HYDROGEN ABSTRACTION REACTIONS

OF

BISTRIFLUOROMETHYLAMINO-OXYL

by

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TO MY PARENTS

This dissertation is submitted in part
fulfilment of the requirements for the
degree of Doctor of Philosophy at the
Victoria University of Manchester.
Unless otherwise stated, the work described
is that of the author and has not
previously been submitted in whole or in
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SUMMARY

Since the first syntheses of the stable free radical bistrifluoromethylamino-oxyl, $(CF_3)_2NO^\cdot$, were reported in 1965, its hydrogen abstraction, addition and combination reactions have been extensively studied.

Compared with other stable radicals it has been found to be an unusually active, although still highly selective, hydrogen abstractor.

The free radicals formed by hydrogen abstraction from alkanes have been found to react further with $(CF_3)_2NO^\cdot$ by either combination or disproportionation. The reaction between $(CF_3)_2NO^\cdot$ and isobutane has been particularly well studied by a number of workers.

In the present work the influence of polar and steric effects on this reaction have been studied by reacting $(CF_3)_2NO^\cdot$ with a number of substituted isoalkyl compounds of general formula $(CH_3)_2CHCH_2X$, the group X being varied through CH_3CH_2, $(CH_3)_3C$, Cl, Br, NO_2, $COCH_3$, $OOCCH_3$, CH_2Cl, CH_2Br, CH_2NO_2 and CH_2CH_2Br.

The inductive effect of the group X has been shown to exert a controlling influence over (a) the rate of initial hydrogen abstraction and (b) the ratio of disproportionation to combination of the intermediate tertiary radical with $(CF_3)_2NO^\cdot$. The two effects parallel one another, increased electron withdrawal by X leading to slower hydrogen abstraction by the electrophilic $(CF_3)_2NO^\cdot$, from $(CH_3)_2CHCH_2X$ in the initial hydrogen abstraction, and from $(CH_3)_2\overset{\cdot}{C}CH_2X$ in the disproportionation step, hence favouring the combination reaction.

Both reaction times and ratios of disproportionation to combination (k_d/k_c) have been found to correlate well with Taft polar substituent constants σ^*. In the case of the k_d/k_c ratios the correlation is good enough for $\log(k_d/k_c)$ to be directly proportional to σ^*, within

close limits.

In the reactions of $(CF_3)_2NO^{\cdot}$ with the isoalkanes the size of X has been shown to be of prime importance in determining the ratio of external to internal olefin formed in the disproportionation step. In the extreme case of 2,2,4-trimethylpentane no internal olefin was detected. Furthermore one of the major products was a tri-amino-oxy compound apparently formed via an intermediate allylic substitution product which was itself formed as a result of severe steric hindrance.

Where X is an electron-attracting group the olefin formed in the disproportionation reaction is almost exclusively the external olefin. This has been attributed to a combination of polar and steric factors. The stability of the olefins formed appears to be of little importance in determining the distribution of the products.

Varying the ratio of $(CF_3)_2NO^{\cdot}$ to isoalkyl compound from 2:1 to 1:1 to 1:2 had virtually no effect on the k_d/k_c ratios.

The intermediate olefins involved in the alkane reactions were trapped using HCl, to give tertiary chloroalkanes in high yields, a reaction originally carried out successfully for isobutane by previous workers.

The reactions of $(CF_3)_2NO^{\cdot}$ with isoalkyl iodides are complicated by replacement of iodine competing with abstraction of the tertiary H atom and the subsequent disproportionation-combination reaction.

In the reactions of $(CF_3)_2NO^{\cdot}$ with isoalkyl alcohols there is competition between initial abstraction from the tertiary C-H bond and from the C-H bonds α to the OH group. Both the resulting radicals then apparently undergo combination and disproportionation reactions.

The major product from the reaction of isopentylbenzene with $(CF_3)_2NO^{\cdot}$ is the result of benzylic substitution. The lack of a disproportionation product in this reaction is attributed to a steric

effect.

The reactions of $(CF_3)_2NO^{\cdot}$ with isoalkyl compounds led, via the reaction with isobutylamine, into a study of the reactions of $(CF_3)_2NO^{\cdot}$ with amines and Schiff's bases.

Isobutylamine and benzylamine were both found to give the Schiff's bases (N-isobutylideneisobutylamine and N-benzylidenebenzylamine respectively), via formation of the imines and their condensation with excess amine.

$(CF_3)_2NO^{\cdot}$ reacts further with N-isobutylideneisobutylamine to give two products, one the substitution product from replacement of the tertiary hydrogen α to the C=N and the other the iminol compound $(CH_3)_2CHC(OH)=NCH_2CHMe_2$. This latter compound is only stable in the presence of the slightly acidic N,N-bistrifluoromethylhydroxylamine, $(CF_3)_2NOH$. Removal of the $(CF_3)_2NOH$ converts the iminol compound to the amide.

Benzylamine reacts with excess $(CF_3)_2NO^{\cdot}$ to give a mixture of N-benzylidenebenzylamine, hydrobenzamide (from self-condensation of 3 moles of benzaldimine) and 1,2,3,4-tetrahydro-2,4,6-triphenyl-1,3,5-triazine (from cyclisation of 3 moles of benzaldimine followed by abstraction of 2 hydrogens). This last compound is a solid only stable as a 1:1 adduct with $(CF_3)_2NOH$. Removal of the $(CF_3)_2NOH$ results in the formation of 2,4,6-triphenyl-1,3,5-triazine.

N-benzylidenebenzylamine has been found to react with $(CF_3)_2NO^{\cdot}$ to give an almost quantitative yield of the benzylic substitution product $C_6H_5CH=NCH[ON(CF_3)_2]C_6H_5$.

The reactions of $(CF_3)_2NO^{\cdot}$ with N-alkylanilines are very fast and exothermic. The products are $(CF_3)_2NOH$, bistrifluoromethylamine $(CF_3)_2NH$, black tarry solids and N^1-alkyl-N^1-phenyl-N^2-(trifluoromethyl)-fluoroformamidines, $C_6H_5(alkyl)NCF=NCF_3$, from reaction of $(CF_3)_2NH$ with

the original N-alkylanilines.

N-benzylaniline reacts similarly except that it also gives benzaldehyde and a number of unidentified $(CF_3)_2NO-$ compounds among the products.

N-benzylideneaniline which reacts much more slowly, is apparently not an intermediate in the N-benzylaniline reaction although it gives rather similar products. It is possible that both these reactions occur via a common intermediate.

The reaction of N-methylbenzylamine with $(CF_3)_2NO^{\bullet}$ has features in common with both the benzylamine and N-alkylaniline reactions. The products include N-benzylidenemethylamine ($C_6H_5CH{=}NCH_3$), benzaldehyde, $(CF_3)_2NO$-substituted benzaldehyde and N^1-benzyl-N^1-methyl-N^2-(trifluoro-methyl)-fluoroformamidine from reaction of $(CF_3)_2NH$ with N-methylbenzyl-amine. The $(CF_3)_2NH$ is thought to be produced in the same reaction step which yields benzaldehyde.

ABBREVIATIONS

APL   = Apiezon L

assign.   = assignment

b.p.   = boiling point

D   = bond dissociation energy

DCB   = para-dichlorobenzene

def.   = deformation

DNP   = dinonyl phthalate

DPPH   = diphenylpicrylhydrazyl

Δ = heat

e.s.r.   = electron spin resonance

ev   = electron volt

Fig.   = Figure

g.l.c.   = gas liquid chromatography

int.   = intensity

i.r.   = infrared

kcal.   = kilocalorie

m   = metre, medium

M   = molecular weight

m/e   = mass/charge

m.p.   = melting point

mins.   = minutes

mmole   = 1/1000 gram-molecular weight

mole   = gram-molecular weight

μ = microns

n.m.r.   = nuclear magnetic resonance

ppm   = parts per million

R   = functional group [usually $(CF_3)_2NO$]

ref.   = reference

r.t.   = room temperature

s   = strong

str.   = stretch

SE30   = silicone oil

t   = tertiary

TFA   = trifluoroacetic acid

u.v.   = ultraviolet

v.   = very

w   = weak

wt.   = weight

INTRODUCTION

BISTRIFLUOROMETHYLAMINO-OXYL

The synthesis, isolation and characterisation of the stable free radical bistrifluoromethylamino-oxyl, $(CF_3)_2NO^\cdot$, was first reported almost simultaneously in the U.S.S.R.[1] and the U.S.A.[2]. Its existence had been postulated some years previously as an intermediate in the dimerisation of trifluoronitrosomethane to O-nitrosobistrifluoromethyl-hydroxylamine[3], as shown in Scheme 1.

$$CF_3NO \longrightarrow CF_3^\cdot + NO$$

$$CF_3^\cdot + CF_3NO \longrightarrow (CF_3)_2NO^\cdot$$

$$(CF_3)_2NO^\cdot + NO \longrightarrow (CF_3)_2NONO$$

$$\text{or} \quad (CF_3)_2NO^\cdot + CF_3NO \longrightarrow (CF_3)_2NONO + CF_3^\cdot$$
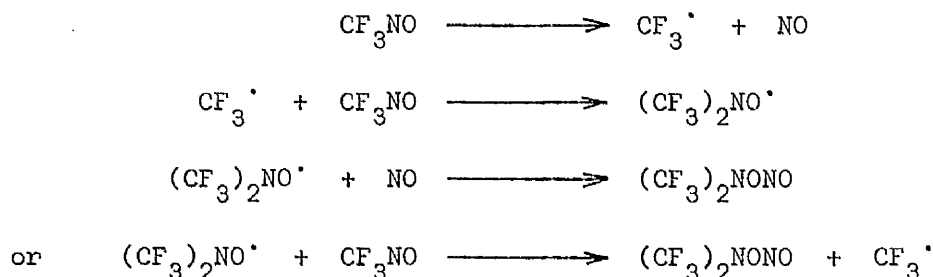
Scheme 1

Bistrifluoromethylamino-oxyl (referred to as $(CF_3)_2NO^\cdot$ or $R^\cdot$ throughout this thesis) is a stable, purple, monomeric gas at room temperature. It condenses to a brown liquid at $-25^\circ C$ and a yellow solid at $-70^\circ C$.[1,2] The solid has been assigned the formula $(CF_3)_2\overset{+}{N}\!-\!\overset{+}{N}(CF_3)_2$.[4]
$$\underset{\underline{O}\quad\underline{O}}{}$$

STABILITY OF BISTRIFLUOROMETHYLAMINO-OXYL

The stability of "stable" organic free radicals is generally attributed to electron delocalisation, steric inhibition to dimerisation or both (e.g. 2,4,6-tri-t-butylphenoxyl).[5] Amino-oxyl radicals were thought to fit in well with these views.

However, it is now accepted that amino-oxyls have an inherently stable electronic arrangement around the N and O atoms, and that steric and mesomeric effects of groups attached to the N atom are mainly

important in preventing the amino-oxyls from reacting with themselves in ways other than dimerisation.[6]

Thus, amino-oxyls with β-hydrogens are known to be unstable, undergoing disproportionation to give a hydroxylamine and a nitrone.[7] Di-t-alkylamino-oxyls[8], having no β-hydrogens cannot disproportionate and hence are stable, although it has been postulated that in this case additional stability against dimerisation is conferred by steric effects of the bulky alkyl groups.[8] t-Butylphenyl- and diphenylamino-oxyls are of relatively low stability, tending to dimerise via attack on the para position to give unstable adducts which rapidly decompose.[5] More stable t-alkylaryl- and diarylamino-oxyls are only produced when attack at the para ring position is blocked by an "inactive" group, approach to it is sterically hindered or the phenyl group is twisted out of conjugation with the NO group. Thus, increase in electron delocalisation around a phenyl ring may merely increase the number of reactive sites in the molecules and not its stability.[6]

This stability of the amino-oxyl group can be accounted for by several representations.

(a)   Delocalisation of the unpaired electron between the N and O atoms as described by the canonical forms A and B[9]:

A   B
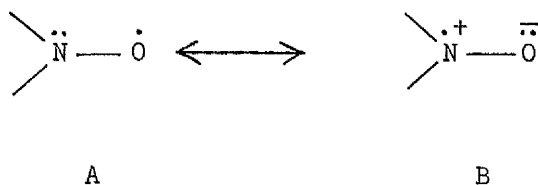
<u>Fig. 1</u>

Protonation of both t-alkyl-[10] and arylamino-oxyls[11] has been carried out without loss of the paramagnetic centre, indicating that structure B makes some contribution.

(b)   Using LCAO-MO theory. The amino-oxyl function can be described by a similar set of molecular orbitals to the carbonyl group[12], namely, a bonding orbital π, an antibonding orbital π^* and a non-bonding orbital n (mainly the 2p orbital on oxygen). The nitrogen may be considered to donate two π electrons to the system whereas only one π electron comes from oxygen. The unpaired electron is assumed to be in the π^* orbital (see Fig. 2).
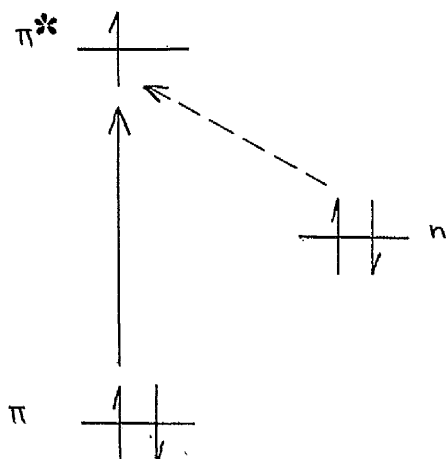
Fig. 2.   Energy-level diagram for the N-O group in amino-oxyls

(c)   Linnett[13] has described amino-oxyl stability using a variation of the Langmuir-Lewis octet rule in which there is a 3 electron N-O π system. The amino-oxyl group may be represented as in Fig. 3.
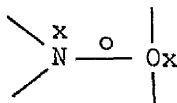
where ⸺ signifies a bonding or lone pair and x or o unpaired electrons of a given spin.

Fig. 3

It can be seen that each atom is surrounded by an octet (or double quartet) of electrons. The stability of the amino-oxyl to dimerisation is attributed to the fact that there is no net gain in the number of bonds in the process.

Support for the 3 π-electron system is given by the facts[6] that the N-O bond lengths and the characteristic N-O frequency in the infrared spectrum are consistent with an N-O bond order of 1.5.

The stability of bistrifluoromethylamino-oxyl can be attributed to the inherent stability of the amino-oxyl group, the absence of reactive groups β to the nitrogen and to the inert nature of fluorine to radical abstraction. However, it is unusually stable compared to other non-fluorinated amino-oxyls. Other amino-oxyls with two CF_2 groups bonded to the N atom form a general class of radical species of high stability.[14]

Blackley and Reinhard[2] have proposed that the stability of $(CF_3)_2NO^{\cdot}$ is due to the strong electronegative character of the CF_3 groups and some delocalisation of the unpaired electron by the six F atoms. Additional evidence to support this delocalisation has been provided by a study[15] of the temperature dependence of the e.s.r. spectrum of $(CF_3)_2NO^{\cdot}$, which showed that the fluorine splitting increases as the temperature is lowered, whereas that due to nitrogen decreases. The mechanism proposed to account for this anomalous temperature effect involved partial conjugation between the N and F atoms.

The e.s.r. spectrum of $(CF_3)_2NO^{\cdot}$ was originally reported as a nine line spectrum, consistent with the theoretical assignments for six equivalent F atoms in two CF_3 groups attached to nitrogen with the splitting due to F and N being equal. However, a later study described the spectrum as a triplet of septets, attributed to the splitting for N being greater than that for F.

INFRARED, NUCLEAR MAGNETIC RESONANCE AND MASS SPECTRA OF BISTRIFLUORO-METHYLAMINO-OXYL

The infrared spectrum[17] shows bands at 1310 cm^{-1} (7.63 μ), 1269 (7.88), 1227 (8.15) [C-F stretch], 992 (10.08) [C-N stretch],

728 (13.74), 723 (13.83), 718 (13.93) [triplet, CF_3 deformation].

The ^{19}F n.m.r. spectrum[2] shows a singlet 73.6 ppm to high field of $CFCl_3$ in $CFCl_3$ at $25^{\circ}C$.

The mass spectrum[17] gives the following fragments:

m/e	Ion	%	m/e	Ion	%
168	$C_2F_6NO^+$	11.8	81	$C_2F_3^+$	38.8
152	$C_2F_6N^+$	12.7	69	CF_3^+	100.0
114	$C_2F_4N^+$	2.4	50	CF_2^+	5.6
85	CF_3O^+	5.9	31	CF^+	4.7
83	CF_3N^+	4.7	30	NO^+	34.1

Table 1

MOLECULAR STRUCTURE OF BISTRIFLUOROMETHYLAMINO-OXYL

The values given in column I of Table 2 for the principal structural parameters are those determined experimentally in the vapour phase by electron diffraction studies.[18] The values given in column II have been calculated[19] by assuming a geometry based on reasonable bond lengths and angles and then systematically varying each of these parameters to obtain the geometry corresponding to the lowest total energy of the system.
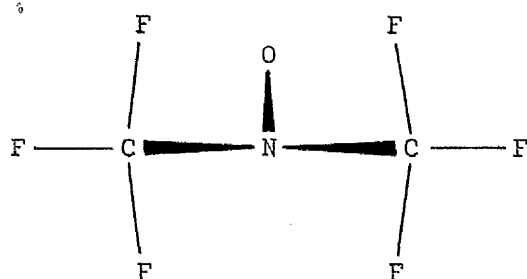
Table 2

Fig. 4

	I	II
r(C-F)	1.32 Å	1.26 Å
r(C-N)	1.44 Å	1.41 Å
r(N-O)	1.26 Å	1.34 Å
F-C-F	109.8±1°	
C-N-C	120.9±2°	
C-N-O	117.2±0.6°	117±1°
Δ	21.9±3°	10°
N-C-F		111°

Δ is the angle between the C-N-C plane and the N-O bond. In the case of the calculated values, where Δ = 10°, it was also calculated that the energy required for deformations of up to 30° from planarity is small (600 cal.) and that the barrier to inversion is 53 calories.

SYNTHESES OF BISTRIFLUOROMETHYLAMINO-OXYL

$(CF_3)_2NO^{\cdot}$ is prepared by oxidation of N,N-bistrifluoromethyl-hydroxylamine, $(CF_3)_2NOH$. This was first prepared[36] from the product of the dimerisation of trifluoronitrosomethane, by reaction with aqueous HCl or methanol.

$$2CF_3NO \longrightarrow (CF_3)_2NONO \xrightarrow{\text{aq. HCl or CH}_3\text{OH}} (CF_3)_2NOH$$
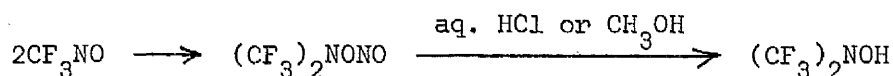
In fact, the isolation of $(CF_3)_2NOH$ and its subsequent conversion to the known bistrifluoromethylamine, $(CF_3)_2NH$,[20] was one of the crucial factors in assigning the correct structure to $(CF_3)_2NONO$.[3b]

Blackley and Reinhard[2], in the first preparation of $(CF_3)_2NO^{\cdot}$

in the U.S.A. used the same route to $(CF_3)_2NOH$ which they then oxidised using fluorine or silver(I) oxide.

Makarov and his co-workers[4] in the U.S.S.R. also prepared $(CF_3)_2NOH$ via the O-nitroso-N,N-bistrifluoromethylhydroxylamine. However, their most useful synthesis was via a single stage reaction of trifluoronitrosomethane with ammonia (Scheme 2).

$$CF_3N=O \ + \ NH_3 \ \xrightarrow[\text{gas phase}]{\text{r.t.}} \ CF_3N=NH \ + \ H_2O$$

$$\downarrow CF_3NO$$
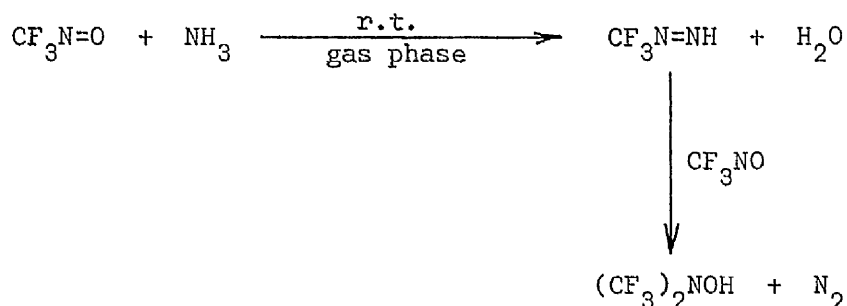
$$(CF_3)_2NOH \ + \ N_2$$

Scheme 2

For the final oxidation stage of hydroxylamine to amino-oxyl they employed potassium permanganate in acetic acid.[1,4]

Other oxidising agents which have been reported to give satisfactory (90-100%) yields of $(CF_3)_2NO^{\cdot}$ from $(CF_3)_2NOH$ are silver(II) oxide[2], cerium(II) sulphate or lead(IV) oxide in aqueous sulphuric acid[21], and a Pt anode in N KOH solution in an electrochemical method.[22]

The synthesis of $(CF_3)_2NO^{\cdot}$ from the perfluoronitrone has been reported[23].

$$CF_3 \overset{\overset{\bar{O}}{|}}{-N}=CF_2 \ + \ HF \ \xrightarrow{-78^{\circ}C} \ (CF_3)_2NOH \ \xrightarrow{ox.} \ (CF_3)_2NO^{\cdot}$$

Neopentane

$$Me_4C + 2R^{\cdot} \xrightarrow[\text{4 days}]{\text{r.t. dark}} Me_4C + RH + Me_3CCH_2R + Me_3CCOR$$

$$\text{23\% rec.} \quad \text{50\%} \quad \text{56\%} \quad \text{23\%}$$

$$+ (CF_3)_2NON(CF_3)_2$$

$$\text{17\%}$$

Propane,[26] with secondary hydrogens available for abstraction, reacts more quickly, to give amino-oxy substituted products, acetone and bistrifluoro-methylamine.

$$C_3H_8 + 2R^{\cdot} \xrightarrow[\text{4 hours}]{\text{r.t. dark}} C_3H_8 + RH + (CF_3)_2NH + Me_2CHR$$

$$\text{36\% rec.} \quad \text{53\%} \quad \text{2\%} \quad \text{55\%}$$

$$+ MeCHRCH_2R + Me_2CO$$

$$\text{23\%} \quad \text{8\%}$$
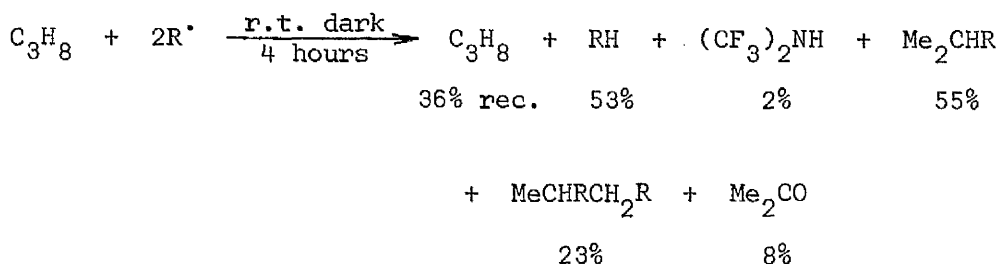
There is good evidence that the mechanism of formation of the carbonyl containing compounds is as given in Scheme 3.

$$XCH_3 \longrightarrow X\overset{\cdot}{C}H_2 \longrightarrow XCH_2ON(CF_3)_2 \longrightarrow X\overset{\cdot}{C}HON(CF_3)_2$$

$$XC{=}O \longleftarrow X\overset{\cdot}{C}{=}O \longleftarrow XCHO$$
$$\underset{R}{|}$$
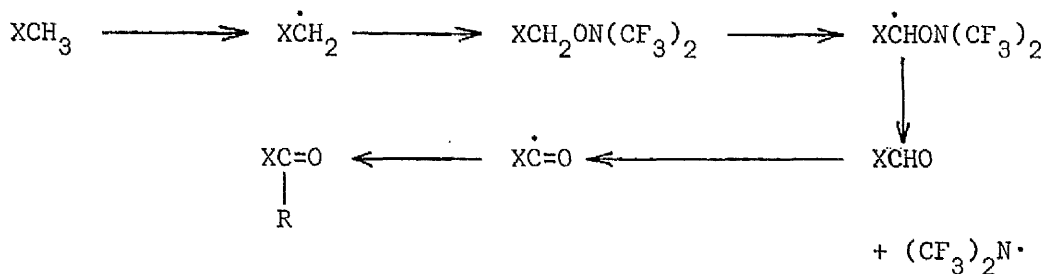
$$+ (CF_3)_2N^{\cdot}$$

Scheme 3   (X = alkyl)

That the mono-bistrifluoromethylamino-oxyalkanes are intermediates in these reactions was shown by reacting them with $(CF_3)_2NO^{\cdot}$.[26]

$$Me_3CCH_2R \xrightarrow{R^{\cdot}} Me_3CCOR + (CF_3)_2NON(CF_3)_2 + RH$$

$$Me_2CHR \xrightarrow{R^{\cdot}} Me_2CO + (CF_3)_2NON(CF_3)_2 + RH$$
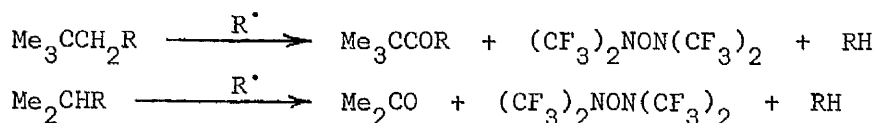
The postulation that aldehydic intermediates might be involved was later given weight by a study[27] of the reactions of aldehydes with $(CF_3)_2NO^{\cdot}$ which showed the reaction

$$XCHO + 2R^{\cdot} \longrightarrow XCOR + RH$$
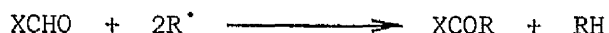
to be extremely facile.

Isobutane and isopentane[26], with tertiary hydrogens available for abstraction, react still faster, giving amino-oxy substituted products but no carbonyl compounds.

Isobutane

$$Me_3CH + 2R^{\cdot} \xrightarrow[\text{15 mins.}]{\text{r.t. dark}} Me_3CH + RH + Me_3CR + Me_2CRCH_2R$$

$$\phantom{Me_3CH + 2R^{\cdot}} \quad 42\% \text{ rec.} \quad 50\% \quad 39\% \quad 51\%$$

Isopentane

$$Me_2CHEt + 2R^{\cdot} \xrightarrow[\text{1 hour}]{\text{r.t. dark}} Me_2CHEt + RH + \underset{\overset{|}{R}}{Me_2CEt} + \underset{\overset{|}{R}}{RCH_2C(Me)Et}$$

$$\phantom{Me_2CHEt + 2R^{\cdot}} \quad 44\% \text{ rec.} \quad 53\% \quad 29\% \quad 45\%$$

$$+ \quad \underset{\overset{|}{R} \ \overset{|}{R}}{Me_2C\text{---}CHMe}$$

$$14\%$$
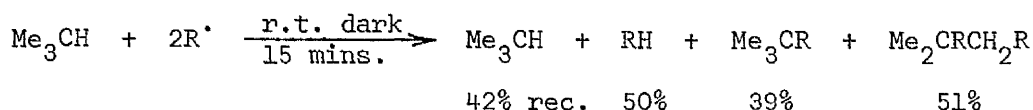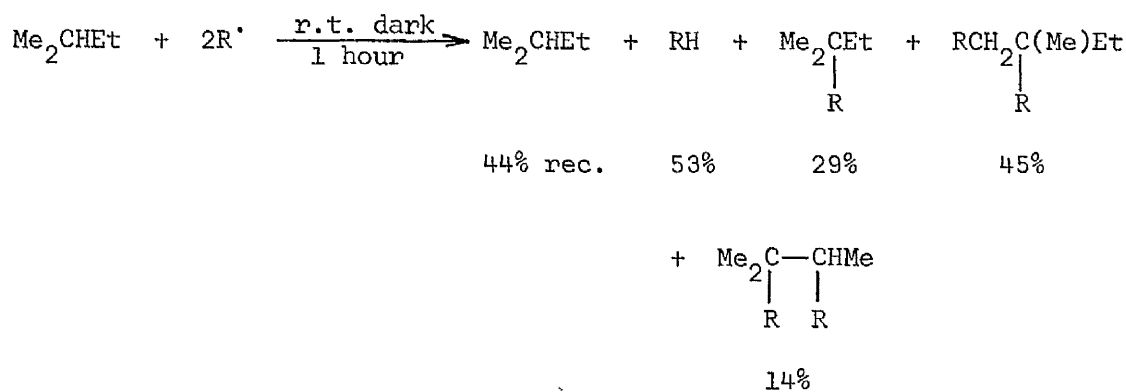
Reactions of alkanes to give di-amino-oxyalkanes were believed to involve olefin formation. That this is certainly the case with isobutane was shown by[26]:

(a)   reacting the two possible mono-bistrifluoromethylamino-oxybutane intermediates, Me_3CR and Me_2CHCH_2R with $(CF_3)_2NO^{\cdot}$. Although the di-amino-

11

oxy compounds were formed in both cases the reactions were too slow to make a significant contribution.

(b)   trapping the isobutene intermediate with HCl using CCl_4 as solvent.

$$Me_3CH + R^{\cdot} + HCl \xrightarrow[\text{3 hours}]{\text{r.t. dark}} HCl + RH + Me_3CR + Me_3CCl$$

$$\phantom{Me_3CH + R^{\cdot} + HCl \xrightarrow{} HCl +} \text{91\% rec.} \quad \text{95\%} \quad \text{9\%} \quad \text{91\%}$$
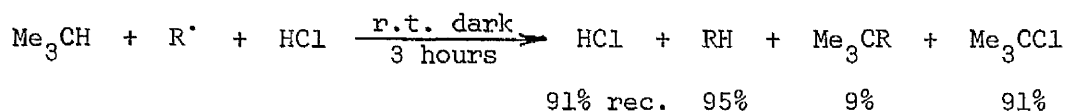
2.   CYCLOALKANES

Cyclopropane[28] is unreactive towards $(CF_3)_2NO^{\cdot}$ at room temperature. Reaction at $70^{\circ}C$ for three weeks resulted in the formation of 71% of bistrifluoromethylamino-oxycyclopropane.

With cyclobutane, cyclopentane, cyclohexane and cycloheptane[28] hydrogen abstraction occurs readily. The resulting cycloalkyl radicals then undergo combination to yield a bistrifluoromethylamino-oxycycloalkane and disproportionation to yield a cycloalkene intermediate which undergoes H abstraction or addition across the double bond depending on the nature of the ring.

These reactions are typified by reaction scheme 4, for cyclopentane.
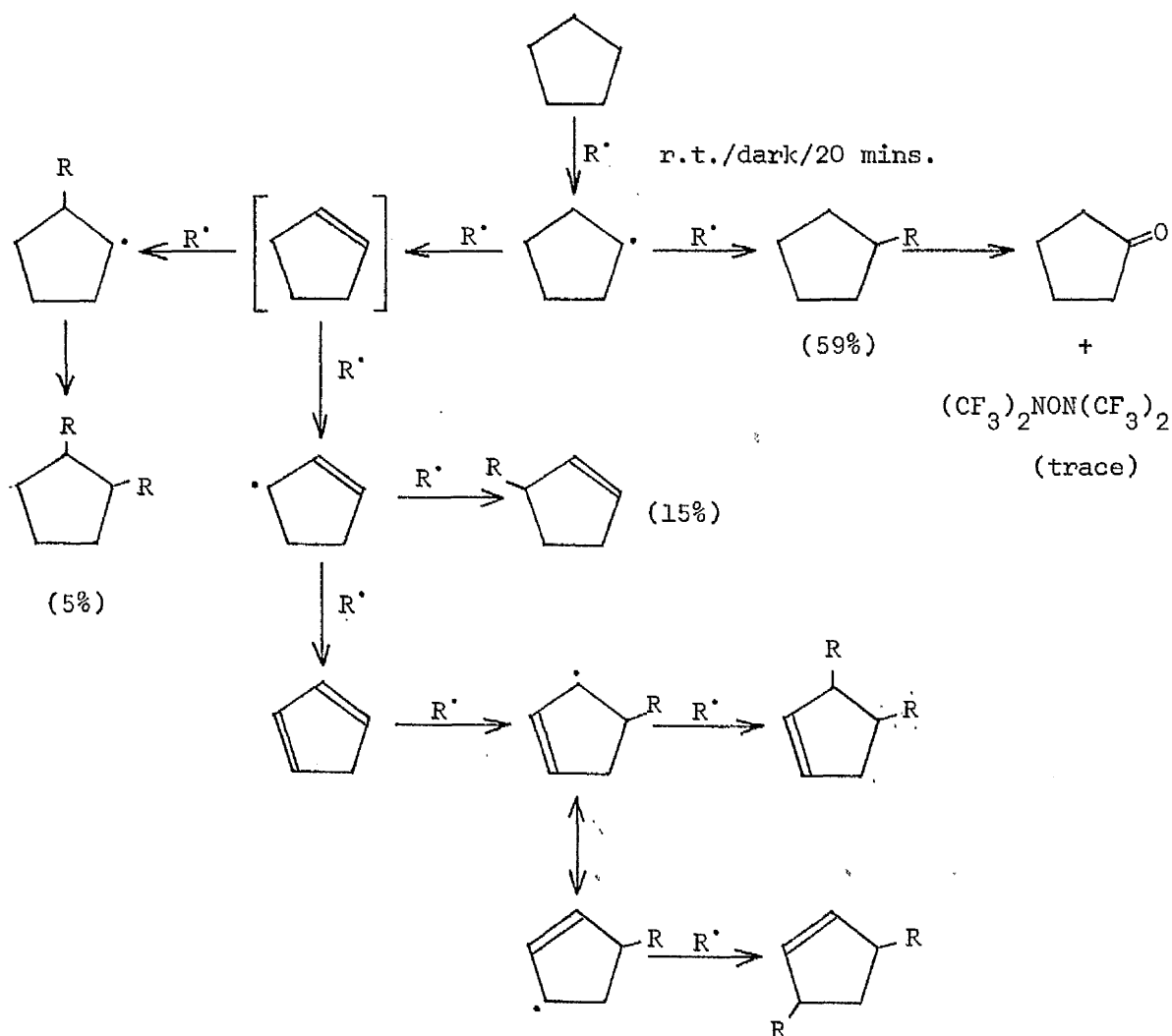
Scheme 4

With norbornane[28] abstraction is from a 2-position to give both the exo-(45%) and endo-(28%) mono-substituted isomers. The 2,3-disubstituted compounds (total 16%) are produced presumably via formation of norbornene.

With methylcyclopentane and methylcyclohexane[28] abstraction of the tertiary hydrogen is rapid. Extremely complex mixtures of products result from radical combination and disproportionation.

e.g.

For methylcyclohexane

79% rec   61%   16%

22%   16%   16%   9%

+ 9% unknowns
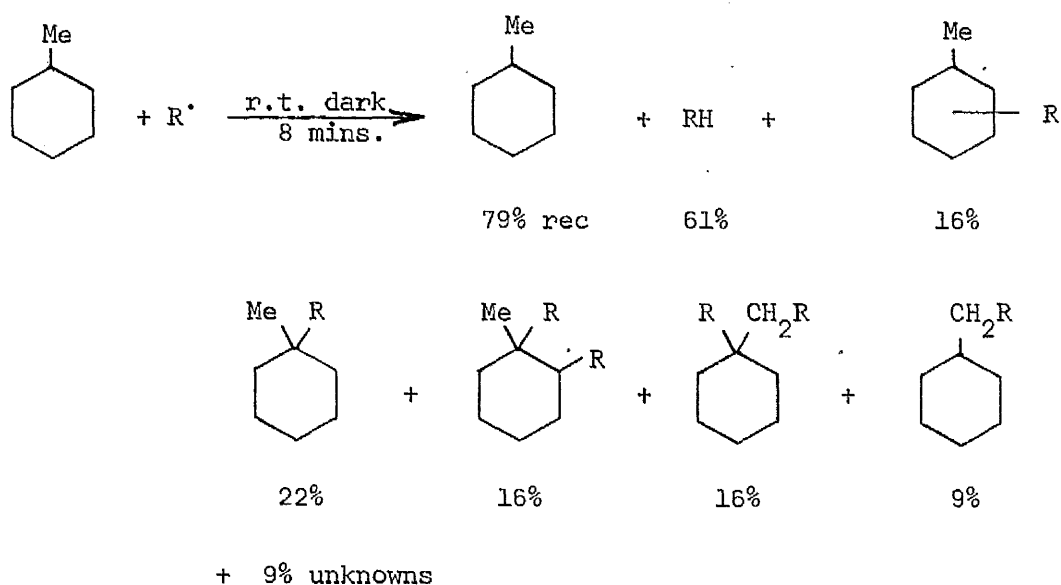
A general trend was observed[28] in these reactions of cycloalkanes with $(CF_3)_2NO \cdot$ in that the more the ring strain is relieved in going from cycloalkane to cycloalkene the greater the extent of the disproportionation reaction and hence the greater the yield of products arising from the intermediate olefin.

3.   ALIPHATIC ALKENES

Ethylene has been widely reported[17,24,29] to undergo addition with $(CF_3)_2NO \cdot$ at room temperature to give the 1,2-addition product. Isobutene, 2-methylbut-1-ene, 2-methylbut-2-ene and tetramethylethylene[26] react in a similar manner giving between 70 and 95% addition across the double bond, the remaining 5 to 30% of the products remaining unidentified but presumably being the result of allylic hydrogen abstraction.

3-Methylbut-1-ene[26] however, which contains a tertiary allylic hydrogen undergoes abstraction to the virtual exclusion of addition giving a 1:1 mixture of the isomeric amino-oxybutenes in almost quantitative yield.

$$Me_2CHCH=CH_2 \longrightarrow Me_2\overset{\bullet}{C}CH=CH_2 \longrightarrow Me_2\underset{\overset{|}{R}}{C}CH=CH_2$$

$$Me_2C=\overset{\bullet}{C}HCH_2 \longrightarrow Me_2C=CHCH_2R$$
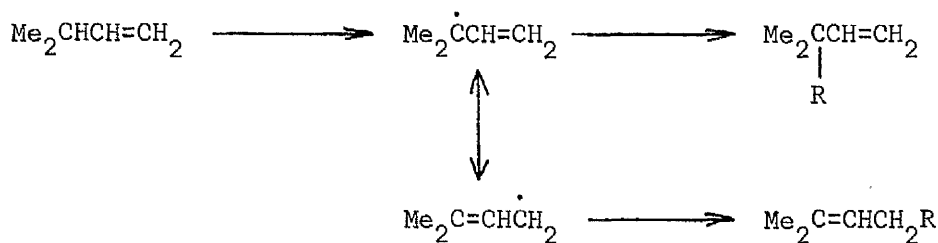
Scheme 5

4.   HALOGENATED ALIPHATIC ALKENES

With tetrafluoroethylene[17,24,29] rapid addition occurs to give the 1,2-addition product. When this reaction was carried out in the presence of NO[24,29] a mixture of products was formed via reaction Scheme 6.

$$NO \xrightarrow{R^{\bullet}} (CF_3)_2NONO$$

$$CF_2=CF_2 \xrightarrow{R^{\bullet}} RCF_2\overset{\bullet}{C}F_2 \xrightarrow{R^{\bullet}} RCF_2CF_2R$$

$$\downarrow NO$$

$$RCF_2CF_2NO$$
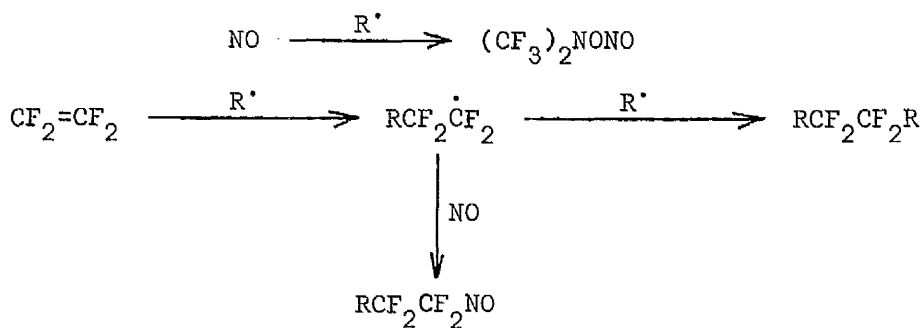
Scheme 6

The polymerisation of C_2F_4 to a solid polymer at $240^{\circ}C$ using $(CF_3)_2NO^{\bullet}$ as initiator has been reported.[30]

When mixed with an excess of an equimolar mixture of ethylene

and tetrafluoroethylene $(CF_3)_2NO^{\cdot}$ combines almost exclusively (98%) with the fluoroolefin.[17] This was taken as an indication that the amino-oxyl is a strongly nucleophilic radical.[17]
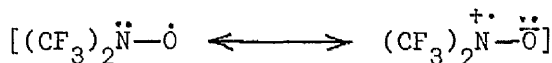
$$[(CF_3)_2\ddot{N}\!\!-\!\!\dot{O} \quad \longleftrightarrow \quad (CF_3)_2\overset{+\cdot}{N}\!\!-\!\!\ddot{\ddot{O}}]$$

Justin,[26b] however, carried out a series of reactions of $(CF_3)_2NO^{\cdot}$ with various fluoroolefins and ethylene and found the following relative rates of addition to the double bond:

$CF_2=CF_2$	1.0
$CHF=CF_2$	7.6×10^{-2}
$CH_2=CH_2$	2.1×10^{-3}
$CH_2=CHF$	1.8×10^{-3}
$CH_2=CF_2$	9.3×10^{-4}

i.e. $CF_2=CF_2 > CHF=CF_2 > CH_2=CH_2 > CH_2=CHF > CH_2=CF_2$.

This is in contrast to the expected rate of addition of a nucleophilic radical to this series which would be in the order $CF_2=CF_2 > CHF=CF_2 > CH_2=CF_2 > CH_2=CHF > CH_2=CH_2$. Furthermore $(CF_3)_2NO^{\cdot}$ addition to tetra-methylethylene and similar hydrocarbon olefins occurs rapidly to give the 2:1 adducts in good yield.[26] Were it assumed that the rapid reaction of $(CF_3)_2NO^{\cdot}$ with C_2F_4 was due to the low electron density of the double bond and the nucleophilicity of the amino-oxyl then the rate of addition to these hydrocarbon olefins would be extremely slow.

Justin suggested that the results with $CF_2=CF_2$ and $CHF=CF_2$ are in fact anomalous and arise as a consequence of the unusual nature of these olefins. These undergo a number of reactions, e.g. thermal dimerisation[31], which are not given by either of the 1,2- or 1,1-difluoroethylenes.[32]

A possible theoretical basis for their anomalous behaviour is provided by the suggestion that C atoms in gem-CF_2 groups in double bonds are sp^3 hybrids and not sp^2.[32] It is further suggested that the driving force for the dimerisation of $CF_2=CF_2$ and the dimerisation and cyclo-addition reaction of the $CF_2=CF-$ group in general is the relief of strain in the double bond.

Justin[26b] concluded that bistrifluoromethylamino-oxyl is an electrophilic radical.

$(CF_3)_2NO\cdot$ has been shown to react readily with perfluoropropene[17] to give 98% of the addition product, a result in good agreement with the expected rate of addition to a $CF_2=CF-$ group based on the above reasoning.

Recent measurements have produced values for the π bond dissociation energies in $CF_2=CF_2$[33] and $CH_2=CF_2$[34] of 52.5 and 62.1 kcal mole^{-1} respectively. These compare with a value for ethylene[35] of 59.1 kcal mole^{-1}. It is suggested[34] that the difference in the electro-negativity of the π bond centres may be the important factor in the unexpectedly high value for $CH_2=CF_2$. It can be seen that the order of π bond dissociation energies [$CF_2=CF_2 < CH_2=CH_2 < CH_2=CF_2$] fits in well with the relative rates of addition of $(CF_3)_2NO\cdot$ to these compounds.

Justin[26b] also studied the relative rates of addition of $(CF_3)_2NO\cdot$ to several chloroolefins and found the order of reactivity to be $CH_2=CCl_2 >> CH_2=CHCl >> CH_2=CH_2$. In these reactions the intermediate free radicals are stabilised by the chlorine substituents and inductive effects are relatively unimportant.

5.   CYCLOALKENES

These compounds are considerably more susceptible to attack by $(CF_3)_2NO\cdot$ than are the corresponding cycloalkanes.[28]

With cyclopentene, cyclohexene and cycloheptene allylic substitution predominates over addition.

e.g. Cyclohexene

56% rec.   52%   87%

trans - 6%   5%

cis - 2%
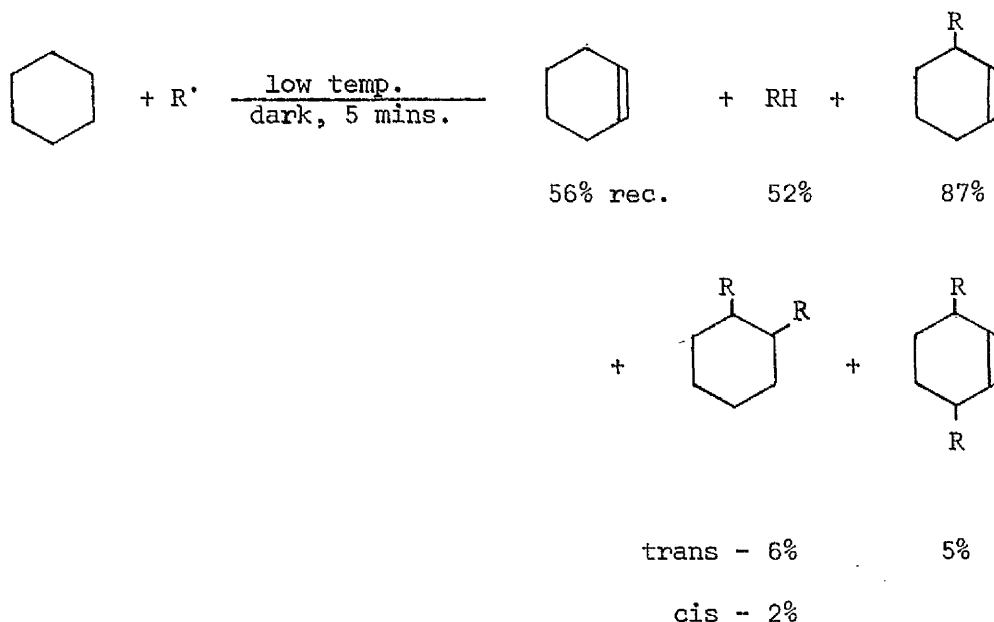
With norbornene or cyclopentadiene[28] the reverse is true, addition taking place across the double bond to the total exclusion of hydrogen abstraction.

6.   PERFLUOROCYCLOALKENES

Perfluorocyclobutene[17] and perfluorocyclohexene[36] both undergo addition across the double bond fairly readily with $(CF_3)_2NO\cdot$.

7.   PERFLUORODIENES

Perfluorobuta-1,3-diene

With a 2:1 molar ratio of amino-oxyl to diene, at room temperature

a very vigorous reaction gives mainly decomposition products plus some (14%) di-amino-oxy adducts.[36b]

At -72°C the yield of di-amino-oxy adducts is 98%, divided between the three isomers as follows:
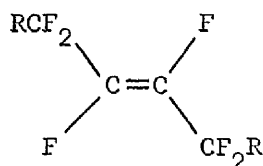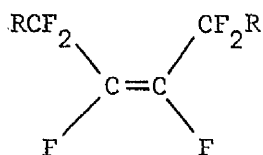
57%   14%   29%

Reaction of a 4:1 molar ratio of $(CF_3)_2NO^{\cdot}$ to diene, after one day at 80°C, gave 95% of $RCF_2CFRCFRCF_2R$ and no detectable di-amino-oxy adduct.[36b]

The following have also been reported[37]:
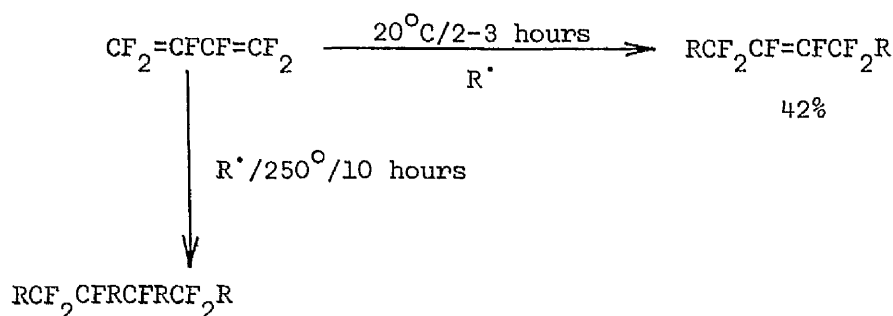
$(CF_3)_2NO^{\cdot}$ has been reported[38] to act as an initiator for the polymerisation of perfluorobuta-1,3-diene. Yields using the amino-oxyl were found to be only about 25% of those obtained using the same concentration of benzoyl peroxide.

With perfluorocyclohexa-1,3-diene[36b] the following reactions take place:

$$\text{[F cyclohexadiene]} \xrightarrow{\quad 2R^{\bullet}/85^{\circ}C/7 \text{ days} \quad} \text{[R-F-R product]} \quad \text{and/or} \quad \text{[R-R-F product]}$$

93%

4R$^{\bullet}$/85°C/14 days ↓

[R,R,R,F substituted cyclohexane] 49%

$+ \quad C_6F_8R_2 \quad + \quad R^{\bullet}$

50%   23% rec.
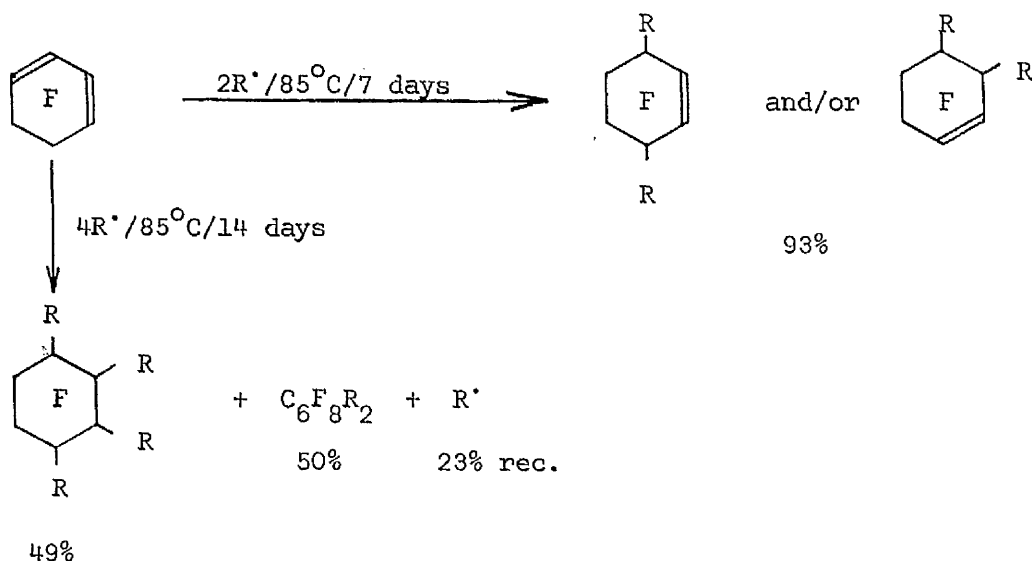
The reaction using the 4:1 molar concentration of $(CF_3)_2NO^{\bullet}$ to cyclodiene presents a contrast to the equivalent reaction with perfluoro-buta-1,3-diene where reaction was complete to give a completely saturated product after only one day.

Hexafluorobicyclo[2,2,0]hexa-2,5-diene adds $(CF_3)_2NO^{\bullet}$ across the double bonds fairly efficiently[39], a 2:1 molar ratio of amino-oxyl to diene giving a mixture of di-amino-oxy adducts after 18 hours at 20°C and a 4:1 molar ratio giving 83% of the completely saturated product after 20 days at 20°C.

8.   ALKYNES

Russian workers[24,29] have claimed that the reaction between $(CF_3)_2NO^{\bullet}$ and acetylene is very slow and gives $(CF_3)_2NOH$ and polymeric unsaturated liquid hydrocarbons containing neither F nor N.

However, workers in this Department[40] have found the main product of the reaction to be the trisubstituted aldehyde, R_2CHCOR. The other major products are $(CF_3)_2NOH$ and either $(CF_3)_2NON(CF_3)_2$ or $(CF_3)_2NH$, depending on the proportions of reactants used. They have proposed that the reaction proceeds by the mechanism shown in Scheme 7.

$$CH\equiv CH \xrightarrow{2R\cdot} RCH=CHR \xrightarrow{R\cdot} R_2CH\overset{\cdot}{C}H-ON(CF_3)_2$$

$$R_2CHC=O \xleftarrow{R\cdot} R_2CH\overset{\cdot}{C}=O \xleftarrow{R\cdot} R_2CHCHO + \cdot N(CF_3)_2$$
$$\underset{R}{|}$$
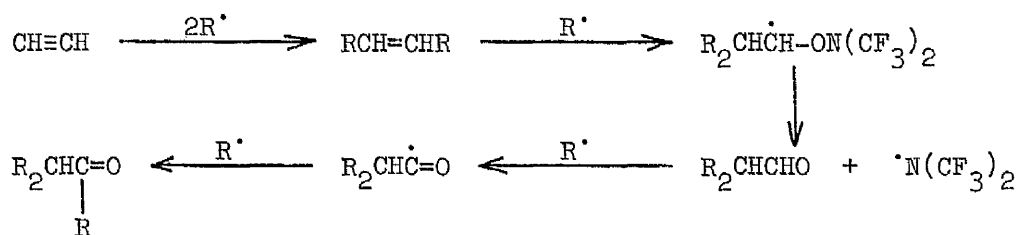
Scheme 7

This mechanism was suggested in the knowledge that aldehydic hydrogens are readily substituted by $(CF_3)_2NO\cdot$.[27]

Perfluoropropyne and perfluorobut-2-yne[40] give a complex array of products with $(CF_3)_2NO\cdot$. Taking perfluorobut-2-yne as the example the products may be rationalised via the mechanism shown in Scheme 8.

$$CF_3C\equiv CCF_3 \xrightarrow{2R\cdot} \underset{R\ R}{CF_3-C=C-CF_3} \longrightarrow \begin{bmatrix} \underset{R\ O\cdot}{CF_3-C=C-CF_3} \\ \updownarrow \\ \underset{R\ O}{CF_3-\overset{\cdot}{C}-C-CF_3} \end{bmatrix}$$

$$(CF_3)_2NON(CF_3)_2 \xleftarrow{R\cdot} (CF_3)_2N\cdot +$$
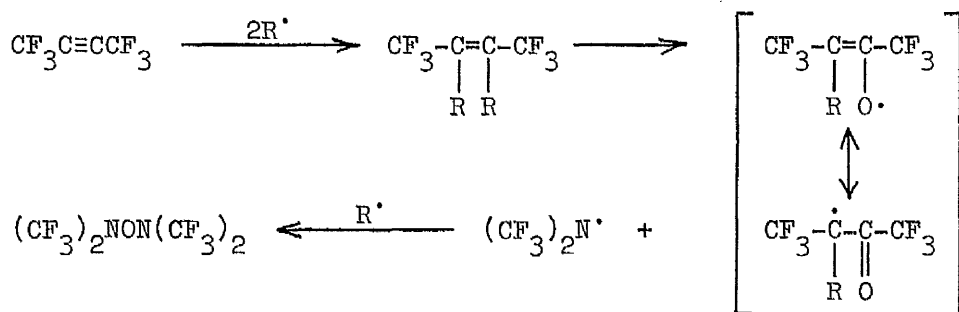
The intermediate radical can then react in a number of different ways:

(a)   with $(CF_3)_2NO\cdot$ $\longrightarrow$ $\underset{CF_3}{R_2C}\text{---}\underset{CF_3}{C=O}$ (I)

(b)   with $(CF_3)_2N\cdot$ $\longrightarrow$ $R\text{---}\overset{CF_3}{\underset{N(CF_3)_2}{C}}\text{---}COCF_3$ (II)

(c)   by loss of $(CF_3)_2N\cdot$ $\longrightarrow$ $\underset{O\ \ O}{CF_3-C-C-CF_3}$ (III)
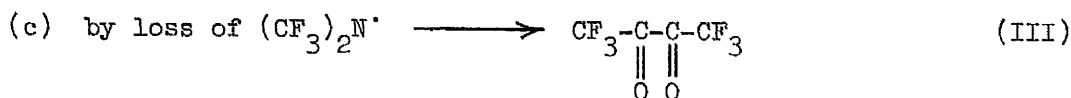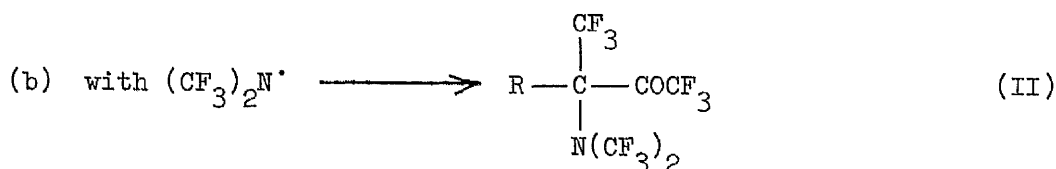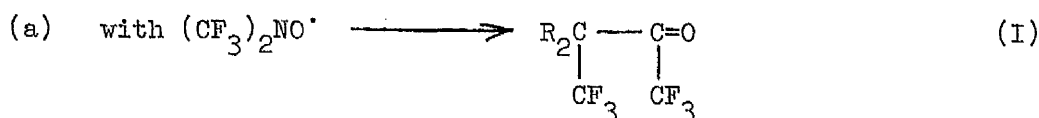
An alternative route to II is via reaction of $CF_3C\equiv CCF_3$ with $(CF_3)_2NON(CF_3)_2$.

i.e. $CF_3C\equiv CCF_3$ + $(CF_3)_2NON(CF_3)_2$ $\longrightarrow$ $R-\underset{\underset{CF_3}{|}}{C}=\underset{\underset{CF_3}{|}}{C}-N(CF_3)_2$

$\downarrow -(CF_3)_2N^{\cdot}$

$II \xleftarrow{\quad R^{\cdot}\quad} \left[O=\underset{\underset{CF_3}{|}}{C}-\overset{\cdot}{\underset{\underset{CF_3}{|}}{C}}-N(CF_3)_2 \longleftrightarrow {}^{\cdot}O-\underset{\underset{CF_3}{|}}{C}=\underset{\underset{CF_3}{|}}{C}-N(CF_3)_2 \right]$
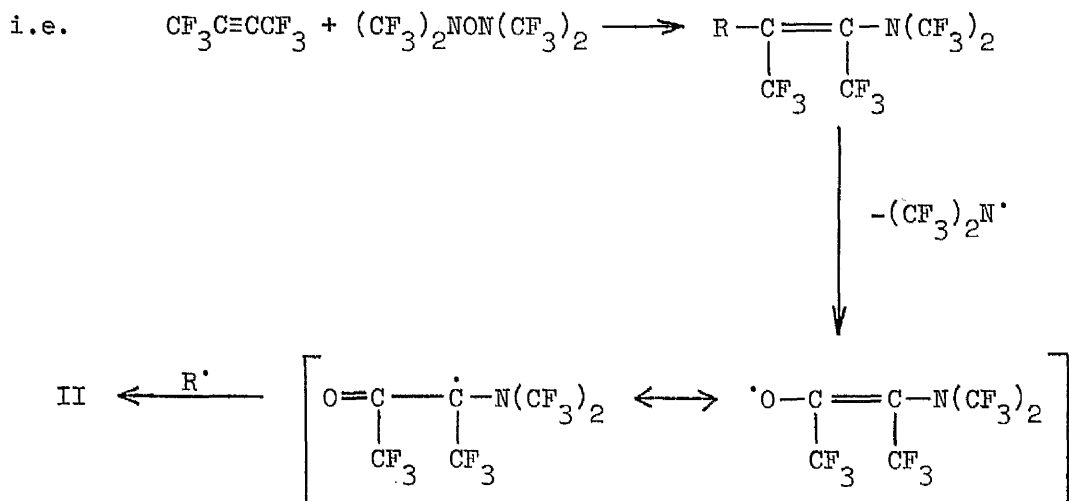
Scheme 8

Reaction of perfluorobut-2-yne with $(CF_3)_2NO^{\cdot}$, after 48 hours at $85^{\circ}C$ gives 21% of I, 10% of II, 73% of III and 79% of $(CF_3)_2NON(CF_3)_2$.

Reaction of perfluoropropyne with $(CF_3)_2NO^{\cdot}$, after 15 days at room temperature gives $R_2\underset{\underset{CF_3}{|}}{C}-\underset{\underset{F}{|}}{C}=O$ + $R-\underset{\underset{N(CF_3)_2}{|}}{C}(CF_3)COF$ + $CF_3-\overset{\overset{O}{||}}{C}-\overset{\overset{O}{||}}{C}-CF_3$

    35%   1%   52%
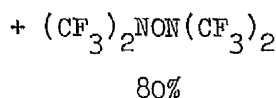
+ $(CF_3)_2NON(CF_3)_2$
80%

Similar mechanisms are thought to be involved in the next two reactions. 3,3,3-Trifluoropropyne[40] reacts slowly (4 months) with $(CF_3)_2NO^{\cdot}$ to give CF_3COCHR_2 + $CF_3COCHRN(CF_3)_2$ + $(CF_3)_2NON(CF_3)_2$.

    85%   15%   45%

Perfluorodiphenylacetylene[40] after 20 hours with $(CF_3)_2NO^{\cdot}$ at room temperature gives $(CF_3)_2NON(CF_3)_2$ +

+ unidentified compounds.

9.   TETRAFLUOROALLENE

Tetrafluoroallene readily undergoes free radical homopolymerisation even in cases where telomer production might be expected.[41] This ease of polymerisation had prevented the determination of the orientation of free radical attack on its cumulene system, although attack on the central carbon giving an allylic radical had seemed most likely.[41] In the reaction of $(CF_3)_2NO^\cdot$ it was hoped, by analogy with the reaction of C_2F_4 with $(CF_3)_2NO^\cdot$, that polymerisation of the allene would not prevent a comparison being drawn between the allene and its acetylenic isomer, perfluoropropyne. The following reactions were observed[42]:

$$CF_2=C=CF_2$$

$$\swarrow 6R^\cdot \qquad\qquad 2R^\cdot/r.t. \searrow$$

$$RCF_2\underset{\underset{O}{\|}}{C}CF_2R \;+\; R^\cdot \qquad\qquad RCF_2\underset{\underset{O}{\|}}{C}CF_2R \;+\; CF_2=\underset{\underset{N(CF_3)_2}{|}}{C}-CF_2R$$

89%   40% rec.   31%   42%

$+\; (CF_3)_2NON(CF_3)_2$ $+$ polytetrafluoroallene

16%

$+\; (CF_3)_2NON(CF_3)_2$

The mechanistic scheme for the reaction is given below.[42]

$$CF_2=C=CF_2 \xrightarrow{R^\cdot} CF_2=\underset{\underset{R}{|}}{\overset{\cdot}{C}}CF_2 \xrightarrow{R^\cdot} CF_2=\underset{\underset{R}{|}}{C}-CF_2R$$

$$\downarrow R^\cdot$$

$$(CF_3)_2N^\cdot \;+\; RCF_2-\underset{\underset{O}{\|}}{C}-CF_2R \;\longleftarrow\; RCF_2-\underset{\underset{R}{|}}{\overset{\cdot}{C}}-CF_2R$$

Scheme 9

If a large excess of $(CF_3)_2NO\cdot$ is used, the reaction stops here, the $(CF_3)_2N\cdot$ being converted to $(CF_3)_2NON(CF_3)_2$. In the absence of an excess of amino-oxyl, unreacted tetrafluoroallene can react further, either with $(CF_3)_2NON(CF_3)_2$ or with $(CF_3)_2N\cdot$ followed by $(CF_3)_2NO\cdot$ to yield

$$CF_2=\underset{\underset{N(CF_3)_2}{|}}{C}-CF_2R$$

10.   ALIPHATIC ALDEHYDES

Reactions of $(CF_3)_2NO\cdot$ with acetaldehyde, propionaldehyde and pivaldehyde, Me_3CCHO,[27] set in at low temperatures and proceed rapidly, exothermically and cleanly to completion as indicated by the equation:

$$Alkyl\text{-}CHO + R\cdot \longrightarrow Alkyl\text{-}\overset{\cdot}{C}=O \xrightarrow{R\cdot} Alkyl\text{-}C\overset{\displaystyle O}{\underset{\displaystyle R}{<}}$$

$$+ RH$$
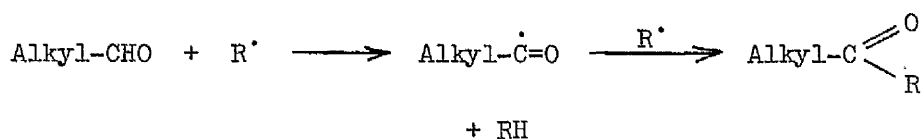
The efficiency of the scavenging of the presumed intermediate alkanoyl radicals was revealed by the detection of traces of CO (plus traces of Me_3CR) in only the products from pivaldehyde.

$(CF_3)_2NO\cdot$ also abstracts the aldehydic hydrogens from glyoxal.[40]

$$\underset{\underset{O\ O}{||\ ||}}{HC\text{-}CH} + 4R\cdot \xrightarrow[\text{12 hours}]{\text{r.t.}} R\cdot + RH + \underset{\underset{O\ O}{||\ ||}}{RC\text{-}CR} + CO$$

$$\text{11\% rec.} \qquad \text{57\%} \qquad \text{84\%} \qquad \text{7\%}$$
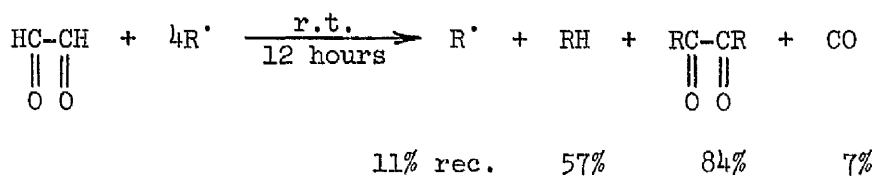
11.   AROMATIC ALDEHYDES

The aldehydic hydrogen is also abstracted from aromatic aldehydes very easily, to give almost quantitative yields of (bistrifluoromethylamino-oxy)-carbonylarenes.[27]

Attack at the aldehydic function takes preference over nuclear attack in the cases of benzaldehyde, terephthaldehyde and pentafluoro-benzaldehyde and over side chain attack in the case of m-tolualdehyde. Only in the case of p-tolualdehyde was any evidence of side chain attack found, in that a room temperature reaction gave a small amount of material which was possibly $p-RCH_2C_6H_4COR$. However a reaction at $-24^{\circ}C$ gave $p-MeC_6H_4COR$ almost exclusively (98%).

An anomalous report has been published by Russian workers[43] claiming that heating pentafluorobenzaldehyde with $(CF_3)_2NO^{\cdot}$ in a sealed tube for 1 to 4 hours at temperatures up to $150^{\circ}C$ results in addition to the ring giving two isomers of $R_4C_6F_5CHO$ plus $R_6C_6F_5CHO$, and apparently leaving the aldehydic H intact.

Reaction of $PhCO_2N(CF_3)_2$ with 4 mole equivalents of $(CF_3)_2NO^{\cdot}$ at $70^{\circ}C$ does lead to nuclear substitution,[27] the major products being $(CF_3)_2NOH$, the para-substituted derivative RC_6H_4COR and either the ortho- or meta-isomer of the latter.

12. KETONES

Acetone has been found to react slowly with $(CF_3)_2NO^{\cdot}$ giving the disubstituted product $R_2CHCOCH_3$ after 47 days at room temperature and this compound (85%) plus some of the trisubstituted R_3CCOCH_3 (15%) after 3 days at $70^{\circ}C$.[44]

The mechanism of the reaction is believed to involve attack on the enol form of acetone, the slow reaction time being attributed to the slow rate of enolisation,

$$CH_3\underset{\underset{O}{\|}}{C}CH_3 \quad \underset{\longleftarrow}{\overset{\text{slow}}{\longrightarrow}} \quad CH_2=\underset{\underset{OH}{|}}{C}-CH_3 \; , \quad 0.00025\% \text{ at r.t.}[45]$$
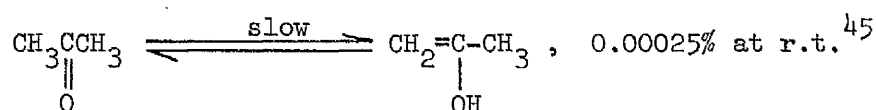
$$K = 2.8 \times 10^{-8} \; min^{-1}$$

and the low yield of the trisubstituted acetone to steric effects.

$$CH_2=\underset{\underset{OH}{|}}{C}-CH_3 \quad \xrightarrow{R^{\cdot}} \quad RCH_2-\underset{\underset{OH}{|}}{\overset{\cdot}{C}}-CH_3 \quad \xrightarrow{R^{\cdot}} \quad RCH=\underset{\underset{OH}{|}}{C}-CH_3$$
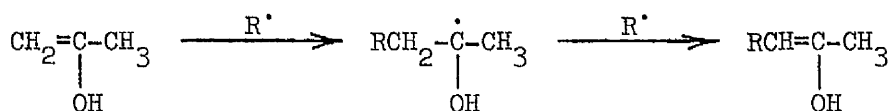
<div align="center">Scheme 10</div>

The monosubstituted enol may then react further giving the disubstituted enol which may react further again.

Evidence for the involvement of the enol form was provided by (a) the result of an investigation of acid catalysis on the reaction. Strong acids catalyse the rate of enolisation and the reaction was found to be faster in the presence of hydrochloric acid.
(b) the reaction of $(CF_3)_2NO^{\cdot}$ with acetylacetone[44] (80%[45] enol form at room temperature) is rapid, being complete on allowing the reactants to warm from $-196^{\circ}C$ to room temperature. The product, however, is unstable.

13. ALCOHOLS

Methanol. Russian workers[46] have claimed that reaction of $(CF_3)_2NO^{\cdot}$ with methanol (2:1 molar ratio) for one day at room temperature gives 43% of the adduct $(CF_3)_2NOCH_2OH$.

This reaction was repeated by Connell[44] in this Department but the adduct could not be isolated. His liquid product, while boiling at the same temperature as that quoted by the Russians, was shown by g.l.c. to consist not of one component but of three. During manipulation of the product quantities of white solid were produced. He repeated the reaction more carefully and obtained 53% of carbon monoxide, approximately 90% $(CF_3)_2NOH$ and some methanol. He postulated from this that the adduct could be decomposing according to Scheme 11.

$$RCH_2OH \longrightarrow HCHO \xrightarrow{R^\bullet} {}^\bullet CHO \xrightarrow{R^\bullet} RCHO$$

$$+ \ RH$$

$$R^\bullet + CO \longleftarrow RC{=}O$$

(with $R^\bullet$ arrow downward from $RCHO$ to $R\overset{\bullet}{C}{=}O$)
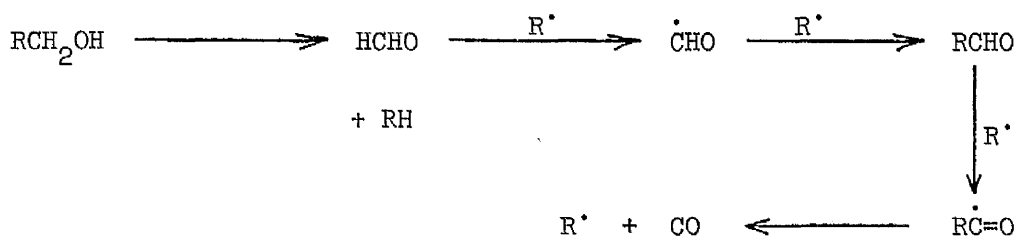
<div align="center">Scheme 11</div>

Certainly it is accepted that hydrogen abstraction by selective radicals, e.g. Br$^\bullet$, usually takes place from the methyl group of methanol,[47] in agreement with bond energy data, $D[MeO-H] = 102 \ kcal \ mole^{-1}$, $D[H-CH_2OH] = 92 \ kcal \ mole^{-1}$.[47] In photobromination of methanol, carbon monoxide is produced in high yield via Scheme 12.[47]

$$CH_3OH \xrightarrow{Br^\bullet} {}^\bullet CH_2OH \xrightarrow{Br^\bullet} BrCH_2OH \longrightarrow HCHO + HBr$$

$$\downarrow 2Br^\bullet$$

$$CO$$
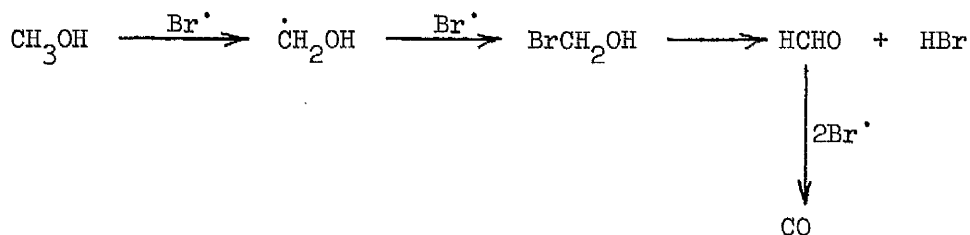
<div align="center">Scheme 12</div>

<u>Isopropanol</u>.[44] Using a 2:1 molar ratio of $(CF_3)_2NO^\bullet$ to isopropanol, a fast reaction takes place giving 95% acetone and 100% $(CF_3)_2NOH$.

Using a 4:1 molar ratio the reaction gives:

$$Me_2CHOH + 4R^\bullet \longrightarrow Me_2C{=}O + R_2CHCOMe + R^\bullet + RH$$

$$ 63\% \qquad 23\% \qquad 14\% \ rec. \ 77\%$$
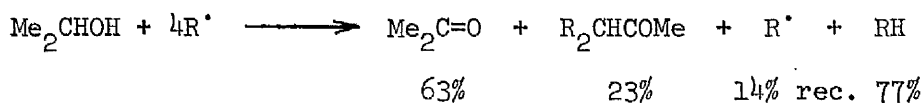
The initial hydrogen abstraction presumably gives the radical Me$_2\overset{\bullet}{C}$OH. An e.s.r. investigation of ·OH radicals with isopropanol[48] revealed the presence of an intense signal due to the intermediate radical Me$_2\overset{\bullet}{C}$OH and a much weaker signal due to $\overset{\bullet}{C}H_2CHOHCH_3$.

14.   FORMIC ACID

Formic acid[44] is slowly dehydrogenated by $(CF_3)_2NO^{\bullet}$ (3 months at room temperature) to give carbon dioxide and $(CF_3)_2NOH$ as the main products of the reaction. A small amount (2%) of CF_3NO_2 is found in the products.

15.   ETHERS

With dimethyl ether, diethyl ether and anisole[28] $(CF_3)_2NO^{\bullet}$ abstracts a hydrogen atom from a carbon α to the O atom.

With dimethyl ether the main product is RCH_2OMe plus some of the disubstituted RCH_2OCH_2R.

Diethyl ether has vicinal hydrogens and disproportionation of the initially formed radical appears to compete with combination, the intermediate olefin undergoing addition to yield an α,β-di-amino-oxy compound.

$$Et_2O \; + \; 2R^{\bullet} \; \xrightarrow[\text{30 mins.}]{\text{r.t./dark}} \; Et_2O \; + \; RH \; + \; \underset{\displaystyle R}{MeCHOEt}$$

$$\qquad\qquad\qquad\qquad\quad 16\%\ rec. \quad 51\% \qquad 76\%$$

$$+ \; \underset{\displaystyle R}{RCH_2CHOEt} \; + \; \underset{\displaystyle R\ \ R}{MeCHOCHMe}$$

$$\qquad\qquad 17\% \qquad\qquad\quad 1\%$$
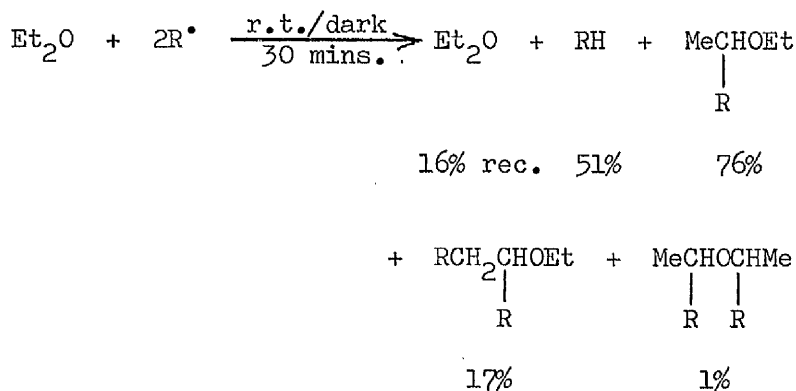
Anisole reacts over 24 hours at room temperature to give 87% of $PhOCH_2R$, traces of $(CF_3)_2NH$ and 10% of unknowns.

16.   ISOCYANIDES

t-Butyl isocyanide[49] reacts readily as follows:

$$t\text{-BuNC} \xrightarrow[\text{r.t./3 days}]{R^\bullet} t\text{-BuN=C=O} \;+\; t\text{-BuN=}\underset{\underset{R}{|}}{C}\text{-N(CF}_3)_2$$

$$\downarrow \; 2R^\bullet/0^\circ C/2 \text{ days}$$

$$\qquad\qquad\qquad\qquad\qquad 50\% \qquad\qquad\qquad 47\%$$

$$t\text{-BuN=C=O} \;+\; t\text{-BuN=CR}_2 \;+\; t\text{-BuN=C-N(CF}_3)_2 \;+\; (\text{CF}_3)_2\text{NON(CF}_3)_2$$

$$\quad 60\% \qquad\qquad 17\% \qquad\qquad 21\% \qquad\qquad\qquad 47\%$$
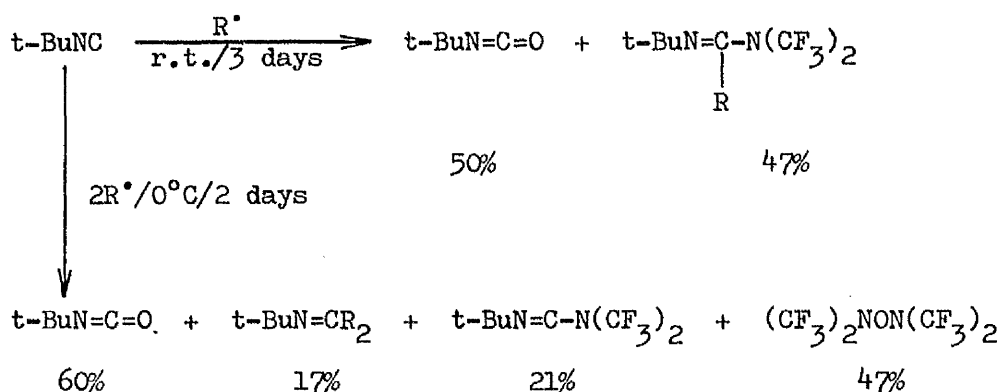
The mechanism proposed to account for these products is shown in Scheme 13.

$$\left[t\text{-BuN}\overset{+}{\equiv}\overset{..}{C} \longleftrightarrow t\text{-BuN=C:} \right] \xrightarrow{R^\bullet} t\text{-BuN=}\overset{\bullet}{C}R \xrightarrow{R^\bullet} t\text{-BuN=CR}_2$$

$$\downarrow \; \beta\text{-scission}$$

$$(\text{CF}_3)_2\text{NON(CF}_3)_2 \xleftarrow{R^\bullet} (\text{CF}_3)_2\text{N}^\bullet + t\text{-BuN=C=O}$$
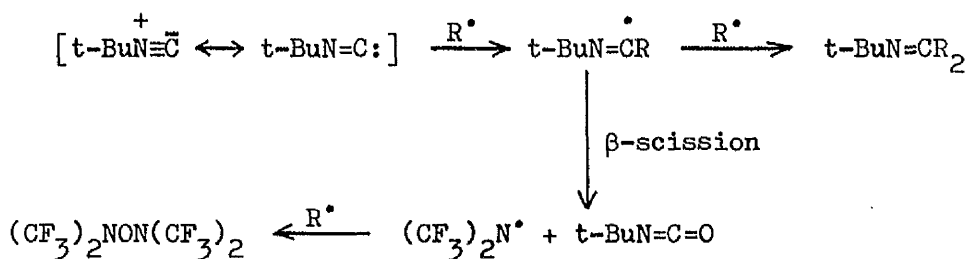
$(\text{CF}_3)_2\text{NON(CF}_3)_2$ undergoes a novel insertion reaction with t-BuNC:

$$t\text{-BuNC} \;+\; (\text{CF}_3)_2\text{NON(CF}_3)_2 \longrightarrow t\text{-BuN=}\underset{\underset{R}{|}}{C}\text{-N(CF}_3)_2$$
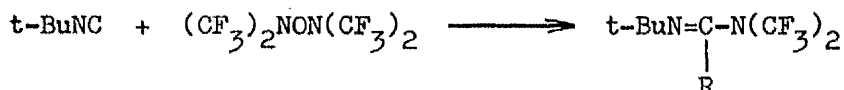
Scheme 13

Trifluoromethyl isocyanide[49] gives

$$\text{CF}_3\text{NC} + R^\bullet \xrightarrow[\text{12 hours}]{\text{r.t.}} \text{CF}_3\text{N=C=O} \;+\; \text{CF}_3\text{N=CR}_2$$

$$\qquad\qquad\qquad\qquad\qquad\qquad 13\% \qquad\qquad 27\%$$

$$+\; \text{CF}_3\text{N=CRCR=NCF}_3 \;+\; (\text{CF}_3)_2\text{NON(CF}_3)_2$$

$$\qquad\qquad 52\% \qquad\qquad\qquad 12\%$$
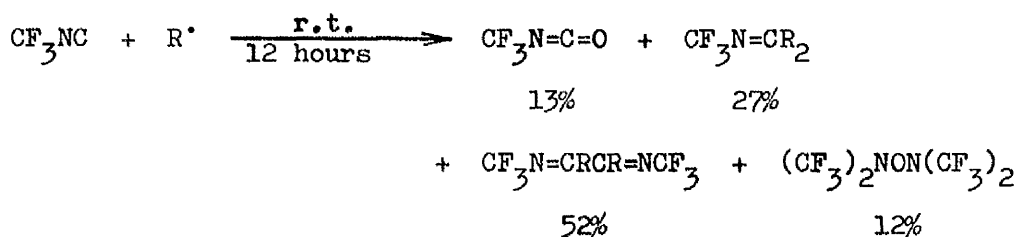
The initial part of the proposed mechanism is the same as in Scheme 13,

leading to $\text{CF}_3\text{N=C=O}$ and $(\text{CF}_3)_2\text{NON(CF}_3)_2$. However the intermediate radical

can also react via Scheme 14.

$$CF_3N=\overset{\bullet}{C}R \xrightarrow{\quad CF_3NC \quad} CF_3N=C-\overset{\bullet}{C}=NCF_3$$

dimerisation

$$CF_3N=C-C=NCF_3$$

Scheme 14
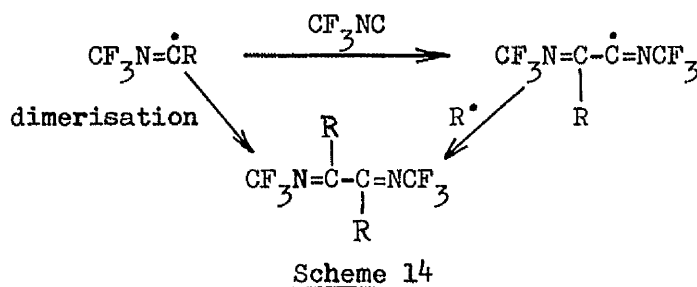
17.   DIMETHYLAMINE

Connell[44], in this Department, found that the reaction of $(CF_3)_2NO^{\bullet}$ with dimethylamine (2:1 molar basis) gave, on warming from -196°C to room temperature, 46% $(CF_3)_2NOH$, traces of $(CF_3)_2NH$ and $(CF_3)_2NON(CF_3)_2$, a colourless gas [15% by weight of the products] and a high boiling oil. The colourless gas and the oil were found to be mixtures displaying i.r. absorptions in the region 1600-1800 cm^{-1} indicating some form of unclarified unsaturation.

Subsequent to this work a report[50] on this reaction appeared which stated that "the product $(CF_3)_2NONMe_2$ was formed if the reaction ampoule was allowed to warm up overnight from -65°C. At room temperature, especially if set aside for about a day, a heavy intractable oil was formed." The phraseology used renders the report somewhat ambiguous, and no further clarification was given.

A careful study of this reaction[51], since carried out in this Department, at low temperature (-78°C to -40°C), resulted in a complex mixture of products which included material containing $(CF_3)_2NO$ groups. An extensive spectroscopic investigation failed to detect any $(CF_3)_2NONMe_2$ in the product mixture.

18.   AROMATIC AMINES

Diphenylamine, 4,4'-dicumyl-, 4,4'-dimethoxy- and 4,4'-dinitrodiphenylamine[51] react rapidly with $(CF_3)_2NO^\bullet$ even at low temperatures (below $-20°C$) giving in all cases $(CF_3)_2NOH$ (10-43%) and $(CF_3)_2NH$ (21-32%) as the only isolable products; intractable multi-component tars containing the corresponding amine and compounds with $(CF_3)_2NO$ groups were also formed.

In no reaction was the corresponding stable diarylamino-oxyl found. Consequently a reaction mechanism involving formation of $Ar_2NON(CF_3)_2$ and $Ar_2NO^\bullet$ and $(CF_3)_2N^\bullet$ as intermediates was considered doubtful. Alternative routes were suggested, e.g. Scheme 15.
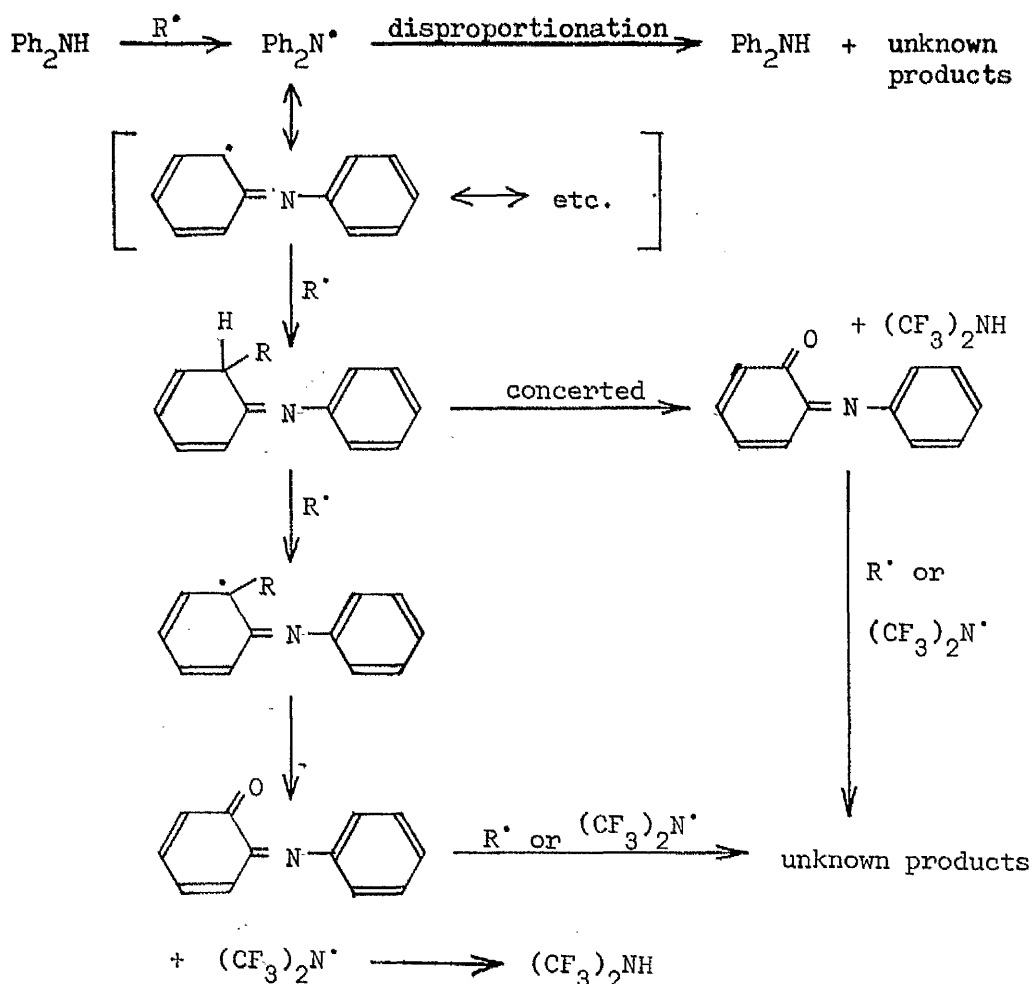
19. ACETANILIDE

Acetanilide[51] reacts in a similar way to the diarylamines, giving $(CF_3)_2NOH$, $(CF_3)_2NH$, a trace of $(CF_3)_2NON(CF_3)_2$, unreacted acetanilide and tar.

20. HYDRAZOBENZENE

Reaction of $(CF_3)_2NO^{\bullet}$ with hydrazobenzene[44] gives, on warming from -196°C to room temperature:

$$PhNHNHPh + 2R^{\bullet} \xrightarrow{CCl_4} PhN=NPh + 2RH + \text{some tar}$$
$$82\%$$
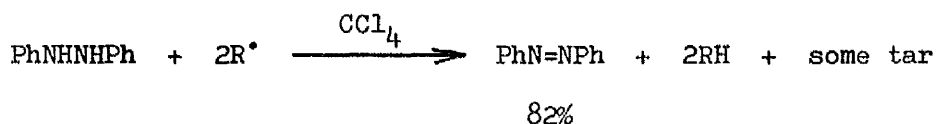
The tarry material is thought to originate from attack of $(CF_3)_2NO^{\bullet}$ on the aromatic nucleus of azobenzene since, in a separate experiment, $(CF_3)_2NO^{\bullet}$ was found to attack azobenzene at room temperature to give an intractable tar.

21. PHTHALIMIDE

$(CF_3)_2NO^{\bullet}$ failed to abstract the amido hydrogen from phthalimide[51] (almost quantitative recovery of reactants after 20 hours at room temperature), probably because of the very high N-H bond energy (ca. 100 kcal mole^{-1}).

22. BENZENE

Benzene was originally reported to be inert to $(CF_3)_2NO^{\bullet}$ attack.[2] Russian workers,[29,46] however, have claimed to have isolated the 1,2,4-trisubstituted product from the reaction.

More recent work,[36b,44] in this Department, has shown that the reaction gives an oil containing at least nine components, and $(CF_3)_2NOH$, suggesting that both hydrogen abstraction and addition to the aromatic

system take place. The oil was found to contain approximately 4 $(CF_3)_2NO$ groups per molecule and was postulated to be a mixture of olefinic and dienic compounds.

On the basis of a later reaction which gave 4% $(CF_3)_2NON(CF_3)_2$ in the products it has been suggested that carbonyl compounds are amongst the extremely complex products.

23. HALOGENATED BENZENES

Russian workers have reported the following reactions:

Fluorobenzene,[46] after 2-3 days with $(CF_3)_2NO\cdot$ at room temperature gives 12% of (bistrifluoromethylamino-oxy)-fluorobenzene.

Pentafluorochlorobenzene,[43] after 1-4 hours with $(CF_3)_2NO\cdot$ at 150°C gives $ClC_6F_5R_2$, $ClC_6F_5R_4$ (2 isomers) and $ClC_6F_5R_6$.

Hexafluorobenzene,[43] after 1-4 hours with $(CF_3)_2NO\cdot$ at 150°C gives $C_6F_6R_2$ (2 isomers), $C_6F_6R_4$ (2 isomers) and $C_6F_6R_6$.

Shaw,[36b] in this Department, observed rather similar products.

$$C_6F_6 \ + \ 6R\cdot \ \xrightarrow[\substack{\text{followed by 120°C} \\ \text{for 14 days}}]{\text{80°C for 14 days}} \ C_6F_6R_6 \ + \ C_6F_6R_4$$

$$50\% \qquad 41\%$$

$$+ \ R\cdot$$

$$25\% \ \text{rec.}$$
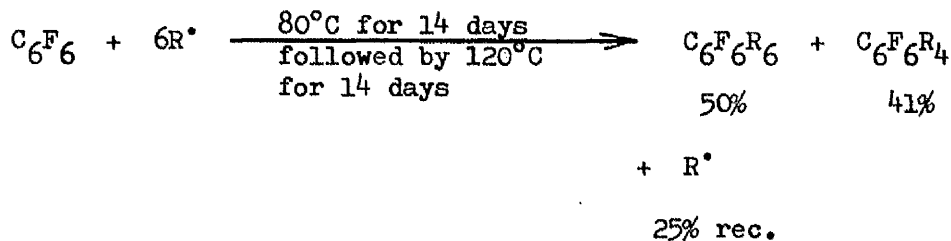
24. ALKYLBENZENES

$(CF_3)_2NO\cdot$ prefers to abstract benzylic hydrogens from toluene,[17] 2,3,4,5,6-pentafluorotoluene[36b] and cumene[52] rather than attack their ring systems.

The reaction between toluene and $(CF_3)_2NO\cdot$ was studied in depth.[53]

$$PhCH_3 + 2R^\bullet \xrightarrow[\text{exothermic}]{\text{rapid}} PhCH_3 + PhCH_2R + PhCOR + RH$$

$$\phantom{PhCH_3 + 2R^\bullet \xrightarrow[\text{exothermic}]{\text{rapid}} PhCH_3}\text{7\% rec.}\quad\text{65\%}\quad\text{3\%}\quad\text{48\%}$$

$$+ \text{ traces } (CF_3)_2NON(CF_3)_2 + (CF_3)_2NH$$

$$PhCH_3 + 6R^\bullet \longrightarrow PhCHR_2 + PhCOR + R^\bullet + RH$$

$$\text{10\%}\quad\text{64\%}\quad\text{10\% rec.}\quad\text{47\%}$$

$$+ (CF_3)_2NON(CF_3)_2$$

$$\text{27\%}$$

To confirm that PhCOR is formed via $PhCH_2R$ and PhCHO as intermediates, rather than via $PhCH_2R$ and $PhCHR_2$ these two latter compounds were also reacted with $(CF_3)_2NO^\bullet$. The ease of substitution of aldehydic hydrogens had already been discovered.[27]

$\underline{(CF_3)_2NO^\bullet \text{ with } PhCH_2ON(CF_3)_2}$ [53]

This reaction proceeded smoothly at room temperature, although it was slower and less exothermic than that between the amino-oxyl and toluene.

$$PhCH_2R \xrightarrow{2R^\bullet} PhCOR + PhCHR_2 + RH + R^\bullet + PhCH_2R$$

$$\phantom{PhCH_2R \xrightarrow{2R^\bullet}}\text{71\%}\quad\text{14\%}\quad\text{44\%}\quad\text{4\% rec.}\quad\text{40\% rec.}$$

$$\big\downarrow 4R^\bullet \qquad\qquad\qquad + (CF_3)_2NON(CF_3)_2$$

$$\text{38\%}$$

$$PhCOR + PhCHR_2 + RH + R^\bullet + (CF_3)_2NON(CF_3)_2$$

$$\text{78\%}\quad\text{18\%}\quad\text{77\%}\quad\text{9\% rec.}\quad\text{42\%}$$

$\underline{(CF_3)_2NO^\bullet \text{ with } PhCH[ON(CF_3)_2]_2}$ [53]

This reaction occurred only slowly at room temperature, 85% of $PhCHR_2$ being recovered after 14 days. Abstraction of hydrogen occurred as indicated by the formation of 33% $(CF_3)_2NOH$, but the yield of PhCOR, the only identifiable non-volatile product, was only 4%. This ruled out $PhCHR_2$ as an important intermediate in the formation of PhCOR and confirmed

that the overall mechanism for the reaction of toluene with $(CF_3)_2NO^{\bullet}$ is as shown in Scheme 16.

$$PhCH_3 \xrightarrow{\ R^{\bullet}\ } Ph\overset{\bullet}{C}H_2 \xrightarrow{\ R^{\bullet}\ } PhCH_2R \xrightarrow{\ R^{\bullet}\ } Ph\overset{\bullet}{C}HR \xrightarrow{\ R^{\bullet}\ } PhCHR_2$$

$\downarrow$ β-scission

$$PhCHO \quad + \quad (CF_3)_2N^{\bullet}$$

$\downarrow R^{\bullet} \qquad\qquad \downarrow R^{\bullet}$

Scheme 16

$$Ph\overset{\bullet}{C}=O \qquad (CF_3)_2NON(CF_3)_2$$

$\downarrow R^{\bullet}$

$$PhC=O$$
$$|$$
$$R$$
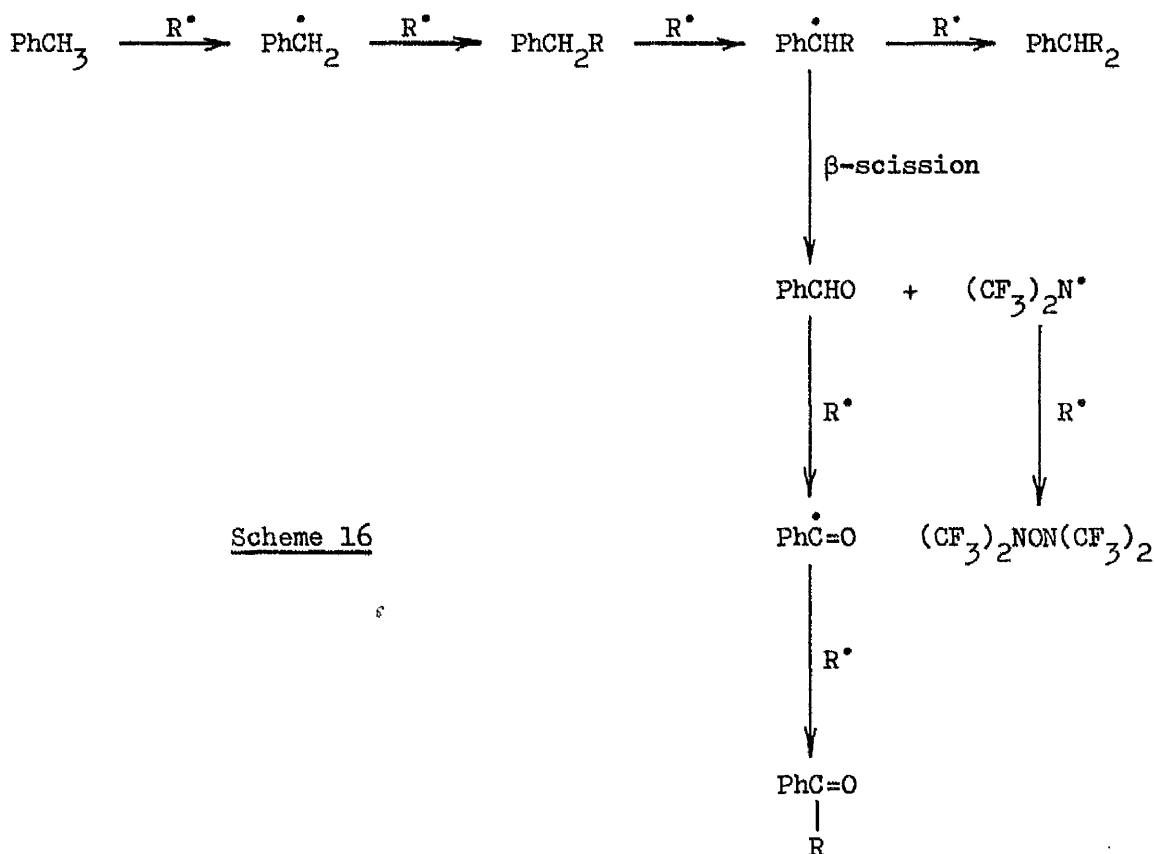
The reactivity order $PhCH_3 > PhCH_2R \gg PhCHR_2$ with respect to abstraction of a benzylic hydrogen atom by $(CF_3)_2NO^{\bullet}$ may be ascribed primarily to a polar effect, the transition state being represented by[53]

$$[(CF_3)_2NO^{\bullet} \quad H:CX_2Ph \iff (CF_3)_2N\overset{-}{O:} \quad \overset{\bullet}{H} \quad \overset{+}{C}X_2Ph]$$
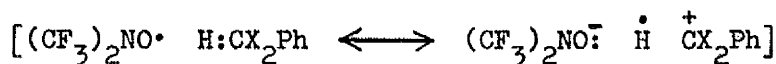
where $X = H$ or $(CF_3)_2NO$.

In these reactions $(CF_3)_2NO^{\bullet}$ is behaving as an electrophilic radical, in line with Justin's suggestion.[26b] The resonance form on the right would be expected to assume importance in this reaction[54] where $(CF_3)_2NO^{\bullet}$ is a relatively unreactive (selective) species forming a weakish bond [i.e. $(CF_3)_2NO-H$[55] ... ca. 71 kcal mole^{-1}], therefore

suggesting a considerable amount of bond breaking in the transition state.[56]

Another possible explanation for the observed resistance to abstraction of the $PhCHR_2$ benzylic hydrogen is the steric crowding created by the two amino-oxy groups.[57] A combination of both steric and polar factors might be responsible.

<u>2,3,4,5,6-pentafluorotoluene</u>[53] is noticeably more resistant to attack by $(CF_3)_2NO^{\bullet}$ than toluene or p-chlorotoluene, presumably owing to the relatively powerful polar effect of the C_6F_5 group.

$$C_6F_5CH_3 \ + \ 2R^{\bullet} \ \longrightarrow \ C_6F_5CH_2R \ + \ RH \ + \ C_6F_5CH_3 \ + \ C_6F_5CHR_2$$

$$\qquad\qquad\qquad\qquad\qquad\quad 76\% \qquad 44\% \quad 18\% \ rec. \qquad trace$$

$$+ \ (CF_3)_2NON(CF_3)_2$$

$$trace$$
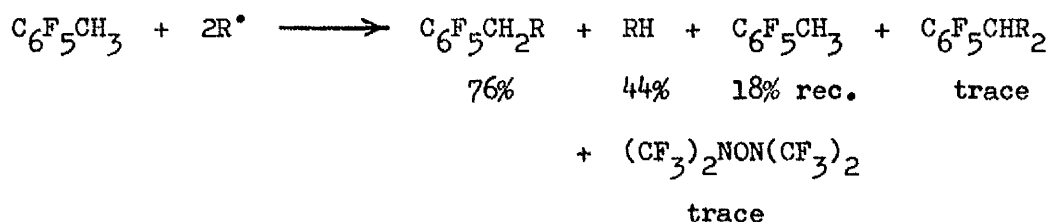
Reaction of the monosubstituted $C_6F_5CH_2R$ with $(CF_3)_2NO^{\bullet}$ over 2 days gave 3% C_6F_5COR, 39% $C_6F_5CHR_2$, $(CF_3)_2NON(CF_3)_2$, $(CF_3)_2NOH$ and unsaturated multi-component high boiling material.

<u>p-Chlorotoluene</u>

The introduction of a <u>para</u>-chlorine substituent does not affect the reaction pattern.[53]

Reaction of $(CF_3)_2NO^{\bullet}$ with the monosubstituted $p\text{-}ClC_6H_4CH_2R$ gives a relatively higher yield of the compound $p\text{-}ClC_6H_4CHR_2$ than in the corresponding reaction of $(CF_3)_2NO^{\bullet}$ with $C_6H_5CH_2R$. This is ascribed[57] to the stabilisation of the intermediate radical by the ring chlorine, leading to a greater part of it being scavenged before it can undergo β-scission.

<u>Cumene</u>[52] reacts readily with $(CF_3)_2NO^{\bullet}$ at room temperature as follows:

$$PhCHMe_2 \ + \ 2R^{\bullet} \ \longrightarrow \ PhCRMe_2 \ + \ RH \ + \ PhCHMe_2 \ + \ yellow \ oil$$

$$\qquad\qquad\qquad\qquad\qquad\quad 70\% \qquad\qquad 28\% \ rec. \qquad 11\%$$
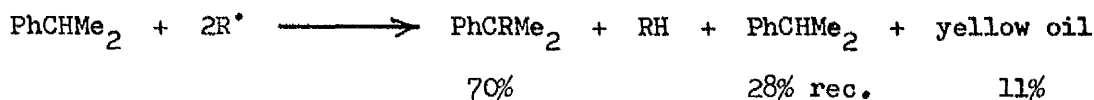
Ethylbenzene

A rapid, exothermic reaction occurs between $(CF_3)_2NO^\bullet$ and ethylbenzene (2:1 molar ratio) giving mainly PhCHRMe (75%), PhCHRCH$_2$R (6%) and $(CF_3)_2NOH$ (49%).[53]

The monosubstituted derivative PhCHRMe was found to react only slowly with $(CF_3)_2NO^\bullet$ to give mainly acetophenone (76%) plus the disubstituted PhCHRCH$_2$R (19%), $(CF_3)_2NON(CF_3)_2$ and $(CF_3)_2NOH$. It was therefore concluded that the monosubstituted derivative is not an important intermediate in the formation of PhCHRCH$_2$R and that the reaction mechanism is analogous to that adopted for the reaction of certain alkanes with $(CF_3)_2NO^\bullet$,[26] i.e. according to Scheme 17.

$$PhCH_2CH_3 \xrightarrow{R^\bullet} Ph\overset{\bullet}{C}HCH_3 \xrightarrow{R^\bullet} PhCH=CH_2 \xrightarrow{2R^\bullet} \underset{\underset{R}{|}}{PhCHCH_2R}$$

$$Ph\overset{\bullet}{C}HCH_3 \xrightarrow{R^\bullet} \underset{\underset{R}{|}}{PhCHCH_3}$$
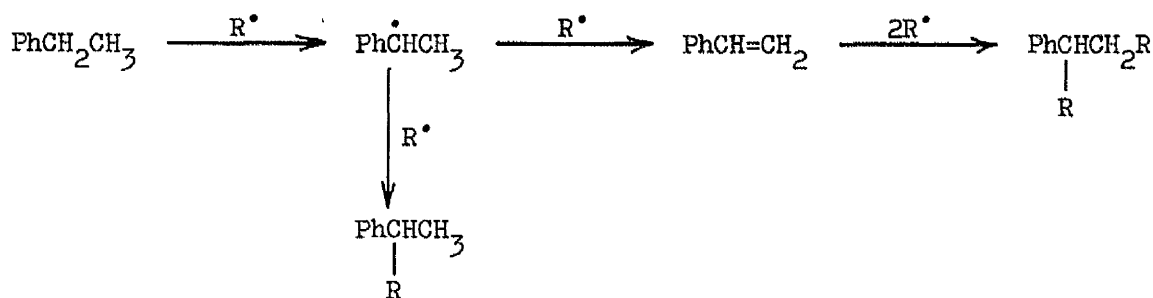
Scheme 17

25.   FLUORINATED HETEROCYCLES

Pentafluoropyridine[36]

$$\xrightarrow{R^\bullet/80^\circ C/7 \text{ days}} \quad 97\%$$
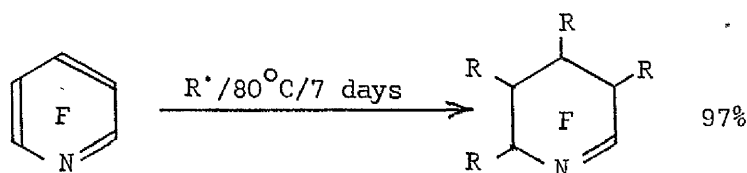
Pentafluoropyridine with chlorine under ultraviolet light gives an analogous reaction.

The C=N bond in perfluoro-imines seems generally resistant to radical attack. e.g. Perfluoro-2,3,4,5-tetrahydropyridine can be recovered in high yield after treatment with $(CF_3)_2NO^{\bullet}$ at 80°C for long periods or with chlorine under u.v. light.[36] This can be compared with the carbon analogue perfluorocyclohexene which can be converted fairly readily into $C_6F_{10}X_2$[36] $[X = Cl$ or $(CF_3)_2NO]$.

Tetrafluoro-4-methylpyridine[36b]

In this reaction competition occurs between hydrogen abstraction from the methyl group and addition to the ring system. All the products retain the C=N bond.
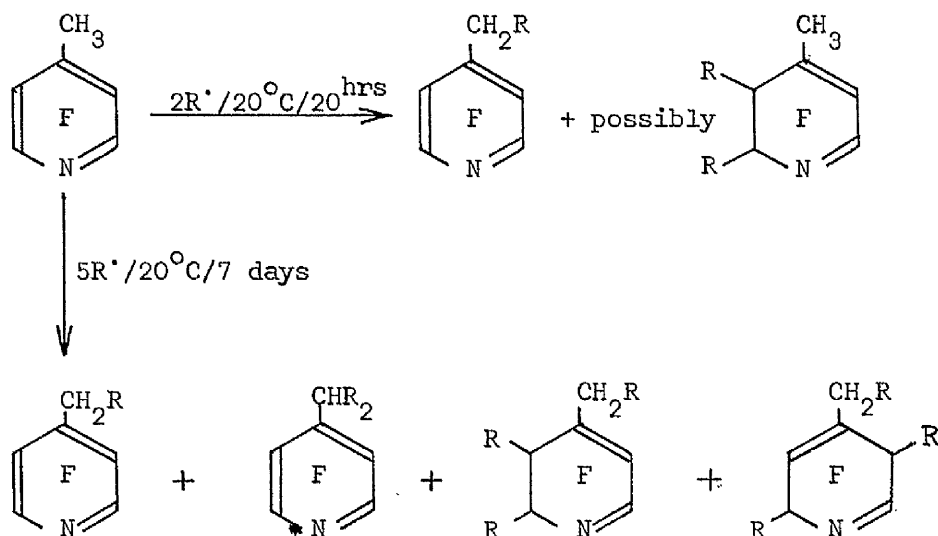
Tetrafluoropyrimidine

There was little reaction at room temperature or after 9 days at 100°C. At 130°C (10-14 days) pyrolysis of the product gave a complex mixture. Eventually, after 35 days at 90°C, a product analysing as $C_4F_4N_2R_2$ was obtained (93%). Mainly on the basis of the i.r. spectrum it was thought to contain several of the following isomers.

The formation of the last three of these isomers can be rationalised via F⁻ isomerisation,
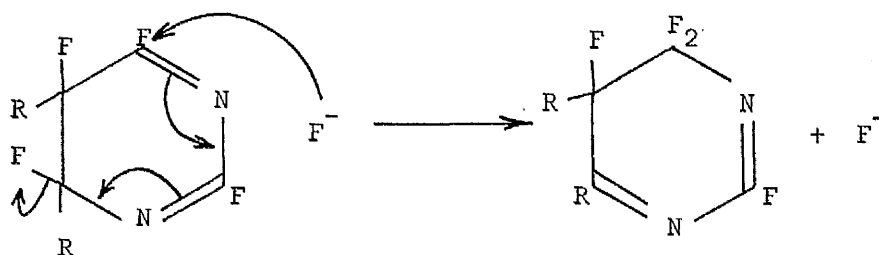
the traces of fluoride ion being produced by reaction between tetrafluoro-pyrimidine and traces of moisture on the glass.

BISTRIFLUOROMETHYLAMINO-OXYL AS A PSEUDO-HALOGEN

Much of the chemistry of $(CF_3)_2NO^{\bullet}$ can be predicted on the basis that it behaves as a pseudo-halogen.[58,59] For instance, $(CF_3)_2NO^{\bullet}$

(a) combines with hydrogen to form an acid $(CF_3)_2NOH$ which may be oxidised to the free radical either chemically or electrochemically,

(b) combines with some metals to form salts,

(c) forms covalent compounds, with a variety of non-metals, which resemble the corresponding halides in their composition and in their physical and chemical behaviour,

(d) easily undergoes addition to double bonds and abstracts hydrogen from organic and inorganic substances,

(e) will displace bromine and iodine from certain bromides and iodides, and in a few instances chlorine from chlorides.

Its oxidising power has been placed in the series

$$F_2 > Cl_2 \geqslant (CF_3)_2NO^{\bullet} > Br_2 > (CN)_2 > (SCN)_2 > I_2.$$
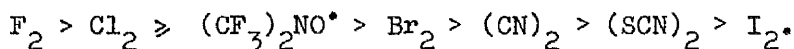
The electronegativity of the $(CF_3)_2NO$ group has been measured, as an approximation, from the infrared spectra of phosphoryl and carbonyl bistrifluoromethylamino-oxy compounds and placed in a series of decreasing electronegativity as follows:

$$F > (CF_3)_2NO > CF_3 > C_3F_7 > Cl > Br > C_2H_5 > CH_3.$$
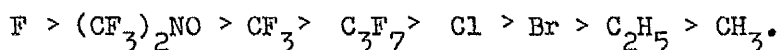
REAGENTS OTHER THAN BISTRIFLUOROMETHYLAMINO-OXYL USED FOR THE INTRODUCTION OF THE $(CF_3)_2NO$ GROUP INTO COMPOUNDS

(a)   N,N-Bistrifluoromethylhydroxylamine, $(CF_3)_2NOH.$[3b]

(b)   The adduct of $(CF_3)_2NOH$ with Caesium Fluoride or Potassium Fluoride.

(c)   Sodium Bistrifluoromethylnitroxide,[62] $(CF_3)_2NO^{-}Na^{+}$.

(d)   Mercury(II) Bistrifluoromethylnitroxide,[63] $[(CF_3)_2NO]_2Hg$.

(e)   Perfluoro-(2,4-dimethyl-3-oxa-2,4-diazapentane),[17,64]

$(CF_3)_2NON(CF_3)_2.$

The reactions of bistrifluoromethylamino-oxyl with inorganic compounds have been covered by several reviews.[59,65]

RESULTS AND DISCUSSION

RESULTS AND DISCUSSION, PART I

INTRODUCTION

Transition states in disproportionation and combination

When organic free radicals are produced in a reaction they eventually undergo a termination reaction producing stable molecules. The paths available to a pair of radicals are combination and, if one of the radicals has a hydrogen atom β to the radical centre, disproportionation.

$$XCH_2CH_2{}^\bullet \;+\; Y^\bullet \longrightarrow \begin{cases} XCH_2CH_2Y & \cdots\cdots\cdots \text{combination} \\[2ex] XCH=CH_2 \;+\; YH & \cdots\cdots \text{disproportionation} \end{cases}$$
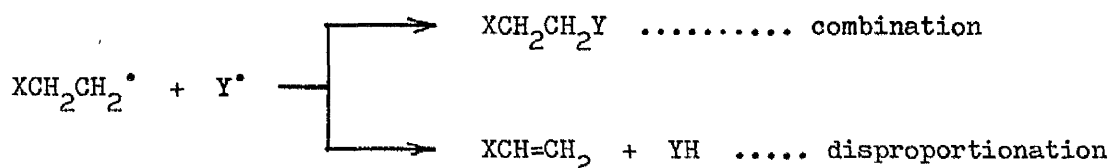
Disproportionation, formally a radical hydrogen abstraction, is more exothermic than a normal hydrogen abstraction.[66]

An indication of the activated complexes was given by the products of the disproportionation of $CH_3CD_2{}^\bullet$ radicals. As all the ethylene formed was $CH_2=CD_2$ it was concluded that a head-to-tail complex was involved.[67,68]

The similarity in the pre-exponential factors for disproportionation and combination (A $\sim 10^{11}$) implies that the radicals in the activated complexes of both processes enjoy the same freedom of movement and that this freedom of movement is considerably greater than that in the activated complex of a typical hydrogen abstraction process (A $\sim 10^8$).[66] Several workers,[69,70] considering that this freedom is not easily reconciled with a head-to-tail structure, have proposed four-centred transition states.

$$2CH_3CH_2^{\bullet} \longrightarrow \begin{array}{c} CH_2 \text{----} H \\ \| \quad\quad | \\ \| \quad\quad | \\ CH_2 \text{----} CH_2 \text{----} CH_3 \end{array} \longrightarrow \begin{cases} CH_2{=}CH_2 \ + \ CH_3CH_3 \\[4pt] CH_3CH_2CH_2CH_3 \end{cases}$$
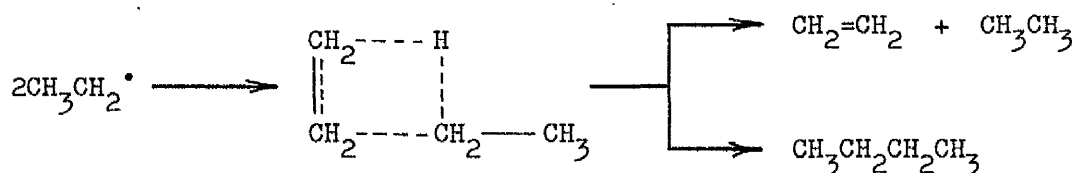
Opinions differ as to whether the transition state is directly identifiable with an excited dimer.[71]

Benson[72] ruled out such models on the basis of a number of observations. He used the approach of regarding radical combination as the reverse of unimolecular decomposition of the dimer. Analysing the transition state for $C_2H_6 \rightleftharpoons 2CH_3^{\bullet}$ he concluded that it is too loose to fit into a framework of normally strongly oriented, covalent bonds, and proposed that at distances involved in the transition state the interactions between the alkyl groups must involve a good deal of ionic character. As the efficiencies of disproportionation and combination are about equal Benson[72] proposed structures such as

$$\underset{H}{\overset{H}{\underset{|}{\overset{|}{CH_3{-}C{:}^{-}}}}} \qquad \underset{H}{\overset{H}{\underset{|}{\overset{|}{H{-}C}}}}{-}\underset{H}{\overset{H}{\underset{|}{\overset{+}{C}}}}{<}\overset{H}{_{H}} \longrightarrow \underset{H}{\overset{H}{\underset{|}{\overset{|}{CH_3{-}C^{+}}}}} \qquad \underset{H}{\overset{H}{\underset{|}{\overset{|}{H{-}C}}}}{-}\underset{H}{\overset{H}{\underset{|}{\overset{\cdot\cdot}{C}}}}{<}\overset{H}{_{H}}$$
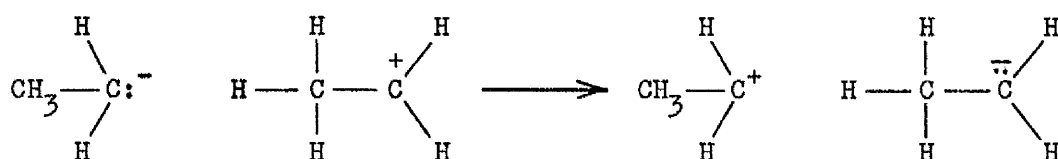
within the activated complex for disproportionation.

However, recent estimates[73,74] of the combination rate constants of higher alkyl radicals have shown them to be well below that for methyl radicals, suggesting much tighter and more orientated transition states for both combination and disproportionation than was previously assumed.

Whether combination and disproportionation proceed via a common or two distinctly different transition states is an argument yet to be resolved. If the latter is the case it would seem that the energies and volumes of the two transitions are very similar.[75]

The high efficiencies of combination and disproportionation

reactions have led a number of workers[66] to conclude that the activation

energies must be close to zero. This calls into question the validity of

the conventional transition state, defined by the saddle point of the

potential energy hypersurface, in describing combination and disproportion-

ation. When a process proceeds without an activation energy the potential

energy hypersurface exhibits a plateau instead of a saddle point, and

the transition state is "loose".[76]

Disproportionation versus combination as a function of structure

Most of the information available for the relation between

disproportionation to combination ratios and structure relates to pairs

of alkyl radicals. Most of the k_d/k_c (rate of disproportionation

compared to rate of combination) ratios have been measured in the gas

phase, many fewer in solution.

Alkyl-alkyl radical reactions

A much quoted generalisation is that for alkyl radicals there

is an almost quantitative correlation between k_d/k_c and the number of β-

hydrogens available for the disproportionation reaction. This was based

on early k_d/k_c values[77] since shown to be inaccurate.[66]

Available data for pairs of the same radicals in both gas phase

and liquid solution (solvents n-pentane and decalin) are given in

Table 3.[66]

For both sets of values it can be seen that while there is no

quantitative relation between k_d/k_c and numbers of β-hydrogens, the

k_d/k_c values remain within a narrow range for primary, secondary and

tertiary radicals and that k_d/k_c increases going from primary to secondary

to tertiary radicals.

Disproportionation-combination reactions between radicals other

than two alkyls have not been as well studied. The following have been

reported.

Table 3

Radical	gas phase		liquid solution	
	k_d/k_c	k_d/k_c per β-H	k_d/k_c	k_d/k_c per β-H
$CH_3CH_2^\bullet$	0.13	0.022	0.15,0.12	0.025,0.020
$CH_3CH_2CH_2^\bullet$	0.15	0.038	0.15,0.13	0.038,0.032
$CH_3CH_2CH_2CH_2^\bullet$	0.14	0.035	0.14,0.13	0.035,0.032
$Me_2CHCH_2^\bullet$	0.076	0.037		
$CH_3\overset{\bullet}{C}HCH_3$	0.66	0.055	1.2	0.10
$CH_3CH_2\overset{\bullet}{C}HCH_3$	0.63,0.77	0.063,0.077	1.0,1.1	0.10,0.11
$Me_3C^\bullet$	2.3,3.1,2.7	0.13,0.17,0.15	7.2	0.4
$CH_3CH_2\overset{\bullet}{C}Me_2$	2.2	0.14		
$Me_2CHCH_2\overset{\bullet}{C}Me_2$	3.6	0.22		

Alkyl-alkoxy radical reactions

Values of k_d/k_c for alkyl-alkoxy radical pairs have been found to be approximately twice as large as those for alkyl-alkyl radical pairs. Related transition states for disproportionation have been proposed:[78]
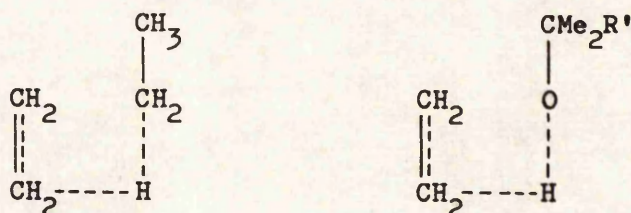
The latter is somewhat unexpected as alkoxy radicals generally show considerably different selectivities to alkyl radicals. This discrepancy can be minimised if bond breaking has not proceeded very far in the transition state of the disproportionation reaction, a conclusion

consistent with the large exothermicity of the reaction.

Alkoxy-alkoxy radical reactions

Alkoxy radicals have been found to give very high k_d/k_c values. The k_d/k_c ratio for ethoxy radicals has been found to be 12 ± 2,[79] and that for methoxy radicals to be greater than 60.[80] It has been suggested[80] that the very polar character of the alkoxy radical leads to an appreciable dipole-dipole interaction which effectively orients approaching alkoxy radicals to favour disproportionation over combination. The increased polar contributions to the transition state for disproportionation can be expressed as:
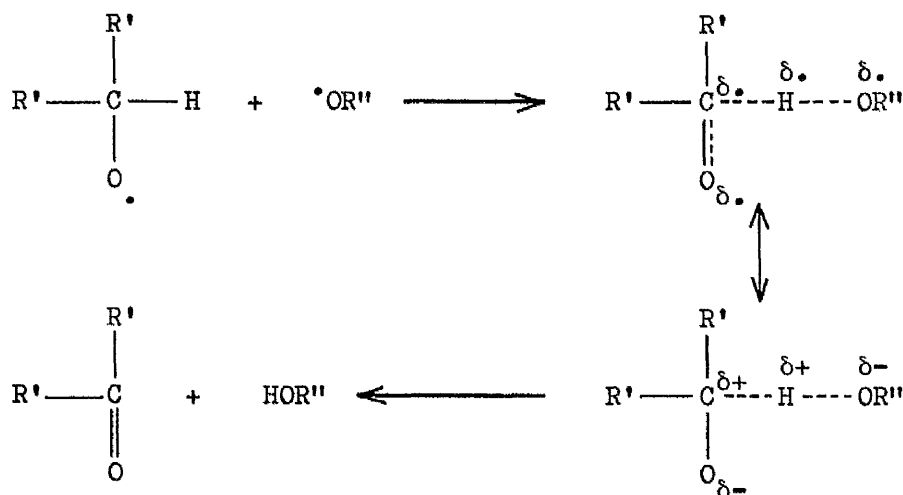
Alkoxy radicals with nitric oxide

The k_d/k_c ratios for a number of alkoxy radicals with NO are given in Table 4. The k_d/k_c ratio divided by the number of β-Hs is approximately constant. This is not unexpected as the radicals are all of the same type, i.e. not primary, secondary and tertiary radicals.

Radical	k_d/k_c	k_d/k_c per β-H	Ref.
$CH_3O^\bullet$	0.5	0.17	81
$CH_3CH_2O^\bullet$	0.3	0.15	81
$Me_2CHO^\bullet$	0.16	0.16	82
$EtMeCHO^\bullet$	0.26	0.26	83
$CH_3CH_2CH_2O^\bullet$	0.4-0.5	0.2-0.25	84

Difluoroamino radicals with isopropyl and t-butyl radicals

The k_d/k_c ratio of isopropyl radicals with $\overset{\bullet}{N}F_2$ radicals was found to be less than that of t-butyl radicals with $\overset{\bullet}{N}F_2$, as expected.[85] The rates of disproportionation and combination were both found to be very slow which was taken as indicating a connection between the transition states for disproportionation and combination. It was thought that the reaction could possibly be occurring via an energised molecule:

$$Me_2CH^\bullet + \overset{\bullet}{N}F_2 \longrightarrow Me_2CH\text{-}NF_2^* \longrightarrow \begin{array}{l} CH_3CH=CH_2 + HNF_2 \\ \\ Me_2CHNF_2 \end{array}$$
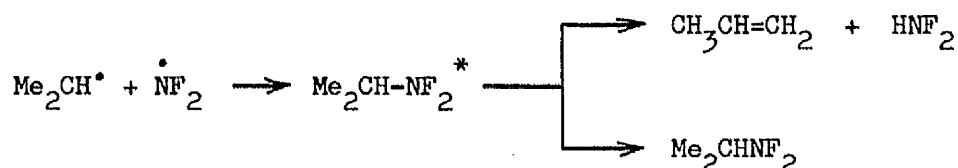
Disproportionation-combination reactions have also been reported to occur between alkyl and amino radicals,[86] alkyl and $CF_3^\bullet$ radicals[87] and between alkyl and bistrifluoromethylamino-oxyl radicals.[26,28] This last set of reactions provides the starting point for the research described in this thesis and is considered in detail in the next section.

Disproportionation-combination reactions of alkyl radicals with bistrifluoromethylamino-oxyl, $(CF_3)_2NO^\bullet$

The reactions of bistrifluoromethylamino-oxyl with a number of

alkanes were first studied by Justin.[26] The reaction with isobutane was studied in depth and the scheme shown below was proposed to explain the formation of the observed products.

$$Me_3CH \xrightarrow{R^\bullet} Me_3C^\bullet \xrightarrow[R^\bullet]{disproportionation} CH_2=CMe_2$$

combination $\Big\downarrow R^\bullet$

Me_3CR

$CH_2=CMe_2 \Big\downarrow R^\bullet$

$RCH_2-\overset{\bullet}{C}Me_2$

$\Big\downarrow R^\bullet$

$RCH_2-\underset{R}{\overset{|}{C}}Me_2$
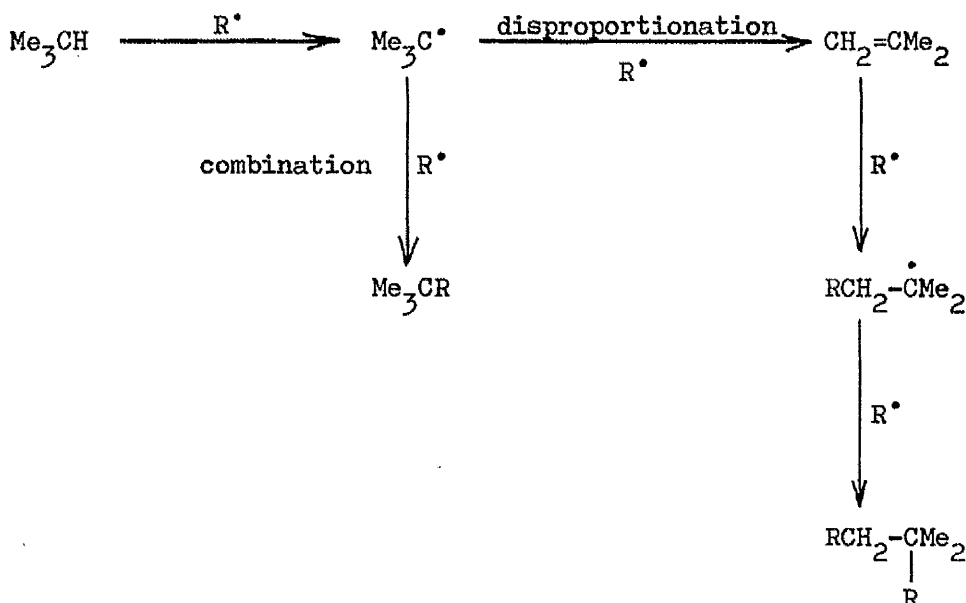
Scheme 18

Other possible reaction schemes involving Me_3CR or Me_2CHCH_2R as intermediates in the formation of the di-amino-oxy product were discarded as although both these compounds were found to react with $(CF_3)_2NO^\bullet$ to give the di-amino-oxy compound, both reactions were found to be too slow to make a significant contribution.

In the reaction of isobutane with $(CF_3)_2NO^\bullet$ Justin did not detect isobutene in the reaction products, but he did trap the alkene using hydrogen chloride gas, obtaining 96% t-butyl chloride.[26]

These reactions were repeated by Brown[28] who observed the same products although in slightly different yields (see Table 5). In the reaction using a 2:1 molar ratio of $(CF_3)_2NO^\bullet$ to isobutane he also observed a small amount (3%) of the carbonyl compound Me_2CRCOR from further reaction of the di-amino-oxy compound RCH_2CRMe_2 with $(CF_3)_2NO^\bullet$.

Using an equimolar ratio of $(CF_3)_2NO^\bullet$ to isobutane he obtained a

significant amount (8%) of the allylic substitution product $RCH_2C(Me)=CH_2$.

Coles,[88] in a preliminary kinetic study of this reaction observed

the presence of traces of isobutene in the products using g.l.c.

Owen,[89] in a much more detailed kinetic study of the reaction, observed

combination $[Me_3CR]$ and disproportionation $[Me_2CRCH_2R$ and $CH_2=C(Me)CH_2R]$

products. He found the overall reaction to be complex and investigated

the kinetic behaviour only for the initial rates of reaction, concluding

that the reaction is second order, being first order with respect to both

isobutane and the amino-oxyl, over the temperature range used. He

suggested a slightly modified reaction scheme, incorporating formation

of the allylic substitution product.
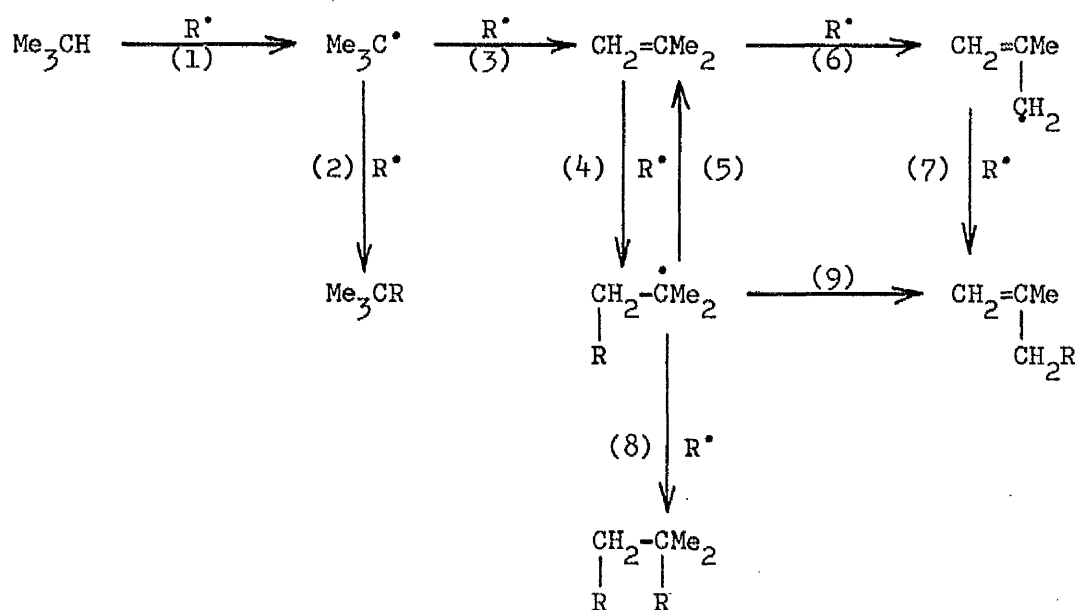
Scheme 19

He suggested that reversibility of addition to the double bond is possible

at high temperature (step 5), favouring the allylic abstraction (step 6),

and also that at higher temperatures a second route (step 9,

disproportionation) leading to the allylic product becomes significant.
Other alkanes[26] (ethane, propane and isopentane) which were found to give
mono- and di-amino-oxy products were presumed to react via a similar
mechanism. Carbonyl compounds were also found among the products of the
ethane andpropane reactions and were shown to be formed by further attack
of $(CF_3)_2NO^\bullet$ on the mono-amino-oxy compounds.

The ratio of the combined yields of the di-amino-oxy products
to the combined yields of the combination products gives a measure of the
relative rates of disproportionation to combination (k_d/k_c ratios) for
reaction of the intermediate alkyl radicals with $(CF_3)_2NO^\bullet$. These are
tabulated below for reactions in which a 2:1 molar ratio of $(CF_3)_2NO^\bullet$
to alkane was used.

Table 5

Alkyl radical	no. of β-Hs	% combination products	% disprop. products	$\dfrac{k_d}{k_c}$	k_d/k_c per β-H	reference
$CH_3CH_2^\bullet$	3	69	11	0.16	0.05	26
$Me_2CH^\bullet$	6	63	23	0.37	0.06	26
$Me_3C^\bullet$	9	39,26	51,70	1.31,2.69	0.15,0.30	26,28
$Me_2\overset{\bullet}{C}Et$	8	28	58	2.07	0.26	26

Again there is no quantitative relation between k_d/k_c and numbers of
β-hydrogens but as with the radicals already considered k_d/k_c increases
going from primary to secondary to tertiary radicals.

Similar schemes to that of isobutane with $(CF_3)_2NO^\bullet$, involving
alkene intermediates, have been proposed for reactions of $(CF_3)_2NO^\bullet$ with
ethylbenzene[53] and with various cycloalkanes.[28]

The tendency of alkyl and $(CF_3)_2NO^\bullet$ radicals to disproportionate
has been attributed to[26]

(a)   the high concentration of the $(CF_3)_2NO^\bullet$ radical,

(b)   the low strengths of the C-H bonds adjacent to the radical centre,

(c)   steric effects, and

(d)   the low O-H bond strength in $(CF_3)_2NOH$ which is thought to be in the region of 71 kcal/mole, a value in keeping with the high selectivity of $(CF_3)_2NO^\bullet$.

REACTIONS OF BISTRIFLUOROMETHYLAMINO-OXYL WITH ALKANES AND SUBSTITUTED

ALKANES OF GENERAL FORMULA Me_2CHCH_2X

These reactions were all carried out initially using a 2:1 molar
ratio of bistrifluoromethylamino-oxyl to alkane or substituted alkane in
300 cm^3 sealed tubes. The reactants were allowed to warm from $-196°C$
to room temperature and left in the dark, overnight in most cases, to
proceed to completion.

The products were examined initially by g.l.c. Unreacted substrate
and N,N-bistrifluoromethylhydroxylamine were identified and their yields
calculated by comparative g.l.c. In most of the reactions the other major
products were isolated by preparative g.l.c. and identified by their
n.m.r. and i.r. spectra, and by g.l.c.-mass spectral data. In a few
unambiguous cases the products were identified from their mass spectra
alone or by comparative g.l.c. Minor products were identified, where
possible, from their mass spectra. Yields of the amino-oxy substituted
compounds were based on g.l.c. peak areas. In the reactions of
$(CF_3)_2NO^•$ with (i) 2,2,4-trimethylpentane, (ii) isobutyl acetate,
(iii) isopentyl bromide and (iv) isohexyl bromide sufficient quantities
of mono- and di-amino-oxy substituted compounds were isolated for mixtures
of these compounds to be compared directly by g.l.c. In all four cases it
was found that, within experimental error, equimolar amounts of mono-
and di-amino-oxy compounds gave g.l.c. peaks of equal area. Kosinski[90]
found a similar relationship for mono- and di-amino-oxy substituted
cycloalkanes and cycloalkenes.

Full practical details for all the reactions discussed are given
in the experimental section. Spectroscopic data are recorded in the
appendices.

Yields for the products are given as percentages. For N,N-

bistrifluoromethylhydroxylamine, $(CF_3)_2NOH$, yields are based on $(CF_3)_2NO^•$ used. For unreacted substrate the percentage is based on substrate used in the reaction. For $(CF_3)_2NO$-substituted compounds percentage yields are based on substrate reacted.

1. <u>Reaction of $(CF_3)_2NO^•$ with isohexane</u>

This reaction was carried out twice as summarised below.

$$Me_2CHCH_2CH_2CH_3 \;+\; 2R^• \longrightarrow Me_2CHCH_2CH_2CH_3$$

(a) 42%, (b) 44% unreacted

$$+\quad Me_2\underset{R}{\overset{|}{C}}CH_2CH_2CH_3 \quad+\quad \text{possibly}\; Me_2CHCH_2\underset{R}{\overset{|}{C}}HCH_3$$

(a) 28%, (b) 22%   (a) 11%, (b) 7%

$$+\quad \underset{R}{\overset{|}{C}}H_2-\underset{R}{\overset{|}{C}}(Me)CH_2CH_2CH_3 \quad+\quad Me_2\underset{R}{\overset{|}{C}}-\underset{R}{\overset{|}{C}}HCH_2CH_3$$

(a) 51%, (b) 57%   (a) 6%, (b) 7%

$$+\quad \text{unidentified} \quad+\quad (CF_3)_2NOH$$

(a) 4%, (b) 7%   (a) 52%, (b) not determined
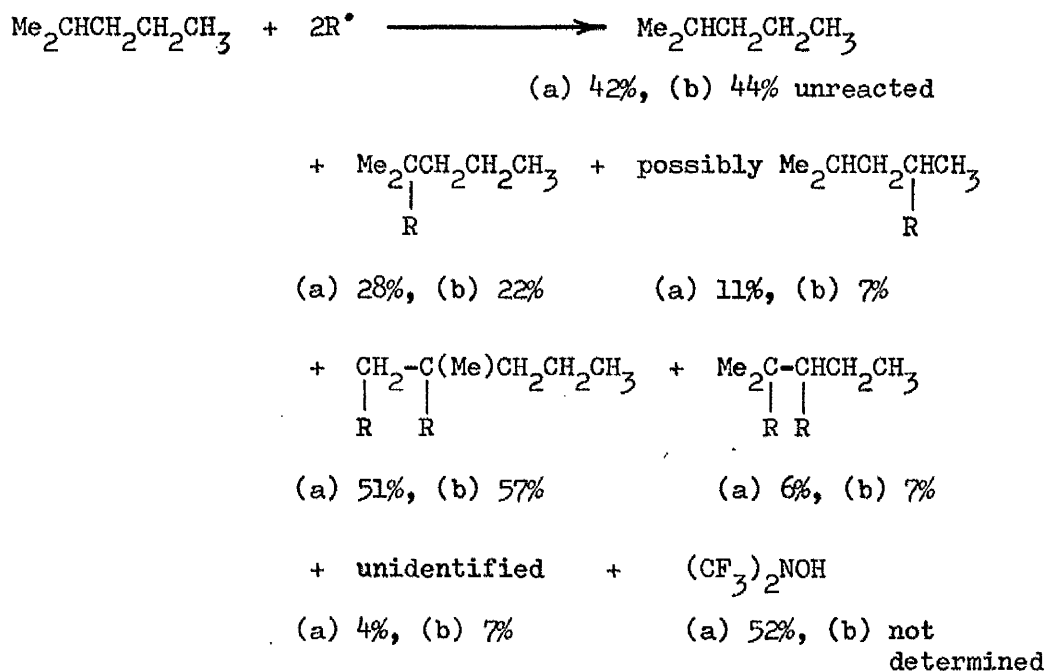
The ratio of disproportionation to combination (k_d/k_c) for reaction of 2-methyl-2-pentyl radicals with $(CF_3)_2NO^•$ equals the ratio of the sum of the yields of the two di-amino-oxy products to the yield of 2-(bis-trifluoromethylamino-oxy)-2-methylpentane.

i.e.   For reaction (a), $\dfrac{k_d}{k_c} = \dfrac{51 + 6}{28} = 2.04$

and for reaction (b), $\dfrac{k_d}{k_c} = \dfrac{57 + 7}{22} = 2.91$.

The ratio of the yields of 1,2-bis(bistrifluoromethylamino-oxy)-2-methylpentane to 2,3-bis(bistrifluoromethylamino-oxy)-2-methylpentane

is assumed to be the same as the ratio of the yields of the intermediate

olefins from which they are formed.
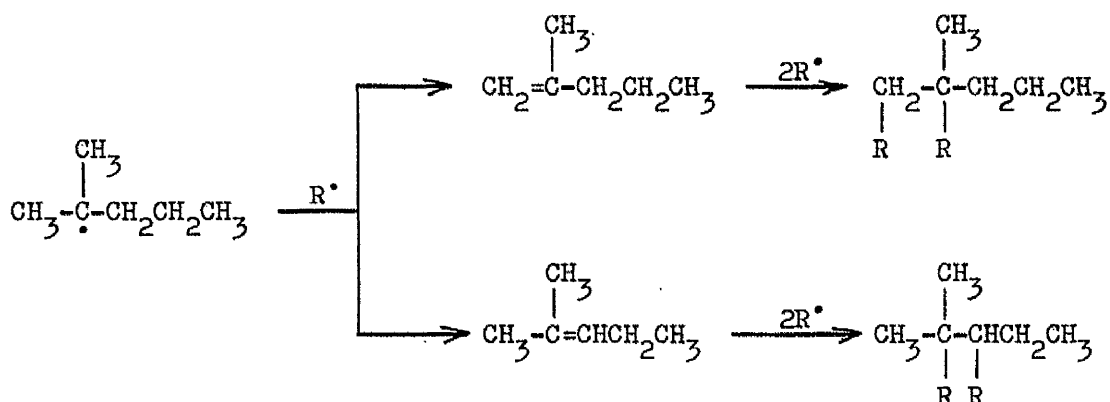
Scheme 20

The ratio of external to internal olefin can be seen to be 51:6 and

57:7 for reactions (a) and (b) respectively, i.e. 8.5:1 and 8.1:1

respectively.

In the reaction of $(CF_3)_2NO^\bullet$ with isopentane, Justin[26] ascribed

the slight deviation (45%:14%) from the expected statistical ratio of

external to internal olefin of 3:1 to steric hindrance to approach by

the bulky $(CF_3)_2NO^\bullet$ to the internal CH_2 in the 2-methyl-2-butyl radical.

An indication of the steric hindrance effect due to $(CF_3)_2NO^\bullet$ is given

by the products of the self-disproportionation of the 2-methyl-2-butyl

radical in the gas phase, which shows a slight preference (2.7:1) for the

internal olefin.[66]

It is not surprising then that the approach to the α-CH_2 is even

more hindered in the case of the reaction of the 2-methyl-2-pentyl radical

with $(CF_3)_2NO^\bullet$, leading to a greater preponderance of external over

internal olefin.

Two monosubstituted compounds were identified in the products,

2-(bistrifluoromethylamino-oxy)-2-methylpentane from substitution of a

tertiary hydrogen, and another tentatively identified from its mass spectrum as 2-(bistrifluoromethylamino-oxy)-4-methylpentane, from substitution of a secondary hydrogen. The formation of this compound gives an approximate value for the relative selectivity of $(CF_3)_2NO^\bullet$ for secondary as compared to tertiary hydrogen atoms. Presuming that both intermediate olefins are formed by disproportionation of the tertiary radical $Me_2\overset{\bullet}{C}CH_2CH_2CH_3$ then the total percentage abstraction at the tertiary position equals

$$51 + 6 + 28 = 85\% \text{ for reaction (a)}$$

and

$$57 + 7 + 22 = 86\% \text{ for reaction (b)}.$$

The relative reactivities of tertiary to secondary C-H bonds (per H atom) to $(CF_3)_2NO^\bullet$ are then $85/5.5 = 15.5$ for reaction (a) and $86/3.5 = 24.6$ for reaction (b).

On this basis $(CF_3)_2NO^\bullet$ appears to be rather less selective than the bromine atom for which the relative reactivity of tertiary to secondary C-H bonds has been calculated to be approximately 25.[91]

2.   Reaction of $(CF_3)_2NO^\bullet$ with 2,2,4-trimethylpentane

This reaction was carried out twice as summarised below.

$$Me_2CHCH_2CMe_3 + 2R^\bullet \longrightarrow Me_2CHCH_2CMe_3$$

(a) 45%, (b) 47% unreacted

$$+ \quad \underset{R}{Me_2CCH_2CMe_3} \quad + \quad \underset{R}{\underset{}{CH_2}}-\underset{R}{C(Me)CH_2CMe_3}$$

(a) 28%, (b) 25%   (a) 56%, (b) 57%

$$+ \quad \underset{R}{(RCH_2)_2CCH_2CMe_3} \quad + \quad 2 \text{ compounds } C_8H_{17}R$$
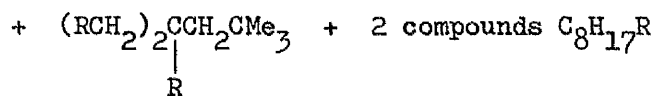
(a) 13%, (b) 16%   (a) 3.5%, (b) 2%
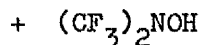
$$+ \quad (CF_3)_2 NOH$$

(a) 47%, (b) not determined.

The intermediate olefin formed in this reaction is exclusively the external olefin, steric hindrance due to the t-butyl group presumably being great enough to completely prevent approach of $(CF_3)_2 NO^{\bullet}$ to the internal CH_2.

There would appear to be two plausible routes to the tri-aminooxy compound, from 2,4,4-trimethylpent-1-ene, shown in Scheme 21.
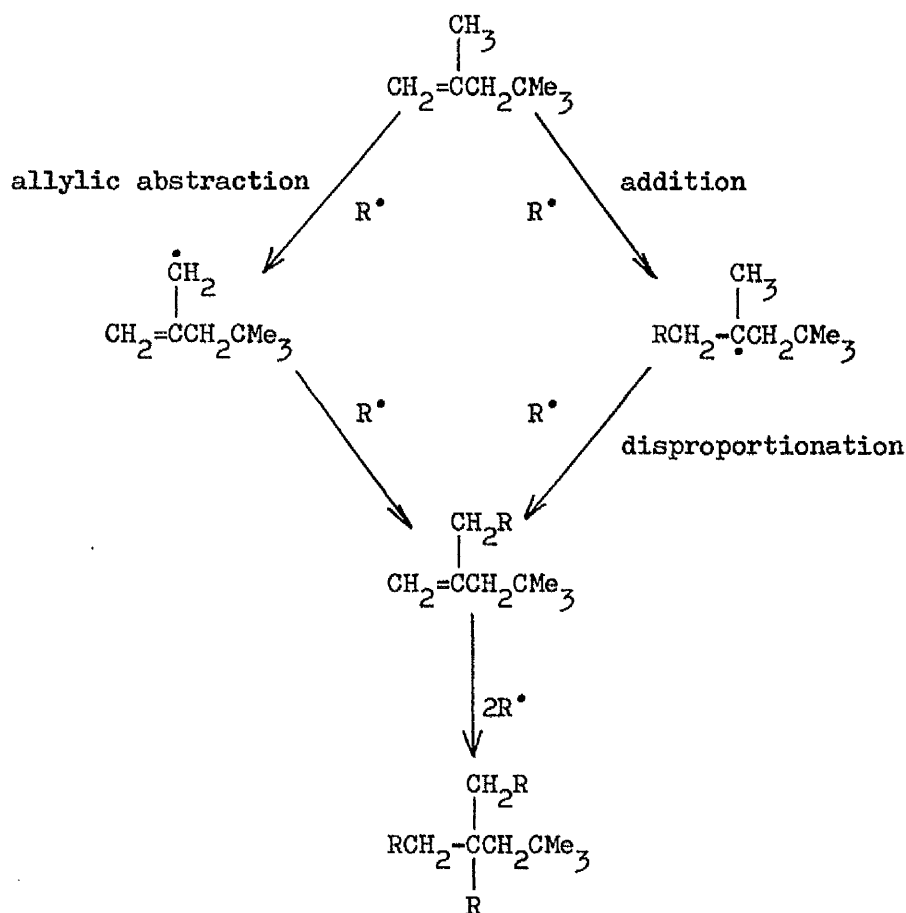
Scheme 21

Both routes could be the result of steric hindrance due to the t-butyl group, in one case steric hindrance to addition across the double bond

favouring allylic abstraction and in the other case steric hindrance to addition of a second $(CF_3)_2NO^\bullet$ radical leading to disproportionation of the tertiary radical.

Kosinski,[90] in the reaction of $(CF_3)_2NO^\bullet$ with t-butylcyclohexane, obtained 8 or 9 products all of which appeared to be the result of disproportionation reactions. The simple combination product 1-(bis-trifluoromethylamino-oxy)-1-t-butylcyclohexane was not observed among the products, presumably due to shielding of the tertiary radical centre by the t-butyl group.

It is interesting that this reaction of 2,2,4-trimethylpentane with $(CF_3)_2NO^\bullet$ is the only one in the series of reactions of compounds of formula Me_2CHCH_2X with $(CF_3)_2NO^\bullet$ in which an allylic substitution product was observed, apparently as a result of severe steric hindrance.

In the reaction of $(CF_3)_2NO^\bullet$ with isobutane neither Justin[26] nor Brown[28] found the allylic substitution product in reactions where they used molar ratios of $(CF_3)_2NO^\bullet$ to isobutane of 2:1, but Brown[28] identified it in the products of a reaction using equimolar quantities of reactants. Owen[89] found the allylic substitution product present in the products of all his reactions, which were carried out at intervals over the temperature range 80 to 155°C with initial reactant pressures varying from a 1:1 to a 4:1 ratio of amino-oxyl to isobutane and total pressures varying from 20 to 50 torr. He also found it present in a reaction where 0.5 cm^3 of liquid $(CF_3)_2NO^\bullet$ and 0.25 cm^3 of liquid isobutane were allowed to warm to room temperature, giving a vigorous reaction complete within 30 seconds.

Allylic substitution in radical reactions is normally favoured by high temperatures and low radical concentrations,[92] and hence would not normally be expected to be a significant route in reactions where olefins are generated as intermediates in the presence of a very large excess of radicals, as in the $(CF_3)_2NO^\bullet$ reactions. In the case of the isobutane-

$(CF_3)_2NO^•$ reaction, the reaction was complete within half a minute[89] and is much faster than any of the reactions considered in this work (see reaction times given later). Hence the temperature of the reaction would be expected to build up to a much higher level, tending to favour the allylic abstraction.

The k_d/k_c ratio for the reaction of the 2,4,4-trimethyl-2-pentyl radical with $(CF_3)_2NO^•$ equals the sum of the yields of the di- and tri-amino-oxy products to the yield of 2-(bistrifluoromethylamino-oxy)-2,4,4-trimethylpentane.

i.e.   For reaction (a), $\dfrac{k_d}{k_c} = \dfrac{56 + 13}{28} = 2.46$

and for reaction (b), $\dfrac{k_d}{k_c} = \dfrac{57 + 16}{25} = 2.92$

Reactions of $(CF_3)_2NO^•$ with the isobutyl compounds

3.   isobutyl chloride, Me_2CHCH_2Cl,

4.   isobutyl bromide, Me_2CHCH_2Br,

5.   isobutyl methyl ketone, Me_2CHCH_2COMe,

6.   isobutyl acetate, Me_2CHCH_2OOCMe,

7.   2-methyl-1-nitropropane, $Me_2CHCH_2NO_2$

Reactions of $(CF_3)_2NO^•$ with the isopentyl compounds

8.   isopentyl chloride, $Me_2CHCH_2CH_2Cl$,

9.   isopentyl bromide, $Me_2CHCH_2CH_2Br$,

10.   3-methyl-1-nitrobutane, $Me_2CHCH_2CH_2NO_2$

Reaction of $(CF_3)_2NO^•$ with the isohexyl compound

11.   isohexyl bromide, $Me_2CHCH_2CH_2CH_2Br$

These reactions will be considered together. They were carried out, using 2:1 molar ratios of $(CF_3)_2NO^•$ to substrate, and analysed in exactly the same way as the reactions of the alkanes with $(CF_3)_2NO^•$.

This investigation, of reactions of various compounds of general formula Me_2CHCH_2X (where X is an electron attracting group) with $(CF_3)_2NO^•$, was initiated by the discovery that reaction of isobutyl chloride with $(CF_3)_2NO^•$ gave a complete change round of yields of mono- and di-amino-oxy products compared to the alkane reactions, resulting in a very small k_d/k_c ratio.

$$Me_2CHCH_2Cl \xrightarrow{R^•} Me_2\overset{•}{C}CH_2Cl \xrightarrow[k_d]{R^•} CH_2=C(Me)CH_2Cl$$

$$\frac{k_d}{k_c} = 0.14$$

$R^• \downarrow k_c$

$2R^• \downarrow$

$$\underset{\overset{|}{R}}{Me_2CCH_2Cl}$$

84%

$$\underset{\overset{|}{R}\ \ \overset{|}{R}}{CH_2-C(Me)CH_2Cl}$$

12%
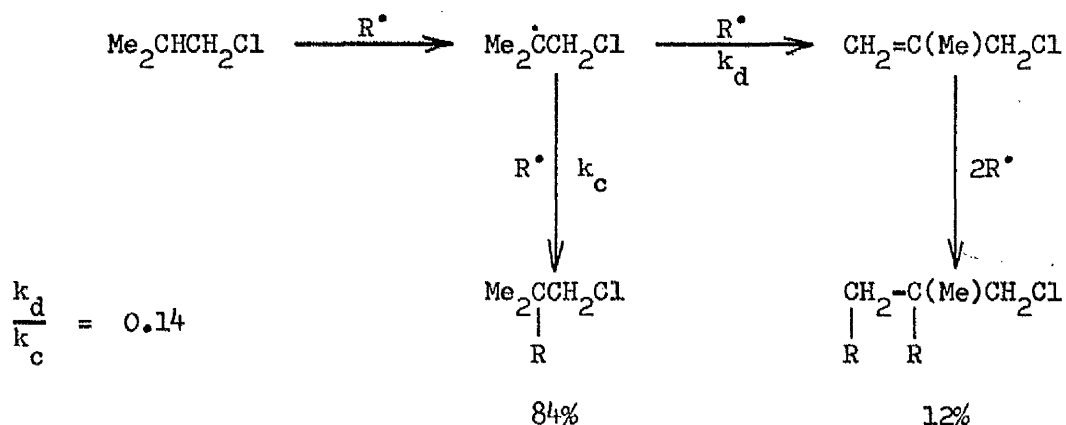
Scheme 22

Each of these reactions was found to give four major products:

N,N-bistrifluoromethylhydroxylamine, $(CF_3)_2NOH$,

unreacted Me_2CHCH_2X,

a mono-amino-oxy compound, $\underset{\overset{|}{R}}{Me_2CCH_2X}$,

a di-amino-oxy compound, $\underset{\overset{|}{R}\ \ \overset{|}{R}}{CH_2-C(Me)CH_2X}$,

plus minor products.

The products of these reactions are summarised in Table 6.

It can be seen from Table 6 that the di-amino-oxy compounds formed are almost exclusively those derived from the external rather than the internal olefin, i.e. $CH_2\text{-}C(Me)CH_2X$, with R and R substituents. In only one case was the product of $(CF_3)_2NO^\bullet$ addition across the double bond of an internal olefin identified, one of the minor products of the reaction of $(CF_3)_2NO^\bullet$ with isopentyl chloride being tentatively identified as 2,3-bis(bistrifluoro-methylamino-oxy)-1-chloro-3-methylbutane on the basis of its mass spectrum. This preponderance of external over internal olefin formation in the disproportionation reaction can be attributed to a combination of two factors:

(a)   steric hindrance to approach of the $(CF_3)_2NO^\bullet$ to the internal CH_2. This has been shown to be of importance in the reactions of $(CF_3)_2NO^\bullet$ with alkanes, the ratio of external to internal olefin increasing as the size of the alkyl group X in Me_2CHCH_2X is increased.

(b)   polar factors. The C-H bonds of the internal CH_2 are rendered electron deficient by the electron-withdrawing group and are therefore less likely to be abstracted by the electrophilic $(CF_3)_2NO^\bullet$.

The reactions do not appear to be influenced by the stability of the olefins formed, or at least if this is important it is overridden by the other factors. In the cases of the isobutyl compound reactions the internal olefins would have their double bonds stabilised by forms such as

$$Me_2C{=}CH{-}Cl \longleftrightarrow Me_2\overset{..}{C}{-}CH{=}\overset{+}{Cl}$$

$$\text{or} \quad Me_2C{=}CH\overset{O}{\overset{\|}{-}C}{-}CH_3 \longleftrightarrow Me_2\overset{+}{C}{-}\underset{H}{C}{=}\overset{O^-}{C}{-}CH_3$$
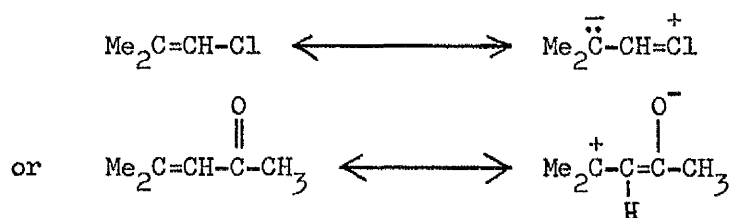
whereas the external olefins are not.

Table 6

REACTANTS	PRODUCTS				
	Unreacted Me_2CHCH_2X	$(CF_3)_2NOH$	$\underset{\overset{\vert}{R}}{Me_2CCH_2X}$	$\underset{\overset{\vert}{R}\ \overset{\vert}{R}}{CH_2C(Me)CH_2X}$	Minor products
$(CF_3)_2NO^{\bullet}$ +					
Me_2CHCH_2Cl	13%	not determined	84%	12%	poss. a mono-amino-oxy compound, 3%.
Me_2CHCH_2Br	21%	45%	78%	10%	5 unidentified compounds, 12%.
Me_2CHCH_2COMe	28%	48%	48%	34%	4 unidentified compounds, 8%.
Me_2CHCH_2OOCMe	(a) 23%	48%	65%	23%	probably 2% $\underset{\overset{\vert}{R}}{Me_2CHCHOOCMe}$ + another mono-amino-oxy compound, 4% + 6% unidentified.
	(b) 16%	49%	68%	25%	7% unidentified
$Me_2CHCH_2NO_2$	16%	not determined	82%	probably this compound, 7%	6 unidentified compounds, 11%.
$Me_2CHCH_2CH_2Cl$	38%	47%	50%	39%	2% probably $\underset{\overset{\vert}{RR}}{Me_2CCHCH_2Cl}$ + 4 unidentified compounds, 9%.

Table 6 continued:

REACTANTS	PRODUCTS				
$(CF_3)_2NO^\bullet$ +	Unreacted Me_2CHCH_2X	$(CF_3)_2NOH$	Me_2CCH_2X $\quad$ R	$CH_2C(Me)CH_2X$ $\quad$ R R	Minor products
$Me_2CHCH_2CH_2Br$	(a) 32%	49%	55%	38%	4 unidentified compounds, 6%.
	(b) 25%	53%	55%	36%	4 unidentified compounds, 8%.
$Me_2CHCH_2CH_2NO_2$	30%	not determined	55%	39%	4 unidentified compounds, 6%
$Me_2CHCH_2CH_2CH_2Br$	36%	not determined	41%	49%	5 unidentified compounds, 10%

Values of k_d/k_c for reactions of the intermediate $Me_2\overset{\bullet}{C}CH_2X$ radicals with $(CF_3)_2NO^{\bullet}$ are calculated from

$$\frac{k_d}{k_c} = \frac{\%\text{ yield of di-amino-oxy products}}{\%\text{ yield of mono-amino-oxy product}}$$

Table 7 gives values for k_d/k_c, $\log_{10}(k_d/k_c)$ and values for the Taft substituent constant σ^* for each group CH_2X. Table 7 includes the values from reactions of isohexane and 2,2,4-trimethylpentane with $(CF_3)_2NO^{\bullet}$ and Justin's value[26] for the reaction of isopentane with $(CF_3)_2NO^{\bullet}$.

The change in values of k_d/k_c with change in the group X in the Me_2CHCH_2X molecule would appear to be attributable to the strength of the inductive effect of X, as the tertiary radical centre is insulated from mesomeric effects due to X by the CH_2 group and steric effects might be expected to be fairly constant throughout the series of compounds. Taft[93] found that rates and equilibria for reactions of such compounds, where the reaction centre is not part of a conjugated system and the degree of steric interaction between substituent and reaction site does not change appreciably as the reaction progresses, obey a relationship analogous to the Hammett equation:

$$\log\left(\frac{k}{k_o}\right) = \sigma^* \rho^*$$

where k is the rate or equilibrium constant for a particular member of the reaction series, k_o is the corresponding constant for the parent compound (generally the methyl compound), ρ^* is the reaction constant and σ^* is the polar substituent constant, representing the electron-attracting ability of the substituent as transmitted through an aliphatic chain. Taft derived the σ^* values from an evaluation of the polar effects of substituents on the rate of hydrolysis of esters. That the polar substituent constants σ^* are measures of inductive effect is shown to be

sound by a quantitative parallel between them and the σ' values of Roberts and Moreland[94] obtained from 4-substituted bicyclo-(2,2,2)-octane-1-carboxylic acids.

Most of the σ^* values in Table 7 are those derived by Taft.[93] The values for CH_2CH_2Br, $CH_2CH_2CH_2Br$ and CH_2NO_2 were derived from the values for CH_2Br and $CH_2CH_2NO_2$ by using a conversion factor of 2.8. This is the factor for reduction of the inductive effect of a substituent resulting from the interposition of a methylene group.[93c] The σ^* value for the acetate group is derived from the σ' value for acetate of Roberts and Moreland.[94] The σ' values closely parallel the σ^* values, the best value of the σ'/σ^* ratio being 0.45.[95]

<div align="center">Table 7</div>

$(CF_3)_2NO^\bullet + Me_2\dot{C}CH_2X$	$\dfrac{k_d}{k_c}$	$\log_{10}\left(\dfrac{k_d}{k_c}\right)$	σ^* for CH_2X
$Me_2\dot{C}CH_2Cl$	0.14	-0.87	+1.05
$Me_2\dot{C}CH_2Br$	0.13	-0.89	+1.00
$Me_2\dot{C}CH_2COMe$	0.71	-0.15	+0.60
$Me_2\dot{C}CH_2OOCMe$	0.35, 0.37	-0.44	+0.87
$Me_2\dot{C}CH_2NO_2$	0.09	-1.07	+1.40
$Me_2\dot{C}CH_2CH_2Cl$	0.82	-0.09	+0.39
$Me_2\dot{C}CH_2CH_2Br$	0.69, 0.65	-0.17	+0.36
$Me_2\dot{C}CH_2CH_2NO_2$	0.71	-0.15	+0.50
$Me_2\dot{C}CH_2CH_2CH_2Br$	1.20	0.08	+0.13
$Me_2\dot{C}CH_2CH_2CH_3$	2.04, 2.91	0.39	-0.12
$Me_2\dot{C}CH_2CMe_3$	2.46, 2.92	0.43	-0.17
$Me_2\dot{C}CH_2CH_3$[26]	2.07	0.32	-0.10

Graph I: k_d/k_c versus σ^* for the disproportionation-combination of $Me_2\dot{C}CH_2X$ with $(CF_3)_2NO^{\cdot}$
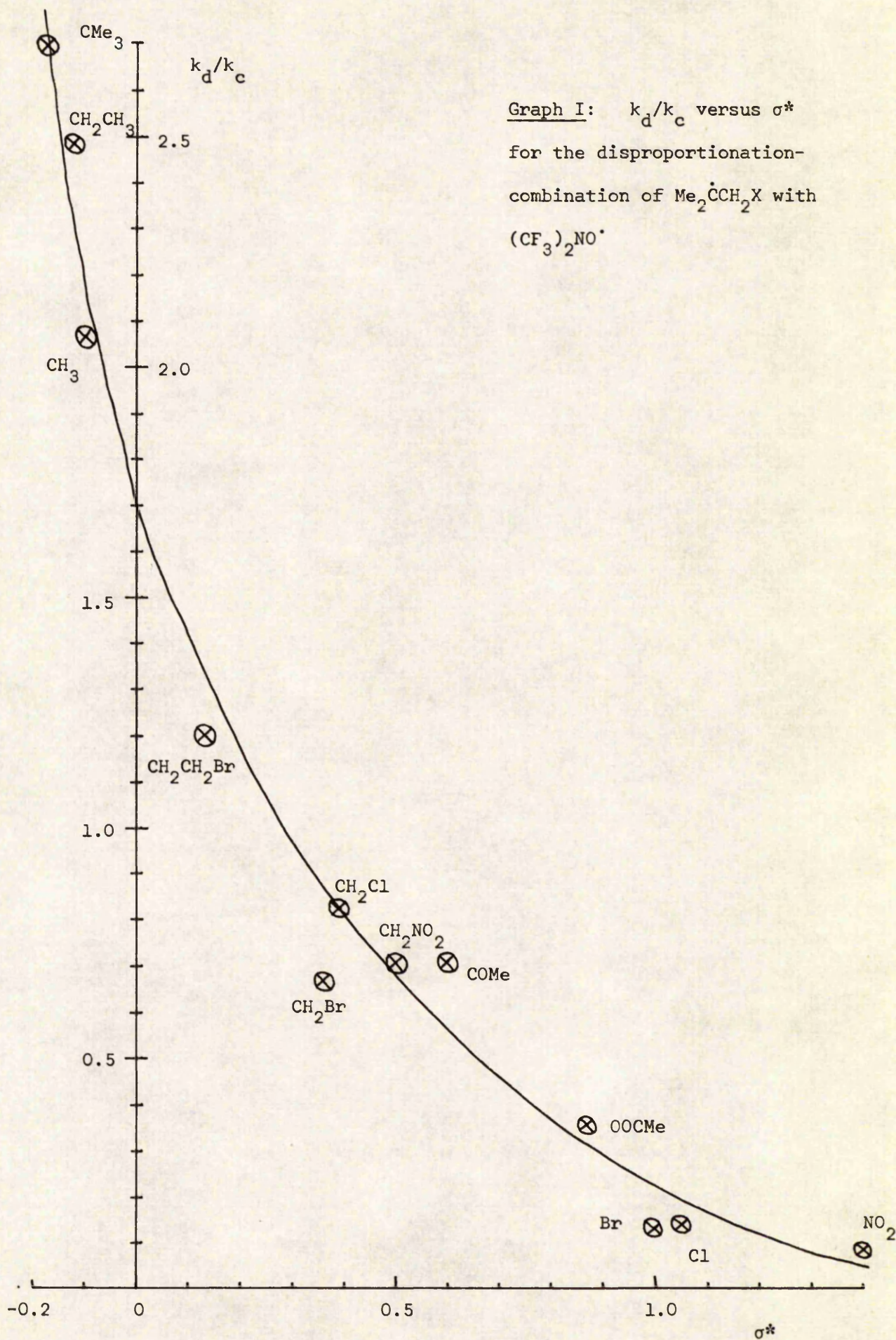
Graph II: $\log_{10}(k_d/k_c)$ versus σ^* for the disproportionation-combination of $Me_2\dot{C}CH_2X$ with $(CF_3)_2NO^{\cdot}$
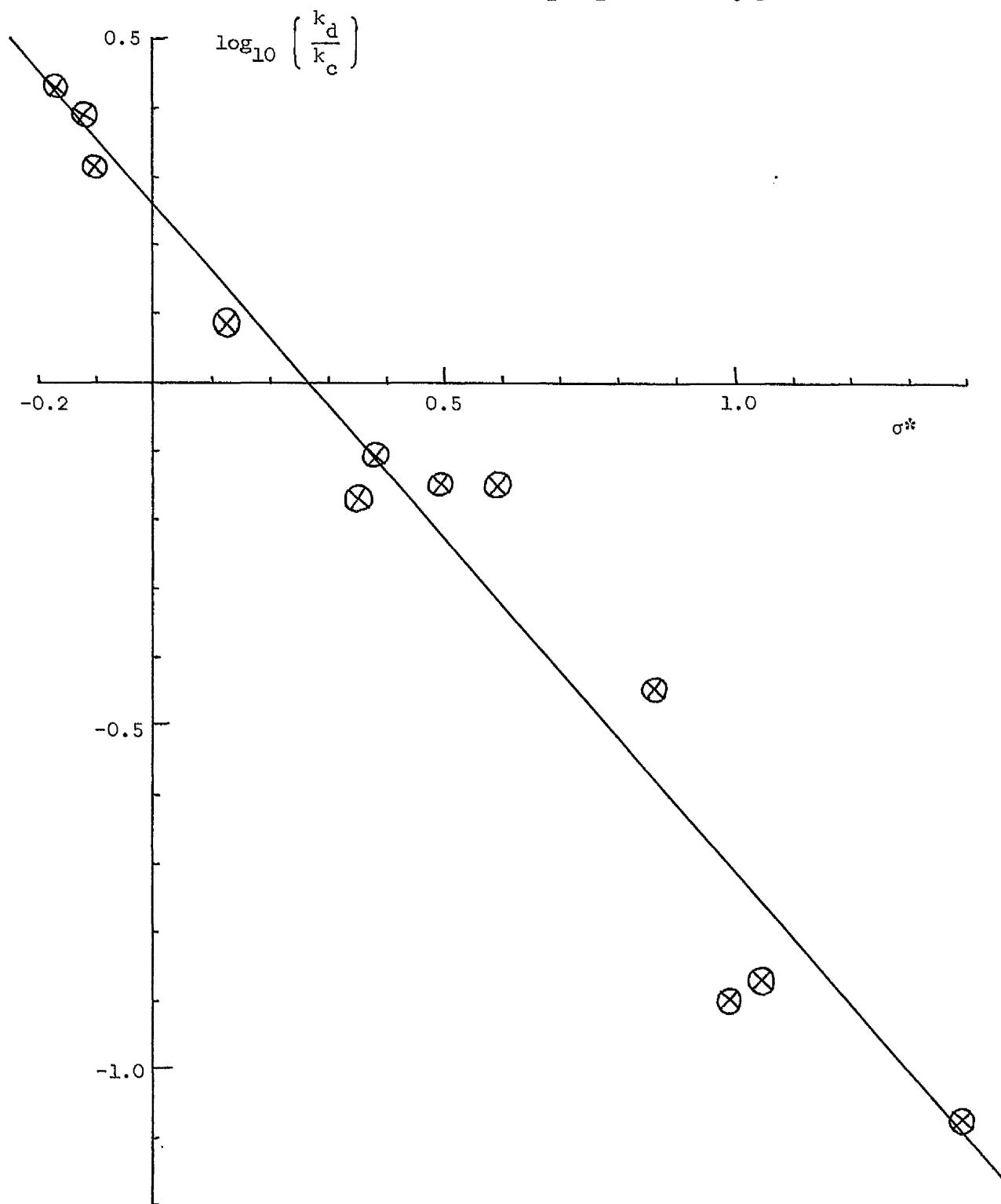
In Graph I, k_d/k_c values are plotted against σ^*.

In Graph II, $\log_{10}(k_d/k_c)$ values are plotted against σ^*.

From consideration of the data in Tables 6 and 7 and Graphs I and II it can be seen that the group X exercises a controlling influence on the ratio of disproportionation to combination. As the group X becomes more electron-withdrawing the values of k_d/k_c decrease. i.e. Combination is favoured by electron-withdrawing groups and disproportionation is favoured by electron-donating groups.

The k_d/k_c values correlate well with the Taft polar substituent constants σ^*. From Graph II it can be seen that, within close limits, $\log_{10}(k_d/k_c)$ is directly proportional to σ^*.

The decrease in disproportionation with increase in electron withdrawal by X can be explained as follows. Electron withdrawal by X renders the methyl C-H bonds electron deficient and hence less liable to abstraction by the electrophilic $(CF_3)_2NO^\bullet$ in the disproportionation step. Slowing down the disproportionation step will obviously favour the closely related combination reaction.

The transition state for disproportionation can be pictured as a resonance hybrid of the structures:
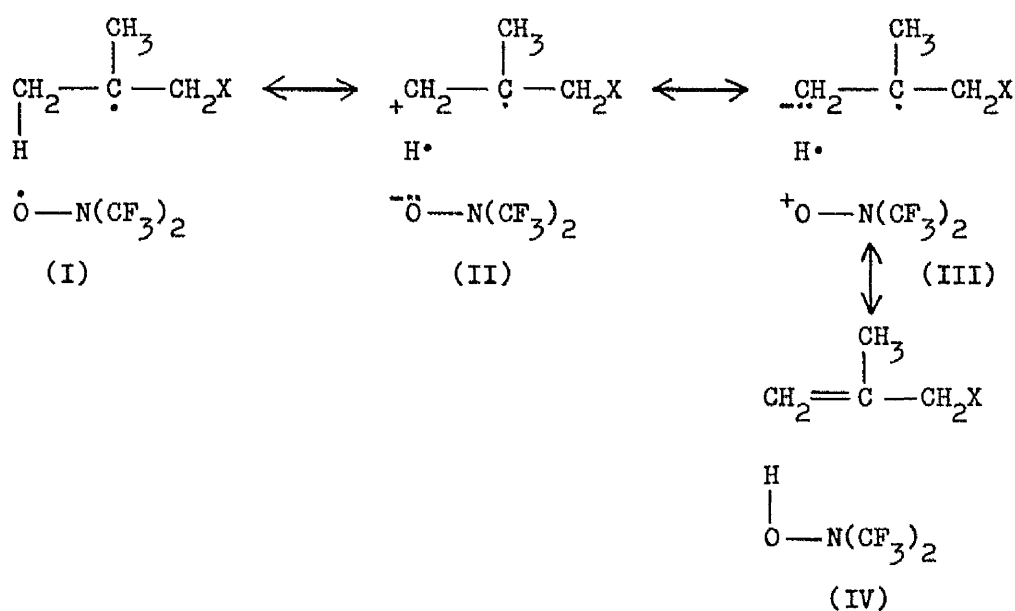
where (I) resembles the reactants, (IV) resembles the products and (II) and (III) are the possible polar structures. Structure (III) would be expected to make little contribution as $(CF_3)_2NO^•$ is electrophilic. Disproportionation is thought to proceed with little or no energy of activation and to be highly exothermic which implies that the transition state, if it can be described at all, resembles the reactants (I) more closely than the products (IV). Structure (IV) might therefore be expected to make little contribution. Structure (II) would be expected to make a major contribution to the transition state as $(CF_3)_2NO^•$ is an electrophile. Such a structure would be progressively destabilised as the electron-withdrawing power of X is increased.

Reaction times for reactions of bistrifluoromethylamino-oxyl with alkanes and substituted alkanes of general formula Me_2CHCH_2X.

The reactions described in the preceding section were carried out in 300 cm^3 sealed tubes by allowing the reactants to warm up from $-196°C$ to room temperature and leaving them in the dark until reaction was complete. In many cases they were left overnight. Consequently, no accurate information on reaction times was obtained. Some of the reactions were therefore repeated in much smaller (25 cm^3) tubes using 2:1 molar ratios of $(CF_3)_2NO^•$ to substrate as before. Instead of allowing the reaction tubes to slowly warm up in air they were transferred directly from liquid nitrogen to a water bath maintained at $23-24°C$. The reaction times were taken as the lengths of time for complete disappearance of the coloured $(CF_3)_2NO^•$.

The products of each reaction were analysed by g.l.c., the products being identified by comparison of the g.l.c. traces with those of the original reactions. Experimental details and percentage yields of the mono- and di-amino-oxy products are given in the experimental section. Table 8 gives the reaction times, the k_d/k_c values derived from

the percentage yields and the σ^* values for CH_2X in Me_2CHCH_2X.

Table 8

REACTANTS $(CF_3)_2NO^\bullet$ +	Reaction time (minutes)	σ^*	k_d/k_c
Me_2CHCH_2Cl	99	+1.05	0.18
Me_2CHCH_2Br	93	+1.00	0.15
Me_2CHCH_2COMe	48	+0.60	0.62
$Me_2CHCH_2CH_2Cl$	34	+0.39	0.68
$Me_2CHCH_2CH_2Br$	35	+0.36	0.71
$Me_2CHCH_2CH_2NO_2$	70	+0.50	0.83
$Me_2CHCH_2CH_2CH_3$	4	−0.12	1.87
$Me_2CHCH_2CMe_3$	11	−0.17	2.31

There is little difference between these k_d/k_c values and those found using 300 cm^3 tubes (Table 7), and certainly no systematic variation, 4 of the k_d/k_c values being slightly greater and 4 slightly less than those obtained previously.

The reaction times are plotted against σ^* in Graph III.

The reaction of 1-nitro-3-methylbutane can be seen from Graph III to be much slower than would be predicted from consideration of the other reaction times and the corresponding σ^* values. This may be due to the gaseous $(CF_3)_2NO^\bullet$ being less soluble in 1-nitro-3-methylbutane than in the other compounds. A greater proportion of the $(CF_3)_2NO^\bullet$ appeared to remain as vapour during this reaction, the purple colour in the liquid being restricted to a narrow surface band rather than being spread uniformly through the liquid, as was the case with the other slow-reacting compounds.

Graph III: Reaction time versus σ* for reactions of Me_2CHCH_2X with $(CF_3)_2NO^•$
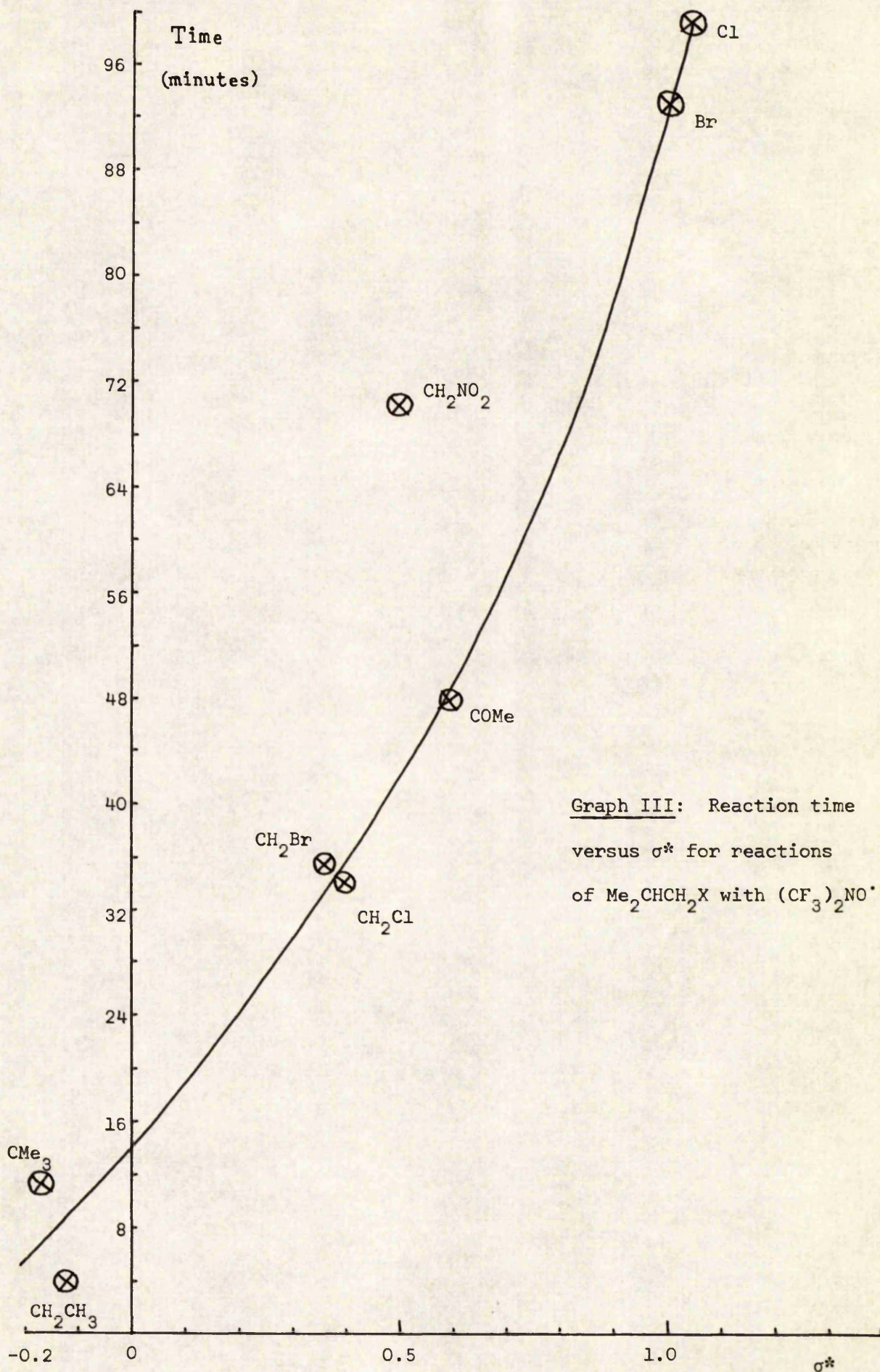
Owen,[89] in his study of the kinetics of the reaction of
$(CF_3)_2NO^{\bullet}$ with isobutane, found the overall reaction to be complex but
that for the initial rates of reaction the reaction is first order with
respect to both $(CF_3)_2NO^{\bullet}$ and isobutane.

It seems reasonable to suppose that in the reactions considered
here the rate determining step is the initial abstraction of the tertiary
H atom and that the reaction times are approximately inversely proportional
to the reaction rates.

It can be seen from Table 8 and Graph III that the more electron-
attracting X is, the longer the reaction time. This is as expected for
attack by a highly electrophilic radical such as $(CF_3)_2NO^{\bullet}$. The more
electron-withdrawing is X the more electron deficient the tertiary C-H
bond becomes and hence the slower the abstraction of this H atom by
$(CF_3)_2NO^{\bullet}$.

The transition state for abstraction of the tertiary hydrogen can
be written as a resonance hybrid of three canonical forms:
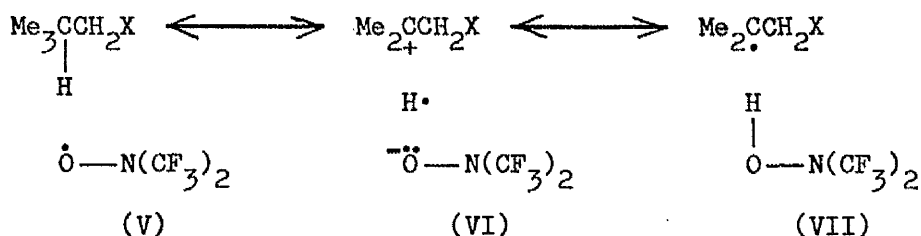
are resembling the reactants (V), another resembling the products (VII)
and one in which electron transfer is regarded as having taken place
between the radical and the substrate (VI). According to Russell[54]
polar effects should be most important in form (VI) and the more
electronegative the attacking radical the more important (VI) becomes.
Structure (VI) would be progressively destabilised as X becomes more
electron-withdrawing and hence the more electron attracting X is the
slower the abstraction reaction would be expected to be.

To summarise, the group X in Me_2CHCH_2X can be seen to exert a controlling influence over

(a)   the rate of initial hydrogen abstraction and

(b)   the ratio of disproportionation to combination of the intermediate tertiary radical with $(CF_3)_2NO^{\bullet}$.

The two effects appear to parallel one another, increased electron withdrawal by X leading to slower hydrogen abstraction by the electrophilic $(CF_3)_2NO^{\bullet}$ from Me_2CHCH_2X, and in the disproportionation step, from $Me_2\overset{\bullet}{C}CH_2X$, hence favouring the combination reaction.

Reactions of bistrifluoromethylamino-oxyl with alkanes and chloroalkanes using 1:1 and 1:2 molar ratios of reactants

The reactions of $(CF_3)_2NO^{\bullet}$ with isohexane, 2,2,4-trimethylpentane, isobutyl chloride and isopentyl chloride were previously carried out using a 2:1 molar ratio of $(CF_3)_2NO^{\bullet}$ to substrate.

The reactions of $(CF_3)_2NO^{\bullet}$ with these four compounds were repeated but using first equimolar and then 1:2 molar ratios of $(CF_3)_2NO^{\bullet}$ to substrate, in 25 cm^3 sealed tubes which were transferred directly from liquid nitrogen to a water bath at 23-24°C and left there until the reactions reached completion. The products were analysed by g.l.c. Full details are given in the experimental section. The k_d/k_c values for these reactions are given in Table 9 alongside the k_d/k_c values obtained using 2:1 molar ratios of $(CF_3)_2NO^{\bullet}$ to substrate.

Only in the case of isohexane with $(CF_3)_2NO^{\bullet}$ is there any significant change in k_d/k_c although even here only a variation of about 8% is needed to move from a k_d/k_c ratio of 1.87 (58% : 31%) to one of 1.21 (47% : 39%).

In the reactions of $(CF_3)_2NO^{\bullet}$ with 2,2,4-trimethylpentane, isobutyl chloride and isopentyl chloride there is virtually no change in k_d/k_c with

REACTANTS $(CF_3)_2NO^\bullet$ +	k_d/k_c values from reactant ratios of $(CF_3)_2NO^\bullet$: Me_2CHCH_2X of			
	2:1 (300 cm^3 tube)	2:1 (25 cm^3 tube)	1:1 (25 cm^3 tube)	1:2 (25 cm^3 tube)
$Me_2CHCH_2CH_2CH_3$	2.04,2.91	1.87	1.51	1.21
$Me_2CHCH_2CMe_3$	2.46,2.92	2.31	2.13	2.13
Me_2CHCH_2Cl	0.14	0.18	0.17	0.20
$Me_2CHCH_2CH_2Cl$	0.82	0.68	0.74	0.70

Table 9

change in molar ratio of the reactants. These results are in contrast to Brown's results[28] from the $(CF_3)_2NO^\bullet$-isobutane reaction. Using a 2:1 molar ratio he obtained a value for k_d/k_c of 2.69 and found 3% of the compound Me_2CRCOR in the products. Using a 1:1 molar ratio he obtained a value for k_d/k_c of 1.23 and found 8% of the compound $CH_2=C(Me)CH_2R$ in the products. Even so, this variation in k_d/k_c in the isobutane case is still less than that found between the extreme values (2.91 and 1.21) for the isohexane reaction, although these two reactions were carried out under slightly different conditions.

Reactions of bistrifluoromethylamino-oxyl with alkanes using hydrogen chloride to trap the alkene intermediate

The reactions of $(CF_3)_2NO^\bullet$ with isobutane, isopentane, isohexane and 2,2,4-trimethylpentane using a 2:1 molar ratio of $(CF_3)_2NO^\bullet$ to alkane were repeated in 300 cm^3 sealed tubes in the presence of a large excess of hydrogen chloride and carbon tetrachloride as solvent. The reactants were allowed to warm from $-196°C$ to room temperature and left in the dark

overnight to proceed to completion. The products were identified by comparative g.l.c. with the products of the reactions of $(CF_3)_2NO^\bullet$ with the alkanes and from g.l.c.-mass spectral data. Full details are given in the experimental section. The results are summarised in Table 10.

Table 10

Alkane	% tertiary halide	total % mono-amino-oxy products	total % di-amino-oxy products
isobutane	90	10	0
isopentane	74	19	5
isohexane	77	15	4
2,2,4-trimethylpentane	73	16	9

The reaction with isobutane was a repeat of that carried out by both Justin[26] and Brown[28] and a very similar result was obtained. In all the reactions, except that of isobutane, the di-amino-oxy products were found to be present in low yields, showing that ionic addition of HCl across the double bond in the intermediate olefins does not totally exclude addition of $(CF_3)_2NO^\bullet$.

The yields of mono-amino-oxyalkanes were also reduced in all the reactions. Brown[28] has suggested that the lowering of yields of the combination products could be due to solvation of the tertiary alkyl radicals by the carbon tetrachloride, leading to steric inhibition of the close approach of $(CF_3)_2NO^\bullet$ radicals, thus reducing the proportion of combination.

In the reaction of isopentane with $(CF_3)_2NO^\bullet$ a significant amount (6%) of a second mono-amino-oxy compound was present in the products.

It was tentatively identified from its mass spectrum as 2-(bistrifluoro-methylamino-oxy)-3-methylbutane, resulting from substitution of one of the secondary hydrogens in $Me_2CHCH_2CH_3$.

The reaction of isohexane was repeated using a 2.7:1 molar ratio of $(CF_3)_2NO^\bullet$ to alkane. In this case the yield of 2-chloro-2-methylpentane was only 60% and the total yields of mono- and di-amino-oxy compounds were 27% and 9% respectively. Presumably the higher concentration of $(CF_3)_2NO^\bullet$ is able (i) to overcome the solvent effect working against combination and in favour of disproportionation and (ii) to compete more effectively with the HCl for the alkene intermediate.

The reaction of $(CF_3)_2NO^\bullet$ with isobutyl chloride was also carried out in the presence of HCl and carbon tetrachloride (molar ratio of $(CF_3)_2NO^\bullet$: Me_2CHCH_2Cl : HCl was 2 : 1 : 10) but the products were virtually identical to those for the reaction where no HCl was used. However the reaction of HCl with the olefin intermediate 3-chloro-2-methylprop-1-ene would be expected to be much slower than with unsubstituted alkenes. In fact little or no reaction had taken place between a 43:1 molar ratio of HCl and 3-chloro-2-methylprop-1-ene in CCl_4 after two hours in the dark at room temperature in a 300 cm^3 sealed tube. HCl addition in this case is obviously much too slow to compete with $(CF_3)_2NO^\bullet$ addition across the double bond.

Reactions of bistrifluoromethylamino-oxyl with isobutyl iodide and isopentyl iodide

The reactions of $(CF_3)_2NO^\bullet$ with these two alkyl iodides were carried out using a 2:1 molar ratio of $(CF_3)_2NO^\bullet$ to alkyl iodide in 300 cm^3 sealed tubes, using exactly the same method as previously described for other Me_2CHCH_2X compounds. The reactions were complicated by replacement of iodine competing with abstraction of the tertiary hydrogen

atom and the subsequent disproportionation-combination reaction.

12.   <u>Reaction of $(CF_3)_2NO^{\bullet}$ with isobutyl iodide</u>

This is summarised below.

$$Me_2CHCH_2I + 2R^{\bullet} \longrightarrow Me_2CHCH_2I + (CF_3)_2NOH$$

9% unreacted   46%

$$+ \quad Me_2\underset{\underset{R}{|}}{C}CH_2I \quad + \quad Me_2\underset{\underset{R}{|}}{C}CH_2R$$

75%   3%
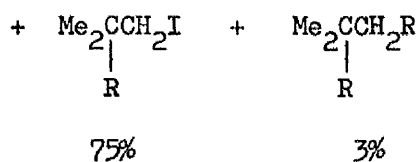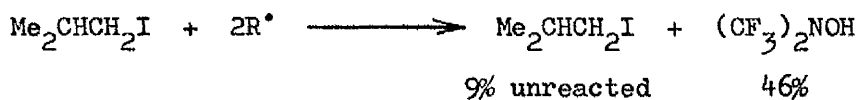
+   possibly another di-amino-oxy compound, 3%

+   possibly C_4H_6IR, 6%

+   4 unidentified compounds, 13%   + iodine.

The high yield of 2-(bistrifluoromethylamino-oxy)-1-iodo-2-methylpropane
is about as expected compared with the yields of the corresponding
chloro- (84%) and bromo- (78%) compounds.

Several routes for the formation of 1,2-bis(bistrifluoromethyl-
amino-oxy)-2-methylpropane can be postulated, as shown in Scheme 23.
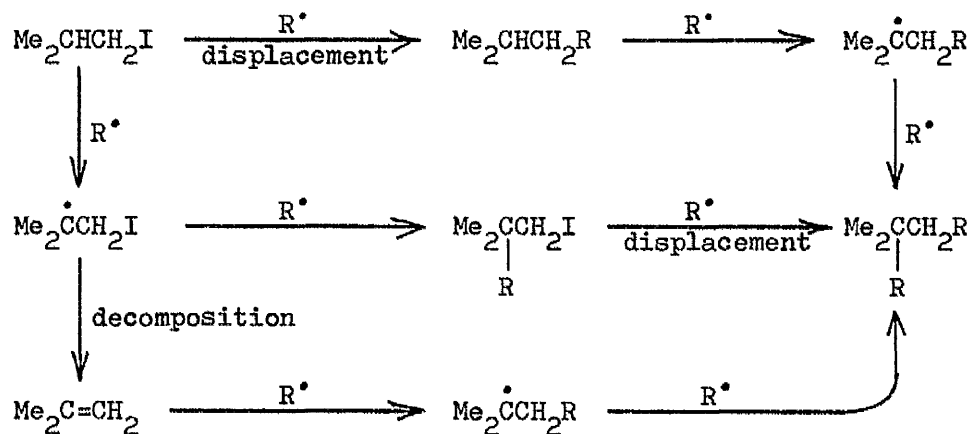
Scheme 23

Justin[26] investigated the reaction of Me_2CHCH_2R with $(CF_3)_2NO^\bullet$ and

found that a slow reaction took place giving the di-amino-oxy product

Me_2CRCH_2R.

The route involving decomposition of the intermediate tertiary

radical by loss of iodine must be regarded as a distinct possibility, as

iodoalkyl radicals of this type are known to be unstable, the equilibrium

$Me_2\overset{\bullet}{C}CH_2I \rightleftharpoons Me_2C=CH_2 + I^\bullet$ lying well to the right.[96]

13.   <u>Reaction of $(CF_3)_2NO^\bullet$ with isopentyl iodide</u>

This reaction was carried out twice as summarised below.

$$Me_2CHCH_2CH_2I + 2R^\bullet \longrightarrow Me_2CHCH_2CH_2I$$

(a) 21%, (b) 28% unreacted

$$+ (CF_3)_2NOH + Me_2\underset{R}{\overset{|}{C}}CH_2CH_2I$$

(a) 46%, (b) not   (a) 28%, (b) 27%
        determined

$$+ \underset{R}{\overset{|}{C}}H_2-\underset{R}{\overset{|}{C}}(Me)CH_2CH_2I + \text{probably } C_5H_9R$$

(a) 11%, (b) 16%   (a) 5%, (b) 10%

$+ \text{probably } C_5H_{10}R_2 + 3 \text{ compounds}, C_5H_9R_3$

(a) 14%, (b) 15%   (a) 8%, (b) 15%

$+ \text{unidentified} + \text{iodine}$
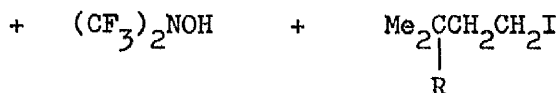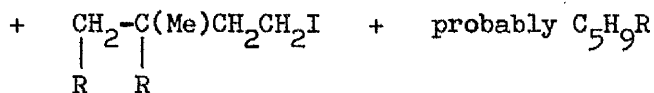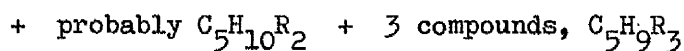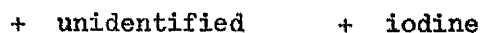
(a) 34%, (b) 17%

In this case a route involving decomposition of the intermediate tertiary

radical by loss of an iodine atom is unlikely as an extra CH_2 group has

been interposed between the radical centre and the iodine atom.

Other than 3-(bistrifluoromethylamino-oxy)-1-iodo-3-methylbutane

and 1,2-bis(bistrifluoromethylamino-oxy)-4-iodo-2-methylbutane which were

isolated by preparative g.l.c. and identified by their n.m.r., i.r.

and mass spectra, the products contained a number of compounds containing

one, two or three $(CF_3)_2NO$-groups but no iodine. The low yields and

close retention times of these compounds prevented their separation by

g.l.c. and they could only be identified tentatively on the basis of

g.l.c.-mass spectral data.

$(CF_3)_2NO^{\bullet}$, which behaves in many of its reactions as a pseudo-

halogen,[59] has been found to replace iodine, bromine and, in some cases

chlorine, from several metallic and metalloid halides,[58,59] and to

liberate iodine from di-iodomethane and iodoform at room temperature.[59]

Reactions of bistrifluoromethylamino-oxyl with isobutyl and isopentyl alcohols

The reactions of $(CF_3)_2NO^{\bullet}$ with these alcohols were carried out

using a 2:1 molar ratio of $(CF_3)_2NO^{\bullet}$ to alcohol in 300 cm^3 sealed tubes,

using exactly the same method as previously described for other

Me_2CHCH_2X compound reactions.

14.   ## Reaction of $(CF_3)_2NO^{\bullet}$ with isobutyl alcohol

This was carried out twice as summarised below.

$$Me_2CHCH_2OH + 2R^{\bullet} \longrightarrow Me_2CHCH_2OH \quad + \quad (CF_3)_2NOH$$

(a) 42%, (b) 36% unreacted   (a) 68%, (b) not
                                                                   determined

$+ \quad Me_2CHCHO \quad + \quad Me_2CHCOR$

(a) 12%, (b) 12%   (a) 31%, (b) 38%

$+ \quad Me_2\overset{|}{\underset{R}{C}}CH_2OH \quad + \quad$ possibly $Me_2CHCHROH$

(a) 18%, (b) 14%   mixed with 5 unidentified

$(CF_3)_2NO$-compounds

(a) 14%, (b) 21%
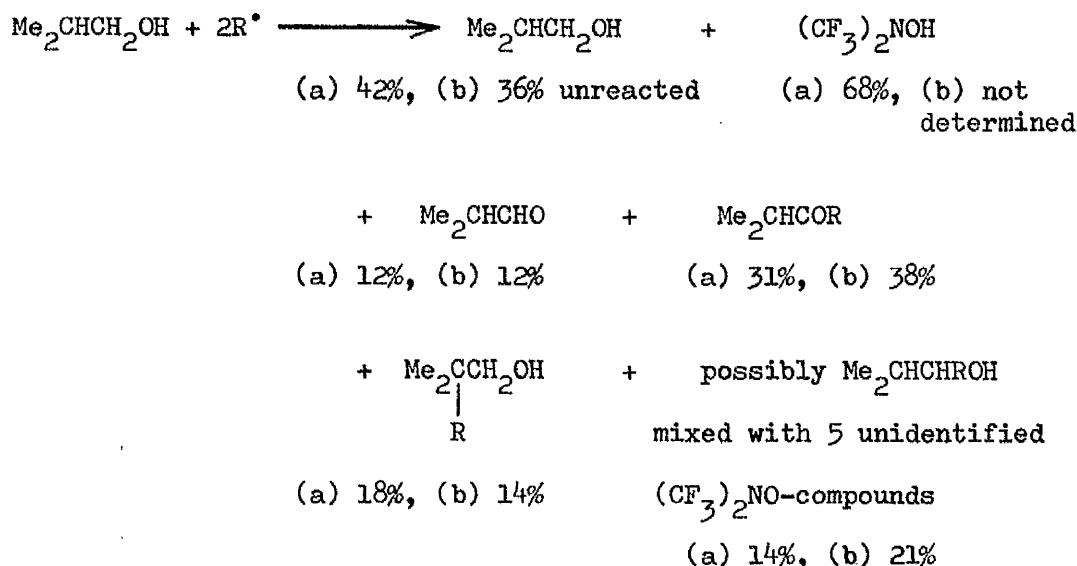
$$+ \text{ possibly } C_4H_7(OH)R_2$$

(a) 4%, (b) 3%

The isobutyraldehyde and $(CF_3)_2NO$-substituted isobutyraldehyde were identified by g.l.c. and i.r. comparison with the products of the reaction of isobutyraldehyde and $(CF_3)_2NO^\bullet$:

$$Me_2CHCHO + R^\bullet \longrightarrow Me_2CHC{\overset{\displaystyle \nearrow O}{\underset{\displaystyle \searrow R}{}}} + (CF_3)_2NOH$$

100%
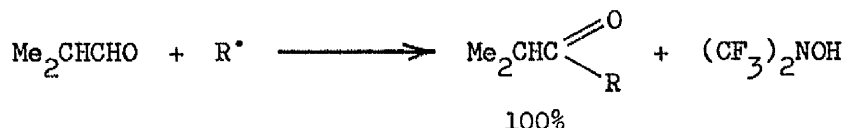
15.   Reaction of $(CF_3)_2NO^\bullet$ with isopentyl alcohol

This reaction was carried out twice with rather differing results as detailed below. The difference in the yields between the two reactions may be at least partly attributed to deterioration of the g.l.c. column used in the analysis.

$$Me_2CHCH_2CH_2OH + 2R^\bullet \longrightarrow Me_2CHCH_2CH_2OH$$

(a) 33%, (b) 45% unreacted

$$+ (CF_3)_2NOH \qquad + \qquad Me_2CHCH_2CHO$$

(a) 70%, (b) not determined   (a) 12%, (b) 0%

$$+ Me_2CHCH_2COR \qquad + \qquad Me_2\underset{\displaystyle R}{\overset{\displaystyle |}{C}}CH_2CH_2OH$$

(a) 25%, (b) 66%   (a) 16%, (b) 11%

$+ 3$ unidentified $(CF_3)_2NO$-compounds

(a) 39%, (b) 23%

$+ 5$ unidentified compounds

(a) 8%, (b) 0%
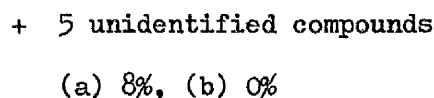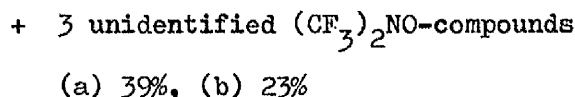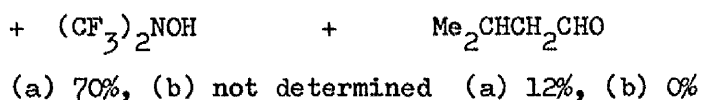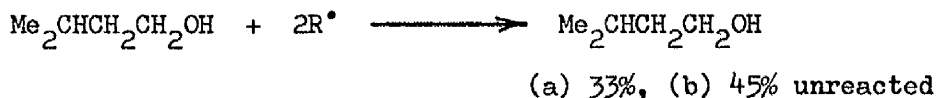
Connell,[44] in the reaction of $(CF_3)_2NO^\bullet$ with methanol, obtained a high

yield of carbon monoxide but found none of the adduct RCH_2OH claimed as the main product of the reaction by Russian workers.[46]

In the reaction of a 2:1 molar ratio of $(CF_3)_2NO^\bullet$ with isopropanol Connell[44] obtained 95% acetone and 100% $(CF_3)_2NOH$. He proposed that initial hydrogen abstraction takes place from the α C-H bond rather than from the hydroxyl group in both the above reactions, in agreement with bond energy data $[D(\text{alkoxy-H}) = 102\text{-}3$ kcal mole^{-1}, $D(HOCH_2\text{-H}) = 92$ kcal mole^{-1}, $D(HOCHMe\text{-H}) = 90$ kcal mole$^{-1}].$[35,97] This is the generally accepted position for radical attack on primary and secondary alcohols in solution.[98] The resulting α-hydroxyalkyl radicals have been trapped by olefins[99] and spin-trapped by nitrones[100]; their e.s.r. spectra have been examined.[48]

Accordingly, the reaction scheme for reactions of $(CF_3)_2NO^\bullet$ with isobutyl and isopentyl alcohols envisages competition between initial abstraction from the tertiary C-H bond and from the α C-H bond in the CH_2OH group. Such competition is expected from bond energy data $[D(Me_3C\text{-H}) = 91$ kcal mole^{-1}, $D(HOCHMe\text{-H}) = 90$ kcal mole$^{-1}].$[35,97] In either case the intermediate radical can then undergo combination or disproportionation with $(CF_3)_2NO^\bullet$, as shown in Scheme 24.

$$Me_2CHCH_2OH$$

$$R^{\bullet} \quad\quad R^{\bullet}$$

$$Me_2\overset{\bullet}{C}CH_2OH \quad\quad\quad\quad Me_2CH\overset{\bullet}{C}HOH$$

$$R^{\bullet} \quad\quad\quad R^{\bullet} \quad\quad\quad\quad\quad R^{\bullet} \quad\quad\quad R^{\bullet}$$

$$Me_2\underset{R}{C}CH_2OH \quad\quad\quad Me_2CH\underset{R}{C}HOH$$

$$CH_2{=}C(Me)CH_2OH \quad\quad\quad\quad\quad\quad Me_2CHCHO$$

$$2R^{\bullet} \quad\quad\quad\quad\quad\quad\quad\quad\quad\quad R^{\bullet}$$

$$\underset{R}{C}H_2{-}\underset{R}{C}(Me)CH_2OH \quad\quad\quad\quad Me_2CH\overset{\bullet}{C}O$$

$$R^{\bullet}$$

$$Me_2CH\underset{R}{C}O$$
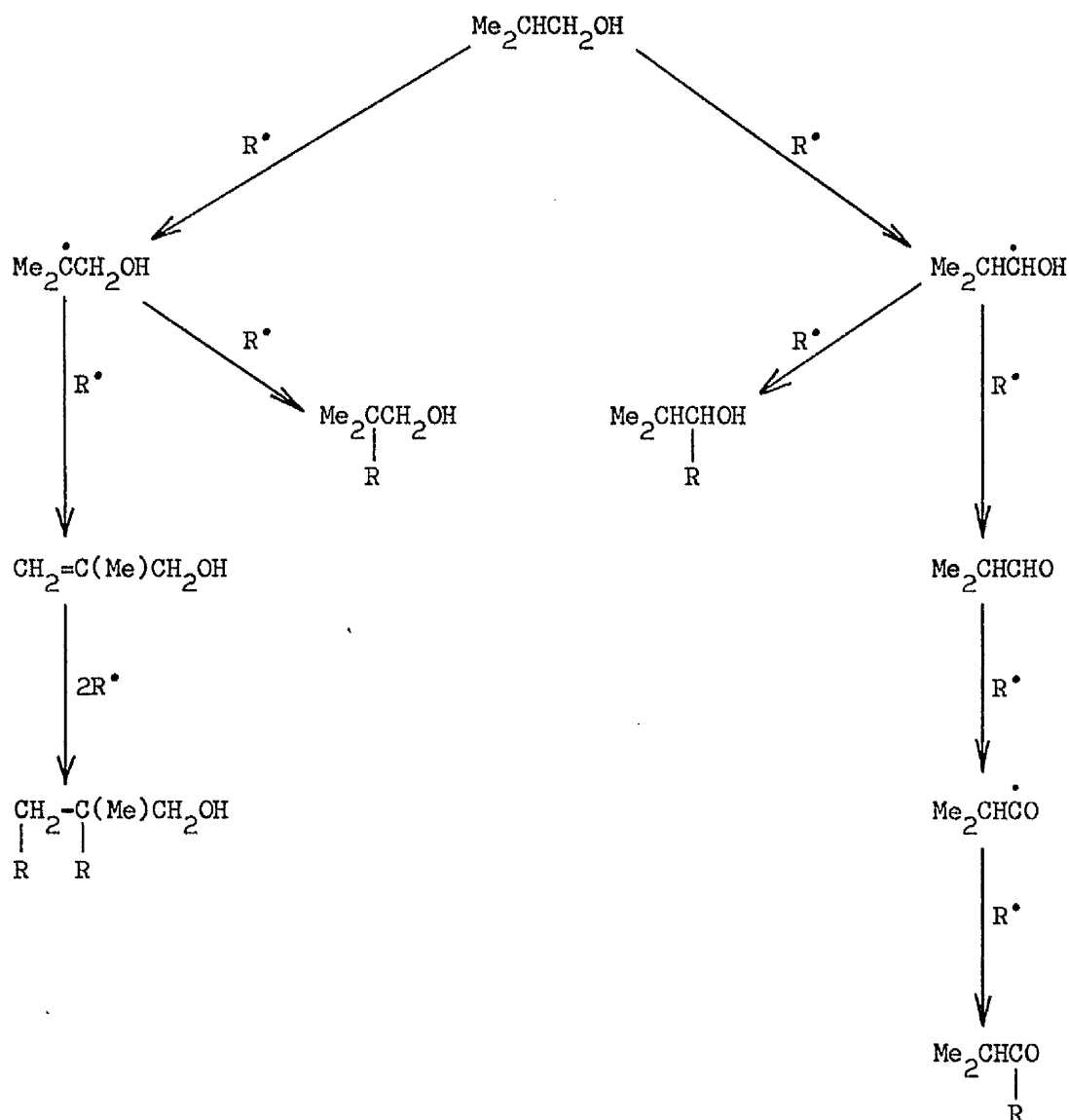
Scheme 24

16.   Reaction of $(CF_3)_2NO^{\bullet}$ with isopentylbenzene

This reaction was carried out using a 2:1 molar ratio of $(CF_3)_2NO^{\bullet}$ to isopentylbenzene in a 300 cm^3 sealed tube using the same method as in the reactions already discussed.

$$Me_2CHCH_2CH_2C_6H_5 \quad + \quad 2R^\bullet \quad \longrightarrow \quad Me_2CHCH_2CH_2C_6H_5$$

<div align="center">11% unreacted</div>

$$+ \quad (CF_3)_2NOH \quad + \quad Me_2CHCH_2\overset{|}{\underset{R}{C}}HC_6H_5$$

<div align="center">not determined   77%</div>

$$+ \quad \text{probably } Me_2\overset{|}{\underset{R}{C}}CH_2\overset{|}{\underset{R}{C}}HC_6H_5 \quad + \quad \text{probably } C_{11}H_{13}R_3$$

<div align="center">7%   2%</div>

<div align="center">+   4 unidentified products</div>

<div align="center">14%</div>
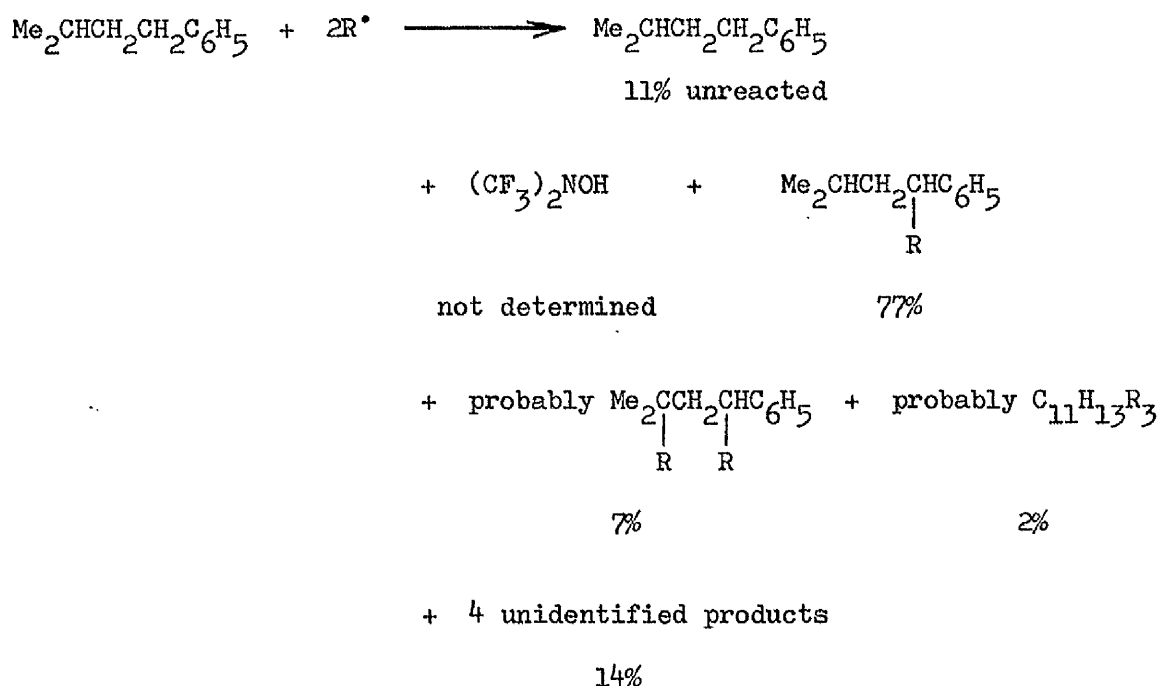
Initial hydrogen abstraction from the benzylic CH_2 rather than from the tertiary C-H bond is as expected on the basis of bond energy data $[D(Me_3C-H) = 91$ kcal mole^{-1}, $D(C_6H_5CH-H) = 85$ kcal mole$^{-1}].$[97]

No disproportionation product from either $Me_2CHCH_2\overset{\bullet}{C}HC_6H_5$ or $Me_2\overset{\bullet}{C}CH_2CH_2C_6H_5$ could be identified.

The reaction of $(CF_3)_2NO^\bullet$ with ethylbenzene[53] (2:1 molar ratio) has been found to yield 75% PhCHRMe and 6% PhCHRCH$_2$R giving a k_d/k_c ratio for reaction of Ph$\overset{\bullet}{C}$HCH$_3$ with $(CF_3)_2NO^\bullet$ of 0.08. This value is comparable with the k_d/k_c value for the self disproportionation-combination of α-phenylethyl radicals, formed by thermal decomposition of the symmetrical azo compound in benzene, of 0.097. An almost identical value of 0.095 was obtained for the $C_6H_5\overset{\bullet}{C}HCH_2CHMe_2$ radical.[66]

The radical $C_6H_5\overset{\bullet}{C}HCH_2CHMe_2$ might therefore be expected to give a k_d/k_c value for its reaction with $(CF_3)_2NO^\bullet$ similar to that of the $C_6H_5\overset{\bullet}{C}HCH_3$ radical. However, in its reactions with isohexane and 2,2,4-trimethylpentane, $(CF_3)_2NO^\bullet$ has been shown to be very susceptible to steric influences. Disproportionation of the $C_6H_5\overset{\bullet}{C}HCH_2CHMe_2$ radical would

entail close approach of $(CF_3)_2NO^\bullet$ to the internal CH_2 and hence it is

not surprising that the only di-amino-oxy product found appears to be

$C_6H_5\underset{R}{CH}CH_2\underset{R}{CMe}_2$ rather than $C_6H_5\underset{R}{CH}\text{-}\underset{R}{CH}CHMe_2$.
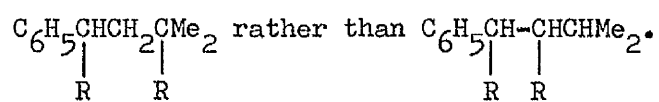
RESULTS AND DISCUSSION, PART II

INTRODUCTION

Free radical hydrogen abstraction from amines

Early literature reports[101,102,103] concerning the position of attack of methyl radicals on amines are conflicting, some stating that attack occurs at C-H, others that it occurs at N-H bonds. Later work[104,105,106] showed such conclusions to be incorrect and that hydrogen abstraction occurs at both alkyl and amine sites, the rate of abstraction being greater at the amine group. For example, on a per-atom basis, the H atom attached to nitrogen is 18 to 20 times[105,106] more reactive towards methyl radicals than the H atom attached to carbon in dimethylamine.

The rate of abstraction increases going from primary to secondary nitrogen. The relative rates of abstraction from NH_3, $MeNH_2$ and Me_2NH are 1 to 11 to 168 at 150°C.[105] In this respect the amines follow the alkanes, the strength of the N-H bond determining to a large extent the rate of radical attack. The reactivity of the C-H bonds in primary, secondary and tertiary amines appears fairly constant on a per H atom basis,[106] the $-NH_2$, $>NH$ and $\geq N$ groups apparently making little difference to the activation of the C-H bonds.

When trifluoromethyl radicals are the abstracting species the disparity between abstraction from N-H and C-H bonds is not as marked (e.g. on a per-atom basis the N-H in Me_2NH is only 3 times as reactive as a C-H)[106], in keeping with the greater reactivity of $CF_3 \cdot$.

Whereas numerous reactions are known involving the abstraction of H atoms by reactive radicals of short life, comparatively few cases have been described of hydrogen abstraction by "stable" free radicals.

A number of stable radicals, for example diphenylpicrylhydrazyl[107] (DPPH) and the amino-oxyls[108] diphenylamino-oxyl, 4,4'-dinitrodiphenylamino-oxyl, Banfield and Kenyon's radical and porphyrexide oxidise hydrazobenzene instantly to azobenzene,

$$PhNHNHPh \longrightarrow PhN=NPh$$

and N-benzylaniline partially or completely to N-benzylideneaniline,

$$PhCH_2NHPh \longrightarrow PhCH=NPh$$

at room temperature. None of these radicals oxidise bibenzyl.

Other stable radicals such as Fremy's radical[109], bistrifluoromethylamino-oxyl[44] and aroxyls[110] dehydrogenate hydrazobenzene; their reactions with N-benzylaniline and bibenzyl have not been reported.

These results reflect the greater ease of dehydrogenation of systems containing N-H rather than C-H bonds. The explanation for the greater reactivity of the N-H bonds is thought to be the greater ease with which N can pass from the tetrahedral (sp^3) to the planar (sp^2) configuration.[107]
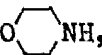
Other radical-amine reactions, particularly those involving aliphatic amines or those where the attacking radicals are intermediate between the highly reactive methyl and the relatively unreactive "stable" radicals, are less clear cut as to whether the initial hydrogen abstraction takes place at N or at the carbon α to the amino group.

Diphenylpicrylhydrazyl (DPPH) reacts quantitatively with NH_3 and N_2H_4[111] forming nitrogen but less cleanly with aliphatic amines.[111,112] These reactions were thought to involve initial abstraction of an amino hydrogen followed by the reaction of the resulting radical in a variety of ways, in part with a second equivalent of DPPH. However t-butylamine gives no appreciable reaction with DPPH; it appears that a hydrogen on

the α-carbon is necessary for aliphatic amines to react.[112]

The reactions of phenyl radicals with a number of amines have been studied,[113] the radicals formed being spin trapped by a nitroso compound and identified by the e.s.r. spectra of the resulting amino-oxyls.

Abstraction from a number of tertiary amines was from the α-carbon atom. One unexpected result was that abstraction from diethyliso-propylamine took place from an ethyl rather than from the isopropyl group.

With the secondary amines piperidine and morpholine abstraction was from the carbon α to the amino group, indicating in the case of morpholine, O⟨ ⟩NH, that the amine N has a greater activating effect than the ether oxygen.

In spite of steric hindrance abstraction took place from the N atom in 2,2,6,6-tetramethyl-4-piperidone, O=⟨ ⟩NH . With diethylamine, abstraction took place from both nitrogen and α-carbon atoms to give the radicals $Et_2N^\bullet$ and $CH_3\overset{\bullet}{C}HNEt$ respectively.

In the radical obtained from n-butylamine abstraction was from the β- or the γ-carbon or possibly from both, but apparently not from the α-carbon as would be expected. The possibility of abstraction from the NH_2 could not be ruled out as the amino-oxyl formed by the reaction of the radical with the nitroso compound would be unstable and liable to disproportionate.

Hydrogen abstractions from benzylamine and N-alkylbenzylamines have been studied in reactions where irradiation of the amines results in the homolytic scission of the benzyl-nitrogen bond only.[114] The reactions considered to contribute to the products are shown in Scheme 25, taking benzylamine as the example.

$$PhCH_2NH_2 \xrightarrow{h\nu} PhCH_2{}^{\bullet} + {}^{\bullet}NH_2$$

$$PhCH_2NH_2 + {}^{\bullet}NH_2 \longrightarrow PhCH_2\overset{\bullet}{N}H + NH_3$$

$$PhCH_2{}^{\bullet} + PhCH_2\overset{\bullet}{N}H \longrightarrow (PhCH_2)_2NH$$

$$\longrightarrow PhCH_3 + PhCH{=}NH$$

$$PhCH{=}NH + PhCH_2NH_2 \longrightarrow PhCH{=}NCH_2Ph + NH_3$$

$$(PhCH_2)_2NH + X^{\bullet} \longrightarrow (PhCH_2)_2N^{\bullet} + XH, \quad etc.$$

$$[X^{\bullet} = {}^{\bullet}NH_2 \text{ or } PhCH_2\overset{\bullet}{N}H]$$
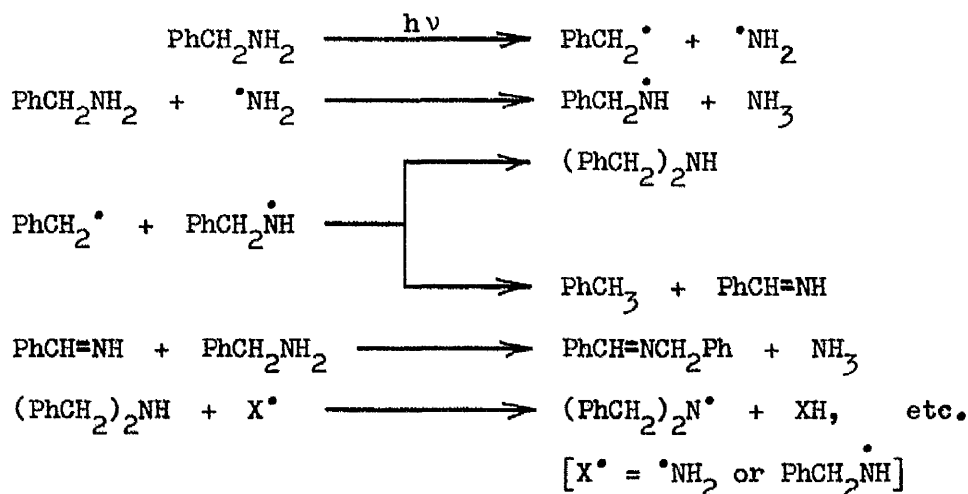
Scheme 25

The N-benzylidenebenzylamine could also be formed via disproportionation of the dibenzylamino radical. Support for N-H rather than C-H hydrogen abstraction derives from the products formed and the absence of dimers involving the radical PhĊHNH$_2$.

Although oxidation of amines to imines using catalytic methods[115] and oxidising agents such as manganese dioxide[116], potassium permanganate[117], lead tetraacetate[118], silver(II) picolinate[119] and sulphur[120] are well documented and some of these oxidations [those using MnO_2,$(Pb(OAc)_4$ and Ag(II) picolinate] are thought to proceed via mechanisms involving free radicals, there have been few reports of direct hydrogen abstractions by radicals from amines to give imines, other than those by stable free radicals from N-benzylaniline to which reference has already been made.

Primary and secondary alkylamines have been found to induce the decomposition of di-t-butylperoxide forming imines.[121] The mechanism proposed is analogous to that postulated for the reaction of primary and secondary alcohols which also induce the decomposition of the peroxide.[122] It was proposed that the aldehyde or ketone produced resulted from the interaction of an α-hydroxyalkyl radical with the O-O linkage of the

peroxide. The mechanism postulated for the amine reaction is shown in Scheme 26.

$$Me_3COOCMe_3 \longrightarrow 2Me_3CO^\bullet$$

$$Me_3CO^\bullet + R_2^1CHNHR^2 \longrightarrow Me_3COH + R_2^{1\bullet}CNHR^2$$

$$R_2^{1\bullet}CNHR^2 + Me_3COOCMe_3 \longrightarrow R_2^1C=NR^2 + Me_3COH + Me_3CO^\bullet$$

$$R_2^1CHNHR^2 + 2Me_3CO^\bullet \longrightarrow R_2^1C=NR^2 + 2Me_3COH$$
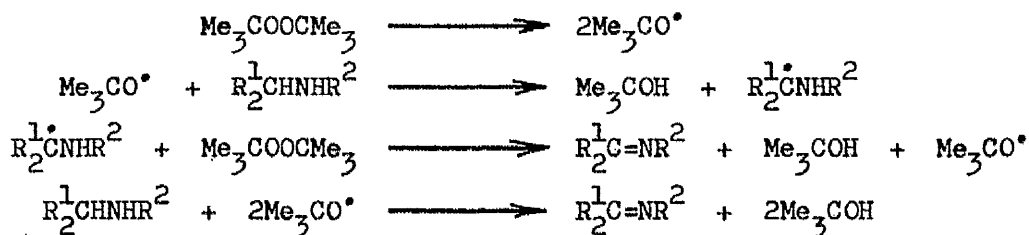
<u>Scheme 26</u>

Tert-butyl hydroperoxide has been found to oxidise primary and secondary amines to give imines[123] which undergo hydrolysis; in the case of primary amines the aldehydes so formed undergo condensation in excess amine to give Schiff's bases. E.s.r. investigation[124] of these reactions revealed the presence of amino-oxyl radicals and a mechanism was proposed in which these radicals take part in chain transfer steps to produce other free radicals which in turn oxidise amine to imine.

$$(R^1CH_2)_2NH + t\text{-BuOOH} \rightleftharpoons (R^1CH_2)_2NH\text{---}t\text{-BuOOH}$$

$$H_2O + t\text{-BuO}^\bullet + (R^1CH_2)_2NO^\bullet \xleftarrow{t\text{-BuOOH}} [(R^1CH_2)_2NOH] + t\text{-BuOH}$$

$$(R^1CH_2)_2NO^\bullet + (R^1CH_2)_2NH \longrightarrow R^{1\bullet}CHNHCH_2R^1 + (R^1CH_2)_2NOH$$

$$\downarrow t\text{-BuO}^\bullet$$

$$R^1CH=NCH_2R^1 + t\text{-BuOH}$$
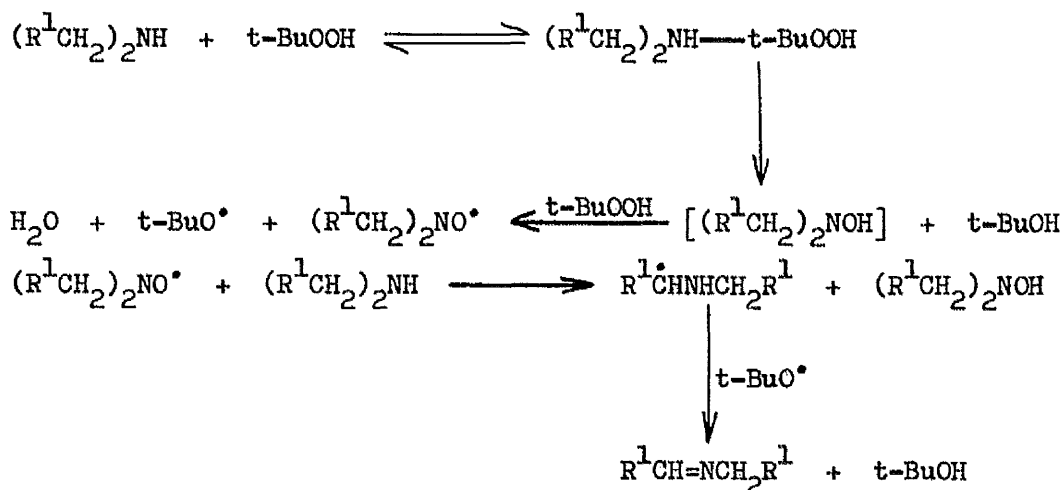
<u>Scheme 27</u>

Numbers of aromatic and aliphatic amino-oxyls have been prepared by oxidation of amines with peroxy radicals and hydroperoxides.[125] However,

as can be seen from Scheme 27 the reactions do not involve straightforward hydrogen abstraction and so will not be considered further.

The reactions of photoexcited unsaturated compounds (e.g. ketones, aldehydes, quinones, nitro compounds, aromatic hydrocarbons) with amines in solution lead to abstraction of an α-hydrogen from the amine and the formation of two radicals[126]:

$$A=B^* \ + \ R_2^1CHNR_2^2 \longrightarrow \overset{\bullet}{A}-BH \ + \ R_2^1\overset{\bullet}{C}NR_2^2$$

For example, primary and secondary amines rapidly photoreduce benzophenone, leading to benzpinacol and Schiff's bases. Primary amines, $R_2^1CHNH_2$, give the Schiff's bases $R_2^1C=NCHR_2^1$ via formation of $R_2^1C=NH$ and its subsequent condensation with amine; secondary amines $R_2^1CHNHR^2$ give $R_2^1C=NR^2$.

REACTIONS OF BISTRIFLUOROMETHYLAMINO-OXYL WITH AMINES AND SCHIFF'S BASES

The investigation into these reactions was initiated when the reaction of $(CF_3)_2NO^{\bullet}$ with isobutylamine, carried out as part of a general study of the reactions of $(CF_3)_2NO^{\bullet}$ with isobutyl compounds, was found to give as its main product the amino-oxy substituted Schiff's base $Me_2CRCH=NCH_2CHMe_2$.

The method used was similar for all the reactions, $(CF_3)_2NO^{\bullet}$ being condensed, in vacuo, into a Pyrex reaction tube containing the amine or Schiff's base cooled to -196°C. The tube was sealed and allowed to warm up, in most cases, to room temperature.

The products were initially analysed by g.l.c. The main products were either isolated and identified by their n.m.r., i.r. and mass spectra or identified by comparison of (i) the spectra and (ii) the g.l.c. retention times with those of prepared products. Product yields were calculated by a combination of g.l.c. and n.m.r. peak areas. Full practical details are given in the experimental section; spectra are given in the appendices.

1. Reactions of $(CF_3)_2NO^{\bullet}$ with isobutylamine

Using a 2:1 molar ratio of $(CF_3)_2NO^{\bullet}$ to isobutylamine the products were as shown below.

$$Me_2CHCH_2NH_2 + 2R^{\bullet} \longrightarrow \underset{\overset{|}{R}}{Me_2C}CH=NCH_2CHMe_2 + \underset{\overset{|}{R}}{Me_2C}CH_2NH_2$$

$$90\% \qquad\qquad 4\%$$

$$+ \underset{\overset{|}{R}}{Me_2C}CH=NCH_2\underset{\overset{|}{R}}{C}Me_2 + (CF_3)_2NOH + NH_3$$

$$1\%$$

Using equimolar quantities of $(CF_3)_2NO^{\bullet}$ and isobutylamine the products

were as follows.

$$Me_2CHCH_2NH_2 \; + \; R^{\bullet} \; \longrightarrow \; Me_2CHCH_2NH_2 \; + \; Me_2CHCH=NCH_2CHMe_2$$

<div style="text-align:center">24% unreacted   62%</div>

$$+ \; Me_2\underset{\underset{R}{|}}{C}CH=NCH_2CHMe_2 \; + \; Me_2\underset{\underset{OH}{|}}{C}HC=NCH_2CHMe_2$$

<div style="text-align:center">25%   4%</div>

$$+ \; (CF_3)_2NOH \; + \; NH_3 \; + \; \text{unidentified, } 9\%$$

The fact that, in the reaction using equimolar quantities of reactants, N-isobutylideneisobutylamine is produced in high yield, suggests that this compound is the main intermediate in the formation of N-[2-(bistrifluoromethylamino-oxy)-2-methylpropylidene]-isobutylamine, i.e. that the reaction proceeds via route B rather than route A in Scheme 28.

In route B initial hydrogen abstraction is presumed to be from the CH_2 group α to the NH_2 rather than from the NH_2 itself, by analogy with the reactions of $(CF_3)_2NO^{\bullet}$ with alcohols. The $Me_2CH\overset{\bullet}{C}HNH_2$ radical would be resonance stabilised:

$$Me_2CH\overset{\bullet}{C}H-\overset{\cdot\cdot}{N}H_2 \longleftrightarrow Me_2CH\overset{\overline{\cdot\cdot}}{C}H-\overset{+\bullet}{N}H_2$$

$$Me_2CHCH_2NH_2$$

R• (left)   R• (right)

$$Me_2\overset{\bullet}{C}CH_2NH_2 \qquad\qquad Me_2CH\overset{\bullet}{C}HNH_2$$

R• (down left)   R• (down right)

$$Me_2\underset{R}{\overset{|}{C}}CH_2NH_2 \qquad\qquad Me_2CHCH=NH$$

Route A   Route B

R• $Me_2CHCH_2NH_2$

$$Me_2\underset{R}{\overset{|}{C}}\overset{\bullet}{C}HNH_2 \qquad\qquad Me_2CHCH=NCH_2CHMe_2$$

R•   R•

$$Me_2\underset{R}{\overset{|}{C}}CH=NH \qquad\qquad Me_2\overset{\bullet}{C}CH=NCH_2CHMe_2$$

$Me_2CHCH_2NH_2$ R•

$$Me_2\underset{R}{\overset{|}{C}}CH=NCH_2CHMe_2$$
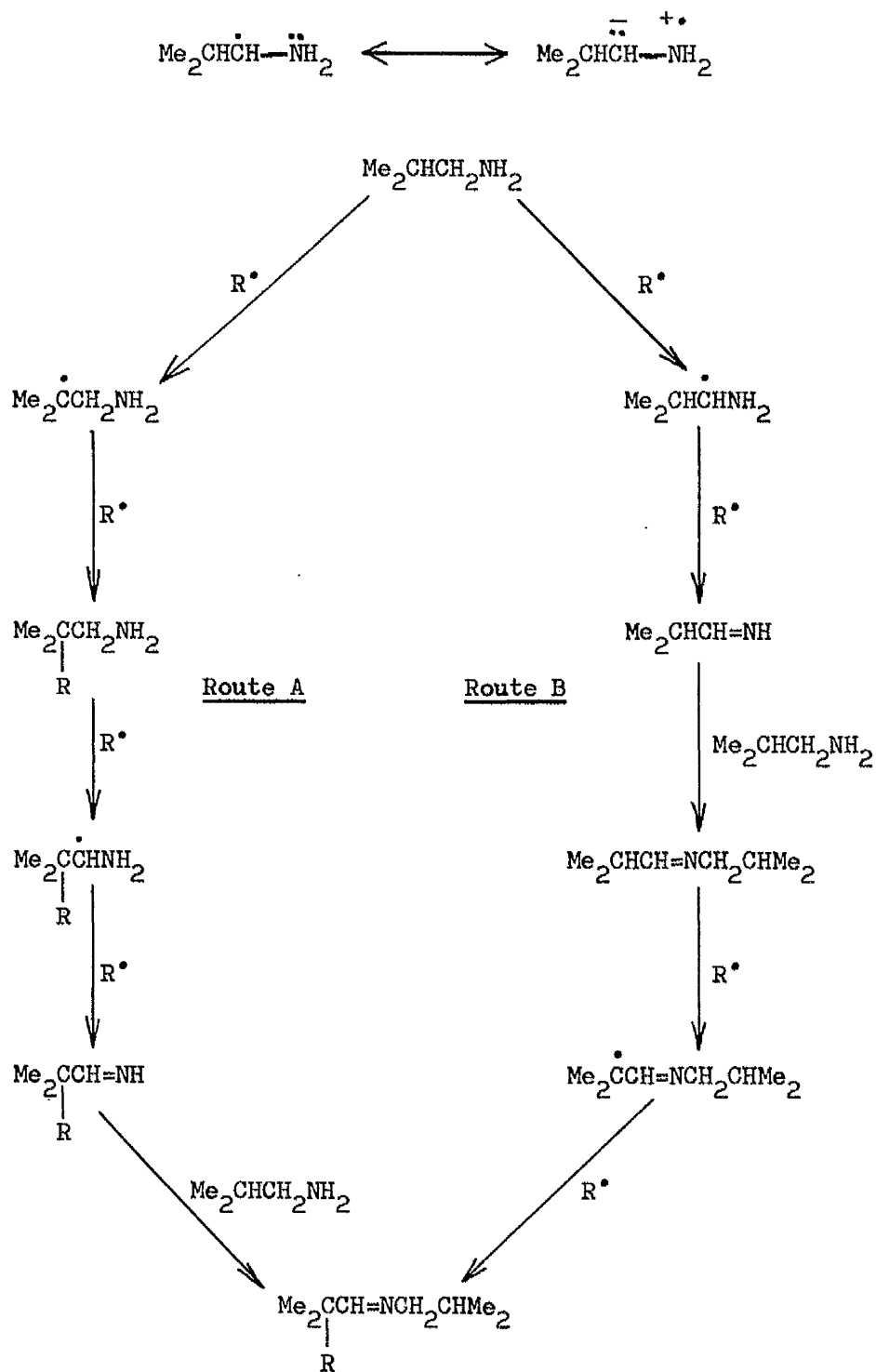
<u>Scheme 28</u>

Other possible reaction schemes involving the formation of isobutyr-
aldehyde as an intermediate in the formation of the Schiff's base, rather

than isobutylimine, can be ruled out, as in the 2:1 molar ratio reaction of $(CF_3)_2NO^{\bullet}$ with isobutylamine the only main fluorine containing products were shown by [19]F n.m.r. to be $(CF_3)_2NOH$ and $Me_2CRCH=NCH_2CHMe_2$.

The formation of the Schiff's base, N-isobutylideneisobutylamine, is the reaction expected when an imine is produced in the presence of an excess of amine.[127,128]

The reaction is simplified by the stability of N-isobutylidene-isobutylamine. Schiff's bases containing an α-CH_2 group often give aldol type condensations.[128]

i.e. $2R^1CH_2CH=NR^2 \longrightarrow R^1CH_2CH=CCH=NR^2 + R^2NH_2$
                                                $\underset{R^1}{|}$
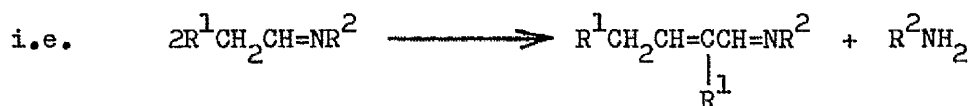
To test the feasibility of route B further, $(CF_3)_2NO^{\bullet}$ was reacted with N-isobutylideneisobutylamine.

2.   Reactions of $(CF_3)_2NO^{\bullet}$ with N-isobutylideneisobutylamine

Using a 2:1 molar ratio of $(CF_3)_2NO^{\bullet}$ to Schiff's base the products were as shown below.

$Me_2CHCH=NCH_2CHMe_2 + 2R^{\bullet} \longrightarrow Me_2CHCH=NCH_2CHMe_2$
                                                        23% unreacted

$+ \underset{R}{\underset{|}{Me_2CCH=NCH_2CHMe_2}} + \underset{OH}{\underset{|}{Me_2CHC=NCH_2CHMe_2}}$

            79%   16%

$+ (CF_3)_2NOH + (CF_3)_2NON(CF_3)_2 +$ unidentified
    50%   11%   5%

Using equimolar quantities of reactants the products were found to be:

$$Me_2CHCH=NCH_2CHMe_2 + R^\bullet \longrightarrow Me_2CHCH=NCH_2CHMe_2$$

<div align="center">58% unreacted</div>

$$+ \quad \underset{\underset{R}{|}}{Me_2CCH=NCH_2CHMe_2} \quad + \quad \underset{\underset{OH}{|}}{Me_2CHC=NCH_2CHMe_2}$$

<div align="center">55%   40%</div>

$$+ \quad Me_2CHCHO \quad + \quad Me_2CHCOR$$

<div align="center">2%   1%</div>

$$+ \quad (CF_3)_2NOH \quad + \quad (CF_3)_2NON(CF_3)_2$$

<div align="center">40%   34%</div>
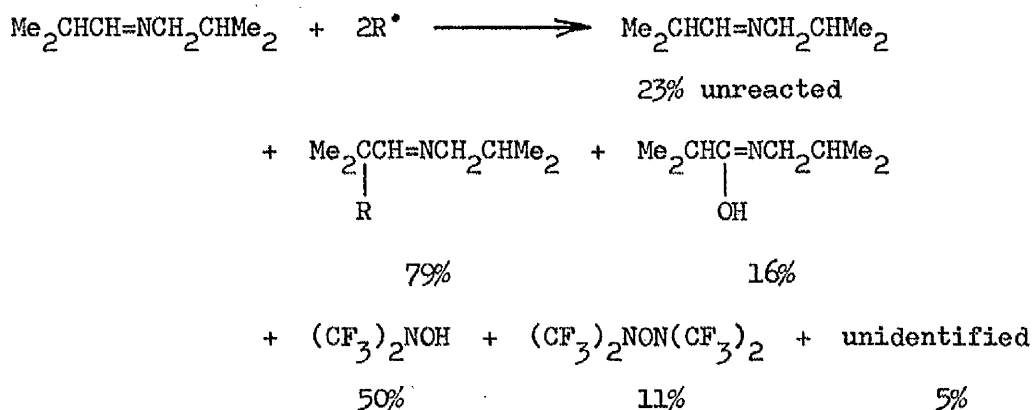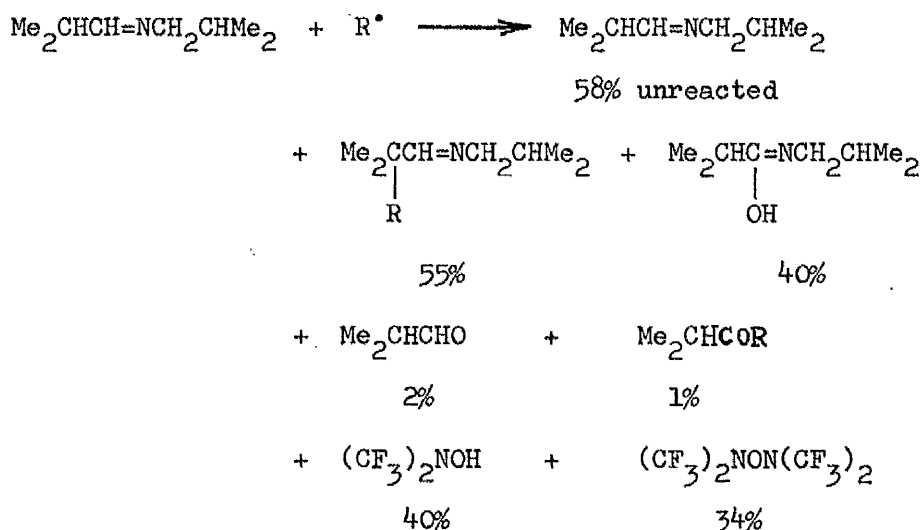
The product $Me_2CHC(OH)=NCH_2CHMe_2$, N-(1-hydroxy-2-methylpropylidene)-isobutylamine is the iminol form of N-isobutyl-2-methylpropanamide and as such would be expected to be unstable and to change to the amide if formed. The evidence for its identification is given in full in the experimental section but will be discussed briefly here.

The compound was isolated by preparative g.l.c. Its n.m.r. spectrum (n.m.r. 22) shows peaks for two isopropyl groups and a doublet ($J \sim 7$ Hz) for the CH_2 group at slightly different chemical shifts to those for the same groups in the parent Schiff's base, N-isobutylidene-isobutylamine (n.m.r. 21). It also shows a broad singlet at -1.24 ppm from external DCB attributed to the OH group. This spectrum is significantly different to that of N-isobutyl-2-methylpropanamide (n.m.r. 23) which shows a triplet for the CH_2 group and a broad peak at -0.36 ppm from external DCB for NH. The triplet is as expected, as in secondary amides the NH proton exchange rate is slow and coupling to adjacent C-H protons is observed.[129] Coupling to both the N-H and the adjacent C-H results in the CH_2 group appearing as a triplet, rather than a doublet.

The ^{19}F n.m.r. shows peaks for $(CF_3)_2NOH$ and some $(CF_3)_2NON(CF_3)_2$.

The mass spectrum (g.l.c./m.s., m.s. 41a) shows a prominent parent peak at m/e 143 (34.5%) and strong peaks for the m/e values 128 (20.8%, M-CH$_3$), 100 (19.1%, M-C$_3$H$_7$), 72 (64.4%, C$_4$H$_{10}$N$^+$), 71 (82.3%, C$_4$H$_7$O$^+$), 57 (62.4%, C$_4$H$_9^+$) and 43 (C$_3$H$_7^+$, 100%). It is virtually identical to the mass spectrum of N-isobutyl-2-methylpropanamide (m.s. 41b), confirming the identity of the compound as either the amido or the iminol form of the amide.

The i.r. spectrum (Fig. 5, experimental section) shows a strong peak at 1710 cm^{-1} for the C=N stretch. In N-isobutylideneisobutylamine the C=N stretching frequency is 1670 cm^{-1}, typical of compounds of the general type alkyl-CH=N-alkyl.[130] The shift to higher frequency is attributed to the inductive effect of the OH group reducing the length of the C=N bond, thus increasing its force constant and the frequency of absorption. The i.r. spectrum also shows peaks due to (CF$_3$)$_2$NO and a broad peak due to OH stretching at 3120 cm^{-1}.

The position of the C=N stretching band at 1710 cm^{-1} rules out the possibility of the compound isolated being the nitrone Me$_2$CHCH=NCH$_2$CHMe$_2$, the C=N stretching frequency of which would be expected[131] to be around 1600 cm^{-1}.

Evaporating the solution of the iminol plus (CF$_3$)$_2$NOH in CCl$_4$ left a white residue. Redissolving this in CCl$_4$ and rerunning the i.r. spectrum (Fig. 6) showed a reduction in the intensity of the C=N stretching and (CF$_3$)$_2$NO peaks and new peaks at 1640 and 1540 cm^{-1}. Repeating this process and heating the residue under vacuum resulted in (Fig. 7) further reduction of the peaks due to C=N and (CF$_3$)$_2$NO, further intensification in the peaks at 1640 and 1540 cm^{-1}, the disappearance of the OH band at 3120 cm^{-1} and the appearance of a band at 3220 cm^{-1}. By comparison with the spectrum of the amide (Fig. 8) it can be seen that the peaks at 3220, 1640 and 1540 cm^{-1} are the N-H stretching, C=O stretching (the

"Amide I" band) and N-H bending (the "Amide II" band) bands respectively of the amide. It was concluded that the process of evaporating the solution and warming the residue was driving off the $(CF_3)_2NOH$ and resulting in the conversion of the iminol form to the more stable amido form.

The inference must be that the inherently unstable iminol form, being more basic than the amido form, is stabilised by the slightly acidic $(CF_3)_2NOH$ in a weak adduct analogous to the amine-$(CF_3)_2NOH$ adducts[132] and that resonance forms (II) to (IV) make some contribution to the stability of the iminol.

$$
\begin{array}{ccc}
\overset{\displaystyle OH}{\underset{\displaystyle |}{Me_2CHC}}=NCH_2CHMe_2 & \longleftrightarrow & Me_2CHC=\overset{+}{N}CH_2CHMe_2 \\
& & \underset{\displaystyle H}{|} \\
HON(CF_3)_2 \quad (I) & & \overline{O}N(CF_3)_2 \quad (II)
\end{array}
$$

$$
\begin{array}{ccc}
Me_2CHC=NCH_2CHMe_2 & \longleftrightarrow & \overset{\displaystyle OH}{\underset{\displaystyle |}{Me_2CHC}}-NCH_2CHMe_2 \\
\underset{\displaystyle H}{|} & & + \quad \underset{\displaystyle H}{|} \\
\overline{O}N(CF_3)_2 \quad (IV) & & \overline{O}N(CF_3)_2 \quad (III)
\end{array}
$$
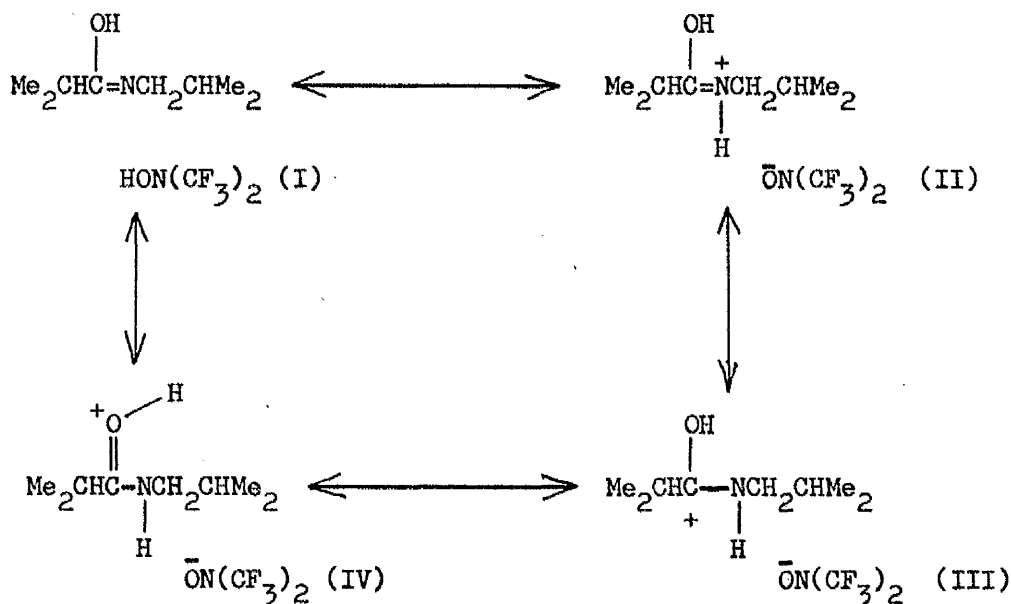
That such an adduct should stabilise the iminol form is given weight by the site of protonation of amides which is predominantly or exclusively at oxygen. Although the amino group is inherently much more basic than the carbonyl group suggesting (VI) as the most likely structure for the protonated amide, structure (VII) is stabilised by important contributions from (VIII) and (IX) to the resonance hybrid.[133]

$$(V) \quad R^1\!-\!\overset{\overset{\displaystyle O}{\|}}{C}\!-\!NR^2R^3 \underset{-H^+}{\overset{H^+}{\rightleftharpoons}} R^1\!-\!\overset{\overset{\displaystyle O}{\|}}{C}\!-\!\overset{+}{N}R^2R^3 \quad (VI)$$

$$\left[R^1\!-\!\overset{\overset{\displaystyle OH}{|}}{\underset{+}{C}}\!-\!NR^2R^3 \longleftrightarrow R^1\!-\!\overset{\overset{\displaystyle \overset{+}{O}\!-\!H}{\|}}{C}\!-\!NR^2R^3 \longleftrightarrow R^1\!-\!\overset{\overset{\displaystyle OH}{|}}{C}\!=\!\overset{+}{N}R^2R^3 \right]$$

$$(VIII) \qquad\qquad (VII) \qquad\qquad (IX)$$
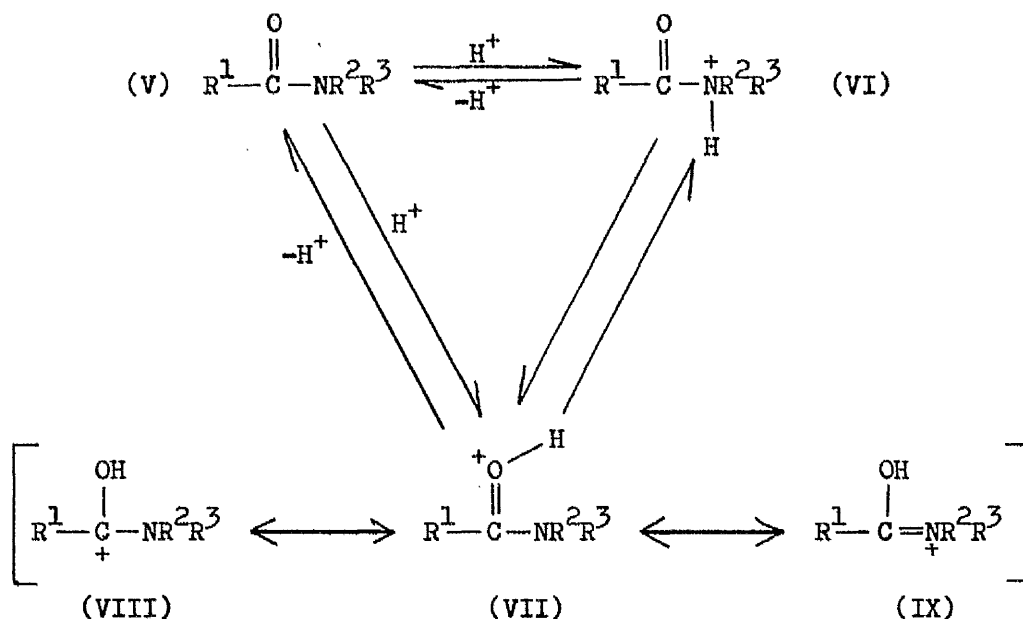
The existence of amides in the iminol form is certainly exceptional although a few claims for this type of geometrical isomerisation have been made.[134]

Two final points regarding the stability of N-(1-hydroxy-2-methylpropylidene)-isobutylamine are worthy of mention.

(a) It is stable enough to survive passage through a preparative g.l.c. column. The fact that when collected it contained an appreciable amount of $(CF_3)_2NOH$ suggests that it may pass through the column in association with the $(CF_3)_2NOH$.

(b) A 1:1 molar ratio mixture of $(CF_3)_2NOH$ and N-isobutyl-2-methylpropanamide was prepared but the i.r. spectrum showed no peak for the iminol form suggesting that the change is irreversible:

$$Me_2CH\overset{\overset{\displaystyle }{|}}{\underset{\displaystyle OH}{C}}\!=\!NCH_2CHMe_2 \cdot (CF_3)_2NOH \longrightarrow Me_2CHCONHCH_2CHMe_2 + (CF_3)_2NOH .$$
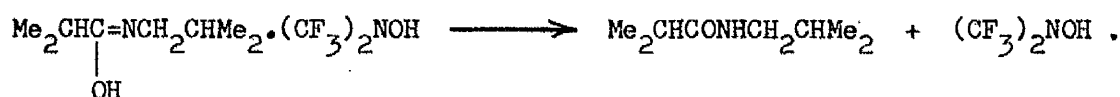
There would appear to be two possible routes to N-(1-hydroxy-2-methylpropylidene)-isobutylamine from N-isobutylideneisobutylamine, as

shown in Scheme 29.

$$Me_2CHCH=NCH_2CHMe_2 \xrightarrow[R^\bullet]{\text{H abstraction}} Me_2CH\overset{\bullet}{C}=NCH_2CHMe_2$$

$R^\bullet$ | addition $R^\bullet$

$$Me_2CHCH-\overset{\bullet}{N}CH_2CHMe_2 \xrightarrow[R^\bullet]{\text{disproportionation}} Me_2CHC=NCH_2CHMe_2$$
$\qquad\qquad |$ $\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad |$
$\qquad\qquad R$ $\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad R$

decomposition

$$(CF_3)_2NON(CF_3)_2 \xleftarrow{\quad R^\bullet \quad} (CF_3)_2N^\bullet \ + \ Me_2CHC=NCH_2CHMe_2$$
$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad |$
$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad O\bullet$

H abstraction

$$Me_2CHC=NCH_2CHMe_2$$
$\qquad\qquad |$
$\qquad\qquad OH$
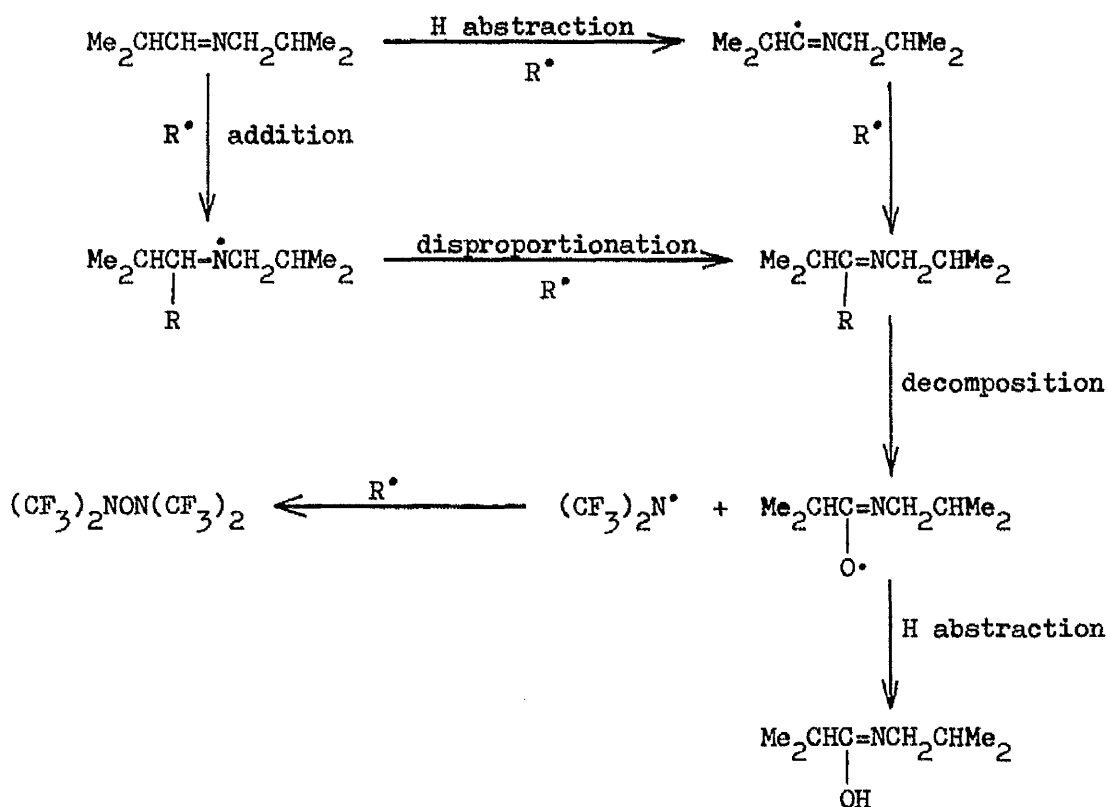
Scheme 29

The route involving H abstraction to give the iminoyl radical seems possible in view of the facile abstraction of aldehydic H atoms by $(CF_3)_2NO^\bullet$,[27] in which case the resulting radical is stabilised by resonance: $-\overset{\bullet}{\underset{}{C}}=\overset{..}{\underset{..}{O}} \xleftrightarrow{\quad} -\overset{..}{\underset{}{C}}=\overset{+\bullet}{\underset{}{O}}$ i.e. overlap between the radical orbital (presumably an sp^2 orbital rather than a p orbital; $-\overset{\bullet}{C}=O$ radicals are σ radicals rather than π radicals) and one of the orbitals containing one of the lone pairs on oxygen.

Iminoyl radicals have been proposed as intermediates in the reactions of N-benzylideneamines (ArCH=NR', R' = t-Bu or $PhCO_2$) with di-isopropylperoxydicarbonate which give benzonitrile as the major product.[135]

$$ArCH=NR^1 + R^2O^\bullet \longrightarrow Ar\overset{\bullet}{C}=NR^1 + R^2OH$$

$$\downarrow \text{fragmentation}$$

$$ArC\equiv N + {}^\bullet R^1$$
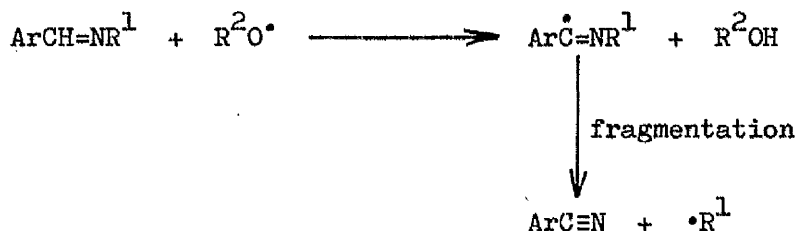
Scheme 30

They have only recently been positively identified by e.s.r. spectroscopy, in reactions of Schiff's bases with t-butoxyl radicals:[136]

$$R^1-CH=N-R^2 \xrightarrow{\ t\text{-}BuO^\bullet\ } R^1-\overset{\bullet}{C}=N-R^2$$

(R^1 and R^2 = Me, Et, n-Bu or t-Bu).

The e.s.r. parameters are consistent with the iminoyl radicals being σ radicals, with a non-linear arrangement about the N=C-C bonds. It is argued that, as the t-butoxyl radical is fairly selective (abstracting tertiary, secondary and primary hydrogens in the respective ratios of 44:12:1 at 40°C[137]) the weakest bond in the Schiff's base must be the C-H bond of the CH=N group, the stabilisation of the radical being due to the adjacent N atom. It is suggested[136] that this stabilisation is similar to that operating in the case of the aldehydes,

i.e.

$$\underset{R^1}{\overset{\bullet}{C}}\overset{\bullet\bullet}{=}N-R^2 \longleftrightarrow \underset{R^1}{\overset{\overline{\bullet\bullet}}{C}}\overset{+\bullet}{=}N-R^2$$
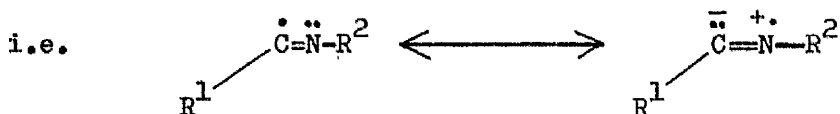
although the positive spin density at the nitrogen nucleus resulting from such resonance is not reflected in the magnitude of the N hyperfine splitting constant.

It seems likely that such resonance stabilisation would not be as important in the case of the iminoyl radicals as in the case of the

radicals from aldehydes as some, at least, of the iminoyl radicals would be expected to be in the syn-configuration where overlap between radical orbital and lone pair would not be possible:
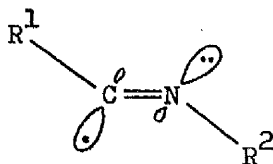
It has already been shown that tertiary hydrogens are abstracted in preference to CH=N hydrogens (the reverse of the aldehyde case,

e.g. $Me_2CHCHO \xrightarrow{2R^\bullet} 100\%$ Me_2CHCOR) and it seems possible that in the case of the reactions of $(CF_3)_2NO^\bullet$ with Schiff's bases abstraction of the CH=N hydrogen may be too slow to compete with alternative reactions.

Several other factors against abstraction of the CH=N hydrogen are that:

(i)   in reactions of $(CF_3)_2NO^\bullet$ with N-benzylidenebenzylamine and N-benzylideneaniline (discussed later) no products from abstraction of this hydrogen were observed, and

(ii)   the formation of $Me_2CHC(OH)=NCH_2CHMe_2$ and $(CF_3)_2NON(CF_3)_2$ is favoured by an increase in the ratio of Schiff's base to $(CF_3)_2NO^\bullet$. There seems no reason why an increase in the concentration of Schiff's base should lead to an increase in abstraction of one type of H atom over another.

The alternative route in Scheme 29 involves addition of one $(CF_3)_2NO^\bullet$ to the double bond followed by disproportionation of the N-centred radical so formed, with another $(CF_3)_2NO^\bullet$. Addition of a second $(CF_3)_2NO^\bullet$ radical would not be expected due to the instability of the $(CF_3)_2NO-N$ linkage.[51]

Such an addition step is not without precedent. It has been proposed that reaction of ethylbenzene peroxide radicals with 35 Schiff's bases proceeds via addition of a peroxide radical to the double bond, forming a free valence on the nitrogen,[138]

i.e. $R^1OO^\bullet$ + $>C=N-$ ⟶ $>C-\overset{\bullet}{N}-$
$\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad |$
$\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad OOR^1$
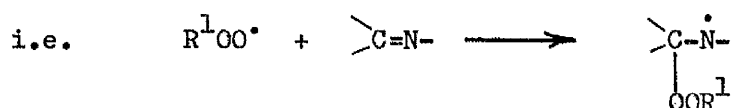
The new free radical probably reacts with a second peroxide radical

$>C-\overset{\bullet}{N}-$ + $R^1O_2^\bullet$ ⟶ $>C-\overset{O^\bullet}{\underset{|}{\underset{|}{N}}}$ + $R^1O^\bullet$.
$\ |$
OOR^1 $\quad\quad\quad\quad\quad\quad\quad\quad OOR^1$

Then follow secondary reactions with cleavage of the C-N bond.

The decomposition step by loss of $(CF_3)_2N^\bullet$ from $Me_2CHC=NCH_2CHMe_2$ is unusual in that most mechanisms proposed to explain the $\quad R$ formation of $(CF_3)_2N^\bullet$ radicals involve the loss of $(CF_3)_2N^\bullet$ by β-scission of a $(CF_3)_2NO$ containing radical.[26,42,53] An exception is the mechanism proposed for reaction of $(CF_3)_2NO^\bullet$ with perfluoropropyne or perfluorobut-2-yne, shown in Scheme 31.[40]

$$CF_3C\equiv CCF_3 \xrightarrow{2R^\bullet} R-C=C-R \longrightarrow \left[\begin{matrix} R-C=C-O^\bullet \\ |\quad\quad | \\ CF_3\quad CF_3 \\ \updownarrow \\ R-\overset{\bullet}{C}-C=O \\ |\quad\quad | \\ CF_3\quad CF_3 \end{matrix} \right] + (CF_3)_2N^\bullet$$
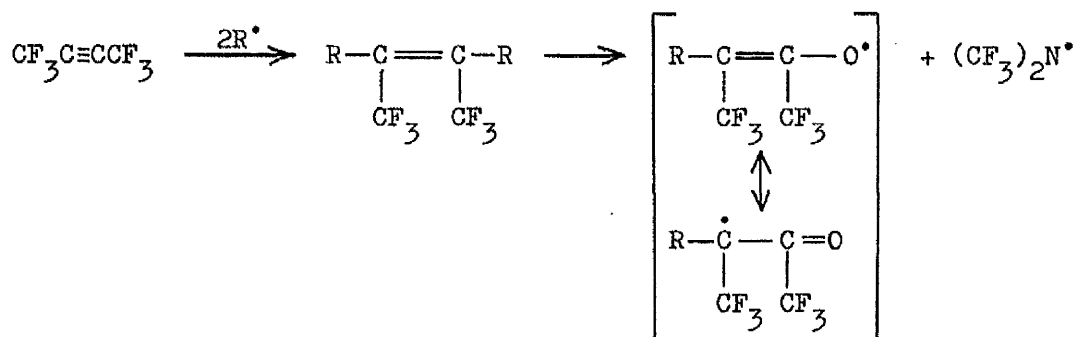
Scheme 31

The full reaction scheme for reaction of $(CF_3)_2NO^\bullet$ with N-isobutylideneisobutylamine is given in Scheme 32.

$$Me_2CHCH=NCH_2CHMe_2 \xrightarrow{\;R^{\bullet}\;} Me_2CH\overset{\bullet}{C}H-NCH_2CHMe_2$$

$$Me_2\overset{\bullet}{C}CH=NCH_2CHMe_2$$

$$Me_2CH\overset{\bullet}{C}=NCH_2CHMe_2 \xrightarrow{\;R^{\bullet}\;} Me_2CHC=NCH_2CHMe_2$$

$$Me_2CCH=NCH_2CHMe_2$$

$$(CF_3)_2N^{\bullet} \;+\; Me_2CHC=NCH_2CHMe_2$$

$$(CF_3)_2NON(CF_3)_2 \qquad Me_2CHC=NCH_2CHMe_2$$
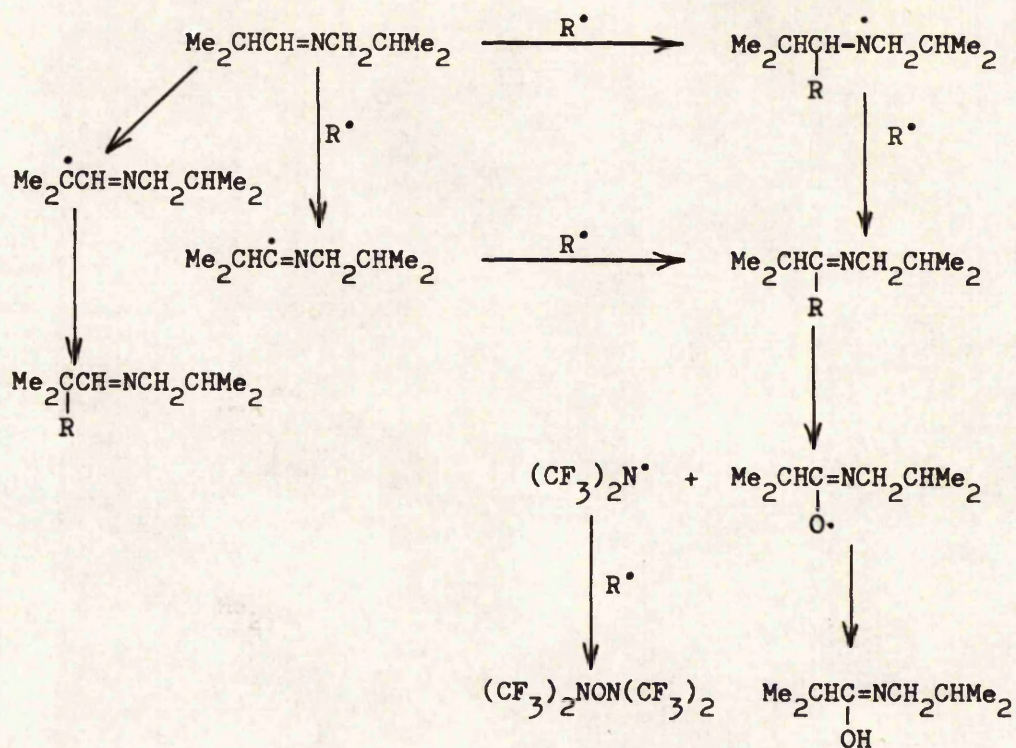
Scheme 32

The full reaction scheme for the reaction of $(CF_3)_2NO^{\bullet}$ with isobutylamine is given in Scheme 33.

$$Me_2CHCH_2NH_2 \longrightarrow Me_2\overset{\bullet}{C}CH_2NH_2$$

$$\downarrow R^\bullet \qquad\qquad\qquad \downarrow R^\bullet$$

$$Me_2CH\overset{\bullet}{C}HNH_2 \qquad\qquad \underset{R}{Me_2\underset{|}{C}CH_2NH_2}$$

minor product

$$\downarrow R^\bullet$$

$$Me_2CHCH{=}NH$$

$$\downarrow Me_2CHCH_2NH_2$$

$$Me_2CHCH{=}NCH_2CHMe_2 \quad\ldots \text{ major product}$$

$$\swarrow R^\bullet \qquad\qquad\qquad\qquad \searrow 2R^\bullet$$

$$Me_2\overset{\bullet}{C}CH{=}NCH_2CHMe_2 \qquad\qquad \underset{R}{Me_2\underset{|}{C}HC{=}NCH_2CHMe_2}$$

$$\downarrow R^\bullet \qquad\qquad\qquad\qquad\qquad \downarrow$$

$$\underset{R}{Me_2\underset{|}{C}CH{=}NCH_2CHMe_2} \qquad (CF_3)_2N^\bullet + \underset{O\bullet}{Me_2CH\underset{|}{C}{=}NCH_2CHMe_2}$$

major product

$$\downarrow$$

$$\underset{OH}{Me_2CH\underset{|}{C}{=}NCH_2CHMe_2}$$

minor product

Scheme 33

There would appear to be two possible routes to the disubstituted Schiff's base found as a minor product in the 2:1 reaction of $(CF_3)_2NO^\bullet$ with isobutylamine:

(a)   further substitution by $(CF_3)_2NO^\bullet$:

$$Me_2\overset{R}{\underset{|}{C}}CH=NCH_2CHMe_2 \quad \xrightarrow{R^\bullet} \quad Me_2\overset{R}{\underset{|}{C}}CH=NCH_2\overset{\bullet}{C}Me_2 \quad \xrightarrow{R^\bullet} \quad Me_2\overset{R}{\underset{|}{C}}CH=NCH_2\overset{R}{\underset{|}{C}}Me_2$$
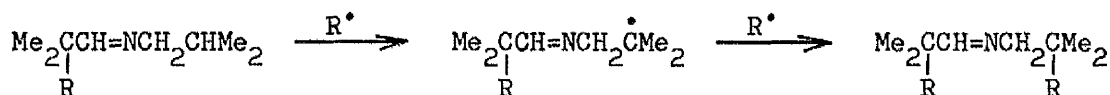
or (b) transalkylidenation (exchange):

$$Me_2\overset{R}{\underset{|}{C}}CH_2NH_2 \; + \; Me_2\overset{R}{\underset{|}{C}}CH=NCH_2CHMe_2 \quad \longrightarrow \quad Me_2\overset{R}{\underset{|}{C}}CH=NCH_2\overset{R}{\underset{|}{C}}Me_2$$

$$+ \; Me_2CHCH_2NH_2$$
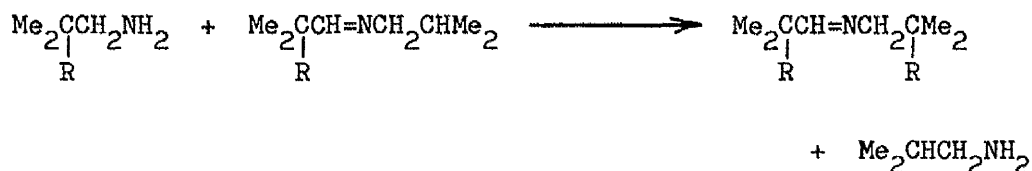
3.   <u>Reactions of $(CF_3)_2NO^\bullet$ with benzylamine</u>

Benzylamine was chosen as the next amine for study as it has no readily abstractable hydrogens other than in the CH_2NH_2 group.

Using equimolar quantities of reactants reaction was complete after 20 to 30 minutes giving the products shown below.

$$PhCH_2NH_2 \; + \; R^\bullet \quad \longrightarrow \quad PhCH=NCH_2Ph \; + \; (CF_3)_2NOH \; + \; NH_3$$
$$95\% \qquad\qquad\qquad 100\%$$

$$+ \quad \text{unidentified}$$
$$5\%$$
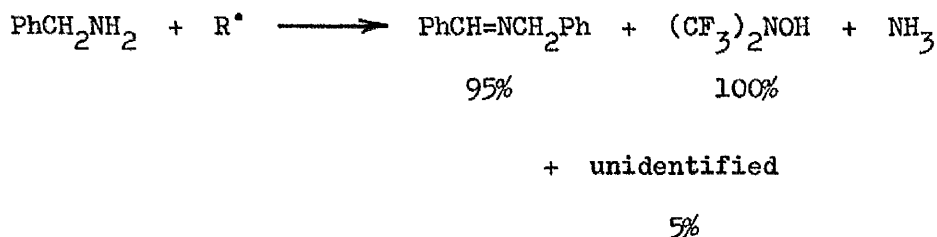
The mechanism proposed to explain the formation of <u>N</u>-benzylidenebenzylamine is shown in Scheme 34.

$$PhCH_2NH_2 \quad \xrightarrow{R^\bullet} \quad Ph\overset{\bullet}{C}HNH_2 \quad \xrightarrow{R^\bullet} \quad PhCH=NH \quad \xrightarrow{PhCH_2NH_2} \quad PhCH=NCH_2Ph$$
$$+ \quad NH_3$$
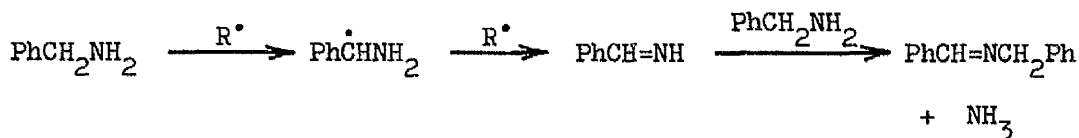
<u>Scheme 34</u>

The abstraction of the first hydrogen from the CH_2 rather than from the NH_2 is even more likely in this case than in the isobutylamine reaction as the resulting radical would be further resonance stabilised by delocalisation of the lone electron around the ring. The disproportionation

of the PhĊHNH$_2$ radical with a second (CF$_3$)$_2$NO$^\bullet$ radical gives benzaldimine PhCH=NH which is unstable, although much more stable than the aliphatic aldimines. The condensation of the imine with the amine to give the Schiff's base is the reaction expected when an imine is generated in the presence of excess amine.[127,128]

An alternative route to the Schiff's base via benzaldehyde can be ruled out as this would involve loss of oxygen from the (CF$_3$)$_2$NO$^\bullet$ resulting in the formation of (CF$_3$)$_2$N$^\bullet$ radicals and then (CF$_3$)$_2$NH, (CF$_3$)$_2$NON(CF$_3$)$_2$ or (CF$_3$)$_2$NN(CF$_3$)$_2$; (CF$_3$)$_2$NOH was the only fluorine containing product.

Using a 2:1 molar ratio of (CF$_3$)$_2$NO$^\bullet$ to benzylamine the products were as shown. Percentage yields from two reactions are given.
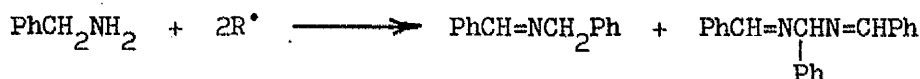
PhCH$_2$NH$_2$ + 2R$^\bullet$ ⟶ PhCH=NCH$_2$Ph + PhCH=NCHN=CHPh
                                                               |
                                                               Ph

(a) 51%, (b) 42%   (a) 19%, (b) 37%

+ probably

(a) 20%, (b) 17%

+ PhCHO   +   PhCOON(CF$_3$)$_2$
(a) trace, (b) 2.5%   (a) - , (b) 1%

+ (CF$_3$)$_2$NOH   +   NH$_3$
97%
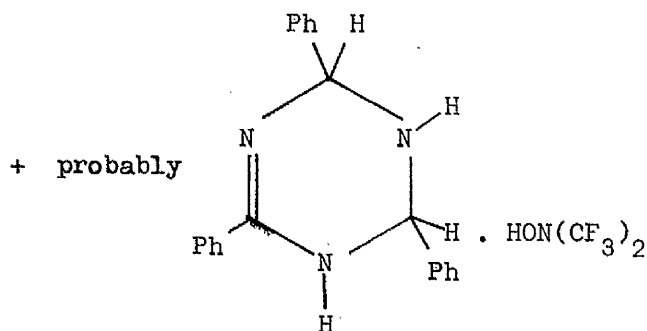
The main products were:

(a) $(CF_3)_2NOH$, 100% in all,

(b) $\underline{N}$-benzylidenebenzylamine, formed as in the equimolar reactant

reaction,

(c)   hydrobenzamide, $(PhCH=N)_2CHPh$. This is the product normally

expected when benzaldimine, formed at room temperature, undergoes self-

condensation, presumably via the reaction sequence shown in Scheme 35.

$$2PhCH=NH \longrightarrow \underset{\underset{Ph}{|}}{PhCH=NCHNH_2} \xrightarrow{PhCH=NH} \underset{\underset{Ph}{|}\ \underset{Ph}{|}}{PhCH=NCHNHCHNH_2}$$

$$\downarrow -NH_3$$

$$\underset{\underset{Ph}{|}}{PhCH=NCHN=CHPh}$$
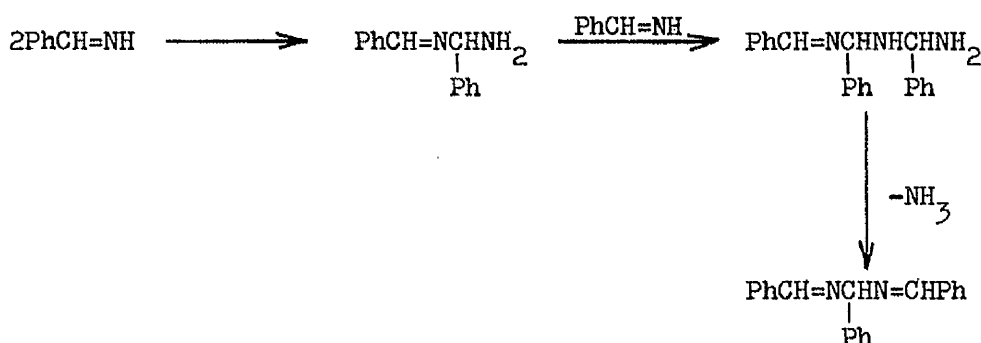
Scheme 35

(d)   the adduct between probably 1,2,3,4-tetrahydro-2,4,6-triphenyl-

1,3,5-triazine and $(CF_3)_2NOH$. The evidence for the identification of

this compound is given in full in the experimental section but will be

discussed briefly here.

The adduct consists of a white solid which was found to be

insoluble in all the solvents tried although it dissolved in acetone on

heating forming 2,4,6-triphenyl-1,3,5-triazine and $(CF_3)_2NOH$. The same

compounds were formed by the action of heat on the solid $\underline{in\ vacuo}$, and

when a melting point determination on the solid was attempted. Decom-

position appears to occur between 135 and 140°C.

The i.r. spectrum of the solid (Fig. 9, experimental section)

showed peaks for C=N stretching (1625 cm^{-1}), N-H stretching (3300 cm^{-1},

sharp) and for $(CF_3)_2NO$. It also showed a broad medium band between

3100 and 2100 cm^{-1} typical of secondary amine-$(CF_3)_2NOH$ adducts.[132] The

presence of the free N-H stretch implies that two amino groups must be present, one free and the other forming the adduct with $(CF_3)_2NOH$.

Analysis of the solid gave figures close to those required by the adduct although two analyses on portions of the same sample indicated that the adduct slowly decomposes, losing $(CF_3)_2NOH$, at room temperature.

No references to 1,2,3,4-tetrahydro-2,4,6-triphenyl-1,3,5-triazine could be found in the literature other than as a postulated intermediate in the hydrogenation of 2,4,6-triphenyl-1,3,5-triazine.[139] It is presumably unstable and only stable in this case as the $(CF_3)_2NOH$ adduct.

1,2-Dihydro-2,4,6-triphenyl-1,3,5-triazine which is stable and well documented was considered as a possibility. However its i.r. spectrum shows bands for C=N at 1605 cm^{-1} and N-H at 3200 cm^{-1}.[140] The position of the C=N stretching frequency is about as expected. Having two conjugated C=N bonds it would be expected to have a lower C=N stretching frequency than the tetrahydro compound. Furthermore, a 1:1 adduct between the dihydro compound and $(CF_3)_2NOH$ would not be expected to show a stretching band for free N-H.

The 1,2-dihydro compound is easily converted to 2,4,6-triphenyl-1,3,5-triazine by heating in refluxing xylene or nitrobenzene.[141]
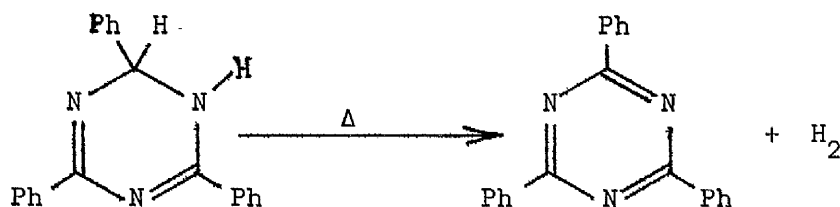
Presumably a similar reaction takes place with the tetrahydro compound when heated:
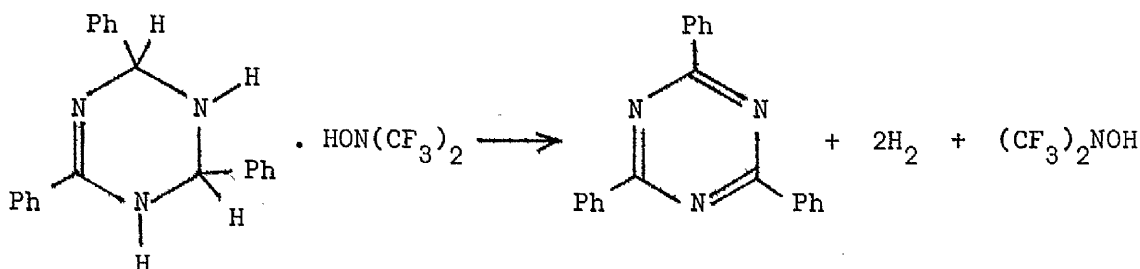
The mechanism proposed for formation of the tetrahydro compound is shown in Scheme 36.

$2PhCH=NH \longrightarrow PhCH=NCHNH_2$
$\qquad\qquad\qquad\qquad\quad |$
$\qquad\qquad\qquad\qquad\ Ph$

$PhCH=NH$

$PhCH=NCHNHCHNH_2$
$\qquad\qquad\quad |\quad\ |$
$\qquad\qquad\ Ph\ \ Ph$

$-NH_3$

$PhCH=NCHN=CHPh$
$\qquad\qquad |$
$\qquad\quad Ph$

$2R^\bullet$
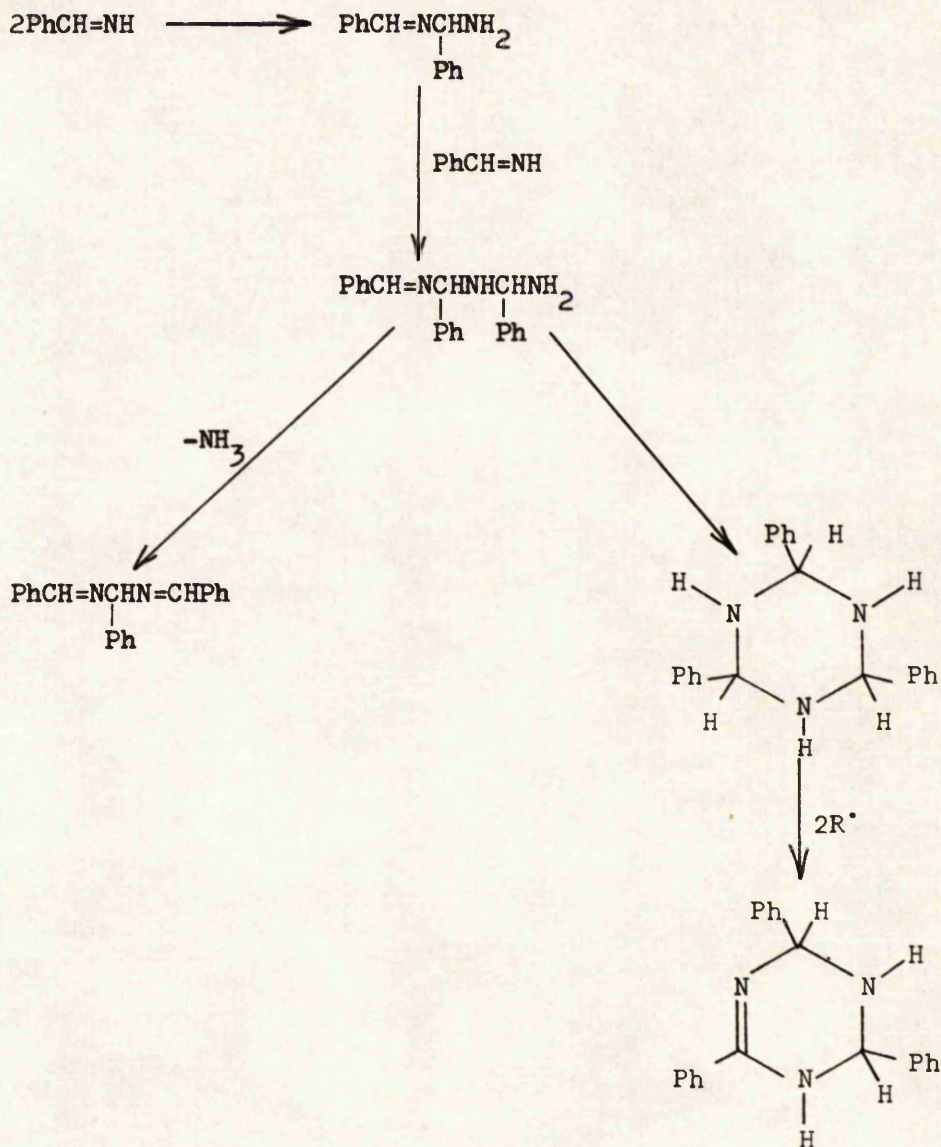
Scheme 36

The driving force for the cyclisation is presumably the presence of excess $(CF_3)_2NO^\bullet$ which can stabilise the intrinsically unstable hexahydro--2,4,6-triphenyl-1,3,5-triazine by removing two hydrogens to give the double bond.

Another possibility for the structure of the compound under discussion was thought to be an adduct between $(CF_3)_2NOH$ and the intermediate compound shown in Scheme 36,

i.e. $PhCH=NCHNHCHNH_2$. $HON(CF_3)_2$.
                 $\underset{Ph}{|}$ $\underset{Ph}{|}$
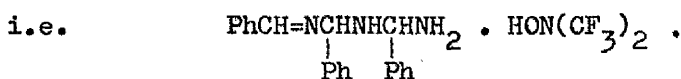
Such a structure would (a) show very nearly the same analysis figures, (b) show peaks in the i.r. spectrum for C=N and free N-H. Loss of ammonia or cyclisation would be prevented by the bonding between the NH_2 group and $(CF_3)_2NOH$. However such an adduct was ruled out as it was considered that removal of the $(CF_3)_2NOH$ would probably result in loss of ammonia giving hydrobenzamide rather than in cyclisation and loss of hydrogen to give 2,4,6-triphenyl-1,3,5-triazine, as there would be no $(CF_3)_2NO^\bullet$ present to abstract hydrogens and stabilise the hexahydro-2,4,6-triphenyl-1,3,5-triazine.

There appears to be only one literature report of the possible isolation of hexahydro-2,4,6-triphenyl-1,3,5-triazine. Russian workers [142] have reported that addition of a solution of benzaldehyde in methanol to a saturated solution of ammonia in methanol gives, on standing at $-10^\circ C$, a previously unknown crystalline base of formula $C_{21}H_{21}N_3$ which is unstable and readily loses ammonia to form hydrobenzamide. It was considered that this compound could be either hexahydro-2,4,6-triphenyl-1,3,5-triazine or $PhCH=NCHNHCHNH_2$. The former of these was thought the
                                                   $\underset{Ph}{|}$ $\underset{Ph}{|}$
most likely, on the basis of the compound's infrared spectrum which showed a band at 3180 cm^{-1} assigned to an N-H stretching vibration but no double band characteristic of NH_2. A strong band at 1680 cm^{-1}, the only one in the region 1600 to 1700 cm^{-1}, is assigned to N-H deformation on the basis that $PhCH=NCH(Ph)NHCH(Ph)NH_2$ should show at least two intense

bands in this region, one for NH_2 deformation and one for C=N stretching.

This reasoning seems slightly dubious as the band due to N-H deformation in the hexahydrotriazine might be expected to be weak and to appear at a lower frequency than 1680 cm^{-1}.

However, whichever of these compounds is preferred it does provide some support for the mechanism shown in Scheme 36, involving as it does both these compounds as unstable intermediates.

Using a 3:1 molar ratio of $(CF_3)_2NO^{\bullet}$ to benzylamine the following products were obtained.

$$PhCH_2NH_2 \ + \ 3R^{\bullet} \ \longrightarrow \ PhCH=NCH_2Ph \ + \ (PhCH=N)_2CHPh$$

$$16\% \qquad\qquad 10\%$$

+ probably

$$.HON(CF_3)_2 \ +$$

45%

30%

+ PhCHO + $PhCOON(CF_3)_2$ + $(CF_3)_2NOH$

trace   trace   not determined
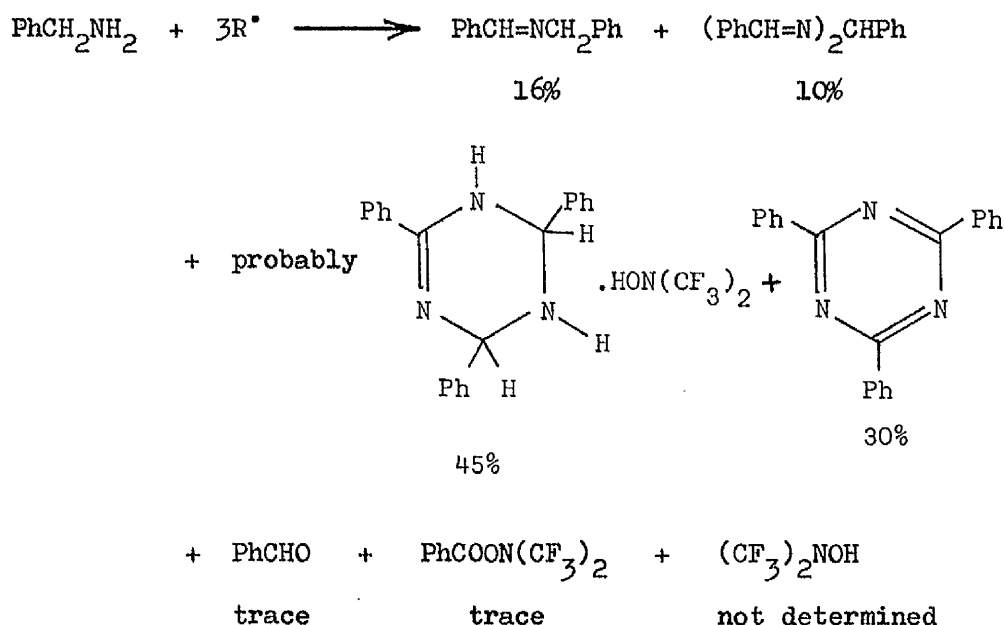
The traces of PhCHO and $PhCOON(CF_3)_2$ found in the products of the 2:1 and 3:1 molar ratio reactions of $(CF_3)_2NO^{\bullet}$ with benzylamine could be formed by hydrolysis of N-benzylidenebenzylamine or hydrobenzamide to benzaldehyde by traces of water and the subsequent reaction of benzaldehyde with $(CF_3)_2NO^{\bullet}$. In one reaction using a 2:1 molar ratio of reactants significant amounts of PhCHO and $PhCOON(CF_3)_2$ were found but rigorous drying of the reactants reduced the amounts of these to barely measurable quantities. No traces of either $(CF_3)_2NH$ or

$(CF_3)_2NON(CF_3)_2$, one of which would probably be formed if the benzaldehyde resulted from reaction of $(CF_3)_2NO^\bullet$ with benzylamine or one of the products, were detected.

The overall reaction scheme for the reaction of $(CF_3)_2NO^\bullet$ with benzylamine is shown in Scheme 37.

$$PhCH_2NH_2$$

$$\downarrow R^\bullet$$

$$Ph\overset{\bullet}{C}HNH_2$$

$$\downarrow R^\bullet$$

$$PhCH=NH \xrightarrow{\;PhCH_2NH_2\;} PhCH=NCH_2Ph + NH_3$$

$$\downarrow 2PhCH=NH$$

$$PhCH=NCHNHCHNH_2$$
$$\qquad\quad |\quad\;\; |$$
$$\qquad\; Ph\quad Ph$$

$$\overset{-NH_3}{\swarrow} \qquad\qquad \searrow$$

$$PhCH=NCHN=CHPh$$
$$\qquad\quad\; |$$
$$\qquad\quad Ph$$

Scheme 37

4.   <u>Reaction of $(CF_3)_2NO^{\bullet}$ with N-benzylidenebenzylamine</u>

This reaction was complete within 30 minutes giving an almost quantitative yield of <u>N</u>-benzylidene-1-(bistrifluoromethylamino-oxy)-benzylamine.

$$PhCH=NCH_2Ph \quad + \quad R^{\bullet} \quad \longrightarrow \quad PhCH=NCH_2Ph \quad + \quad (CF_3)_2NOH$$

4.51 mmoles   7.98 mmoles   17% unreacted   53%

$$+ \quad \begin{array}{c} PhCH=NCHPh \\ | \\ R \end{array}$$

99%
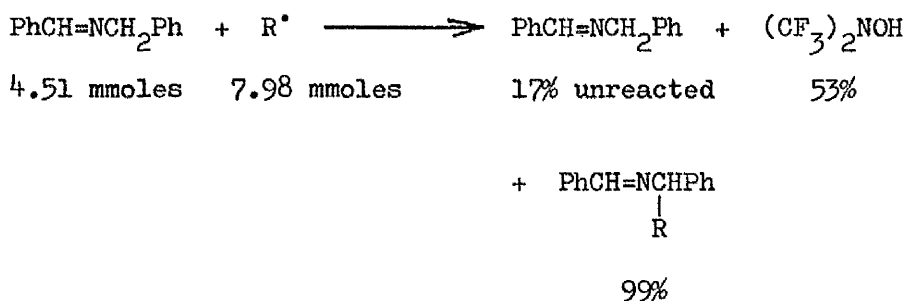
The radical formed by abstraction of the benzylic hydrogen is resonance stabilised as shown:

$$PhCH=N\overset{\bullet}{C}HPh \quad \longleftrightarrow \quad Ph\overset{\bullet}{C}HN=CHPh$$

as well as by delocalisation of the odd electron around the rings.

The ^{19}F n.m.r. spectrum of PhCH=NCHRPh is interesting. At room temperature it displays a very broad singlet (Fig. 10), at higher temperature (60°C) a much narrower singlet, and at low temperature (-10°C) a doublet of quartets (Fig. 11, $\Delta\nu$ = 90 Hz and J = 9.5 Hz). The explanation for this splitting is that the $(CF_3)_2NO$ group is attached to an asymmetric C atom.[143] At high temperature the CF_3 groups are equivalent due to rapid rotation about the N-O bond and inversion of the N atom. At room temperature the rates of rotation and inversion are lower, leading to a certain amount of magnetic non-equivalence of the CF_3 groups. This non-equivalence is exaggerated at low temperature and the CF_3 groups appear as discrete peaks. Coupling between the fluorines of the CF_3 groups splits these peaks into quartets. Similar splitting patterns have been observed previously with compounds of general formula $(CF_3)_2NO-CXYZ$.[143]

Reactions of $(CF_3)_2NO^\bullet$ with N-alkylanilines

5.   N-methylaniline

6.   N-ethylaniline

7.   2-Chloro-4-(N-propylamino)-toluene

8.   4-Chloro-2-(N-propylamino)-toluene

The reactions of $(CF_3)_2NO^\bullet$ with these N-alkylanilines were carried out in the same way as with the other amines, $(CF_3)_2NO^\bullet$ being condensed, in vacuo, onto the N-alkylaniline in a reaction tube at $-196^\circ C$. The tube was sealed and removed from the liquid nitrogen. In each case a very fast, exothermic reaction took place, the reactants quickly turning dark red-purple. Thick white fumes were evolved which settled down to give dark wine-red viscous products. The reactions were complete within about three minutes, before the tubes had reached room temperature.

In reactions using a 2:1 molar ratio of $(CF_3)_2NO^\bullet$ to N-alkylaniline the volatile products were found to consist of mainly N,N-bistrifluoromethylhydroxylamine and bistrifluoromethylamine with traces of perfluoro(methylenemethylamine) and perfluoro-(2,4-dimethyl-3-oxa-2,4-diazapentane).

The involatiles were found to consist of (a) brown-black tarry solids which dried to brown-black clinker-like solids with melting points greater than $300^\circ C$, and (b) viscous liquids which were identified by their n.m.r., i.r. and mass spectra as N^1-alkyl-N^1-aryl-N^2-(trifluoromethyl)-fluoroformamidines of general formula,

$$Ar - \underset{\underset{\text{alkyl}}{|}}{N} - \overset{\overset{F}{|}}{C} = N - CF_3 \quad .$$
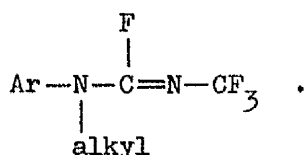
The ^{19}F n.m.r. spectra of these compounds show a doublet between -29.5 and -26.5 p.p.m. from external TFA and a quartet between -38 and -32 p.p.m.,

with coupling constants of approximately 12.4 Hz. By comparison with other compounds, these chemical shifts and coupling constants were shown to be as expected for compounds containing the N^2-(trifluoromethyl)-fluoroformamidine group, $-NCF=NCF_3$.

In the [1]H n.m.r. spectra, replacing the amino H by the $-CF=NCF_3$ group results in a shift of the peak due to the α-CH_2 or CH_3 group to lower field by between 0.7 and 1.4 p.p.m. The β-CH_2 to CH_3 peak is shifted by a much smaller amount and there is a shift downfield of the phenyl protons by between 0.5 and 1.0 p.p.m.

The i.r. spectra show a very strong peak at about 1690 cm^{-1} for the C=N stretching vibration.

The reactions of $(CF_3)_2NO^\bullet$ with these four N-alkylanilines (2:1 molar ratio) are summarised below.

5. $(CF_3)_2NO^\bullet$ with N-methylaniline

$$PhNHMe + 2R^\bullet \longrightarrow (CF_3)_2NOH + (CF_3)_2NH + CF_3N=CF_2$$

                                    64%   16%   trace

$$+ \; PhNCF=NCF_3 \; (Me) \; + \; black \; tarry \; solid$$

36% of amine used   27% total weight of reactants

6. $(CF_3)_2NO^\bullet$ with N-ethylaniline

$$PhNHEt + 2R^\bullet \longrightarrow (CF_3)_2NOH + (CF_3)_2NH + CF_3N=CF_2$$

         60%   20%   trace

$$+ \; (CF_3)_2NON(CF_3)_2 \; + \; PhNCF=NCF_3 \; (Et)$$

3%   26%
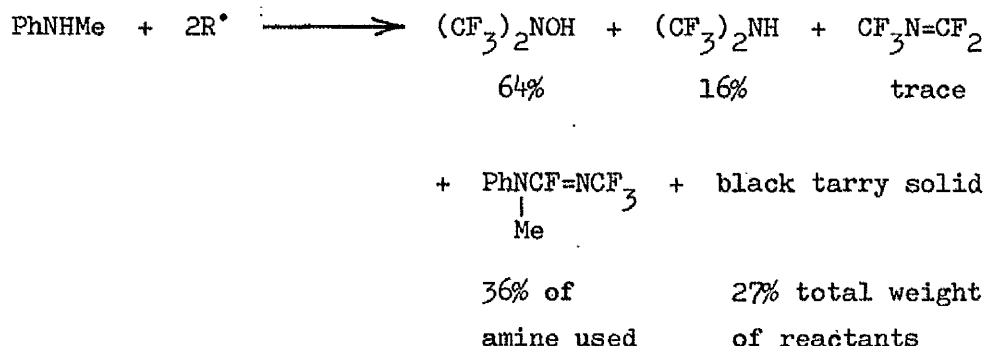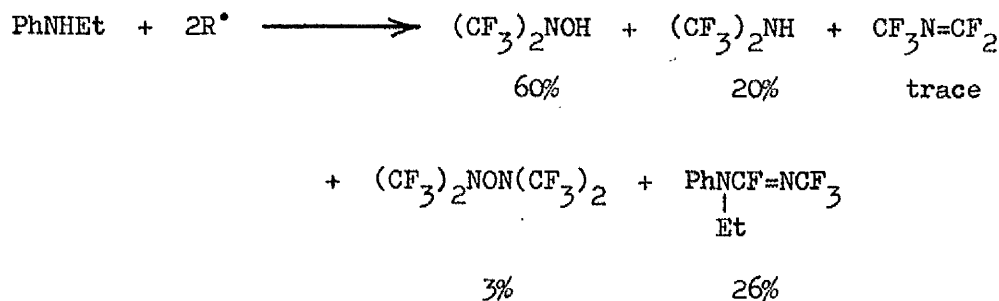
+ black tarry solid

19% total weight of reactants

7.   (CF$_3$)$_2$NO$^\bullet$ with 2-chloro-4-(N-propylamino)-toluene

Me—⟨benzene ring, Cl at position⟩—NHPr + 2R$^\bullet$ ⟶ (CF$_3$)$_2$NOH + (CF$_3$)$_2$NH

                                                                .62%   15%

+ Me—⟨benzene ring, Cl⟩—NCF=NCF$_3$ + black tarry solid
                                |Pr
                                                    29% total weight
                                                    of reactants

24%

8.   (CF$_3$)$_2$NO$^\bullet$ with 4-chloro-2-(N-propylamino)-toluene

⟨benzene ring, Me top, Cl bottom⟩—NHPr + 2R$^\bullet$ ⟶ (CF$_3$)$_2$NOH + (CF$_3$)$_2$NH

                                                                    44%   35%

⟨benzene ring, Me top, Cl bottom⟩—NCF=NCF$_3$ + black tarry solid
                                        |Pr
                                                        21% total weight
                                                        or reactants

41%
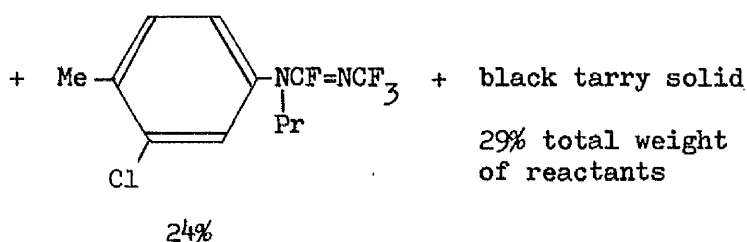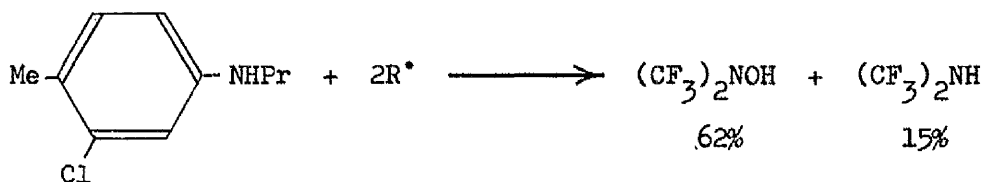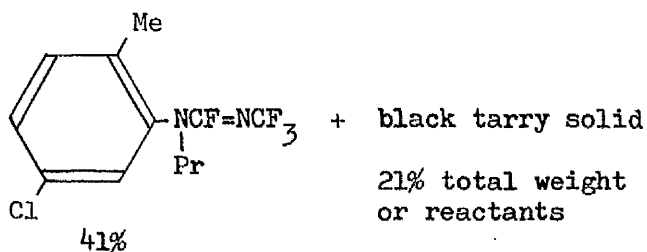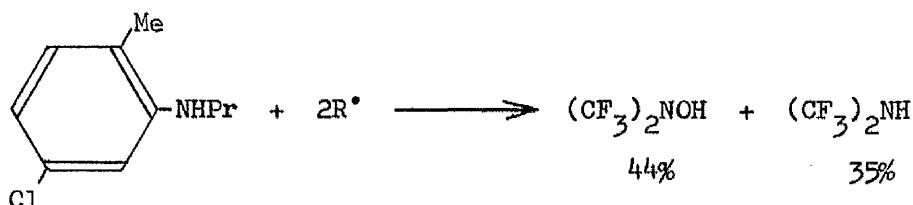
The bistrifluoromethylamine could be formed via several routes, as postulated by Choudhury[51] who studied the reactions of (CF$_3$)$_2$NO$^\bullet$ with diphenylamine, 4,4'-dimethoxydiphenylamine, 4,4'-dicumyldiphenylamine and 4,4'-dinitrodiphenylamine in an attempt to prepare compounds of general formula Ar$_2$NON(CF$_3$)$_2$. In all these reactions the only isolable products

were $(CF_3)_2NOH$ and $(CF_3)_2NH$ together with intractable multi-component mixtures containing the corresponding amine and compounds with $(CF_3)_2NO$ groups. In view of the fact that traces of neither $\ge NON\le$ compounds nor stable diphenylamino-oxyls were found, Choudhury[51] thought a reaction scheme such as that shown in Scheme 38 was unlikely.

$$Ph_2NH \ + \ (CF_3)_2NO^\bullet \longrightarrow (CF_3)_2NOH \ + \ Ph_2N^\bullet \xrightarrow{(CF_3)_2NO^\bullet}$$

$$(CF_3)_2NONPh_2$$

$$\downarrow$$

$$(CF_3)_2N^\bullet \ + \ Ph_2NO^\bullet$$

$$Ph_2NH \downarrow \qquad\qquad \downarrow \text{several steps}$$

$$(CF_3)_2NH \ + \ Ph_2N^\bullet \longrightarrow Ph_2NH$$

$$+ \text{ other products}$$
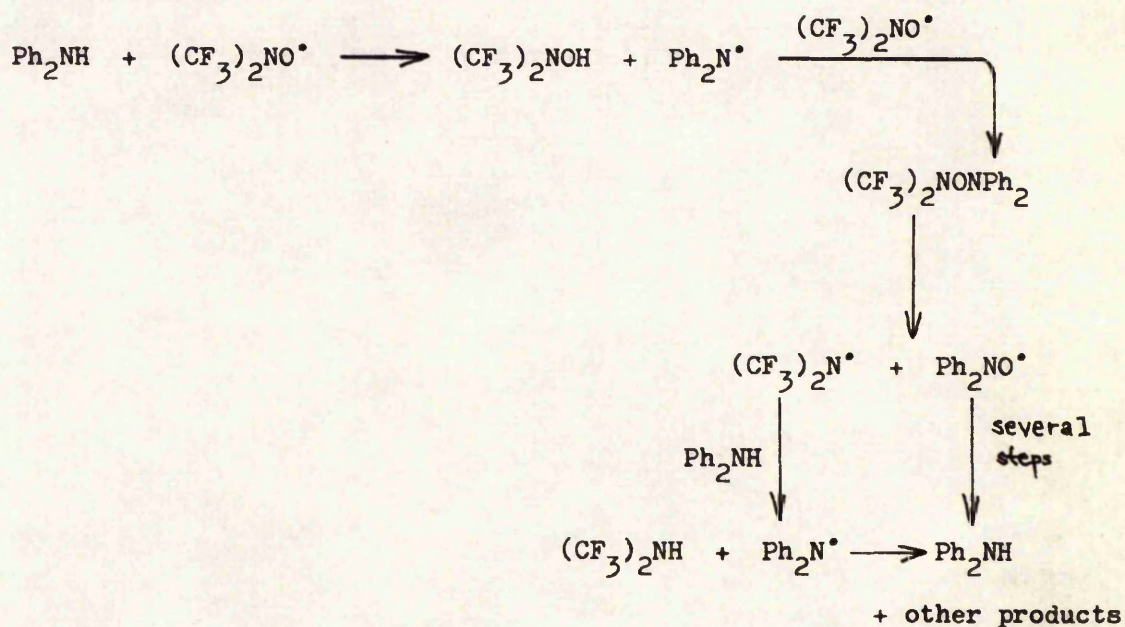
Scheme 38

He suggested alternative routes, shown in Scheme 39, as more likely possibilities.

$$\left(X-\!\!\left\langle\bigcirc\right\rangle\!\!\right)_2 NH \xrightarrow{R^\bullet} RH \ + \ \left(X-\!\!\left\langle\bigcirc\right\rangle\!\!\right)_2 N^\bullet \longrightarrow \left(X-\!\!\left\langle\bigcirc\right\rangle\!\!\right)_2 NH$$

$$+ \text{ unknown products}$$

Scheme 39
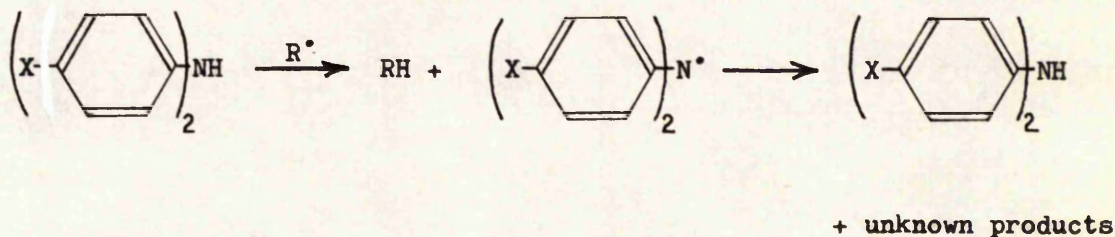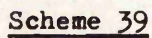
Similar mechanisms have been proposed for reactions of other
amino-oxyls, e.g. the oxidation of phenols to benzoquinones by diphenyl-
amino-oxyl, 4,4'-dinitrodiphenylamino-oxyl, Banfield and Kenyon's radical

and porphyrexide,[108] and the oxidation of aniline and substituted anilines to p-benzoquinones and the oxidation of diphenylamine to p-benzoquinone anil by Fremy's radical[109] (Scheme 40).
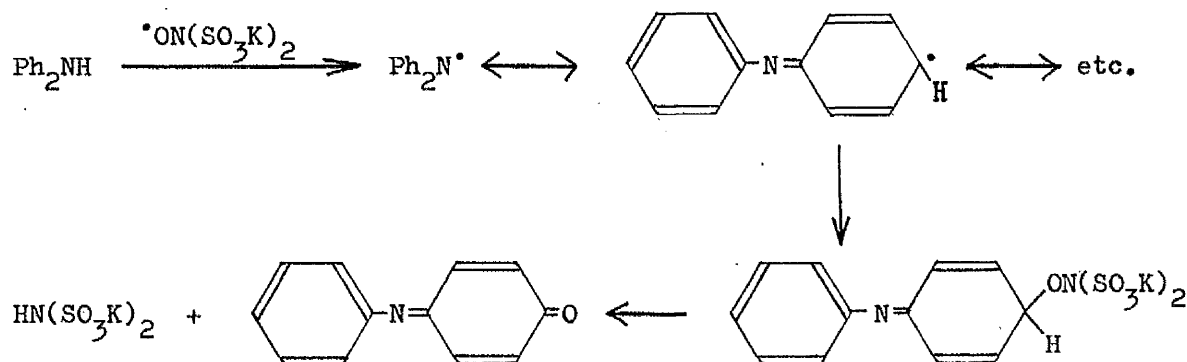
<div align="center">Scheme 40</div>

The $\underline{N}^1$-alkyl-$\underline{N}^1$-aryl-$\underline{N}^2$-(trifluoromethyl)-fluoroformamidines are the result of reaction between $(CF_3)_2NH$ and the original $\underline{N}$-alkylanilines. This is supported by the following evidence.

(a)   Reaction of $(CF_3)_2NO^\bullet$ with an excess (1:4 molar ratio) of $\underline{N}$-ethylaniline gave volatile products consisting of $(CF_3)_2NOH$ (57%) and $(CF_3)_2NON(CF_3)_2$ (2%). These volatile products showed some reluctance to condense from the reaction tube into a -196°C trap, but after strong heating the tube reached constant weight. The difficulty in removing the volatiles was attributed to the presence of excess $\underline{N}$-ethylaniline which would form an adduct with the slightly acidic $(CF_3)_2NOH$. No $(CF_3)_2NH$ was detected in the products. Using an excess of $\underline{N}$-ethylaniline there is enough to react with all the $(CF_3)_2NH$ which is generated in excess in the reactions using a 2:1 molar ratio of $(CF_3)_2NO^\bullet$ to amine.

(b)   When a reaction between $(CF_3)_2NH$ and $\underline{N}$-ethylaniline was carried out using equimolar amounts of reactants the products were as shown below,

$$\text{PhNHEt} + (CF_3)_2\text{NH} \longrightarrow (CF_3)_2\text{NH} + \underset{\overset{|}{Et}}{\text{PhNCF=NCF}_3}$$

44% unreacted   53%

$$+ \quad \text{Ph}\overset{+}{\text{N}}\text{H}_2\text{Et} \ \bar{\text{H}}_2\text{F}_3 \quad + \quad 7\% \text{ total weight}$$

34%   unaccounted for

The mechanism of the reaction of $(CF_3)_2\text{NH}$ with the N-alkylanilines is shown in Scheme 41, using N-methylaniline as an example. Because of the reduction in base strength caused by the two CF_3 groups $(CF_3)_2\text{NH}$ does not react normally with the usual amine reagents. In most reactions it tends to reverse the normal method of synthesis and revert to $CF_3N=CF_2$ and HF.[144] In comparison with the C=C bond in perfluoropropene the C=N bond in perfluoro(methylenemethylamine) is much more susceptible to nucleophilic attack and considerably less prone to free radical attack.[145]

$$(CF_3)_2\text{NH} \longrightarrow CF_2=NCF_3 + HF$$

$$\text{PhNHMe} + CF_2=NCF_3 \xrightarrow{\underset{\text{addition}}{\text{nucleophilic}}} \underset{\overset{|}{Me}}{\text{PhNCF}_2\text{NHCF}_3}$$

$\downarrow$ −HF

$$\underset{\overset{|}{Me}}{\text{PhNCF=NCF}_3}$$

$$\text{and} \quad \text{PhNHMe} + 3HF \longrightarrow \text{Ph}\overset{+}{\text{N}}\text{H}_2\text{Me} \ \bar{\text{H}}_2\text{F}_3$$

Scheme 41

Similar reactions to that proposed above have been reported for alcohols, mercaptans and H_2S with perfluoro(methylenemethylamine).[146] The thoroughness with which these reactions have been investigated is illustrated by the fact that over 50 compounds, patented as plant

protecting fungicides, insecticides and acaricides, have been prepared by reacting perfluoro(methylenemethylamine), bistrifluoromethylamine or $\underline{N}^1,\underline{N}^1,\underline{N}^2$-tris(trifluoromethyl)-fluoroformamidine, $(CF_3)_2NCF=NCF_3$, with compounds containing benzene rings substituted with various nucleophilic groups[147] and with nuclear substituted 2,3-dimercaptoquinoxalines.[148] e.g.
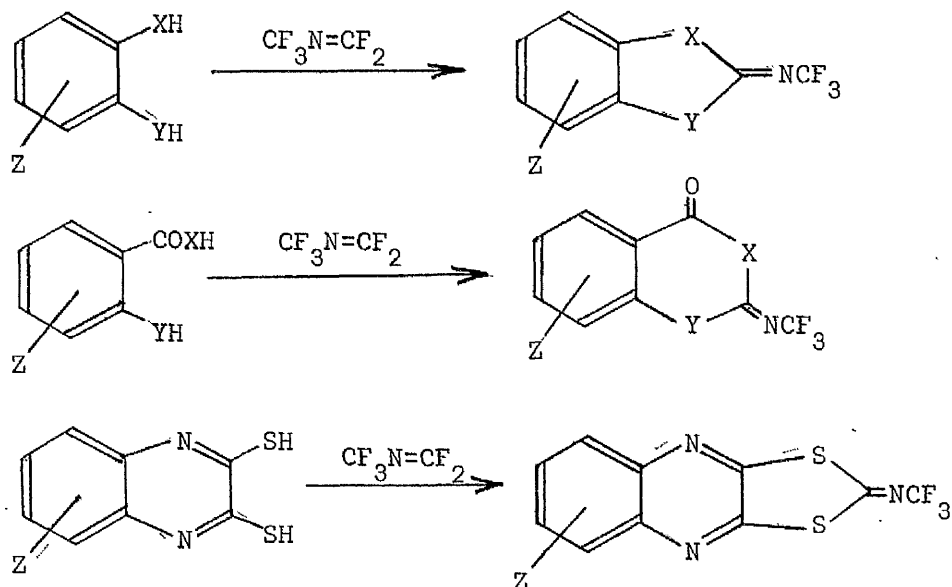
Acid-binding agents such as alkali metal carbonates or fluorides, tertiary aliphatic or aromatic amines have been used as acceptors for the HF liberated in the reactions.

The overall scheme for reaction of $(CF_3)_2NO^\cdot$ with $\underline{N}$-alkylanilines is shown in Scheme 42, using $\underline{N}$-methylaniline as an example.

(a)   PhNHMe $\xrightarrow{R^{\bullet}}$ PhNMe $\longleftrightarrow$ =NMe $\longleftrightarrow$ etc.

unknown products $\longleftarrow$ =NMe $\longleftarrow$ =NMe

$+ (CF_3)_2NH$

(b)   PhNHMe $+$ $(CF_3)_2NH$ $\longrightarrow$ $PhNCF=NCF_3$ $+$ $2HF$
$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad$ |
$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\;\;$ Me

(c)   PhNHMe $+$ $3HF$ $\longrightarrow$ $Ph\overset{+}{N}H_2Me\ \overset{-}{H}_2F_3$ $\longrightarrow$ unknown products

Scheme 42

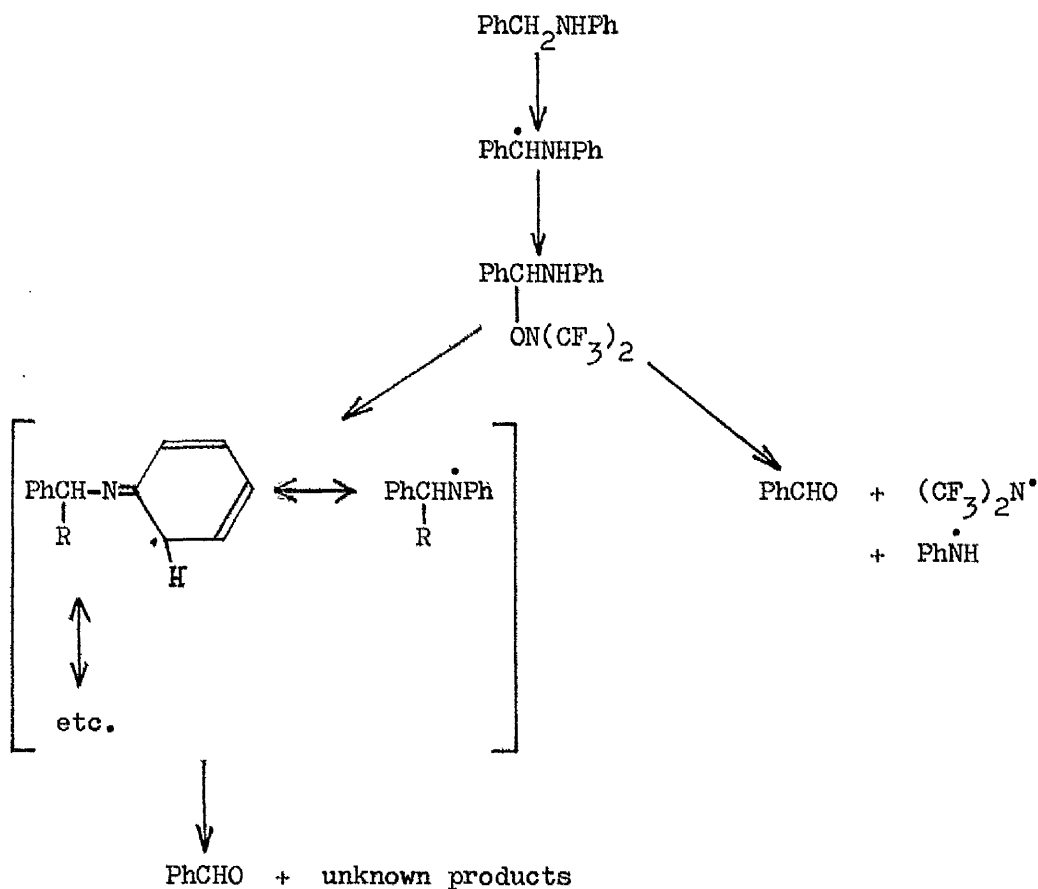## Reactions of $(CF_3)_2NO^{\bullet}$ with N-benzylaniline and N-benzylideneaniline

9.   N-benzylaniline

The reaction of N-benzylaniline with $(CF_3)_2NO^{\bullet}$ showed many points of similarity with the other N-alkylanilines. The reaction time, in a reaction where CCl_4 was used as solvent, was about the same, 3 minutes, although in reactions where no solvent was used the reaction was much slower, taking 10-15 minutes. This was hardly surprising as, in these cases, the $(CF_3)_2NO^{\bullet}$ was reacting with solid N-benzylaniline.

The products were similar in appearance, consisting of dark red liquid. Removal of the volatiles left a brown-black tar. The volatiles consisted of $(CF_3)_2NOH$ and $(CF_3)_2NH$ in comparable yields to the other reactions. The involatile tar was partially soluble in CCl_4, leaving a black residue. The main product of the reaction was N^1-benzyl-N^1-

phenyl-$\underline{N}^2$-(trifluoromethyl)-fluoroformamidine, $PhCH_2(Ph)NCF=NCF_3$, the same type of compound as formed in the other $\underline{N}$-alkylaniline reactions.

However another major product in this reaction was benzaldehyde and the ^{19}F n.m.r. spectrum of the soluble involatile products also showed a complex series of overlapping bands between -12.3 and -10.3 p.p.m. from TFA for unidentified $(CF_3)_2NO$-compounds (molar ratio of $PhCH_2(Ph)NCF=NCF_3$ to unidentified $(CF_3)_2NO$-groups, from the ^{19}F n.m.r. equals 2.3:1). No aldehyde or unidentified $(CF_3)_2NO$-compounds were found in the products of the other reactions of $(CF_3)_2NO^\bullet$ with $\underline{N}$-alkylanilines. The ^1H n.m.r. spectrum of the involatile products showed peaks for the CHO of benzaldehyde, the CH_2 of $\underline{N}^1$-benzyl-$\underline{N}^1$-phenyl-$\underline{N}^2$-(trifluoromethyl)-fluoroformamidine and for C_6H_5 groups, the integration of the phenyl peaks being 38% in excess of that required for PhCHO and $PhCH_2(Ph)CF=NCF_3$. It was concluded that the unidentified compounds contain phenyl and $(CF_3)_2NO$ groups but no other C-H or N-H bonds.

The products of the reaction are summarised below.

$$PhCH_2NHPH + 2R^\bullet \longrightarrow (CF_3)_2NOH + (CF_3)_2NH + PhCHO$$

$$58\% \qquad 23\% \qquad 9\%$$

$$+ \underset{\underset{Ph}{|}}{PhCH_2NCF=NCF_3} + \text{unidentified compounds}$$

containing Ph and $(CF_3)_2NO$

22%

groups.

approx. 19% based on

$PhCH_2NHPh$

+ black tarry solid

18% of total weight

reactants

That the $\underline{N}^1$-benzyl-$\underline{N}^1$-phenyl-$\underline{N}^2$-(trifluoromethyl)-fluoroformamidine is formed by reaction of bistrifluoromethylamine and $\underline{N}$-benzylaniline was shown by carrying out the reaction:

$$2\text{PhCH}_2\text{NHPh} + (\text{CF}_3)_2\text{NH} \longrightarrow \text{PhCH}_2\text{NHPh}$$

$$20\% \text{ unreacted}$$

$$+ \ \text{PhCH}_2\underset{\underset{\text{Ph}}{|}}{\text{N}}\text{CF=NCF}_3 \ + \ \text{PhCH}_2\overset{+}{\text{N}}\text{H}_2\text{Ph} \ \overset{-}{\text{HF}}_2$$

$$50\% \qquad\qquad\qquad 50\%$$

The formation of benzaldehyde must be attributed to substitution of one of the benzylic hydrogens of $\underline{\text{N}}$-benzylaniline, followed by either decomposition of the resulting compound or its further reaction and subsequent decomposition, as shown in Scheme 43.

$$\text{PhCH}_2\text{NHPh}$$

$$\downarrow$$

$$\text{Ph}\overset{\bullet}{\text{C}}\text{HNHPh}$$

$$\downarrow$$

$$\text{PhCHNHPh}$$

$$\underset{\text{ON}(\text{CF}_3)_2}{|}$$

$$\text{PhCHO} + \text{unknown products}$$

Scheme 43

Substitutions of this sort would be much more unlikely in the cases of the $\underline{\text{N}}$-methyl-, $\underline{\text{N}}$-ethyl- or $\underline{\text{N}}$-propylanilines where radicals of the type

PhNHCH$_2$$^\bullet$ and PhNHĊH-alkyl would not be stabilised by delocalisation of the electron around the ring as in the case of the PhNHĊHPh radical, and in fact there is no evidence for aldehyde formation in the reactions of these N̲-alkylanilines with $(CF_3)_2NO^\bullet$.

10. N̲-benzylideneaniline

The reactions of $(CF_3)_2NO^\bullet$ with N̲-benzylideneaniline were carried out using both 2:1 and 1:1 ratios of reactants and CCl$_4$ as solvent. Both reactions were much slower (30-40 minutes) than the reactions of $(CF_3)_2NO^\bullet$ with N̲-benzylaniline (3 minutes). The products are summarised below.

PhCH=NPh + R$^\bullet$ $\longrightarrow$ PhCH=NPh + PhCHO

63% unreacted*   10%*

+ unidentified compounds containing

$(CF_3)_2NO$ and phenyl groups

27%*

+ black tarry solid

7% total weight reactants

+ $(CF_3)_2NOH$ + $(CF_3)_2NH$

32%   20%

PhCH=NPh + 2R$^\bullet$ $\longrightarrow$ PhCH=NPh + PhCHO

53% unreacted*   18%*

+ unidentified compounds containing

phenyl groups and one $CF_3N=CF$,

5 $(CF_3)_2N-$ and approximately

6 $(CF_3)_2NO-$ groups

29%*

+   black tarry solid

18% total weight reactants

+ $(CF_3)_2NOH$ + $(CF_3)_2NH$ + $CF_3N=CF_2$

33%   17%   trace

(* Percentages based on relative molar concentrations of soluble involatile products, not on PhCH=NPh used or reacted.)

There was no evidence for what might be thought the simplest possible hydrogen substitution product, resulting from:

$$PhCH=NPh \xrightarrow{\text{R}^{\bullet}} Ph\overset{\bullet}{C}=NPh \xrightarrow{\text{R}^{\bullet}} Ph\underset{\underset{R}{|}}{C}=NPh$$

This compound would be expected to show a strong band in the i.r. spectrum of the products at a frequency about 100 cm^{-1} higher than that of PhCH=NPh (by analogy with the C=O stretching frequencies of PhCHO and PhCOON$(CF_3)_2$ at 1700 and 1800 cm^{-1} respectively), i.e. at about 1730 cm^{-1}.   No such band was present.

If abstraction of the CH=N hydrogen is ruled out then the most reasonable alternative would seem to be addition to the double bond,

$$PhCHO + (CF_3)_2N^{\bullet} + \text{unknown} \atop \text{products}$$

Scheme 44

to form an intermediate identical to one of those proposed as a

possibility in the reaction of N-benzylaniline with $(CF_3)_2NO^\bullet$, and similar to an intermediate proposed in the reaction of N-isobutylideneisobutyl-amine with $(CF_3)_2NO^\bullet$.

The $(CF_3)_2NOH$ and some of the $(CF_3)_2NH$ could be formed by reactions such as those shown in Scheme 45.
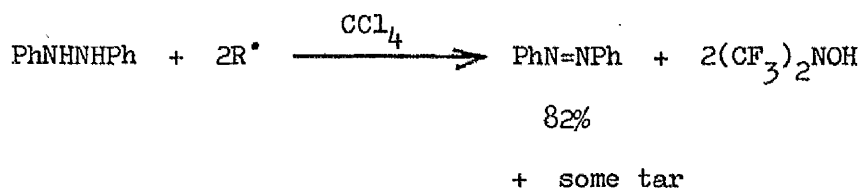

Scheme 45

An alternative mechanism for the formation of benzaldehyde could involve attack on one of the rings, the resulting radical being stabilised by delocalisation over both rings, as shown in Scheme 46.
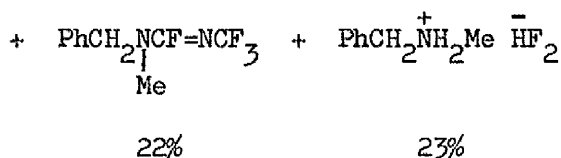
Scheme 46

It is perhaps surprising that in the reactions of N-benzylaniline with $(CF_3)_2NO^•$, N-benzylideneaniline is not found among the products, particularly as benzylamine and N-methylbenzylamine (see next section), in their reactions with $(CF_3)_2NO^•$, lose hydrogen to give $PhCH=NH$ and $PhCH=NCH_3$ respectively. The formation of N-benzylideneaniline as an intermediate, which then reacts further to give benzaldehyde and unknown products, can be ruled out by the fact that the N-benzylaniline reaction is complete within 3 minutes (in CCl_4 as solvent) whereas the N-benzylidene-aniline reaction (in CCl_4) takes 30 to 40 minutes. The Schiff's base, if formed, would not therefore be expected to undergo appreciable further reaction.

$(CF_3)_2NO^•$ has been found[44] to react with hydrazobenzene, on warming from -196°C to room temperature, as follows.

$$PhNHNHPh + 2R^• \xrightarrow{CCl_4} PhN=NPh + 2(CF_3)_2NOH$$

82%

+ some tar

Other amino-oxyls, e.g. diphenylamino-oxyl, 4,4'-dinitrodiphenylamino-oxyl, Banfield and Kenyon's radical and porphyrexide, also oxidise hydrazobenzene to azobenzene instantly at room temperature.[108] These same amino-oxyls were found to partly oxidise N-benzylaniline slowly at room temperature to N-benzylideneaniline.[108] Diphenylpicryl-hydrazyl is another stable radical which readily dehydrogenates N-benzyl-aniline to N-benzylideneaniline and also converts hydrazobenzene to azo-benzene almost instantaneously at room temperature.[107]

On this basis also, $(CF_3)_2NO^{\bullet}$ might be expected to oxidise N-benzylaniline to N-benzylideneaniline, particularly as it is a much more active hydrogen abstractor than the stable radicals named above. Presumably in this reaction however, the efficiency of $(CF_3)_2NO^{\bullet}$ as a radical scavenger is of paramount importance leading to attack at one of the delocalisation sites around the ring.

Reactions of $(CF_3)_2NO^{\bullet}$ with N-methylbenzylamine and N-benzylidenemethyl-amine

The reactions of $(CF_3)_2NO^{\bullet}$ with the amine and with the corresponding Schiff's base were carried out using the same methods as in the reactions of $(CF_3)_2NO^{\bullet}$ previously described. In both cases the reactions were complete in about 50 minutes giving yellow liquid products.

11.   N-methylbenzylamine

The products from the N-methylbenzylamine reaction are summarised below.

$$PhCH_2NHMe \; + \; 2R^{\bullet} \longrightarrow (CF_3)_2NOH \; + \; PhCH=NMe$$

$$83\% \qquad\qquad 24\%$$

$$+ \; PhCHO \; + \; PhCOON(CF_3)_2$$

$$12\% \qquad\qquad 9\%$$

+ $PhCH_2\underset{Me}{N}CF=NCF_3$ + $PhCH_2\overset{+}{N}H_2Me\ \overset{-}{H}F_2$

22%   23%

The $\underline{N}$-benzylidenemethylamine, PhCH=NMe, formed by abstraction of a benzylic hydrogen and disproportionation of the resulting radical with a second $(CF_3)_2NO^\bullet$ radical,

i.e. $PhCH_2NHMe \xrightarrow{R^\bullet} Ph\overset{\bullet}{C}HNHMe \xrightarrow{R^\bullet} PhCH=NMe$

is expected by analogy with the reaction of benzylamine with $(CF_3)_2NO^\bullet$.

The formation of $\underline{N}^1$-benzyl-$\underline{N}^1$-methyl-$\underline{N}^2$-(trifluoromethyl)-fluoroformamidine requires the presence of bistrifluoromethylamine as an intermediate and is formed by nucleophilic attack of $\underline{N}$-benzylmethylamine on perfluoro(methylenemethylamine) and loss of HF, a similar reaction to that already discussed for the $\underline{N}$-alkylanilines.

$(CF_3)_2NH \xrightarrow{-HF} CF_2=NCF_3$

$PhCH_2NHMe + CF_2=NCF_3 \xrightarrow{-HF} PhCH_2\underset{Me}{N}CF=NCF_3$

$PhCH_2NHMe + 2HF \longrightarrow PhCH_2\overset{+}{N}H_2Me\ \overset{-}{H}F_2$

Scheme 47

That $(CF_3)_2NH$ is the intermediate was shown by carrying out the reaction of $(CF_3)_2NH$ and $\underline{N}$-methylbenzylamine:

$PhCH_2NHMe + (CF_3)_2NH \longrightarrow PhCH_2NHCH_3 + PhCH_2\underset{Me}{N}CF=NCF_3$

2.07 mmoles   0.65 mmoles   38% unreacted   51%

+ $PhCH_2\overset{+}{N}H_2Me\ \overset{-}{H}F_2$

48%

The formation of $(CF_3)_2NH$ in this reaction must also involve the production of benzaldehyde. A number of reaction routes can be postulated, as shown in Scheme 48.

$$PhCH_2NHCH_3$$
$$\downarrow R^\bullet$$
$$Ph\overset{\bullet}{C}HNHCH_3$$

$R^\bullet$ (left) $\qquad$ $R^\bullet$ (right)

$$PhCHO \xleftarrow{(A)} \underset{R}{PhCHNHCH_3} \qquad PhCH=NCH_3 \xrightarrow{R^\bullet} PhCH=N\overset{\bullet}{CH_2}$$

$$+ (CF_3)_2N^\bullet$$
$$+ CH_3\overset{\bullet}{NH}$$

$R^\bullet$ (B) $\qquad$ (C) $R^\bullet$

$$Ph\overset{\bullet}{CH}-N=CH_2$$

$$Ph\overset{\bullet}{C}HNCH_3$$
$$R$$

$$(D) \quad R^\bullet$$

$$PhCH-N=CH_2$$
$$R$$

$$PhCHO + (CF_3)_2N^\bullet$$
$$+ CH_2=NH$$

$$PhCHO + (CF_3)_2N^\bullet$$
$$+ CH_2=N^\bullet$$

and

$$(CF_3)_2N^\bullet \xrightarrow{PhCH_2NHMe} (CF_3)_2NH$$

$$\left. \begin{array}{l} CH_3\overset{\bullet}{NH} \\ CH_2=NH \\ CH_2=N^\bullet \end{array} \right\} \longrightarrow \text{unknown products}$$

Scheme 48

12. N-benzylidenemethylamine

The reaction of $(CF_3)_2NO^\bullet$ with N-benzylidenemethylamine also gives benzaldehyde and the amino-oxy substituted benzaldehyde as major products.

$$PhCH=NMe \ + \ 2R^\bullet \ \longrightarrow \ (CF_3)_2NOH \ + \ (CF_3)_2NON(CF_3)_2$$

$$52\% \qquad\qquad 15\%$$

$$+ \ PhCH=NMe \ + \ PhCHO$$

$$48\% \ unreacted \qquad 29\%$$

$$+ \ PhCOON(CF_3)_2 \ + \ unidentified$$

$$14\% \qquad\qquad 57\% \ based \ on$$
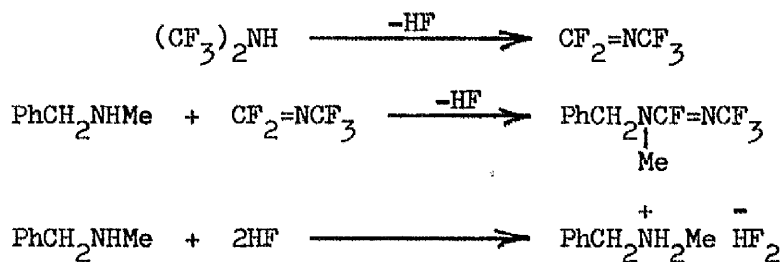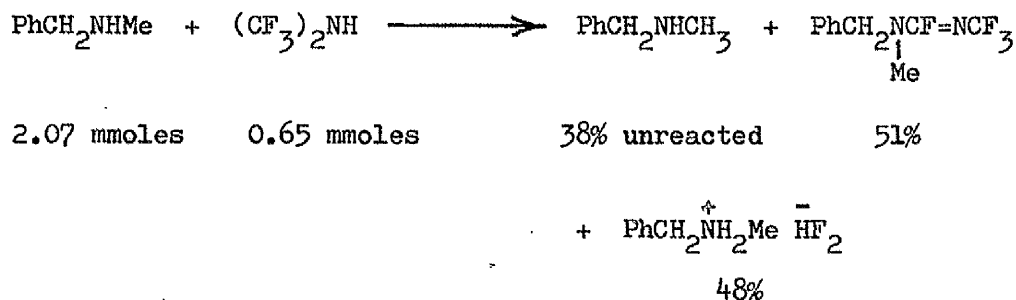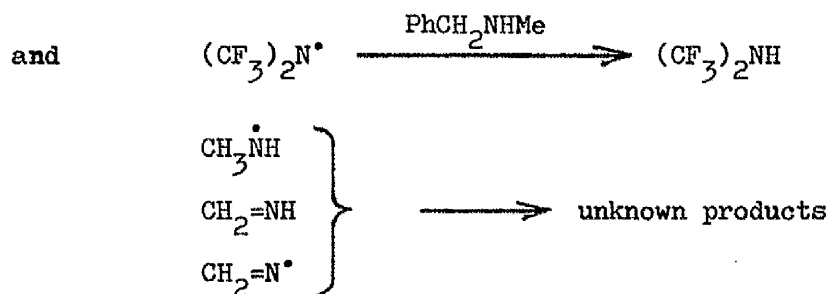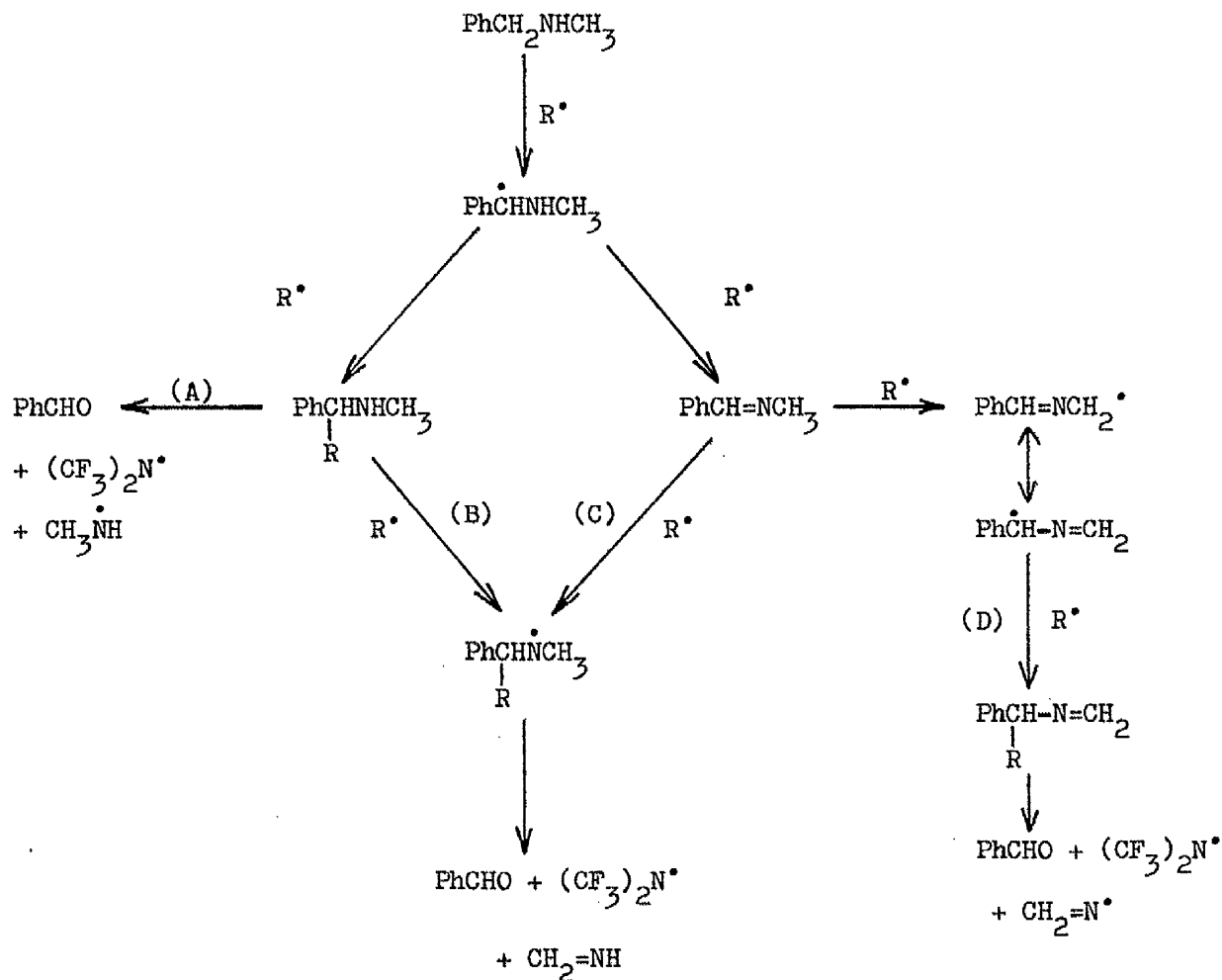
PhCH=NMe reacted;

27% based on

$R^\bullet$ used.
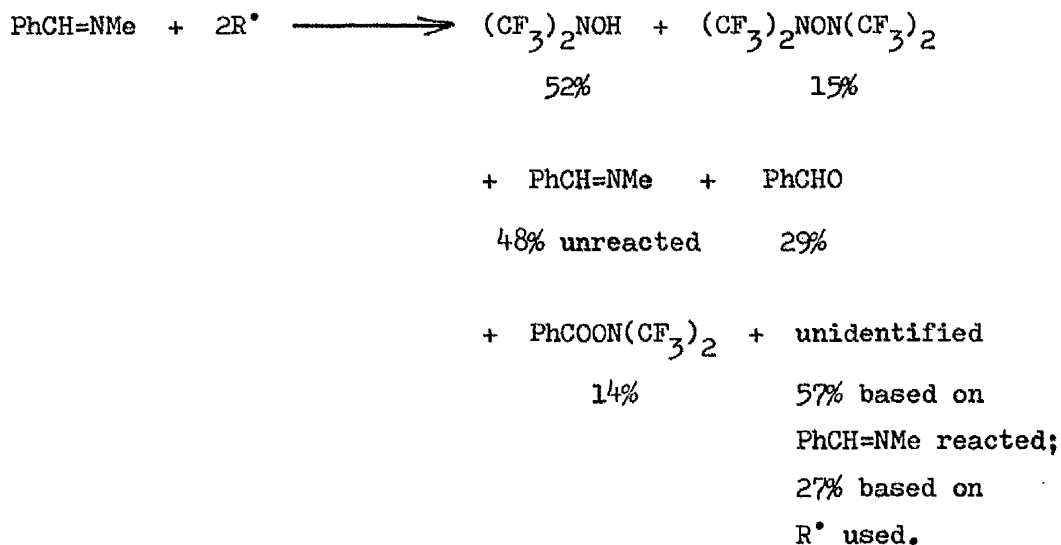
The reaction was rather more complex than that starting with N-methyl-benzylamine and a large proportion of the products remained unidentified.

There would appear to be two routes to the identified products, already shown as part of Scheme 48.

i.e.

and   PhCHO $\xrightarrow{\text{R}^\bullet}$ Ph$\overset{\bullet}{\text{C}}$O $\xrightarrow{\text{R}^\bullet}$ PhCOR

$(\text{CF}_3)_2\text{N}^\bullet \xrightarrow{\text{R}^\bullet} (\text{CF}_3)_2\text{NON}(\text{CF}_3)_2$
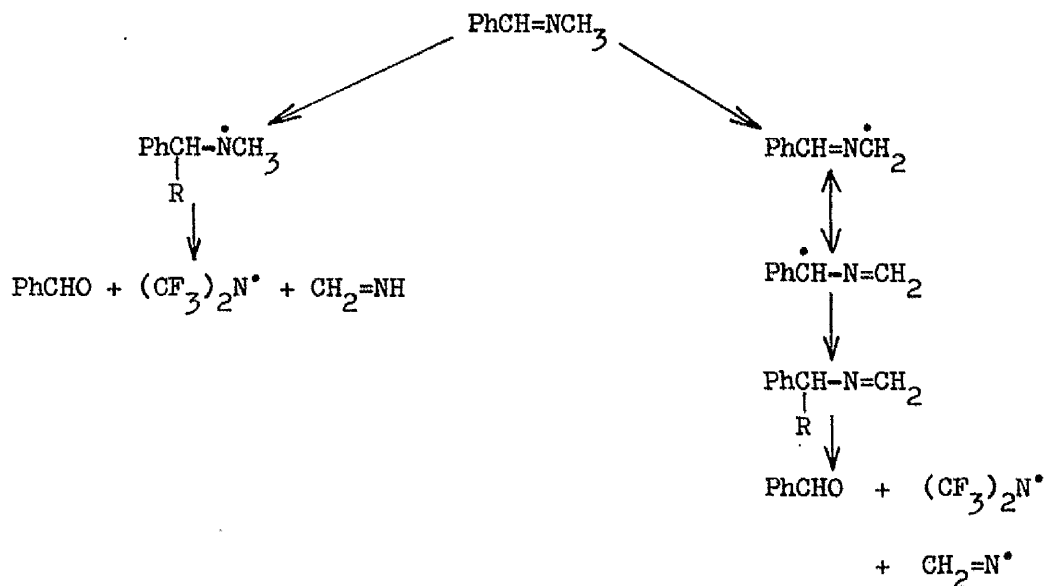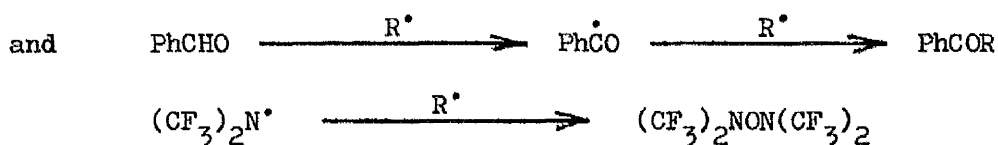
<div align="center">Scheme 49</div>

The formation of $(\text{CF}_3)_2\text{NON}(\text{CF}_3)_2$ rather than $(\text{CF}_3)_2\text{NH}$ can be attributed to the fact that hydrogens in PhCH=NCH$_3$ are less labile than those in N-methylbenzylamine and the $(\text{CF}_3)_2\text{N}^\bullet$ radicals are therefore likely to be scavenged by the excess $(\text{CF}_3)_2\text{NO}^\bullet$ before abstracting hydrogen.

The route involving addition of $(\text{CF}_3)_2\text{NO}^\bullet$ to the C=N double bond and the subsequent decomposition of the PhCHR$\overset{\bullet}{\text{N}}CH_3$ radical is similar to routes proposed for the reactions of $(\text{CF}_3)_2\text{NO}^\bullet$ with N-isobutylideneiso-butylamine (Scheme 29) and with N-benzylideneaniline (Scheme 44).

The route involving abstraction of hydrogen from the CH$_3$ group seems a strong possibility, the radical so formed being resonance stabilised:

<div align="center">PhCH=NCH$_2^\bullet$ ⟷ PhĊH-N=CH$_2$ ⟷ [benzene ring]=CH-N=CH$_2$ ⟷ etc.</div>
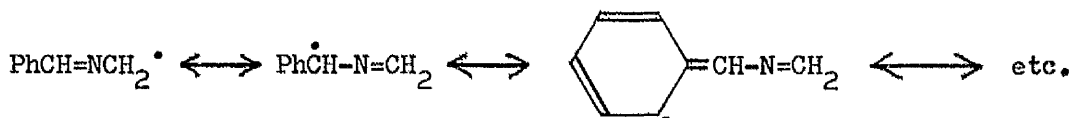
The second resonance form would be more stable than the first and subsequent reaction might therefore be expected to take place at the benzylic position. Against this route are the following facts.

(i)   In the reaction of N-isobutylideneisobutylamine with $(\text{CF}_3)_2\text{NO}^\bullet$ the major product results from substitution of the tertiary hydrogen to give Me$_2$CRCH=NCH$_2$CHMe$_2$, and the second product apparently results from addition of $(\text{CF}_3)_2\text{NO}^\bullet$ to the C=N double bond followed by disproportionation, or substitution of the CH=N hydrogen, in either case followed by decomposition of the compound so formed, Me$_2$CHCR=NCH$_2$CHMe$_2$. There was no indication that any abstraction from the CH$_2$ took place.

(ii)   The reaction between N-benzylidenebenzylamine and $(CF_3)_2NO^{\bullet}$,

which gives an almost quantitative yield of PhCH=NCHRPh, is not

particularly fast (reaction time 30 minutes at room temperature) even

though the radical PhCH=N$\overset{\bullet}{C}$HPh is extensively resonance stabilised.

The fact that the reaction of N-benzylidenemethylamine with

$(CF_3)_2NO^{\bullet}$ gives PhCHO, PhCOON$(CF_3)_2$ and $(CF_3)_2NON(CF_3)_2$ as major

products is good evidence that PhCH=NCH$_3$ is also the intermediate in the

formation of PhCHO, PhCOON$(CF_3)_2$ and $(CF_3)_2NH$ in the reaction of N-

methylbenzylamine with $(CF_3)_2NO^{\bullet}$.

It seems most likely, therefore, that the reaction of $(CF_3)_2NO^{\bullet}$

with N-methylbenzylamine proceeds via route C or D in Scheme 48, although

the other two routes cannot be completely ruled out.

No product could be identified from further reaction of the other

fragment (CH$_3\overset{\bullet}{N}$H, CH$_2$=NH or CH$_2$=N$^{\bullet}$) involved in formation of benzaldehyde

and $(CF_3)_2N^{\bullet}$, although the ^{1}H n.m.r. spectrum of the volatiles from

reaction of PhCH=NCH$_3$ with $(CF_3)_2NO^{\bullet}$ showed a singlet (int. 4.2) at +0.97

ppm from external DCB for $(CF_3)_2NOH$ and broad singlets at +2.15 ppm (int.

0.2), +4.17 ppm (int. 0.1) and +4.92 ppm (int. 0.6), the latter peak

being at about the correct chemical shift for CH$_3$N. (e.g. CH$_3$ in the

CH$_3$NH$_2 \cdot (CF_3)_2$NOH adduct gives a peak at 7.55 τ,[132] approximately +4.8 ppm

from external DCB).

The overall reaction scheme for reaction of $(CF_3)_2NO^{\bullet}$ with

N-methylbenzylamine is shown below.

$PhCH_2NHCH_3$

$\downarrow R^{\bullet}$

$Ph\overset{\bullet}{C}HNHCH_3$

$\downarrow R^{\bullet}$

$PhCH=NCH_3$

$\downarrow R^{\bullet}$

$Ph\overset{\bullet}{C}=O \quad\overset{R^{\bullet}}{\longleftarrow}\quad PhCHO \;+\; (CF_3)_2N^{\bullet} \quad\xrightarrow{PhCH_2NHMe}\quad (CF_3)_2NH$

$\downarrow R^{\bullet}$

$+$ unknown products

$PhC=O$
$\;\;|$
$\;\;R$

$\downarrow PhCH_2NHMe$

$PhCH_2\underset{Me}{\overset{|}{N}}CF=NCF_3$

$+\quad 2HF$

$\downarrow PhCH_2NHMe$

$PhCH_2\overset{+}{N}H_2CH_3\;\; \overset{-}{H}F_2$
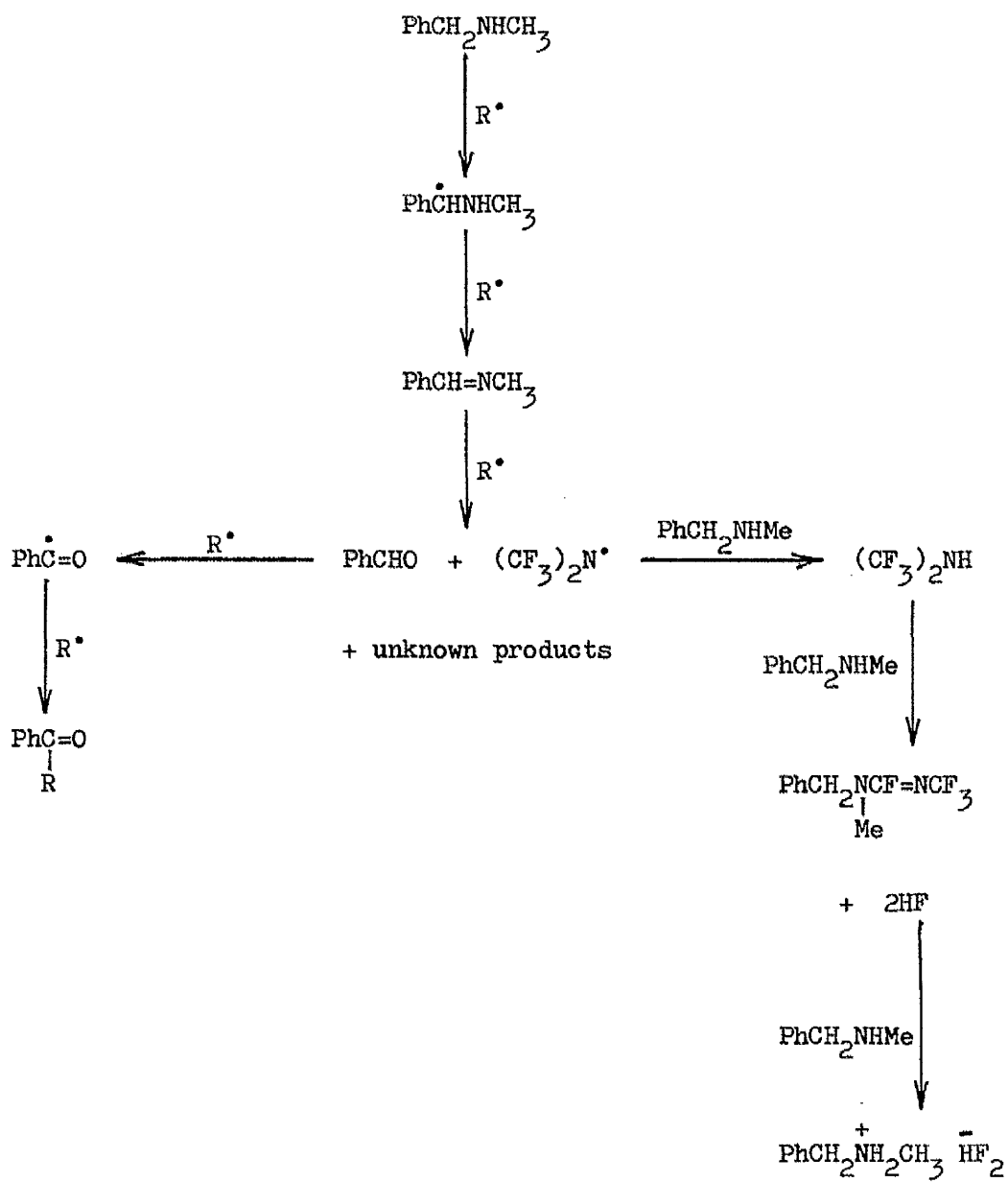
Scheme 50

SUMMARY OF CONCLUSIONS

1.   In reactions of $(CF_3)_2NO^\bullet$ with isoalkyl compounds of general

formula Me_2CHCH_2X (X = Et, t-Bu, Cl, Br, NO_2, COMe, OCCMe, CH_2Cl,

CH_2Br, CH_2NO_2 and CH_2CH_2Br) the inductive power of the group X exercises

a controlling influence over the following.

(a)   The ratio of disproportionation to combination (k_d/k_c) for

$(CF_3)_2NO^\bullet$ with the initially formed $Me_2\overset{\bullet}{C}CH_2X$ radicals. Combination is

favoured by electron-withdrawing groups and disproportionation by

electron-donating groups. The k_d/k_c values correlate well with the Taft

polar substituent constants σ^* of CH_2X. Within close limits, $\log (k_d/k_c)$

is directly proportional to σ^*.

(b)   The rate of initial hydrogen abstraction from Me_2CHCH_2X.

2.   Steric effects are important in determining the ratio of external

to internal olefin formed in the disproportionation step. When X is an

alkyl group, increase in the size of X favours formation of the external

olefin. When X is an electron-withdrawing group the external olefin

is formed almost exclusively. This is attributed to a combination of

polar and steric effects.

3.   The reactions of $(CF_3)_2NO^\bullet$ with isoalkyl iodides are complicated

by replacement of iodine by $(CF_3)_2NO^\bullet$.

4.   In the reactions of $(CF_3)_2NO^\bullet$ with isoalkyl alcohols abstraction

takes place from the tertiary C-H and from the CH_2 group α to OH. Both

resulting radicals give disproportionation and combination reactions.

5.   In the reaction of $(CF_3)_2NO^\bullet$ with isopentylbenzene the main

product is the result of benzylic substitution. The lack of

disproportionation is attributed to a steric effect.

6. $(CF_3)_2NO^\bullet$ reacts with isobutylamine and benzylamine to give

the imines which condense with excess amine to give the Schiff's bases.

Benzylamine, with excess $(CF_3)_2NO^\bullet$, gives a mixture of N-benzylidenebenzyl-

amine, hydrobenzamide and 1,2,3,4-tetrahydro-2,4,6-triphenyl-1,3,5-triazine, the last two compounds being formed by self-condensation and cyclisation of benzaldimine respectively.

7. $(CF_3)_2NO^{\cdot}$ substitutes the tertiary hydrogen of $\underline{N}$-isobutylidene-isobutylamine to give $Me_2CRCH=NCH_2CHMe_2$, and also forms the unstable iminol compound $Me_2CHC(OH)=NCH_2CHMe_2$.

8. $(CF_3)_2NO^{\cdot}$ substitutes a benzylic hydrogen in $\underline{N}$-benzylidene-benzylamine to give an almost quantitative yield of $PhCH=NCHRPh$.

9. $(CF_3)_2NO^{\cdot}$ reacts with $\underline{N}$-alkylanilines to give $(CF_3)_2NOH$, $(CF_3)_2NH$, black tarry solids and N^1-alkyl-N^1-aryl-N^2-(trifluoromethyl)-fluoroformamidines, from reaction of $(CF_3)_2NH$ with the $\underline{N}$-alkylanilines, as the only other isolable products.

10. $\underline{N}$-benzylaniline gives similar products to the other $\underline{N}$-alkylanilines plus benzaldehyde and some unidentified $(CF_3)_2NO$-compounds. $\underline{N}$-benzylideneaniline is thought not to be an intermediate in this reaction although it reacts with $(CF_3)_2NO^{\cdot}$ to give fairly similar products. Possibly the two reactions proceed via the same intermediate.

11. $\underline{N}$-methylbenzylamine reacts with $(CF_3)_2NO^{\cdot}$ to give $PhCH=NCH_3$ which reacts further to give benzaldehyde and $(CF_3)_2NH$. The latter reacts with $\underline{N}$-methylbenzylamine in the same way as with the $\underline{N}$-alkylanilines.

12.   Possible extensions of the work of $(CF_3)_2NO^{\cdot}$ with amines could involve the following.

(a)   Trapping the imine with suitable substituent groups to effect ring closure.

(b)   Introducing C=N bonds into saturated or partially unsaturated heterocyclics.

(c)   The fact that $(CF_3)_2NO^{\cdot}$ abstracts hydrogens from carbon atoms adjacent to both ends of the C=N bond rather than abstracting the CH=N hydrogen could be used in the preparation of $(CF_3)_2NO$-substituted

aldehydes or $_a$mines in which the CHO or NH_2 group is intact, by reaction of $(CF_3)_2NO^{\bullet}$ with a suitable Schiff's base followed by hydrolysis.

EXPERIMENTAL

GENERAL TECHNIQUES

Almost all the reactions carried out during this work, other than preparations of starting materials, involved gases or volatile liquids of high toxicity. These were therefore manipulated in a conventional Pyrex vacuum system.

The reactions were carried out in sealed, evacuated, thick walled (2-3 mm) Pyrex "Carius" tubes capable of withstanding pressures of up to 10 atmospheres, or in thick walled Pyrex "Carius" tubes fitted with PTFE stoppered "Rotaflo" valves and capable of withstanding pressures of up to 5 atmospheres.

Volatile reactants were condensed into the reaction tubes in vacuo at -196°C; involatile reactants were poured into the tubes as the first stage of the loading process. After sealing, the tubes were placed in heavy metal guard tubes or, in cases where reaction times were being taken, in room temperature water baths behind blast screens.

In some cases volatile reaction products were condensed into the vacuum system and separated by trap-to-trap fractionation, the gaseous mixture being passed at pressures of 1-2 mmHg through a series of traps cooled to progressively lower temperatures. The cooling baths were prepared by the careful addition of the coolant to an organic liquid until a slush of adequate consistency was obtained. The solvents used for the low temperature baths and the temperatures attained are shown below.

Acetone/liquid nitrogen	-42°C
Methylated spirits/solid carbon dioxide	-78°C
Toluene/liquid nitrogen	-96°C
Diethyl ether/liquid nitrogen	-120°C
Liquid nitrogen	-196°C

Gas liquid chromatographic analyses were carried out using Pye Series 104 instruments fitted with flame ionisation detectors. Samples were injected with 1 μl syringes onto columns packed with acid-washed Celite coated with ca. 10% by weight of stationary phase.

Preparative g.l.c. was usually carried out using a Perkin-Elmer F21 machine or occasionally with an adapted Pye Series 104 instrument fitted with a 100:1 stream splitter. The carrier gas was nitrogen.

Infrared spectra were recorded on Perkin-Elmer spectrophotometers (Models 137 and 735) fitted with sodium chloride optics. Volatile samples were examined in a gas cell of path length 10 cm equipped with sodium chloride plate windows; involatile liquids were examined as capillary films; solids were run as mulls with nujol and hexachlorobutadiene or as melts.

N.m.r. and mass spectra were run by members of the technical staff of the Department.

Most of the nuclear magnetic resonance spectra were recorded on Perkin-Elmer R10 and R20A spectrometers, both operating at 60 MHz for ^{1}H and 56.5 MHz for ^{19}F investigations, and on an R32 machine operating at 90MHz for ^{1}H and at 84.6 MHz for ^{19}F. A few ^{1}H spectra were recorded on a Varian Associates HA 100 spectrometer operating at 100 MHz.

Mass spectra were recorded on an A.E.I. MS902 double beam focussing spectrometer operating with an ionising beam energy of 70 eV and a resolving power of 1250. G.l.c.-mass spectrometry was carried out using a Pye Series 104 chromatograph which separated out and trapped the components on elution in reservoirs; their mass spectra were then recorded.

Elemental analyses were carried out by the Departmental analysts using recognised techniques. Carbon and hydrogen were estimated by

combustion of the sample in oxygen at about 1000°C in a conventional analytical train fitted with a tube packed with sodium fluoride to remove silicon tetrafluoride and hydrogen fluoride from the combustion products; nitrogen was estimated as nitrogen gas by Dumas' method; fluorine was estimated colourimetrically as the alizarin-fluorine blue complex.

PRESENTATION

Experiments described in the experimental section are presented in the same order as in the discussion.

The percentages quoted for the products are calculated as follows.

(i)   The compounds $(CF_3)_2NOH$, $(CF_3)_2NON(CF_3)_2$ and $(CF_3)_2NH$ ... percentages are based on $(CF_3)_2NO^{\bullet}$ used.

(ii)   Unreacted substrate ... percentages are based on substrate used.

(iii)   Other products derived from the substrate ... percentages are based on substrate reacted.

(iv)   Unidentified products ... percentages are based on substrate reacted or are based on the total weight of reactants.

Nuclear magnetic resonance, infrared and mass spectra are given in the text for unidentified and unknown structures. Spectra of identified compounds, unless illustrated as figures in the text, are to be found in the appendices and are numbered, e.g. n.m.r. 1, i.r. 2, m.s. 3.

SECTION I

REACTIONS OF BISTRIFLUOROMETHYLAMINO-OXYL WITH (a) ALKANES AND SUBSTITUTED
ALKANES OF GENERAL FORMULA Me$_2$CHCH$_2$X, (b) AN ALKENE AND A SUBSTITUTED
ALKENE OF GENERAL FORMULA CH$_2$=C(Me)CH$_2$X, (c) ISOBUTYRALDEHYDE

1.   WITH ISOHEXANE

This reaction was carried out twice as follows. Bistrifluoro-
methylamino-oxyl [(a) 2.80 g, 16.67 mmoles, (b) 5.97 g, 35.54 mmoles]
was condensed, in vacuo, into a Pyrex reaction tube (ca. 300 cm^3)
containing isohexane [(a) 0.74 g, 8.60 mmoles, (b) 1.55 g, 18.02 mmoles]
cooled to -196°C. The tube was sealed, allowed to warm to room
temperature and left in the dark, for 20 hours in the first case and for
one hour in the second. Reaction appeared to be complete after one hour,
as evidenced by the disappearance of the purple gas.

The products were analysed by g.l.c. (2m SE30 and 2m DNP columns
at 60°C). Two of the products gave retention times identical to N,N-
bistrifluoromethylhydroxylamine and isohexane. The yields of these two
compounds were calculated by comparative g.l.c. The other products were
identified, from g.l.c. analysis linked with mass spectrometry, as:
2-(bistrifluoromethylamino-oxy)-2-methylpentane (mass spectrum 1),
probably 2-(bistrifluoromethylamino-oxy)-4-methylpentane (m.s. 2),
1,2-bis(bistrifluoromethylamino-oxy)-2-methylpentane (m.s. 3), and 2,3-
bis(bistrifluoromethylamino-oxy)-2-methylpentane (m.s. 4). Additionally,
1,2-bis(bistrifluoromethylamino-oxy)-2-methylpentane was separated by
preparative g.l.c. (4m SE30 column at 60°C, Pye 104 instrument) and its
structure confirmed by its n.m.r. spectrum (n.m.r. 1). The g.l.c.
retention time and the mass spectrum of this compound were found to be
identical to the retention time and the mass spectrum of the major
product of the reaction between (CF$_3$)$_2$NO$^\bullet$ and 2-methylpent-1-ene.

The mass spectra (m.s. 1 and m.s. 2) of the two mono-amino-oxy products both showed strong peaks at m/e 85 ($C_6H_{13}{}^+$). The mono-amino-oxy products from reaction of $(CF_3)_2NO^{\bullet}$ with 2-methylpent-1-ene (i.e. allylic substitution products) showed strong peaks at m/e 83 ($C_6H_{11}{}^+$) but no peaks at m/e 85.

The g.l.c. peak for 2-(bistrifluoromethylamino-oxy)-2-methylpentane had another peak as a shoulder, presumably due to another monosubstituted compound.

The yields of the $(CF_3)_2NO$-compounds were calculated from their g.l.c. peak areas.

Reaction summary

Reactants:	Reaction (a)	Reaction (b)
$(CF_3)_2NO^{\bullet}$	2.80 g, 16.67 mmoles	5.97 g, 35.54 mmoles
$Me_2CHCH_2CH_2CH_3$	0.74 g, 8.60 mmoles	1.55 g, 18.02 mmoles
Products:		
$Me_2CHCH_2CH_2CH_3$	0.31 g, 3.61 mmoles, 42%	0.68 g, 7.93 mmoles, 44%
$(CF_3)_2NOH$	1.46 g, 8.67 mmoles, 52%	not determined
$Me_2CRCH_2CH_2CH_3$	0.35 g, 1.40 mmoles, 28%	0.56 g, 2.22 mmoles, 22%
prob. $Me_2CHCH_2CHRCH_3$	0.14 g, 0.55 mmoles, 11%	0.18 g, 0.71 mmoles, 7%
$\underset{R \quad R}{CH_2\text{-}C(Me)CH_2CH_2CH_3}$	1.07 g, 2.54 mmoles, 51%	2.42 g, 5.75 mmoles, 57%
$\underset{R\ R}{Me_2C\text{-}CHCH_2CH_3}$	0.13 g, 0.30 mmoles, 6%	0.30 g, 0.71 mmoles, 7%
unidentified	4% of isohexane products	7% of isohexane products

2. WITH 2-METHYLPENT-1-ENE

Bistrifluoromethylamino-oxyl (1.39 g, 8.27 mmoles) and 2-methylpent-1-ene (0.47 g, 5.60 mmoles) were caused to react using the same method as in reaction 1. Reaction was complete within one hour.

G.l.c. analysis of the products (2m SE30 column) showed peaks for 7 major and several minor compounds. Two of the major peaks had retention times identical to N,N-bistrifluoromethylhydroxylamine and 2-methylpent-1-ene. The yields of these two compounds were calculated by comparative g.l.c.

G.l.c.-mass spectral data (mass spectra 5-8) showed four of the major products to be the products of allylic substitution. All four mass spectra were very similar and two (mass spectra 7 and 8) were virtually identical, leading them to be tentatively identified as the two isomers of 1-(bistrifluoromethylamino-oxy)-2-methylpent-2-ene. It was thought likely that the other two compounds would be the other two expected allylic substitution products, 2-(bistrifluoromethylamino-oxymethyl)pent-1-ene and 3-(bistrifluoromethylamino-oxy)-2-methylpent-1-ene.

The main product of the reaction was identified, by comparison of its g.l.c. retention time and its mass spectrum with the products of reaction 1, as 1,2-bis(bistrifluoromethylamino-oxy)-2-methylpentane (m.s. 3).

The minor unidentified products, on the basis of their g.l.c. retention times, appeared to include another mono- and another di-amino-oxy product.

The yields of the $(CF_3)_2NO$-compounds were calculated from their g.l.c. peak areas.

Reaction summary

Reactants:

$(CF_3)_2NO^\bullet$ ..... 1.39 g, 8.27 mmoles

$CH_2=C(Me)CH_2CH_2CH_3$ ...... 0.47 g, 5.60 mmoles

Products:

$CH_2=C(Me)CH_2CH_2CH_3$ ...... 0.17 g, 2.02 mmoles, 36% unreacted

$(CF_3)_2NOH$ ...... 0.43 g, 2.56 mmoles, 31%

probably $CH_2=C(CH_2R)CH_2CH_2CH_3$ ...... 0.14 g, 0.55 mmoles, 15%

probably $CH_2=C(Me)CHRCH_2CH_3$ ...... 0.14 g, 0.55 mmoles, 15%
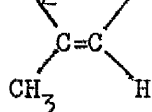
probably

...... 0.05 g, 0.18 mmoles, 5%

probably

...... 0.05 g, 0.18 mmoles, 5%
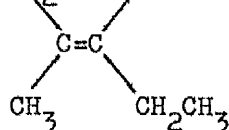
$\underset{R\ \ \ \ R}{CH_2-C(Me)CH_2CH_2CH_3}$ ...... 0.75 g, 1.79 mmoles, 50%

unidentified ...... approximately 10% of 2-methylpent-1-ene products.

3.   WITH 2,2,4-TRIMETHYLPENTANE

This reaction was carried out twice as follows.

Bistrifluoromethylamino-oxyl [(a) 2.67 g, 15.89 mmoles, (b) 3.05 g, 18.15 mmoles] and 2,2,4-trimethylpentane [(a) 0.92 g, 8.07 mmoles, (b) 1.04 g, 9.12 mmoles] were caused to react using the same method as in reaction 1.

G.l.c. analysis (2m SE30, 80-120°C) of the products showed 5 major and 2 very minor peaks. The first two peaks were identified as due to N,N-bistrifluoromethylhydroxylamine and 2,2,4-trimethylpentane. The yields of these compounds were calculated by comparative g.l.c.

The remaining 3 major compounds (g.l.c. retention times of 12.1,

16.0 and 21.4 minutes on a 2m SE30 column at 80°C) were separated by preparative g.l.c. and identified by n.m.r. spectra 2, 3 and 4, mass spectra 9, 10 and 11 and infrared spectra 1 and 2 as 2-(bistrifluoromethyl-amino-oxy)-2,4,4-trimethylpentane (A), 1,2-bis(bistrifluoromethylamino-oxy)-2,4,4-trimethylpentane (B) and 1,2-bis(bistrifluoromethylamino-oxy)-2-(bistrifluoromethylamino-oxymethyl)-4,4-dimethylpentane.

The two minor products appeared from their mass spectra to be mono-amino-oxy compounds.

Sufficient of the monosubstituted compound (A) and the disubstituted compound (B) was isolated for mixtures of these compounds to be compared by g.l.c. The results are shown below.

Mixt.	wt. A	mmoles A	peak area A	wt. B	mmoles B	peak area B	peak area of A/mmole	peak area of B/mmole
(i)	0.048 g	0.17	15.8 cm^2	0.057 g	0.12	13.8 cm^2	93 cm^2	115 cm^2
(ii)	0.048 g	0.17	8.4 cm^2	0.162 g	0.36	19.4 cm^2	49 cm^2	54 cm^2
(iii)	0.048 g	0.17	3.9 cm^2	0.252 g	0.56	13.4 cm^2	23 cm^2	24 cm^2
(iv)	0.048 g	0.17	2.4 cm^2	0.252 g	0.56	8.3 cm^2	14 cm^2	15 cm^2

Within experimental error equimolar mixtures of A and B give approximately equal g.l.c. peak areas.

Reaction summary

Reactants:	Reaction (a)	Reaction (b)
$(CF_3)_2NO^{\bullet}$	2.67 g, 15.89 mmoles	3.05 g, 18.15 mmoles
$Me_2CHCH_2CMe_3$	0.92 g, 8.07 mmoles	1.04 g, 9.12 mmoles
Products:		
$Me_2CHCH_2CMe_3$	0.41 g, 3.63 mmoles, 45%	0.49 g, 4.29 mmoles, 47%

Products:	Reaction (a)	Reaction (b)
$(CF_3)_2NOH$	1.26 g, 7.47 mmoles, 47%	not determined
$Me_2\overset{\displaystyle }{\underset{\displaystyle R}{C}}CH_2CMe_3$	0.35 g, 1.24 mmoles, 28%	0.34 g, 1.21 mmoles, 25%
$\underset{\displaystyle R}{CH_2}-\underset{\displaystyle R}{C(Me)}CH_2CMe_3$	1.12 g, 2.49 mmoles, 56%	1.23 g, 2.75 mmoles, 57%
$(RCH_2)_2\underset{\displaystyle R}{C}CH_2CMe_3$	0.36 g, 0.58 mmoles, 13%	0.47 g, 0.77 mmoles, 16%
2 minor $C_8H_{17}R$ products	0.05 g, 0.16 mmoles, 3.5%	0.03 g, 0.10 mmoles, 2%

4. <u>WITH ISOBUTYL CHLORIDE</u>

Bistrifluoromethylamino-oxyl (3.51 g, 20.89 mmoles) was condensed, in vacuo, into a Pyrex reaction tube (ca. 300 cm^3) containing isobutyl chloride (0.99 g, 10.70 mmoles) cooled to -196°C. The tube was sealed, allowed to warm to room temperature and left in the dark for two hours, after which time a trace of $(CF_3)_2NO^•$ remained, as evidenced by a pale yellow tinge to the frozen down solid and a slight purple colouration in the liquid.

The products were shown by g.l.c. (2m SE30 column at 60°C) to contain <u>N</u>,<u>N</u>-bistrifluoromethylhydroxylamine, isobutyl chloride and 2 other major and one minor components. The two major components were identified from g.l.c.-mass spectral data as 2-(bistrifluoromethylamino-oxy)-1-chloro-2-methylpropane (m.s. 13), and 1,2-bis(bistrifluoromethyl-amino-oxy)-3-chloro-2-methylpropane (m.s. 14).

2-(Bistrifluoromethylamino-oxy)-1-chloro-2-methylpropane was separated by preparative g.l.c. (4m SE30 column at 60°C) and confirmation of its identity obtained from its n.m.r. and i.r. spectra (n.m.r. 5, i.r. 3).

1,2-Bis(bistrifluoromethylamino-oxy)-3-chloro-2-methylpropane
was found to have a g.l.c. retention time and a mass spectrum identical
to the major product of the reaction of $(CF_3)_2NO^{\bullet}$ and 3-chloro-2-
methylprop-1-ene.

Reaction summary

Reactants:

$(CF_3)_2NO^{\bullet}$ ...... 3.51 g, 20.89 mmoles

Me_2CHCH_2Cl ...... 0.99 g, 10.70 mmoles

Products

Me_2CHCH_2Cl ...... 0.13 g, 1.39 mmoles, 13% unreacted

$(CF_3)_2NO^{\bullet}$ ...... trace

$(CF_3)_2NOH$ ...... yield not determined

$Me_2\overset{\displaystyle |}{\underset{\displaystyle R}{C}}CH_2Cl$ ...... 2.03 g, 7.82 mmoles, 84%

$\overset{\displaystyle |}{\underset{\displaystyle R}{C}}H_2\text{-}\overset{\displaystyle |}{\underset{\displaystyle R}{C}}(Me)CH_2Cl$ ...... 0.48 g, 1.12 mmoles, 12%

unidentified, possibly a

mono-amino-oxy product 3%

5. WITH 3-CHLORO-2-METHYLPROP-1-ENE

Bistrifluoromethylamino-oxyl (1.62 g, 9.64 mmoles) and 3-chloro-
2-methylprop-1-ene (0.87 g, 9.61 mmoles) were caused to react using the
same method as in reaction 4. The reaction time was 2 hours.

The products were shown by g.l.c. (2m SE30 at 60°C) to consist
of N,N-bistrifluoromethylhydroxylamine, 3-chloro-2-methylprop-1-ene and
4 other major components. The main one of these was identified, by
comparison of its mass spectrum and its g.l.c. retention time with the
products of reaction 4 as 1,2-bis(bistrifluoromethylamino-oxy)-3-chloro-
2-methylpropane (m.s. 14). Two of the other components were shown by
g.l.c.-mass spectral data to be allylically substituted mono-amino-oxy

compounds, $C_4H_6ClON(CF_3)_2$ (mass spectra 15 and 16), although no structure could be assigned to either compound on the basis of its mass spectrum. The other major product was also possibly a mono-amino-oxy compound. Its mass spectrum showed peaks for m/e values 244 (0.3%, $C_3H_3{}^{37}ClR^+$), 230 (2.9%, $C_2H{}^{37}ClR^+$), 228 (8.9%, $C_2H{}^{35}ClR^+$), 41 (100%, $C_3H_5{}^+$) but only minor peaks for m/e 91 (2.6%, $C_4H_6{}^{37}Cl^+$) and no peak for m/e 89 ($C_4H_6{}^{35}Cl^+$).

Reaction summary

Reactants:

$(CF_3)_2NO^\bullet$ ...... 1.62 g, 9.64 mmoles

$CH_2=C(Me)CH_2Cl$ ...... 0.87 g, 9.61 mmoles

Products:

$CH_2=C(Me)CH_2Cl$ ...... 0.45 g, 5.00 mmoles, 52% unreacted

$(CF_3)_2NOH$ ...... yield not determined

2 compounds C_4H_6ClR ...... 0.18 g, 0.74 mmoles, 16%

0.12 g, 0.46 mmoles, 10%

another possible mono-amino-oxy compound ...... 0.13 g, 0.51 mmoles, 11%

$\underset{R}{CH_2}-\underset{R}{C}(Me)CH_2Cl$ ...... 1.23 g, 2.85 mmoles, 62%

6. WITH ISOBUTYL BROMIDE

Bistrifluoromethylamino-oxyl (1.50 g, 8.93 mmoles) and isobutyl bromide (0.65 g, 4.74 mmoles) were caused to react using the same method as in reaction 4.

Analysis of the colourless liquid products by g.l.c. (2m SE30 at 100°C) showed them to consist of N,N-bistrifluoromethylhydroxylamine, isobutyl bromide, 2 major and 5 very minor products. The 2 major products were identified from g.l.c.-mass spectral data as 2-(bistrifluoromethylamino-oxy)-1-bromo-2-methylpropane (m.s. 17) and 1,2-bis-(bistrifluoromethylamino-oxy)-3-bromo-2-methylpropane (m.s. 18). The fragmentation patterns in the mass spectra of these two compounds are

virtually identical to those of the corresponding chloro-compounds

obtained in reaction 4 (see mass spectra 13 and 14).

The amounts of $(CF_3)_2NOH$ and unreacted isobutyl bromide in the

products were calculated by comparative g.l.c. The yields of the

$(CF_3)_2NO$-substituted products were calculated from their g.l.c. peak

areas.

Reaction summary

Reactants:

$(CF_3)_2NO^•$ ...... 1.50 g, 8.92 mmoles

Me_2CHCH_2Br ...... 0.65 g, 4.74 mmoles

Products:

Me_2CHCH_2Br ...... 0.14 g, 1.00 mmoles, 21% unreacted

$(CF_3)_2NOH$ ...... 0.68 g, 4.01 mmoles, 45%

$Me_2\underset{\underset{R}{|}}{C}CH_2Br$ ...... 0.89 g, 2.92 mmoles, 78%

$\underset{\underset{R}{|}}{C}H_2-\underset{\underset{R}{|}}{C}(Me)CH_2Br$ ...... 0.17 g, 0.37 mmoles, 10%

5 unidentified products ...... total approximately 12% of Me_2CHCH_2Br
reacted

7.   WITH ISOBUTYL METHYL KETONE

This reaction was carried out twice as follows.

Bistrifluoromethylamino-oxyl [(a) 1.75 g, 10.42 mmoles, (b) 3.21

g, 19.11 mmoles] and isobutyl methyl ketone [(a) 0.54 g, 5.45 mmoles,

(b) 1.02 g, 10.30 mmoles] were caused to react using the same method as

in reaction 4. After 2 hours a very slight trace of $(CF_3)_2NO^•$ remained.

The products were shown by g.l.c. (2m SE30 at 85°C) to consist

of N,N-bistrifluoromethylhydroxylamine, isobutyl methyl ketone, 2 major

and 4 minor products. The 2 major products were identified, from g.l.c.-

mass spectral data as 2-(bistrifluoromethylamino-oxy)-2-methylpentan-4-one (m.s. 19) and 1,2-bis(bistrifluoromethylamino-oxy)-2-methylpentan-4-one (m.s. 20). Of the minor products one appeared, from its mass spectrum, to be a mono-amino-oxy compound although it was not possible to decide whether its formula was $C_6H_{11}OR$ or C_6H_9OR, as it showed peaks at the following m/e values: 224 (2.5%, $C_3H_4OR^+$ or $C_4H_8R^+$), 99 (only 0.1%, $C_6H_{11}O^+$), 69 (7.5%, CF_3^+), 43 (100%, $C_2H_3O^+$); there was no peak at m/e 97 ($C_6H_9O^+$). Another appeared to be a trisubstituted compound, as it showed peaks for m/e 515 (0.5%), 448 (0.6%, $C_6H_8O_2R_2^+$), 347 (0.6%), 264 (4.1%, $C_6H_8OR^+$), 69 (22.9%, CF_3^+), 43 (100%, $C_2H_3O^+$).

2-(Bistrifluoromethylamino-oxy)-2-methylpentan-4-one was separated by preparative g.l.c. (4m SE30 at 90°C) and its identity confirmed by its n.m.r. and i.r. spectra (n.m.r. 6, i.r. 4). 1,2-Bis-(bistrifluoromethylamino-oxy)-2-methylpentan-4-one was also separated by preparative g.l.c. but a mix-up over the products resulted in its loss.

The yields of $(CF_3)_2NOH$ and unreacted isobutyl methyl ketone were calculated by comparative g.l.c. The yields of the $(CF_3)_2NO$-substituted compounds were calculated directly from their g.l.c. peak areas.

Reaction summary

Reactants:	Reaction (a)	Reaction (b)
$(CF_3)_2NO^\bullet$	1.75 g, 10.42 mmoles	3.21 g, 19.11 mmoles
Me_2CHCH_2COMe	0.54 g, 5.45 mmoles	1.02 g, 10.30 mmoles
Products:		
Me_2CHCH_2COMe	0.15 g, 1.53 mmoles, 28%	0.29 g, 2.88 mmoles, 28%
$(CF_3)_2NOH$	0.85 g, 5.00 mmoles, 48%	1.55 g, 9.17 mmoles, 48%
Me_2CCH_2COMe R	0.50 g, 1.88 mmoles, 48%	0.95 g, 3.56 mmoles, 48%

Products:	Reaction (a)	Reaction (b)

CH_2-$C(Me)CH_2COMe$
  $\vert$ $\vert$
  R   R
	0.58 g, 1.33 mmoles, 34%	1.09 g, 2.52 mmoles, 34%

another mono- $(CF_3)_2NO$ compd.	0.07 g, 0.27 mmoles, 7%	0.14 g, 0.52 mmoles, 7%
a tri-amino-oxy compound	0.06 g, 0.10 mmoles, 2.5%	0.11 g, 0.19 mmoles, 2.5%
unidentified	8% of Me_2CHCH_2COMe reacted	8% of Me_2CHCH_2COMe reacted

8.   WITH ISOBUTYL ACETATE

This reaction was carried out twice as follows.

Bistrifluoromethylamino-oxyl [(a) 1.54 g, 9.17 mmoles, (b) 4.25 g, 25.30 mmoles] and isobutyl acetate [(a) 0.56 g, 4.83 mmoles, (b) 1.44 g, 12.41 mmoles] were caused to react using the same method as in reaction 4. The reactions were left overnight.

G.l.c. of the colourless liquid products (2m SE30 column at $85°C$) showed peaks for N,N-bistrifluoromethylhydroxylamine, isobutyl acetate, two other major and several minor products. The two major products were identified, from g.l.c.-mass spectral data as 2-(bistrifluoromethylamino-oxy)-2-methylpropyl acetate and 1,2-bis(bistrifluoromethylamino-oxy)-2-methylpropyl acetate (mass spectra 21 and 22).

These two major products were also isolated by preparative g.l.c. (5 m SE30 at $80°C$) and their identities confirmed by their n.m.r. spectra (7 and 8) and i.r. spectra (5 and 6).

One of the minor products was tentatively identified from mass spectrum 23 as 3-(bistrifluoromethylamino-oxy)-2-methylpropyl acetate. Another also appeared to be a mono-amino-oxy product, having peaks at m/e values 282 (8.1%, $C_6H_{10}O_2R^+$), 222 (2.0%), 210 (8.1%, $C_2H_2OR^+$ or

$C_3H_6R^+$), 114 (0.9%, $C_6H_{10}^+$), 69 (8.6%, CF_3^+) and 43 (100%, $C_2H_3O^+$); there was no peak at m/e 115 ($C_6H_{11}O_2^+$). This compound could not be identified further.

Sufficient of 2-(bistrifluoromethylamino-oxy)-2-methylpropyl acetate (A) and 1,2-bis(bistrifluoromethylamino-oxy)-2-methylpropyl acetate (B) were isolated for mixtures of these two compounds to be compared by g.l.c. The results are shown below.

Mixt.	Temp. (°C)	wt.A	mmoles A	peak area A	wt.B	mmoles B	peak area B	peak area A per mmole	peak area B per mmole
(i)	90	0.104 g	0.37	16.6 cm^2	0.076 g	0.17	7.2 cm^2	45 cm^2	42 cm^2
(i)	80	0.104 g	0.37	43 cm^2	0.076 g	0.17	21 cm^2	116 cm^2	124 cm^2
(ii)	90	0.195 g	0.68	36 cm^2	0.085 g	0.19	11 cm^2	53 cm^2	58 cm^2
(ii)	80	0.195 g	0.68	18 cm^2	0.085 g	0.19	5.4 cm^2	26 cm^2	28 cm^2

Within experimental error, equimolar mixtures of A and B give approximately equal g.l.c. peak areas. Yields of $(CF_3)_2$NO-substituted products were accordingly calculated directly from g.l.c. peak areas. Yields of $(CF_3)_2$NOH and isobutyl acetate were calculated by comparative g.l.c.

Reaction summary

Reactants:	Reaction (a)	Reaction (b)
$(CF_3)_2$NO$^\bullet$	1.54 g, 9.17 mmoles	4.25 g, 25.30 mmoles
Me$_2$CHCH$_2$OOCMe	0.56 g, 4.83 mmoles	1.44 g, 12.41 mmoles
Products:		
Me$_2$CHCH$_2$OOCMe	0.13 g, 0.11 mmoles, 23%	0.23 g, 1.99 mmoles, 16%
$(CF_3)_2$NOH	0.75 g, 4.40 mmoles, 48%	2.10 g, 12.40 mmoles, 49%

Products:	Reaction (a)	Reaction (b)
Me$_2$CCH$_2$OOCMe 　　| 　　R	0.68 g, 2.42 mmoles, 65%	2.00 g, 7.09 mmoles, 68%
CH$_2$-C(Me)CH$_2$OOCMe 　|　　| 　R　 R	0.39 g, 0.86 mmoles, 23%	1.17 g, 2.61 mmoles, 25%
probably Me$_2$CHCHOOCMe 　　　 | 　　　 R	0.02 g, 0.07 mmoles, 2%	⎫
another mono- amino-oxy compd.	0.04 g, 0.15 mmoles, 4%	⎬ 7% of isoBuAc reacted
unidentified	6% of isoBuAc reacted	⎭

9.　WITH 2-METHYL-1-NITROPROPANE

2-Methyl-1-nitropropane was prepared in 75% yield from the reaction of isobutyl iodide with sodium nitrite in dimethylformamide.[149]

Bistrifluoromethylamino-oxyl (2.07 g, 12.32 mmoles) and 2-methyl-1-nitropropane (0.64 g, 6.21 mmoles) were caused to react using the same method as in reaction 4. The reaction was left overnight at room temperature.

G.l.c. analysis (2m SE30 at 85°C) of the pale yellow liquid products showed peaks for N,N-bistrifluoromethylhydroxylamine, 2-methyl-1-nitropropane, 1 major and 6 minor products.

G.l.c.-mass spectral data identified the major product as 2-(bistrifluoromethylamino-oxy)-2-methyl-1-nitropropane (m.s. 24). This compound was isolated by preparative g.l.c. (5m SE30) and its identity confirmed from its n.m.r. spectrum (n.m.r. 9). One of the minor products was tentatively identified, from its mass spectrum as 1,2-bis-(bistrifluoromethylamino-oxy)-2-methyl-3-nitropropane (m.s. 25).

A [1]H n.m.r. spectrum (ref. ext. DCB) of the reaction products

showed bands for $(CF_3)_2NOH$ (-0.34 ppm, int. 7.5, very broad),

$Me_2CHCH_2NO_2$ (doublets at +3.20 and +6.42 ppm, integrations approximately

3 and 7 respectively, multiplet at +4.97 ppm), $Me_2CRCH_2NO_2$ (singlets at

+2.86 and +5.92 ppm, integrations approximately 10 and 30 respectively),

several very minor peaks between +8.7 and +9.2 ppm and a small discrete

singlet (int. approximately 0.8) at +2.86 ppm, about the expected chemical

shift for $CH_2-ON(CF_3)_2$.

The ^{19}F n.m.r. (ref. ext. TFA) spectrum showed singlets for

$Me_2CRCH_2NO_2$ (-10.4 ppm, int. 7) and $(CF_3)_2NOH$ (-7.5 ppm, int. 20) and

minor singlets at -9.95 (int. 0.3), -8.2 and -8.1 ppm (total int. 2.4).

Reaction summary

Reactants:

$(CF_3)_2NO^{\bullet}$ ...... 2.07 g, 12.32 mmoles

$Me_2CHCH_2NO_2$ ...... 0.64 g, 6.21 mmoles

Products:

$Me_2CHCH_2NO_2$ ...... 0.10 g, 0.99 mmoles, 16% unreacted

$(CF_3)_2NOH$ ...... yield not determined

$Me_2\underset{R}{C}CH_2NO_2$ ...... 1.16 g, 4.28 mmoles, 82%

probably $\underset{R}{C}H_2-\underset{R}{C}(Me)CH_2NO_2$ ...... 0.16 g, 0.37 mmoles, 7%

6 unidentified compounds ...... 11% of $Me_2CHCH_2NO_2$ reacted

10.   WITH ISOPENTYL BROMIDE

Isopentyl bromide was prepared in approximately 80% yield by

reaction of isopentanol with hydrobromic acid and concentrated sulphuric

acid.[150] It was characterised by its boiling point, n.m.r. and i.r.

spectra and shown to be pure by g.l.c. Its reaction with bistrifluoro-

methylamino-oxyl was carried out twice as follows.

CF_3^+).

Mixtures of the two major products, 3-(bistrifluoromethylamino-oxy)-1-bromo-3-methylbutane (A) and 1,2-bis(bistrifluoromethylamino-oxy)-4-bromo-2-methylbutane (B) were compared by g.l.c. The results are shown below.

Mixt.	wt.A	mmoles A	peak area A	wt.B	mmoles B	peak area B	peak area A per mmole	peak area B per mmole
(i)	0.046 g	0.14	10.1 cm^2	0.044 g	0.095	7.0 cm^2	72 cm^2	74 cm^2
(ii)	0.136 g	0.42	45.0 cm^2	0.044 g	0.095	107 cm^2	107 cm^2	102 cm^2

Within experimental error, equimolar mixtures of A and B give approximately equal g.l.c. peak areas. Yields of $(CF_3)_2NO$-substituted compounds were accordingly calculated directly from g.l.c. peak areas. Yields of $(CF_3)_2NOH$ and unreacted isopentyl bromide were calculated by comparative g.l.c.

Reaction summary

Reactants:	Reaction (a)	Reaction (b)
$(CF_3)_2NO^\bullet$	2.04 g, 12.14 mmoles	4.70 g, 27.97 mmoles
$Me_2CHCH_2CH_2Br$	0.94 g, 6.23 mmoles	2.11 g, 13.97 mmoles
Products:		
$Me_2CHCH_2CH_2Br$	0.30 g, 2.00 mmoles, 32%	0.53 g, 3.49 mmoles, 25%
$(CF_3)_2NOH$	1.01 g, 5.95 mmoles, 49%	2.51 g, 14.82 mmoles, 53%
$Me_2\overset{\text{R}}{\underset{|}{C}}CH_2CH_2Br$	0.74 g, 2.33 mmoles, 55%	1.83 g, 5.76 mmoles, 55%
$\overset{|}{\underset{R}{C}}H_2-\overset{|}{\underset{R}{C}}(Me)CH_2CH_2Br$	0.78 g, 1.61 mmoles, 38%	1.83 g, 3.77 mmoles, 36%
possibly $C_5H_{10}R_2$	0.02 g, 0.06 mmoles, 1.5%	0.06 g, 0.21 mmoles, 2%

Products:	Reaction (a)	Reaction (b)
possibly $C_5H_{10}BrR$	0.02 g, 0.06 mmoles, 1.5%	0.06 g, 0.21 mmoles, 2%
possibly $C_5H_{10}BrR$ or C_5H_8BrR	0.02 g, 0.06 mmoles, 1.5%	0.06 g, 0.21 mmoles, 2%
possibly $C_5H_9BrR_2$	0.04 g, 0.09 mmoles, 2%	0.10 g, 0.21 mmoles, 2%

11.   WITH ISOPENTYL CHLORIDE

Bistrifluoromethylamino-oxyl (1.45 g, 8.63 mmoles) and isopentyl chloride (0.50 g, 4.78 mmoles) were caused to react using the same method as in reaction 4. Reaction was complete within two hours.

Analysis of the colourless liquid products by g.l.c. (2m SE30 at 85°C) showed peaks for N,N-bistrifluoromethylhydroxylamine, isopentyl chloride, 2 major and 5 minor products.

The two major products were identified by g.l.c.-mass spectral data as 3-(bistrifluoromethylamino-oxy)-1-chloro-3-methylbutane (m.s. 29) and 1,2-bis(bistrifluoromethylamino-oxy)-4-chloro-2-methylbutane (m.s. 30). The fragmentation patterns in the mass spectra of these two compounds show marked similarities to those of the corresponding bromo-compounds obtained in reaction 10 (see mass spectra 27 and 28).

Of the minor compounds one was tentatively identified as 2,3-bis(bistrifluoromethylamino-oxy)-1-chloro-3-methylbutane from its mass spectrum [m/e values at 440 (0.1%, $C_5H_9{}^{35}ClR_2{}^+$), 274 (0.3%, $C_5H_9{}^{37}Cl^+$), 272 (1.3%, $C_5H_9{}^{35}Cl^+$), 232 (1.2%, $C_2H_3{}^{37}ClR^+$), 230 (4.3%, $C_2H_3{}^{35}ClR^+$), 210 (1.8%, $C_3H_6R^+$), 69 (53.8%, $CF_3{}^+$), 43 (100%, $C_2H_3O^+$)].

The others appeared from their mass spectra to be amino-oxy substituted compounds but they could not be identified.

The yields of $(CF_3)_2NOH$ and isopentyl chloride were calculated

by comparative g.l.c. The yields of $(CF_3)_2NO$-compounds were calculated directly from their g.l.c. peak areas.

Reaction summary

Reactants:

$(CF_3)_2NO^{\bullet}$ ...... 1.45 g, 8.63 mmoles

$Me_2CHCH_2CH_2Cl$ ...... 0.50 g, 4.78 mmoles

Products:

$Me_2CHCH_2CH_2Cl$ ...... 0.19 g, 1.82 mmoles, 38% unreacted

$(CF_3)_2NOH$ ...... 0.69 g, 4.06 mmoles, 47%

$Me_2\underset{R}{C}CH_2CH_2Cl$ ...... 0.40 g, 1.48 mmoles, 50%

$\underset{R}{C}H_2-\underset{R}{C}(Me)CH_2CH_2Cl$ ...... 0.51 g, 1.15 mmoles, 39%

probably $Me_2\underset{R}{C}-\underset{R}{C}HCH_2Cl$ ...... 0.03 g, 0.06 mmoles, 2%

4 unidentified products ...... 9% of $Me_2CHCH_2CH_2Cl$ reacted

12. WITH 3-METHYL-1-NITROBUTANE

3-Methyl-1-nitrobutane was prepared in 70% yield by the reaction of isopentyl bromide with sodium nitrite in dimethylformamide.[149] It was characterised by its n.m.r. and i.r. spectra and shown to be pure by g.l.c.

Bistrifluoromethylamino-oxyl (2.65 g, 15.77 mmoles) and 3-methyl-1-nitrobutane (0.94 g, 8.03 mmoles) were caused to react using the same method as in reaction 4. The reaction was left overnight at room temperature.

G.l.c. analysis (2m SE30 at 100°C) of the colourless liquid products showed peaks for N,N-bistrifluoromethylhydroxylamine, 3-methyl-1-nitrobutane, 2 major and 4 very minor peaks. The two major products were isolated by preparative g.l.c. (4m SE30 at 100°C) and identified by their

n.m.r. and i.r. spectra as 3-(bistrifluoromethylamino-oxy)-3-methyl-1-nitrobutane (n.m.r. 13, i.r. 10) and 1,2-bis(bistrifluoromethylamino-oxy)-2-methyl-4-nitrobutane (n.m.r. 14, i.r. 11).

Reaction summary

Reactants:

$(CF_3)_2NO^\bullet$ ...... 2.65 g, 15.77 mmoles

$Me_2CHCH_2CH_2NO_2$ ...... 0.94 g, 8.03 mmoles

Products:

$Me_2CHCH_2CH_2NO_2$ ...... 0.28 g, 2.41 mmoles, 30% unreacted

$(CF_3)_2NOH$ ...... yield not determined

$Me_2\underset{R}{C}CH_2CH_2NO_2$ ...... 0.88 g, 3.09 mmoles, 55%

$\underset{R}{CH_2}-\underset{R}{C}(Me)CH_2CH_2NO_2$ ...... 0.99 g, 2.19 mmoles, 39%

4 unidentified compounds ...... 6% of $Me_2CHCH_2CH_2NO_2$ reacted

13.   WITH ISOHEXYL BROMIDE

Isohexyl bromide was prepared in 80% yield by reaction of isohexanol with hydrobromic acid and concentrated sulphuric acid.[150] It was characterised by its boiling point and n.m.r. and i.r. spectra and shown to be pure by g.l.c.

Bistrifluoromethylamino-oxyl (2.62 g, 15.60 mmoles) and isohexyl bromide (1.29 g, 7.82 mmoles) were caused to react using the same method as in reaction 4. The reaction was left overnight at room temperature.

G.l.c. analysis of the colourless liquid products (2m SE30 at 100 to 120°C) showed peaks for N,N-bistrifluoromethylhydroxylamine, isohexyl bromide, 2 other major and 5 very minor products. The two major compounds were isolated by preparative g.l.c. (4m SE30 at 100°C) and identified by their n.m.r. and i.r. spectra as 2-(bistrifluoromethyl-

amino-oxy)-5-bromo-2-methylpentane (A) (n.m.r. 17, i.r. 14) and 1,2-bis-(bistrifluoromethylamino-oxy)-5-bromo-2-methylpentane (B) (n.m.r. 18, i.r. 15).

Mixtures of these two compounds (A and B) were made up from the samples obtained from preparative g.l.c., and compared by g.l.c. (2m SE30 at 100°C) with the following results.

Mixt.	wt. A	mmoles A	peak area of A	wt. B	mmoles B	peak area of B	peak area A per mmole	peak area B per mmole
(i)	0.030 g	0.090	10.4 cm^2	0.120 g	0.24	26.6 cm^2	116 cm^2	111 cm^2
(ii)	0.030 g	0.090	12.6 cm^2	0.210 g	0.42	56.4 cm^2	140 cm^2	134 cm^2

Within experimental error, equimolar mixtures of A and B give approximately equal g.l.c. peak areas. Yields of the $(CF_3)_2NO$-substituted products were accordingly calculated directly from their g.l.c. peak areas. The amount of unreacted isohexyl bromide was calculated by comparative g.l.c.

Reaction summary

Reactants:

$(CF_3)_2NO^\bullet$ ...... 2.62 g, 15.60 mmoles

$Me_2CHCH_2CH_2CH_2Br$ ...... 1.29 g, 7.82 mmoles

Products:

$Me_2CHCH_2CH_2CH_2Br$ ...... 0.46 g, 2.82 mmoles, 36% unreacted

$(CF_3)_2NOH$ ...... not determined

$Me_2\overset{\displaystyle |}{\underset{\displaystyle R}{C}}CH_2CH_2CH_2Br$ ...... 0.68 g, 2.05 mmoles, 41%

$\overset{\displaystyle |}{\underset{\displaystyle R}{C}}H_2-\overset{\displaystyle |}{\underset{\displaystyle R}{C}}(Me)CH_2CH_2CH_2Br$ ...... 1.22 g, 2.45 mmoles, 49%

unidentified, 5 products ...... 10% of $Me_2CHCH_2CH_2CH_2Br$ reacted

14.   WITH ISOBUTYL IODIDE

Bistrifluoromethylamino-oxyl (3.72 g, 22.14 mmoles) and isobutyl iodide (2.04 g, 11.09 mmoles) were caused to react using the same method as in reaction 4. The reaction was left overnight at room temperature. The products consisted of liquid coloured red-brown by liberated iodine.

G.l.c. analysis (2m SE30, 70-100°C) of the products showed peaks for $\underline{N},\underline{N}$-bistrifluoromethylhydroxylamine, isobutyl iodide, one major and 7 minor products.

G.l.c.-mass spectral analysis identified the major product as 2-(bistrifluoromethylamino-oxy)-1-iodo-2-methylpropane (m.s. 26). Separation of the volatile products left a liquid shown by g.l.c. to consist of approximately 90% of this major product. Its identity was confirmed by its n.m.r. (10) and i.r. (7) spectra.

Five of the minor products had g.l.c. retention times less than that of isobutyl iodide. Of these one was identified as 1,2-bis(bistrifluoromethylamino-oxy)-2-methylpropane as its mass spectrum was virtually identical to that given for this compound by Justin[26b] [i.e. main diagnostic peaks at m/e values 376 (3.3%, $C_3H_4R_2^+$), 224 (59.4%, $C_4H_8R^+$), 210 (52.4%, $C_3H_6R^+$), 182 (2.4%, CH_2R^+), 150 (34.8%, $C_2F_5NOH^+$), 72 (42.8%, $C_4H_8O^+$), 43 (100%, $C_2H_3O^+$)].

Another also appeared from its mass spectrum to be a di-amino-oxy product [peaks at m/e values 392 (0.8%, $C_4H_8R_2^+$), 377 (3.6%, $C_3H_5R_2^+$), 226 (24.3%), 206 (18.9%), 182 (18.4%, CH_2R^+), 150 (15.2%, $C_2F_5NOH^+$), 69 (63.8%, CF_3^+), 43 (100%, $C_2H_3O^+$)]. Of the two minor products with longer g.l.c. retention times than isobutyl iodide, one was very tentatively identified as an allylically substituted product, C_4H_6IR, on the basis of its mass spectrum [peaks at m/e values 349 (11.0%, $C_4H_6IR^+$), 222 (2.3%, $C_4H_6R^+$), 210 (1.2%), 198 (13.6%), 182 (5.0%, CH_2R^+), 150 (14.6%, $C_2F_5NOH^+$), 69 (99.6%, CF_3^+), 55 (100%, $C_4H_7^+$ or $C_3H_3O^+$)].

Reaction summary

Reactants:

$(CF_3)_2NO^\bullet$ ...... 3.72 g, 22.14 mmoles

Me_2CHCH_2I ...... 2.04 g, 11.09 mmoles

Products:

Me_2CHCH_2I ...... 0.18 g, 1.00 mmoles, 9% unreacted

$(CF_3)_2NOH$ ...... 1.72 g, 10.18 mmoles, 46%

iodine ...... not determined

$Me_2\underset{\underset{R}{|}}{C}CH_2I$ ...... 2.65 g, 7.56 mmoles, 75%

$Me_2\underset{\underset{R}{|}}{C}CH_2R$ ...... 0.12 g, 0.30 mmoles, 3%

probably another
di-amino-oxy compound ...... 0.30 mmoles, 3%

possibly an allylically substituted
compound, C_4H_6IR ...... 0.60 mmoles, 6%

4 unidentified compounds ...... 13% of Me_2CHCH_2I reacted

15.   WITH ISOPENTYL IODIDE

Isopentyl iodide was prepared in approximately 60% yield by
reaction of isopentanol with potassium iodide in phosphoric acid.[151]
It was shown to be pure by g.l.c. and by its n.m.r. spectrum. Its
reaction with bistrifluoromethylamino-oxyl was carried out twice as
follows.

Bistrifluoromethylamino-oxyl [(a) 1.64 g, 9.76 mmoles, (b)
4.82 g, 28.69 mmoles] and isopentyl iodide [(a) 0.96 g, 4.85 mmoles,
(b) 2.85 g, 14.39 mmoles] were caused to react using the same method
as in reaction 4. The reactions were left overnight at room temperature.
The products consisted of liquid coloured red-brown by liberated iodine.

G.l.c. analysis of the products (2m SE30 at 100°C) showed peaks

for N,N-bistrifluoromethylhydroxylamine, isopentyl iodide, 8 minor

products with retention times between those of $(CF_3)_2NOH$ and isopentyl

iodide and 3 major and 2 minor products with retention times longer

than that of isopentyl iodide.

The 3 major products were isolated by preparative g.l.c. (4m

SE30 at 100°C). Two of these products were identified by their n.m.r.

and i.r. spectra as 3-(bistrifluoromethylamino-oxy)-1-iodo-3-methylbutane

(n.m.r. 15, i.r. 12) and 1,2-bis(bistrifluoromethylamino-oxy)-4-iodo-

2-methylbutane (n.m.r. 16, i.r. 13). Confirmatory evidence for their

identities was provided by g.l.c.-mass spectral data (mass spectra 31

and 32).

The third major product appeared from mass spectral data to be

unambiguously a mono-amino-oxy compound $C_5H_{10}IR$ [m/e values 365 (3.2%,

$C_5H_{10}IR^+$), 238 (11.8%, $C_5H_{10}R^+$), 197 (45.0%, $C_5H_{10}I^+$), 69 (100%, CF_3^+)].

G.l.c. of the sample submitted for n.m.r. showed one major peak

(approximately 95%). However, the ^{19}F n.m.r. spectrum showed 4 peaks

of approximately equal intensity at -11.5 ppm (broad, complex), -11.2,

-10.2 and -10.0 ppm (singlets) from TFA. The ^1H n.m.r. spectrum (ref.

ext. DCB) showed a singlet (int. 1.5) at +2.85 ppm, a doublet (int. 4,

J = 4 Hz) at +5.15 ppm, complex peaks (int. 14) between +6.05 and +6.35

ppm as well as badly defined complex peaks (both int. 1) at +2.6 and

+3.8 ppm. It was concluded that this g.l.c. peak was in fact due to

several compounds with similar retention times.

Of the compounds having g.l.c. retention times less than that of

isopentyl iodide 5 were tentatively identified on the basis of their

mass spectra as shown below.

(1) C_5H_9R, m/e values at 238 (0.6%), 237 (1.4%), 236 (21.3%, $C_5H_8R^+$),

222 (14.0%, $C_4H_6R^+$), 69 (53.1%, CF_3^+), 43 (100%, $C_2H_3O^+$).

(2) $C_5H_{10}R_2$, m/e values at 405 (6.0%, $C_5H_9R_2^+$), 210 (23.2%, $C_3H_6R^+$),

196 (43.6%, $C_2H_4R^+$), 182 (5.1%, CH_2R^+), 69 (45.6%, CF_3^+), 43 (100%, $C_2H_3O^+$).

(3)   A tri-amino-oxy compound, m/e values at 571 (2.7%, $C_5H_7R_3^+$), 403 (9.8%, $C_5H_7R_2^+$), 236 (8.7%), 235 (5.5%, $C_5H_7R^+$), 196 (6.4%, $C_2H_4R^+$), 182 (16.3%, CH_2R^+), 69 (50.5%, CF_3^+), 43 (100%, $C_2H_3O^+$).

(4)   A tri-amino-oxy compound, m/e values at 569.5 (1.5%, $C_5H_6R_3^+$ = 570), 417 (2.0%, $C_5H_5OR_2^+$), 250 (58.2%, $C_5H_6OR^+$), 182 (13.9%, CH_2R^+), 69 (100%, CF_3^+).

(5)   A tri-amino-oxy compound, m/e values at 550 (3.6%), 416 (7.9%, $C_5H_4OR_2^+$), 402 (27.8%, $C_5H_6R_2^+$), 250 (11.8%, $C_5H_6OR^+$), 235 (12.3%, $C_5H_7R^+$), 182 (26.2%, CH_2R^+), 69 (100%, CF_3^+).

Reaction summary

Reactants:	Reaction (a)	Reaction (b)
$(CF_3)_2NO^\bullet$	1.64 g, 9.76 mmoles	4.82 g, 28.69 mmoles
$Me_2CHCH_2CH_2I$	0.96 g, 4.85 mmoles	2.85 g, 14.39 mmoles
Products:		
$Me_2CHCH_2CH_2I$	0.20 g, 1.02 mmoles, 21%	0.80 g, 4.03 mmoles, 28%
$(CF_3)_2NOH$	0.76 g, 4.49 mmoles, 46%	not determined
$Me_2\overset{}{\underset{R}{C}}CH_2CH_2I$	0.39 g, 1.07 mmoles, 28%	1.02 g, 2.80 mmoles, 27%
$\overset{}{\underset{R}{C}H_2{-}\overset{}{\underset{R}{C}}(Me)CH_2CH_2I}$	0.22 g, 0.42 mmoles, 11%	0.88 g, 1.66 mmoles, 16%
probably C_5H_9R	0.05 g, 0.19 mmoles, 5%	0.25 g, 1.04 mmoles, 10%
probably $C_5H_{10}R_2$	0.22 g, 0.54 mmoles, 14%	0.63 g, 1.55 mmoles, 15%
3 compounds, possibly $C_5H_9R_3$, total	0.18 g, 0.31 mmoles, 8%	0.89 g, 1.55 mmoles, 15%
iodine	not determined	not determined

Products:	Reaction (a)	Reaction (b)
unidentified	34% of $Me_2CHCH_2CH_2I$ reacted	17% of $Me_2CHCH_2CH_2I$ reacted

16.   WITH ISOBUTYL ALCOHOL

This reaction was carried out twice as follows.

Bistrifluoromethylamino-oxyl [(a) 2.22 g, 13.21 mmoles, (b) 0.94 g, 5.60 mmoles] and isobutyl alcohol [(a) 0.49 g, 6.62 mmoles, (b) 0.21 g, 2.84 mmoles] were caused to react using the same method as in reaction 4. Reaction was complete within 2 hours giving colourless liquid products.

G.l.c. analysis of the products (2m SE30 at 100°C) showed peaks for N,N-bistrifluoromethylhydroxylamine, isobutyl alcohol, 4 major and 5 minor products. Two of the major products had retention times between those of $(CF_3)_2NOH$ and isobutyl alcohol. The first of these was identified as isobutyraldehyde(2-methylpropanal) on the basis of (a) its g.l.c. retention time which was identical to that of a specimen of isobutyraldehyde over a range of temperatures between 26° and 100°C, (b) its mass spectrum [g.l.c.-mass spectral analysis showed peaks for isobutyraldehyde at m/e values 72 (8.4%, $C_4H_8O^+$), 71 (13.5%, $C_4H_7O^+$), 43 (93.1%, $C_3H_7^+$) mixed with peaks due to the overlapping g.l.c. peak of $(CF_3)_2NOH$] and (c) the i.r. spectrum of the products which showed a strong peak at 1715 cm^{-1} (5.83 μ) due to C=O stretching (the same position as in pure isobutyraldehyde).

The second of these compounds was identified as 2-(bistrifluoromethylamino-oxycarbonyl)propane, $Me_2CHCOON(CF_3)_2$, on the basis of (a) its g.l.c. retention time which was identical to that of the main product of the reaction of isobutyraldehyde with $(CF_3)_2NO^•$ (reaction 17), (b) its mass spectrum (33) and (c) the i.r. spectrum of the products which showed

a strong peak at 1818 cm^{-1} (5.50 μ), typical of C=O stretching in

-COON(CF$_3$)$_2$, and in the same position as that in the products of reaction

17.

Of the major products with g.l.c. retention times greater than

that of isobutyl alcohol one was identified from g.l.c.-mass spectral

data as 2-(bistrifluoromethylamino-oxy)-2-methylpropan-1-ol (m.s. 34)

as it gave a fragmentation pattern typical of a compound of structure

Me$_2$CRCH$_2$X.

The other major product was identified very tentatively from its

mass spectrum as 1-(bistrifluoromethylamino-oxy)-2-methylpropan-1-ol

[m/e values at 224 (5.5%, C$_4$H$_8$R$^+$), 129 (9.8%, C$_2$F$_3$H$_2$NO$_2$$^+$), 73 (25.2%,

C$_4$H$_8$OH$^+$), 69 (10.8%, CF$_3$$^+$), 57 (100%, C$_3H_5O^+$)]. One of the minor products

was tentatively identified from its mass spectrum as a disubstituted

compound, possibly C$_4$H$_7$(OH)R$_2$ [m/e values at 376.5 (2.0%, 377 = C$_3$H$_5$R$_2$$^+$),

240 (1.4%, C$_4$H$_8$OR$^+$), 226 (2.4%, C$_3$H$_6$OR$^+$), 69 (57.4%, CF$_3$$^+$), 43 (100%,

C$_2$H$_3$O$^+$)].

Reaction summary

Reactants:	Reaction (a)	Reaction (b)
(CF$_3$)$_2$NO•	2.22 g, 13.21 mmoles	0.94 g, 5.60 mmoles
Me$_2$CHCH$_2$OH	0.49 g, 6.62 mmoles	0.21 g, 2.84 mmoles
Products:		
Me$_2$CHCH$_2$OH	0.21 g, 2.78 mmoles, 42%	0.08 g, 1.02 mmoles, 36%
(CF$_3$)$_2$NOH	1.52 g, 8.98 mmoles, 68%	not determined
Me$_2$CHCHO	0.03 g, 0.46 mmoles, 12%	0.016 g, 0.22 mmoles, 12%
Me$_2$CHCOR	0.28 g, 1.19 mmoles, 31%	0.16 g, 0.69 mmoles, 38%
Me$_2$CCH$_2$OH \ R	0.17 g, 0.69 mmoles, 18%	0.06 g, 0.25 mmoles, 14%

Products:	Reaction (a)	Reaction (b)
possibly Me$_2$CHCH(OH)—R	0.20 g, 0.81 mmoles, 21%	0.05 g, 0.22 mmoles, 12%
possibly C$_4$H$_7$(OH)R$_2$	0.06 g, 0.15 mmoles, 4%	0.02 g, 0.05 mmoles, 3%
4 unidentified (CF$_3$)$_2$NO-compounds	14% of Me$_2$CHCH$_2$OH reacted	21% of Me$_2$CHCH$_2$OH reacted

17. WITH ISOBUTYRALDEHYDE (2-methylpropanal)

Bistrifluoromethylamino-oxyl (0.70 g, 4.17 mmoles) and isobutyr-aldehyde (0.34 g, 4.72 mmoles) were caused to react using the same method as in reaction 4. The reaction was left overnight at room temperature. G.l.c. analysis of the colourless liquid products (2m SE30) at temperatures between 70° and 100°C showed peaks for N,N-bistrifluoro-methylhydroxylamine, isobutyraldehyde, 2-(bistrifluoromethylamino-oxycarbonyl)propane, which had a retention time identical to the same compound in the products of reaction 16, and several very minor products.

The i.r. spectrum of the products showed C=O stretching absorptions at 1818 cm^{-1} (5.50 μ, strong, sharp) and 1709 cm^{-1} (5.85 μ, strong, broad) from Me$_2$CHCOON(CF$_3$)$_2$ and Me$_2$CHCHO respectively.

Reaction summary

Reactants:

(CF$_3$)$_2$NO$^{\bullet}$ ...... 0.70 g, 4.17 mmoles

Me$_2$CHCHO ...... 0.34 g, 4.72 mmoles

Products:

Me$_2$CHCHO ...... 0.18 g, 2.50 mmoles, 53% unreacted

(CF$_3$)$_2$NOH ...... 0.35 g, 2.08 mmoles, 50%

Me$_2$CHCO—R ...... 0.50 g, 2.11 mmoles, 95%

18.   WITH ISOPENTYL ALCOHOL

This reaction was carried out twice as follows.

Bistrifluoromethylamino-oxyl [(a) 1.57 g, 9.35 mmoles, (b) 3.69 g, 21.96 mmoles] and isopentyl alcohol [(a) 0.42 g, 4.77 mmoles, (b) 0.97 g, 11.02 mmoles] were caused to react using the same method as in reaction 4. The reactions were left overnight at room temperature.

G.l.c. analysis of the colourless liquid products (2m SE30 at 100°C) of the first reaction (a) showed peaks for N,N-bistrifluoromethyl-hydroxylamine, isopentyl alcohol, 6 major products and 5 very minor products. 3 of the major products had retention times between those of $(CF_3)_2NOH$ and isopentyl alcohol. The first of these was identified as 3-methylbutanal from its mass spectrum [m/e values at 86 (5.7%, $C_5H_{10}O^+$), 85 (21.8%, $C_5H_9O^+$), 57 (52.5%, $C_4H_9^+$), 41 (100%, $C_3H_5^+$)] and the presence in the i.r. spectrum of the products of a peak due to a C=O stretching vibration at 1695 cm^{-1} (5.90 μ).

The second of these products was isolated by preparative g.l.c. and identified by its n.m.r. (19) and i.r. (16) spectra as 1-(bistrifluoro-methylamino-oxycarbonyl)-2-methylpropane, $Me_2CHCH_2COON(CF_3)_2$. Its identity was confirmed by its mass spectrum (35). The third showed peaks in its mass spectrum for the m/e values 373 (1.6%), 252 (6.4%, $C_5H_8OR^+$), 224 (38.5%, $C_4H_8R^+$), 210 (8.9%, $C_3H_6R^+$), 83 (9.6%), 72 (50.2%), 69 (45.3%, CF_3^+), 43 (100%, $C_2H_3O^+$) but could not be unambiguously identified. Of the major compounds with retention times greater than that of isopentyl alcohol, one was identified from its mass spectrum as 3-(bis-trifluoromethylamino-oxy)-3-methylpentan-1-ol (m.s. 36). Enough of this compound was isolated by preparative g.l.c. for an i.r. spectrum to be run. This showed peaks for OH and $(CF_3)_2NO$ groups (i.r. 17).

The other two compounds could not be identified from their mass spectra beyond their being amino-oxy substituted.

The second reaction (b) was carried out several weeks later. G.l.c. analysis using the same SE30 column showed the same peaks, with the exception of 3-methylbutanal which was absent. The areas of the peaks also showed pronounced differences. Some of the differences may be attributed to the deterioration of the g.l.c. column which was producing broader peaks with much more tailing off.

Reaction summary

Reactants:	Reaction (a)	Reaction (b)
$(CF_3)_2NO^\bullet$	1.57 g, 9.35 mmoles	3.69 g, 21.96 mmoles
$Me_2CHCH_2CH_2OH$	0.42 g, 4.77 mmoles	0.97 g, 11.02 mmoles
Products:		
$Me_2CHCH_2CH_2OH$	0.14 g, 1.57 mmoles, 33%	0.44 g, 4.96 mmoles, 45%
$(CF_3)_2NOH$	1.11 g, 6.55 mmoles, 70%	not determined
Me_2CHCH_2CHO	0.03 g, 0.38 mmoles, 12%	—
$Me_2CHCH_2\underset{R}{\overset{}{C}}O$	0.20 g, 0.80 mmoles, 25%	1.01 g, 4.00 mmoles, 66%
$Me_2\underset{R}{\overset{}{C}}CH_2CH_2OH$	0.13 g, 0.51 mmoles, 16%	0.17 g, 0.67 mmoles, 11%
3 unidentified $(CF_3)_2NO-$ substituted compounds	10%, 17%, 12% of $Me_2CHCH_2CH_2OH$ reacted	17%, 5%, 1% of $Me_2CHCH_2CH_2OH$ reacted
5 unidentified compounds	8% of $Me_2CHCH_2CH_2OH$ reacted	—

19.   WITH ISOPENTYLBENZENE

Isopentylbenzene was prepared in 20% yield by a Wurtz-Fittig reaction using isopentyl bromide, bromobenzene and sodium.[152] It was

separated from the product mixture by fractional distillation as a

fraction of boiling point 195-196°C, shown to be pure by g.l.c. and

characterised by its n.m.r. spectrum.

Bistrifluoromethylamino-oxyl (2.40 g, 14.29 mmoles) and

isopentylbenzene (1.07 g, 7.23 mmoles) were caused to react using the

same method as in reaction 4. The reaction was left overnight at room

temperature.

G.l.c. analysis of the colourless liquid products (2m SE30 at

200°C) showed peaks for $\underline{N},\underline{N}$-bistrifluoromethylhydroxylamine, isopentyl-

benzene, one main and 6 minor compounds. The major product, which had

a g.l.c. retention time slightly less than that of isopentylbenzene was

identified by g.l.c.-mass spectrometry as 1-(bistrifluoromethylamino-oxy)-

3-methyl-1-phenylbutane (m.s. 37). Isolation of this compound was

attempted using preparative g.l.c. but at all temperatures tried, from

100 to 250°C, with a variety of columns, its retention time was too close

to that of isopentylbenzene to allͦw̫ separation of the two compounds. A

mixture of the two was submitted for n.m.r. and the results compared with

a spectrum of pure isopentylbenzene. The ^{1}H spectrum of the mixture (ref.

int. TMS) showed peaks at 2.76 τ (singlet) for C_6H_5 from the mono-amino-

oxy compound, 2.94 τ (singlet) for C_6H_5 from $Me_2CHCH_2CH_2C_6H_5$, 5.17

(triplet, J ∿ 6 Hz) for $CHON(CF_3)_2$ in $Me_2CHCH_2CHRC_6H_5$, 7.47 (triplet,

J ∿ 7 Hz) for CH_2 from $Me_2CHCH_2\underline{CH_2}C_6H_5$, a complex series of peaks from

7.9 to 9.0 τ for $CHCH_2$ from both compounds and a doublet at 9.10 τ

for Me_2 from both compounds. The ^{19}F n.m.r. spectrum (ref. ext. TFA)

showed a singlet at -11.3 ppm for $(CF_3)_2NO-$. These spectra provided

confirmation of the identity of the mono-amino-oxy compound .

Of the minor products, one was tentatively identified from its

mass spectrum as 1,3-bis(bistrifluoromethylamino-oxy)-3-methyl-1-

phenylbutane [m/e values 481 (4.7%, $C_{11}H_{13}R_2{}^+$), 314 (1.1%, $C_{11}H_{14}R^+$),

258 (3.4%, $C_7H_6R^+$), 210 (2.5%, $C_3H_6R^+$)]. Another appeared to be a tri-amino-oxy compound $C_{11}H_{13}R_3$ [m/e values 648 (4.1%, $C_{11}H_{12}R_3^+$), 480 (1.1%, $C_{11}H_{12}R_2^+$), 314 (3.0%)].

Reaction summary

Reactants:

$(CF_3)_2NO^{\bullet}$ ...... 2.40 g, 14.29 mmoles

$Me_2CHCH_2CH_2Ph$ ...... 1.07 g, 7.23 mmoles

Products:

$Me_2CHCH_2CH_2Ph$ ...... 0.12 g, 0.80 mmoles, 11% unreacted

$(CF_3)_2NOH$ ...... not determined

$Me_2CHCH_2\underset{\overset{|}{R}}{C}HPh$ ...... 1.56 g, 4.95 mmoles, 77%

probably $Me_2\underset{\overset{|}{R}}{C}CH_2\underset{\overset{|}{R}}{C}HPh$ ...... 0.22 g, 0.45 mmoles, 7%

probably $C_{11}H_{13}R_3$ ...... 0.08 g, 0.13 mmoles, 2%

4 unidentified products ...... 14% of $Me_2CHCH_2CH_2Ph$ reacted

SECTION II

REACTION TIMES FOR REACTIONS OF BISTRIFLUOROMETHYLAMINO-OXYL WITH ALKANES AND SUBSTITUTED ALKANES OF GENERAL FORMULA Me_2CHCH_2X

A number of these reactions were repeated, using a slightly different method to that previously employed, in order to compare reaction times.

Bistrifluoromethylamino-oxyl was condensed, in vacuo, into a Pyrex reaction tube (ca. 25 cm^3) containing the alkane or substituted alkane cooled to -196°C. An approximately 2:1 molar ratio of $(CF_3)_2NO^{\bullet}$ to substrate was used each time. The tube was sealed and transferred directly from liquid nitrogen to a water bath maintained at 23-24°C. The reactions were carried out in batches of two or three to allow direct comparison between different reactions. The reactions were judged to be complete when the purple colour of the $(CF_3)_2NO^{\bullet}$ had vanished. This was determined as accurately as possible by refreezing the reactants when the $(CF_3)_2NO^{\bullet}$ seemed to have disappeared and rewarming them in the water bath. Any $(CF_3)_2NO^{\bullet}$ no longer visible to the naked eye was concentrated in the liquid and showed clearly as dark brown and then pink-purple streaks.

The products of each reaction were analysed by g.l.c. (2m SE30, 80-120°C), the products being identified by comparison of the g.l.c. traces with those of the original reactions described in Section I. No attempts were made to calculate yields of unreacted substrate or N,N-bistrifluoromethylhydroxylamine in the products. Percentages quoted were calculated from g.l.c. peak areas and are based on substrate reacted.

Alkane Me_2CHCH_2X	$(CF_3)_2NO^\bullet$ g, mmoles	Products	Reaction time (minutes)
1. isohexane $Me_2CHCH_2CH_2CH_3$ 0.36 g, 4.19 mmoles	1.31, 7.80	$Me_2\underset{R}{C}CH_2CH_2CH_3$ ... 31% $Me_2CHCH_2\underset{R}{C}HCH_3$ ... 11% $\underset{R}{C}H_2-\underset{R}{C}(Me)CH_2CH_2CH_3$ ... 48% $Me_2\underset{R}{C}-\underset{R}{C}HCH_2CH_3$ ... 10%	4
2. 2,2,4-trimethyl- pentane, $Me_2CHCH_2CMe_3$ (a) 0.55 g, 4.82 mmoles (b) 0.18 g, 1.58 mmoles	1.53, 9.11 0.53, 3.15	(a) $Me_2\underset{R}{C}CH_2CMe_3$ ... 29% (b) $\underset{R}{C}H_2-\underset{R}{C}(Me)CH_2CMe_3$ ... 53% (c) $(RCH_2)_2\underset{R}{C}CH_2CMe_3$ ... 14%	(a) 9 (b) 11

Substituted alkane Me_2CHCH_2X	$(CF_3)_2NO^\bullet$ g, mmoles	Products		Reaction time (minutes)
		$Me_2\underset{R}{C}CH_2X$	$\underset{R}{C}H_2-\underset{R}{C}(Me)CH_2X$	
3. isobutyl chloride Me_2CHCH_2Cl (a) 0.38 g, 4.11 mmoles (b) 0.64 g, 6.92 mmoles	 1.26, 7.50 2.31, 13.75	 82% -	 15% -	 100 98
4. isobutyl bromide Me_2CHCH_2Br 0.56 g, 4.09 mmoles	 1.32, 7.86	 81%	 12%	 93

Substituted alkane Me_2CHCH_2X	$(CF_3)_2NO^\bullet$ g, mmoles	Products		Reaction time (minutes)
		$Me_2\overset{\displaystyle }{\underset{\displaystyle R}{C}}CH_2X$	$CH_2=\overset{\displaystyle }{\underset{\displaystyle R}{C}}(Me)CH_2X$	
5. isopentyl chloride $Me_2CHCH_2CH_2Cl$ 0.44 g, 4.13 mmoles	1.32, 7.86	57%	39%	33
6. isopentyl bromide $Me_2CHCH_2CH_2Br$ (a) 0.62 g, 4.11 mmoles (b) 0.40 g, 2.65 mmoles	1.34, 7.98 0.86, 5.11	56% –	40% –	35 34
7. isobutyl methyl ketone Me_2CHCH_2COMe (a) 0.45 g, 4.50 mmoles (b) 0.30 g, 3.00 mmoles	1.46, 8.69 0.94, 5.60	55% –	34% –	45 48
8. 3-methyl-1-nitrobutane $Me_2CHCH_2CH_2NO_2$ (a) 0.46 g, 3.93 mmoles (b) 0.23 g, 1.96 mmoles	1.27, 7.56 0.65, 3.87	54% –	45% –	65 70

SECTION III

REACTIONS OF BISTRIFLUOROMETHYLAMINO-OXYL WITH ALKANES AND CHLOROALKANES
ON 1:1 AND 1:2 MOLAR BASES

The reactions of bistrifluoromethylamino-oxyl with (1) isohexane,
(2) 2,2,4-trimethylpentane, (3) isobutyl chloride and (4) isopentyl
chloride, which had previously been carried out using 2:1 molar ratios
of $(CF_3)_2NO^{\bullet}$ to substrate (see Sections I and II), were repeated using
1:1 and 1:2 molar ratios of reactants.

Bistrifluoromethylamino-oxyl was condensed, in vacuo, into a
Pyrex reaction tube (ca. 25 cm^3) containing the alkane or chloroalkane
cooled to -196°C. The tube was sealed and transferred directly from liquid
nitrogen to a water bath at 23-24°C. Upon completion the products were
analysed by g.l.c. (2m SE30, 80-120°C). The products were identified by
comparison of the g.l.c. traces with those from the 2:1 molar ratio
reactions. No attempts were made to calculate yields of N,N-bistrifluoro-
methylhydroxylamine or unreacted substrate which were major components of
the products. Percentages quoted were calculated from g.l.c. peak areas
and are based on substrate reacted.

1.   Bistrifluoromethylamino-oxyl with isohexane, 1:1 and 1:2 molar
        ratios

Reactants:	1:1 molar ratio reaction	1:2 molar ratio reaction
$(CF_3)_2NO^{\bullet}$	0.54 g, 3.21 mmoles	0.59 g, 3.51 mmoles
$Me_2CHCH_2CH_2CH_3$	0.28 g, 3.33 mmoles	0.60 g, 6.98 mmoles
Products:		
$Me_2CHCH_2CH_2CH_3$	not determined	not determined
$(CF_3)_2NOH$	not determined	not determined

Products:	1:1 molar ratio reaction	1:2 molar ratio reaction
$Me_2CRCH_2CH_2CH_3$	34.5%	39%
$Me_2CHCH_2CHRCH_3$	13%	13.5%
$\underset{R\ \ \ R}{CH_2\text{-}C(Me)CH_2CH_2CH_3}$	48%	45%
$\underset{R\ R}{Me_2C\text{-}CHCH_2CH_3}$	4%	2%

2. **Bistrifluoromethylamino-oxyl with 2,2,4-trimethylpentane, 1:1 and**

    1:2 molar ratios

Reactants:	1:1 molar ratio reaction	1:2 molar ratio reaction
$(CF_3)_2NO^\bullet$	0.73 g, 4.35 mmoles	0.90 g, 5.36 mmoles
$Me_2CHCH_2CMe_3$	0.50 g, 4.39 mmoles	1.22 g, 10.70 mmoles
Products:		
$Me_2CHCH_2CMe_3$	not determined	not determined
$(CF_3)_2NOH$	not determined	not determined
$\underset{R}{Me_2CCH_2CMe_3}$	32%	32%
$\underset{R\ \ \ R}{CH_2\text{-}C(Me)CH_2CMe_3}$	56%	58%
$\underset{R}{(RCH_2)_2CCH_2CMe_3}$	12%	10%

3. **Bistrifluoromethylamino-oxyl with isobutyl chloride, 1:1 and 1:2**

    molar ratios

Reactants:	1:1 molar ratio reaction	1:2 molar ratio reaction
$(CF_3)_2NO^\bullet$	0.98 g, 5.83 mmoles	0.52 g, 3.10 mmoles
Me_2CHCH_2Cl	0.55 g, 5.95 mmoles	0.57 g, 6.16 mmoles

Products:	1:1 molar ratio reaction	1:2 molar ratio reaction
Me_2CHCH_2Cl	not determined	not determined
$(CF_3)_2NOH$	not determined	not determined
$Me_2\underset{R}{C}CH_2Cl$	82%	82%
$\underset{R}{CH_2}-\underset{R}{C}(Me)CH_2Cl$	14%	16%

4. **Bistrifluoromethylamino-oxyl with isopentyl chloride, 1:1 and 1:2 molar ratios**

Reactants:	1:1 molar ratio reaction	1:2 molar ratio reaction
$(CF_3)_2NO^{\bullet}$	0.53 g, 3.15 mmoles	0.39 g, 2.32 mmoles
$Me_2CHCH_2CH_2Cl$	0.34 g, 3.19 mmoles	0.49 g, 4.60 mmoles
Products:		
$Me_2CHCH_2CH_2Cl$	not determined	not determined
$(CF_3)_2NOH$	not determined	not determined
$Me_2\underset{R}{C}CH_2CH_2Cl$	50%	54%
$\underset{R}{CH_2}-\underset{R}{C}(Me)CH_2Cl$	37%	38%

SECTION IV

REACTIONS OF BISTRIFLUOROMETHYLAMINO-OXYL AND HYDROGEN CHLORIDE WITH

ALKANES AND ISOBUTYL CHLORIDE

1.　　　$(CF_3)_2NO^\bullet$, HYDROGEN CHLORIDE AND ISOBUTANE

This was a repeat of a reaction first carried out by B. Justin.[26]

Isobutane (0.35 g, 6.03 mmoles) was condensed, in vacuo, onto

carbon tetrachloride in a Pyrex reaction tube ($\underline{ca}$. 300 cm^3) cooled to

-196°C. The tube was allowed to warm until the reactants had formed a

homogeneous liquid whereupon the tube was recooled to -196°C. Hydrogen

chloride (2.23 g, 61.1 mmoles) and bistrifluoromethylamino-oxyl (2.24 g,

13.33 mmoles) were condensed separately into the tube which was then

sealed and kept in the dark for 20 hours. The products were fractionated

by trap-to-trap condensation as detailed below.

-96°C trap:　A colourless liquid shown by g.l.c. (2m SE30 at room

temperature) to contain 4 components. Three of these gave retention times

identical to those of $\underline{N},\underline{N}$-bistrifluoromethylhydroxylamine, t-butyl chloride

and carbon tetrachloride. The yields of these compounds were calculated

from comparative g.l.c.

-196°C trap:　Hydrogen chloride

Reaction summary

Reactants:

$(CF_3)_2NO^\bullet$ ...... 2.24 g, 13.33 mmoles

Me_3CH ...... 0.35 g, 6.03 mmoles

HCl ...... 2.23 g, 61.1 mmoles

CCl_4 ...... 1.10 g

Products:

$(CF_3)_2NOH$ ...... 1.80 g, 10.66 mmoles, 80%

Me_3CCl ...... 0.50 g, 5.43 mmoles, 90%

one other compound ...... approximately 10% of Me$_3$CH used

CCl$_4$ ...... 1.10 g

HCl ...... not determined

2.   (CF$_3$)$_2$NO$^{\bullet}$, HYDROGEN CHLORIDE AND ISOPENTANE

Hydrogen chloride (2.20 g, 60.3 mmoles) and bistrifluoromethylamino-oxyl (2.00 g, 11.90 mmoles) were condensed separately, in vacuo, onto isopentane (0.43 g, 5.97 mmoles) and carbon tetrachloride (1.00 g) in a 300 cm^3 Pyrex reaction tube cooled to -196°C. The tube was sealed and allowed to warm to room temperature. It was then kept in the dark for 20 hours, after which time the products were fractionated by trap-to-trap condensation as detailed below.

-96°C trap: A colourless liquid shown by g.l.c. (2m SE30, DNP and APL columns) to contain 6 major and 4 minor components. 4 of the major components were identified by their g.l.c. retention times as N,N-bistrifluoromethylhydroxylamine, isopentane, 2-chloro-2-methylbutane and carbon tetrachloride. The other two major components were identified from g.l.c.-mass spectral data as 2-(bistrifluoromethylamino-oxy)-2-methyl-butane [mass spectrum identical to that given for this compound by Justin[26], i.e. main diagnostic peaks are at m/e 225 (1.1%), 224 (17.4%, C$_4$H$_8$R$^+$), 210 (40.3%, C$_3$H$_6$R$^+$), 72 (19.2%), 71 (43.3%, C$_5$H$_{11}$$^+$)] and probably 2-(bistrifluoromethylamino-oxy)-3-methylbutane (m.s. 12). Two of the minor products were identified from g.l.c.-mass spectral data as 1,2- and 2,3-bis(bistrifluoromethylamino-oxy)-2-methylbutane (mass spectra identical to those given for these compounds by Justin[26]). The yields of 2-chloro-2-methylpentane and isopentane were calculated by comparative g.l.c. The yields of (CF$_3$)$_2$NO-substituted compounds were taken as proportional to their g.l.c. peak areas.

-196°C trap: Hydrogen chloride.

Reaction summary

Reactants:

$(CF_3)_2NO^{\bullet}$ ...... 2.00 g, 11.90 mmoles

$Me_2CHCH_2CH_3$ .... 0.43 g, 5.97 mmoles

HCl .... 2.20 g, 60.3 mmoles

CCl_4 .... 1.00 g.

Products:

$Me_2CHCH_2CH_3$ ...... 0.08 g, 1.11 mmoles, 19% unreacted

$(CF_3)_2NOH$ ...... yield not determined

$Me_2CClCH_2CH_3$ ..... 0.38 g, 3.60 mmoles, 74%

$Me_2\overset{\displaystyle |}{\underset{\displaystyle R}{C}}CH_2CH_3$ ...... 0.15 g, 0.63 mmoles, 13%

probably $Me_2CH\overset{\displaystyle |}{\underset{\displaystyle R}{C}}HCH_3$ ...... 0.07 g, 0.29 mmoles, 6%

$Me_2\overset{\displaystyle |}{\underset{\displaystyle R}{C}}-\overset{\displaystyle |}{\underset{\displaystyle R}{C}}HMe$ ...... 0.06 g, 0.15 mmoles, 3%

$\overset{\displaystyle |}{\underset{\displaystyle R}{C}}H_2-\overset{\displaystyle |}{\underset{\displaystyle R}{C}}(Me)CH_2CH_3$ ...... 0.03 g, 0.08 mmoles, 1.6%

HCl ...... not determined

CCl_4 ...... 1.00 g

3. $(CF_3)_2NO^{\bullet}$, HYDROGEN CHLORIDE AND ISOHEXANE

This reaction was carried out twice.

Bistrifluoromethylamino-oxyl [(a) 4.07 g, 24.23 mmoles, (b) 2.33 g, 13.87 mmoles] and hydrogen chloride [1.75 g, 47.9 mmoles in both reactions] were caused to react with isohexane [(a) 0.76 g, 8.84 mmoles, (b) 0.59 g, 6.86 mmoles] in carbon tetrachloride [(a) 1.34 g, (b) 0.96 g] using exactly the same method as in reaction 2.

-96°C trap: A colourless liquid shown by g.l.c. analysis (2m SE30 and 2m DNP at 60°C) to contain 8 components. These were identified, by

comparison of their g.l.c. retention times with 2-chloro-2-methylpentane, carbon tetrachloride and the products of the 2:1 molar ratio reaction of $(CF_3)_2NO^{\bullet}$ with isohexane (Section I, reaction 1) as N,N-bistrifluoromethyl-hydroxylamine, isohexane, carbon tetrachloride, 2-chloro-2-methylpentane, 2-(bistrifluoromethylamino-oxy)-2-methylpentane, probably 2-(bistrifluoro-methylamino-oxy)-4-methylpentane, 1,2- and 2,3-bis(bistrifluoromethylamino-oxy)-2-methylpentane. Yields of the first four of these compounds were obtained by comparative g.l.c.; yields of the $(CF_3)_2NO$-substituted compounds were taken as being proportional to their g.l.c. peak areas.

-196°C trap: Hydrogen chloride

Reaction summary

Reactants:	Reaction (a)	Reaction (b)
$(CF_3)_2NO^{\bullet}$	4.07 g, 24.23 mmoles	2.33 g, 13.87 mmoles
$Me_2CHCH_2CH_2CH_3$	0.76 g, 8.84 mmoles	0.59 g, 6.86 mmoles
HCl	1.75 g, 47.9 mmoles	1.75 g, 47.9 mmoles
CCl_4	1.34 g	0.96 g
Products:		
$Me_2CHCH_2CH_2CH_3$	0.07 g, 0.80 mmoles, 9%	0.16 g, 1.92 mmoles, 28%
$(CF_3)_2NOH$	3.20 g, 18.90 mmoles, 78%	not determined
$Me_2CClCH_2CH_2CH_3$	0.58 g, 4.82 mmoles, 60%	0.46 g, 3.80 mmoles, 77%
$Me_2CRCH_2CH_2CH_3$	0.43 g, 1.69 mmoles, 21%	0.14 g, 0.54 mmoles, 11%
probably $Me_2CHCH_2CHRCH_3$	0.12 g, 0.48 mmoles, 6%	0.05 g, 0.20 mmoles, 4%
$\overset{\vert}{\underset{R}{C}}H_2-\overset{\vert}{\underset{R}{C}}(Me)CH_2CH_2CH_3$	0.13 g, 0.32 mmoles, 4%	0.06 g, 0.15 mmoles, 3%
$Me_2\overset{\vert}{\underset{R}{C}}-\overset{\vert}{\underset{R}{C}}HCH_2CH_3$	0.17 g, 0.40 mmoles, 5%	0.02 g, 0.05 mmoles, 1%
HCl	not determined	not determined
CCl_4	1.34 g	0.96 g

4.   (CF$_3$)$_2$NO$^\bullet$, HYDROGEN CHLORIDE AND 2,2,4-TRIMETHYLPENTANE

Bistrifluoromethylamino-oxyl (1.27 g, 7.56 mmoles) and hydrogen chloride (2.20 g, 60.3 mmoles) were reacted with 2,2,4-trimethylpentane (0.44 g, 3.86 mmoles) in carbon tetrachloride (0.87 g) using exactly the same method as in reaction 2. Reaction was complete within one hour.

The colourless liquid products were shown, by comparative g.l.c. with 2-chloro-2,4,4-trimethylpentane, carbon tetrachloride and the products of the 2:1 molar ratio reaction of (CF$_3$)$_2$NO$^\bullet$ with 2,2,4-trimethylpentane (Section I, reaction 3), to contain as major components N,N-bistrifluoromethylhydroxylamine, 2,2,4-trimethylpentane, 2-chloro-2,4,4-trimethylpentane, 2-(bistrifluoromethylamino-oxy)-2,4,4-trimethylpentane and 1,2-bis(bistrifluoromethylamino-oxy)-2,4,4-trimethylpentane, and as minor components another mono-amino-oxy compound and 1,2-bis(bistrifluoromethylamino-oxy)-2-(bistrifluoromethylamino-oxymethyl)-4,4-dimethylpentane.

Reaction summary

Reactants:

(CF$_3$)$_2$NO$^\bullet$ ...... 1.27 g, 7.56 mmoles

Me$_2$CHCH$_2$CMe$_3$ ... 0.44 g, 3.86 mmoles

HCl .... 2.20 g, 60.3 mmoles

CCl$_4$ .... 0.87 g.

Products:

Me$_2$CHCH$_2$CMe$_3$ ...... 0.09 g, 0.81 mmoles, 21% unreacted

(CF$_3$)$_2$NOH .... yield not determined

Me$_2$CClCH$_2$CMe$_3$ ...... 0.35 g, 2.38 mmoles, 78%

Me$_2$CRCH$_2$CMe$_3$ ...... 0.06 g, 0.21 mmoles, 7%

another mono-amino-oxy compound .... 0.01 g, 0.03 mmoles, 1%

CH$_2$-C(Me)CH$_2$CMe$_3$ ... 0.15 g, 0.34 mmoles, 11%
   | |
   R   R

$(RCH_2)_2\overset{|}{\underset{R}{C}}CH_2CMe_3$ ...... 0.04 g, 0.06 mmoles, 2%

HCl ...... not determined

CCl_4 ...... 0.87 g.

5. (a) $(CF_3)_2NO^\bullet$, HYDROGEN CHLORIDE AND ISOBUTYL CHLORIDE

Bistrifluoromethylamino-oxyl (1.57 g, 9.35 mmoles) and hydrogen chloride (1.75 g, 47.9 mmoles) were reacted with isobutyl chloride (0.44 g, 4.76 mmoles) in carbon tetrachloride (0.83 g) using exactly the same method as in reaction 2. The reaction tube was kept in the dark for two hours at room temperature. A faint trace of $(CF_3)_2NO^\bullet$ remained in the products. The products were analysed by g.l.c. (2m SE30 column) alongside the products of the 2:1 molar ratio reaction of $(CF_3)_2NO^\bullet$ with isobutyl chloride (reaction 4, Section I) and it was found that the products of the two reactions were virtually identical. i.e. The hydrogen chloride made no difference to the reaction.

Reaction summary

Reactants:

$(CF_3)_2NO^\bullet$ ...... 1.57 g, 9.35 mmoles

Me_2CHCH_2Cl ..... 0.44 g, 4.76 mmoles

HCl ...... 1.75 g, 47.9 mmoles

CCl_4 .... 0.83 g.

Products:

Me_2CHCH_2Cl ...... 0.05 g, 0.56 mmoles, 12% unreacted

$(CF_3)_2NO^\bullet$ ...... trace

$(CF_3)_2NOH$ ...... yield not determined

Me_2CRCH_2Cl ...... 0.95 g, 3.65 mmoles, 87%

$\overset{|}{\underset{R}{C}H_2}-\overset{|}{\underset{R}{C}}(Me)CH_2Cl$ ... 0.20 g, 0.46 mmoles, 11%

unidentified, possibly a mono-amino-oxy compound 1.5%

HCl ...... not determined

CCl_4 ..... 0.83 g.

(b) REACTION OF 3-CHLORO-2-METHYLPROP-1-ENE WITH HYDROGEN CHLORIDE

Hydrogen chloride (1.75 g, 47.9 mmoles) was condensed, _in vacuo_, onto 3-chloro-2-methylprop-1-ene (1.00 g, 1.11 mmoles) and carbon tetra-chloride (1.11 g) in a Pyrex reaction tube (_ca._ 300 cm^3) cooled to -196°C. The tube was sealed, allowed to warm to room temperature and kept in the dark for 2 hours. G.l.c. analysis (2m SE30) showed peaks for 3-chloro-2-methylprop-1-ene, carbon tetrachloride and a small peak in area only 8% of the area of the 3-chloro-2-methylprop-1-ene peak. An i.r. spectrum of the products was identical with that of a mixture of 3-chloro-2-methylprop-1-ene and carbon tetrachloride. i.e. Little or no reaction had occurred.

SECTION V

(a)   REACTIONS OF BISTRIFLUOROMETHYLAMINO-OXYL WITH AMINES AND SCHIFF'S

BASES, (b)   SOME REACTIONS OF BISTRIFLUOROMETHYLAMINE WITH AMINES

1.   REACTION OF $(CF_3)_2NO^{\bullet}$ WITH ISOBUTYLAMINE (2:1 MOLAR RATIO)

This reaction was carried out three times as described below.

(a)   Bistrifluoromethylamino-oxyl (4.58 g, 27.3 mmoles) was condensed,

in vacuo, into a Pyrex reaction tube (ca. 300 cm^3) containing isobutylamine

(1.00 g, 13.7 mmoles) cooled to -196°C. The tube was sealed, allowed to

warm to room temperature and left in the dark overnight.

G.l.c. analysis (2m SE30 at 100-120°C) of the colourless liquid

products showed peaks for N,N-bistrifluoromethylhydroxylamine, one other

major product and 5 minor products. The main product was isolated by

preparative g.l.c. and identified by its n.m.r., i.r. and mass spectra

(n.m.r. 20, i.r. 18, m.s. 38) as N-[2-(bistrifluoromethylamino-oxy)-2-

methylpropylidene]-isobutylamine, $Me_2CRCH=NCH_2CHMe_2$.

Two of the minor products were identified from g.l.c.-mass spectral

data as 2-(bistrifluoromethylamino-oxy)-2-methylpropylamine (m.s. 39)

and N-[2-(bistrifluoromethylamino-oxy)-2-methylpropylidene]-2'-

(bistrifluoromethylamino-oxy)-2'-methylpropylamine, $Me_2CRCH=NCH_2CRMe_2$

(m.s. 40).

The yields shown are based on g.l.c. peak areas.

Reaction summary

Reactants:

$(CF_3)_2NO^{\bullet}$ ...... 4.58 g, 27.26 mmoles

$Me_2CHCH_2NH_2$ .... 1.00 g, 13.70 mmoles

Products:

$Me_2\underset{\underset{R}{|}}{C}CH=NCH_2CHMe_2$ ...... 1.81 g, 6.17 mmoles, 90%

$Me_2\underset{\underset{R}{|}}{C}CH_2NH_2$ ...... 0.13 g, 0.55 mmoles, 4%

$Me_2\underset{\underset{R}{|}}{C}CH=NCH_2\underset{\underset{R}{|}}{C}Me_2$ ... 0.03 g, 0.07 mmoles, 1%

$(CF_3)_2NOH$ .... yield not determined

unidentified ..... 5% of $Me_2CHCH_2NH_2$ used

Reaction (b):

The reaction was repeated in order to examine the volatile

products, using 2.08 g (12.38 mmoles) of $(CF_3)_2NO^\bullet$ and 0.45 g (6.19 mmoles)

of isobutylamine in a 50 cm^3 sealed tube fitted with a "Rotaflo" tap.

The reaction was moderated by immersion in a slush bath at $-42°C$. The

products consisted of traces of white solid suspended in colourless liquid.

After completion the reaction tube was connected to the vacuum system

and heated gently over a long period until there was no further weight

loss. The involatile residue consisted of whitish solid and colourless

liquid. The volatiles were separated by trap-to-trap fractionation as

follows.

ice-salt bath trap: A colourless involatile liquid (exerted 0.5 cm Hg

pressure at room temperature). It proved impossible to recover this

liquid by condensation into an external trap.

$-42°C$ trap: White solid forming a volatile liquid at room temperature.

I.r. spectra of the vapour showed peaks for $(CF_3)_2NOH$ and traces of

ammonia. 0.88 g of liquid were condensed out of this trap leaving a

relatively involatile liquid. The i.r. spectrum of the vapour produced

by heating this liquid showed peaks for $(CF_3)_2NOH$ plus very strong peaks

for ammonia. The i.r. spectrum [peaks at 3580 cm^{-1} (m, sharp, OH stretch),

3400 to 2700 (broad series of peaks with maxima at 3310, 3225, 3125 and

3050 cm^{-1}), 2920 (strong, sharp), 1392, 1310, 1270, 1225 (v. strong,

C-F stretching), 1190 (m), 1045, 1060 (s, N-O stretch), 967 (s, C-N

stretch), 928 (w), 700 (s, CF_3 def)] was virtually identical to that of the N,N-bistrifluoromethylhydroxylamine-ammonia adduct.[132]

-78°C trap: Some $(CF_3)_2$NOH

-196°C trap: Trace $(CF_3)_2$NOH.

Reaction (c):

The reaction was repeated using 0.65 g (3.87 mmoles) of $(CF_3)_2$NO· and 0.14 g (1.92 mmoles) of isobutylamine in a 50 cm^3 sealed tube. The tube was allowed to warm to room temperature and reaction appeared to be complete after 15 minutes giving a pale yellow liquid. The products were dissolved in chloroform and submitted for ^{19}F n.m.r. spectroscopy to check that $(CF_3)_2$NOH and Me_2CRCH=NCH$_2$CHMe$_2$ were the only main fluorinated products. The ^{19}F n.m.r. spectrum showed two main singlet peaks, at -11.1 ppm from TFA (int. 1) due to Me_2CRCH=NCH$_2$CHMe$_2$ and at -8.4 ppm (int. 6) due to $(CF_3)_2$NOH. Six very minor peaks (total int. 0.1 to 0.2) were present between -11.3 and -9.8 ppm.

2.   REACTION OF $(CF_3)_2$NO· WITH ISOBUTYLAMINE (1:1 MOLAR RATIO)

This reaction was carried out twice as follows.

Bistrifluoromethylamino-oxyl [(a) 0.98 g, 5.83 mmoles, (b) 0.83 g, 4.94 mmoles] was condensed, in vacuo, into a Pyrex reaction tube (ca. 50 cm^3) fitted with a "Rotaflo" tap, containing isobutylamine [(a) 0.43 g, 5.83 mmoles, (b) 0.37 g, 5.06 mmoles] cooled to -196°C. The tube was sealed and allowed to warm to room temperature. Reaction was complete after about 20 minutes giving a colourless liquid and traces of white solid.

The volatile fraction of the products was condensed into the vacuum system. An i.r. spectrum of the vapour from this fraction showed peaks for $(CF_3)_2$NOH and ammonia. Molecular weight determinations of the

vapour from reactions (a) and (b) gave values of 140 and 113 respectively (the $(CF_3)_2NOH.NH_3$ adduct is thought to be about 50% dissociated in the vapour phase at room temperature; the value of the molecular weight would therefore be expected to be about 124).

G.l.c. analysis (2m SE30, 70-120°C) of the more involatile products showed peaks for the following compounds, in ascending order of retention times:

N,N-bistrifluoromethylhydroxylamine,

unreacted isobutylamine,

a minor unidentified product,

N-isobutylideneisobutylamine, $Me_2CHCH=NCH_2CHMe_2$,

and   N-[2-(bistrifluoromethylamino-oxy)-2-methylpropylidene]-

isobutylamine.

These last two compounds were isolated by preparative g.l.c. and identified by comparison of their n.m.r. and i.r. spectra and g.l.c. retention times with (i) a prepared sample of N-isobutylideneisobutylamine (n.m.r. 21, i.r. 19) and (ii) a previously isolated sample of N-[2-(bistrifluoromethylamino-oxy)-2-methylpropylidene]-isobutylamine.

G.l.c. of the products one week after the reaction showed a considerable decrease in the size of the N-isobutylideneisobutylamine peak, presumably due to hydrolysis, and the appearance of two new peaks, one with much lower retention time and another with a slightly longer retention time which was presumed to have been previously hidden beneath the N-isobutylideneisobutylamine peak.

This peak was found to have a g.l.c. retention time identical over a range of temperatures (70 to 120°C) to that of one of the major products from the reaction of $(CF_3)_2NO^{\bullet}$ with N-isobutylideneisobutylamine, namely N-(1-hydroxy-2-methylpropylidene)-isobutylamine, $Me_2CHC(OH)=NCH_2CHMe_2$ (this compound is the iminol form of N-isobutyl-2-

methylpropanamide, $Me_2CHCONHCH_2CHMe_2$).

Reaction summary

Reactants:	Reaction (a)	Reaction (b)
$(CF_3)_2NO^\bullet$	0.98 g, 5.83 mmoles	0.83 g, 4.94 mmoles
$Me_2CHCH_2NH_2$	0.43 g, 5.83 mmoles	0.37 g, 5.06 mmoles
Products:		
$Me_2CHCH_2NH_2$	0.10 g, 1.40 mmoles, 24%	0.09 g, 1.21 mmoles, 24%
$(CF_3)_2NOH$	not determined	not determined
$Me_2CHCH=NCH_2CHMe_2$	0.17 g, 1.32 mmoles, 62%	0.15 g, 1.19 mmoles, 62%
$Me_2\overset{\displaystyle R}{\underset{\displaystyle \mid}{C}}CH=NCH_2CHMe_2$	0.16 g, 0.55 mmoles, 25%	0.14 g, 0.48 mmoles, 25%
$Me_2CH\overset{\displaystyle \mid}{\underset{\displaystyle OH}{C}}=NCH_2CHMe_2$	0.014 g, 0.10 mmoles, 4%	0.01 g, 0.08 mmoles, 4%
NH_3	not determined	not determined
unidentified	9%	9%

REACTIONS OF $(CF_3)_2NO^\bullet$ WITH N-ISOBUTYLIDENEISOBUTYLAMINE

N-isobutylideneisobutylamine was prepared by adding isobutylamine (14.6 g, 0.20 moles) dropwise to isobutyraldehyde (14.4 g, 0.20 moles) in a cooled flask so that the temperature did not rise above 4°C.[153] The products were dried over sodium sulphate and distilled under reduced pressure. The identity of N-isobutylideneisobutylamine was confirmed by its n.m.r. (21) and i.r. (19) spectra and it was shown to be pure by g.l.c.

3.   REACTION OF $(CF_3)_2NO^\bullet$ WITH N-ISOBUTYLIDENEISOBUTYLAMINE (2:1 MOLAR RATIO)

This reaction was carried out twice as follows.

Bistrifluoromethylamino-oxyl [(a) 1.08 g, 6.43 mmoles, (b) 4.05 g, 24.11 mmoles] was condensed, in vacuo, into a reaction tube [(a) 25 cm^3, (b) 300 cm^3] containing N-isobutylideneisobutylamine [(a) 0.41 g, 3.23 mmoles, (b) 1.53 g, 12.06 mmoles] cooled to -196°C. The tube was sealed and removed from the liquid nitrogen. The reaction appeared to be complete within 10 to 15 minutes, shortly after the tube had reached room temperature.

G.l.c. analysis of the slightly yellowish liquid products (2m SE30, 70 to 100°C) showed peaks for N,N-bistrifluoromethylhydroxylamine, unreacted N-isobutylideneisobutylamine and two other major and several minor products.

The two major products were isolated by preparative g.l.c. (5m SE30, 65°C). The main one of these had g.l.c. retention time, n.m.r. and i.r. spectra identical to the previously isolated N-[2-(bistrifluoro-methylamino-oxy)-2-methylpropylidene]-isobutylamine. The other was identified as N-(1-hydroxy-2-methylpropylidene)-isobutylamine, $Me_2CHC(OH)=NCH_2CHMe_2$ on the basis of its n.m.r. (22), i.r. (Fig. 5) and mass (41a) spectra. G.l.c. of this product showed that it was, in fact, a mixture of $Me_2CHC(OH)=NCH_2CHMe_2$ and $(CF_3)_2NOH$ with about 10% $Me_2CRCH=NCH_2CHMe_2$ as impurity. The i.r. spectrum showed the presence of $(CF_3)_2NO-$ and the ^{19}F n.m.r. spectrum showed peaks for $(CF_3)_2NOH$ (int. 6) and $(CF_3)_2NON(CF_3)_2$ (int. 1).

The possibility of the compound isolated actually being the amide $Me_2CHCONHCH_2CHMe_2$ rather than the iminol form, was ruled out by preparing the amide (from isobutyryl chloride and isobutylamine) and comparing its

i.r. (Fig. 8) and n.m.r. spectra (n.m.r.23) with that of the product
isolated.
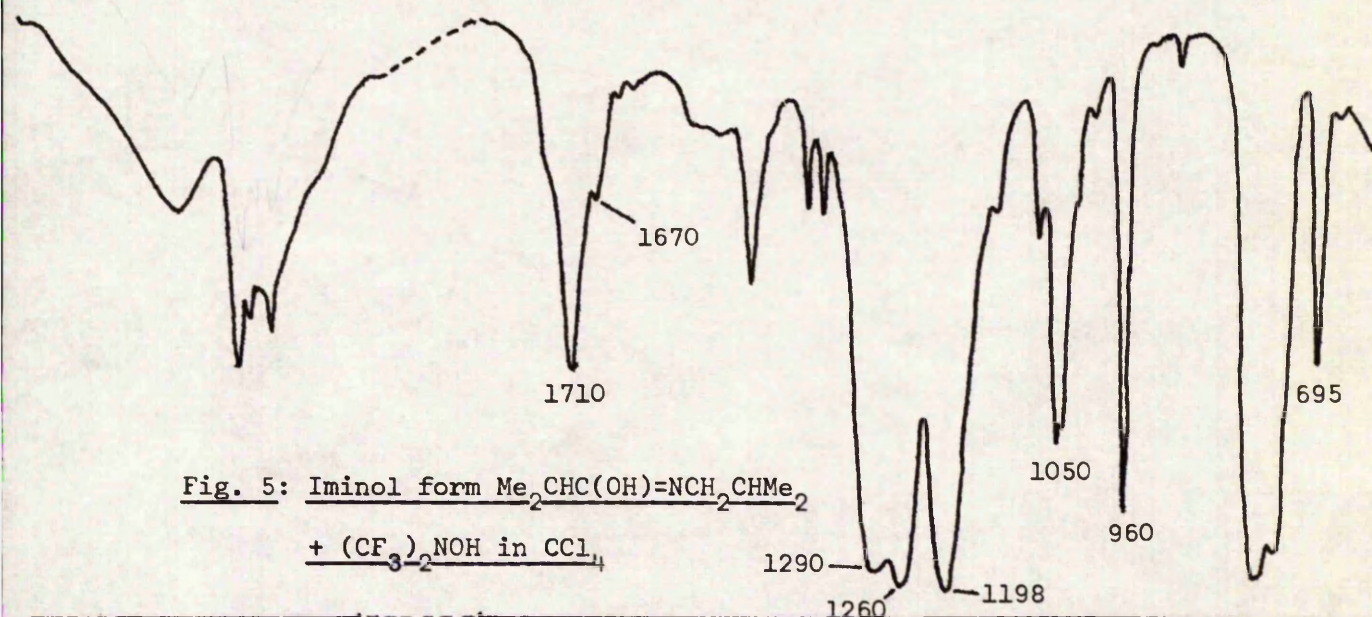
Fig. 5: Iminol form $Me_2CHC(OH)=NCH_2CHMe_2$
+ $(CF_3)_2NOH$ in CCl_4

The solution of $\underline{N}$-(1-hydroxy-2-methylpropylidene)-isobutylamine
with $(CF_3)_2NOH$ in CCl_4 which had been submitted for n.m.r. was evaporated
to a whitish residue under vacuum. This residue was redissolved in CCl_4
and its i.r. spectrum rerun (Fig. 6). It can be seen that the peak due
to C=N at 1710 cm^{-1} and the peaks due to $(CF_3)_2NO-$ at 1290, 1260, 1198,
1050, 960 and 695 cm^{-1} are diminished in intensity while new bands have
appeared at 1640 cm^{-1} (C=O stretch, the "Amide I" band) and 1540 cm^{-1}
(N-H bend, the "Amide II" band). The peak at 1670 cm^{-1} is due to the
C=N stretch in the $Me_2CRCH=NCH_2CHMe_2$ present as impurity.

This procedure was repeated, the CCl_4 being evaporated under
vacuum. The residue was heated using a hair dryer for a few minutes,
then redissolved in CCl_4 and its i.r. spectrum rerun (Fig. 7).
The peaks due to C=N (1710 cm^{-1}) and $(CF_3)_2NO-$ can be seen to be further
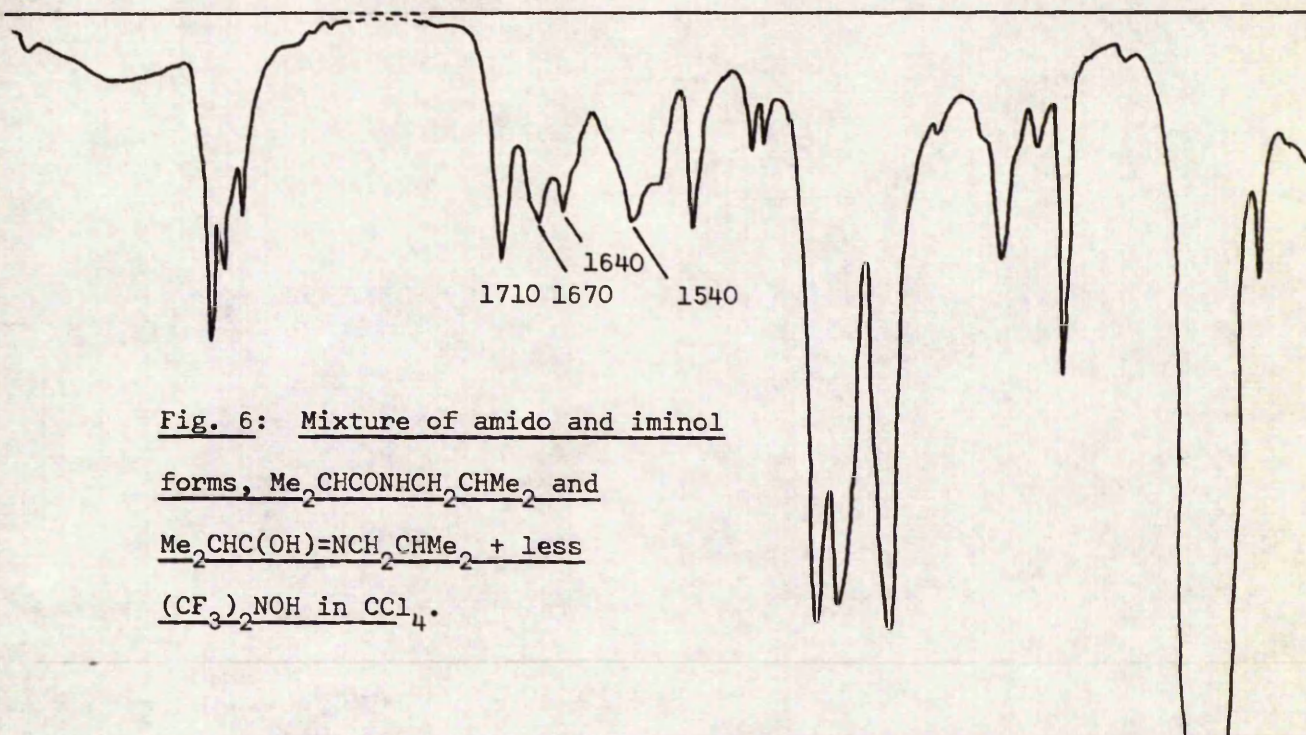
Fig. 6: Mixture of amido and iminol forms, $Me_2CHCONHCH_2CHMe_2$ and $Me_2CHC(OH)=NCH_2CHMe_2$ + less $(CF_3)_2NOH$ in CCl_4.
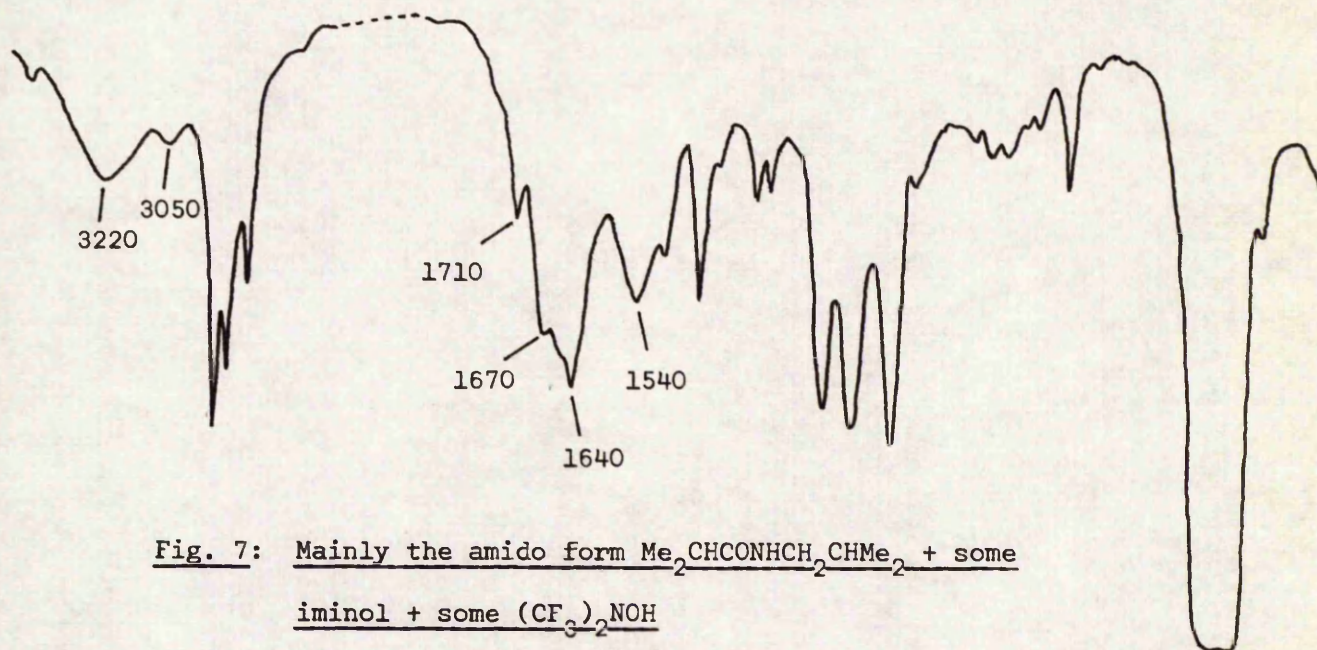
Fig. 7: Mainly the amido form $Me_2CHCONHCH_2CHMe_2$ + some iminol + some $(CF_3)_2NOH$

reduced and those due to the amide (at 3220 cm^{-1}, 3050 cm^{-1}, 1640 cm^{-1} and 1540 cm^{-1}) further accentuated. This spectrum can be compared to that of pure N-isobutyl-2-methylpropanamide in CCl_4 (Fig. 8).
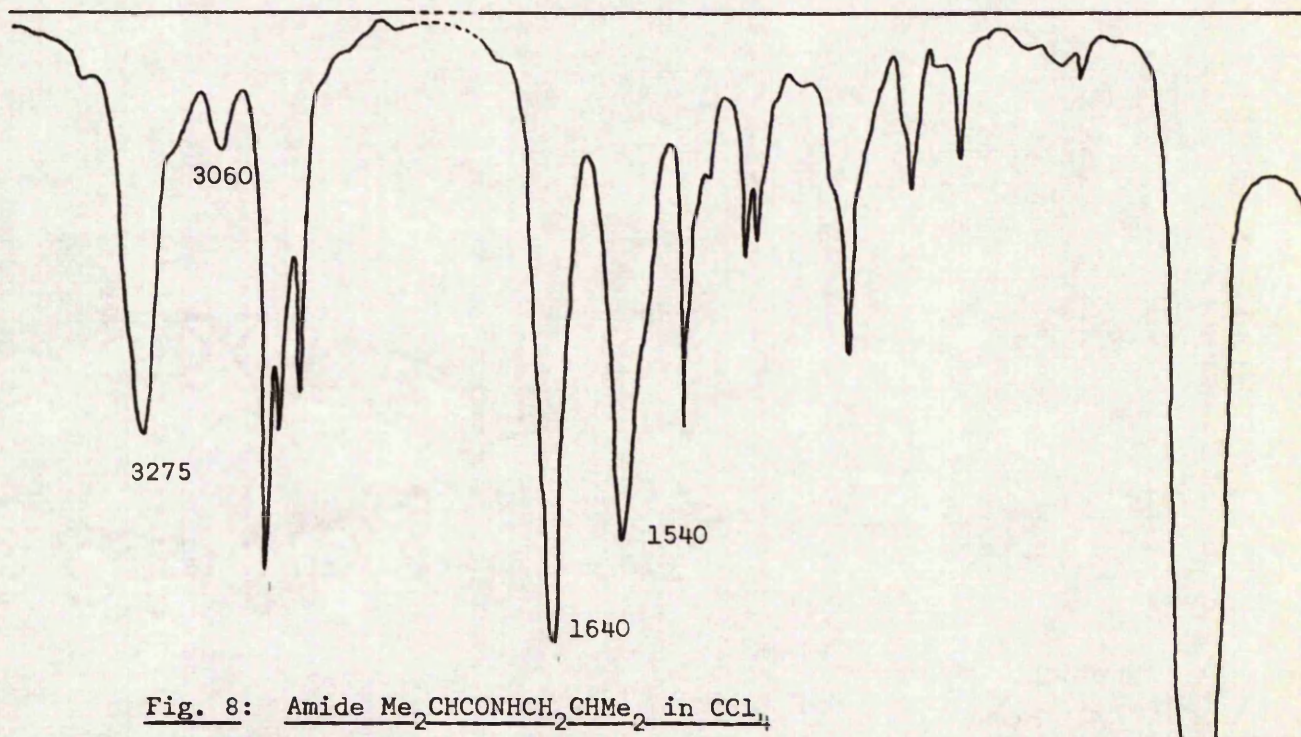
Fig. 8: Amide $Me_2CHCONHCH_2CHMe_2$ in CCl_4

It was concluded that the iminol form $Me_2CHC(OH)=NCH_2CHMe_2$ is stabilised by the presence of $(CF_3)_2NOH$ and that driving off the $(CF_3)_2NOH$ converts the iminol form to the more stable amido form, $Me_2CHCONHCH_2CHMe_2$.

A 1:1 molar ratio mixture of $(CF_3)_2NOH$ and N-isobutyl-2-methylpropanamide was prepared. Its i.r. spectrum showed peaks for the amide but none for the iminol form.

The ^{19}F n.m.r. spectrum (ref. ext. TFA) of the original products of the reaction showed 3 main peaks having areas in the proportions given:

-8.2 ppm	....	$(CF_3)_2NOH$	....	50%
-9.7 ppm	....	$(CF_3)_2NON(CF_3)_2$	..	11%
-10.7 ppm	....	$Me_2CCH=NCH_2CHMe_2$.. R	..	32%

plus 6 other small peaks, total approximately 5%.

The yields shown below are based on g.l.c. peak areas and ^{19}F n.m.r. peak integrations.

Reaction summary

Reactants:	Reaction (a)	Reaction (b)
$(CF_3)_2NO^{\bullet}$	1.08 g, 6.43 mmoles	4.05 g, 24.11 mmoles
$Me_2CHCH=NCH_2CHMe_2$	0.41 g, 3.23 mmoles	1.53 g, 12.06 mmoles
Products:		
$Me_2CHCH=NCH_2CHMe_2$	0.09 g, 0.74 mmoles, 23%	0.35 g, 2.77 mmoles, 23%
$(CF_3)_2NOH$	0.54 g, 3.22 mmoles, 50%	2.04 g, 12.06 mmoles, 50%
$(CF_3)_2NON(CF_3)_2$	0.11 g, 0.35 mmoles, 11%	0.42 g, 1.33 mmoles, 11%
$Me_2CCH=NCH_2CHMe_2$ R	0.58 g, 1.97 mmoles, 79%	2.16 g, 7.34 mmoles, 79%
$Me_2CHC=NCH_2CHMe_2$ OH	0.06 g, 0.40 mmoles, 16%	0.21 g, 1.48 mmoles, 16%
unidentified	5%	5%

4. REACTION OF $(CF_3)_2NO^{\bullet}$ WITH N-ISOBUTYLIDENEISOBUTYLAMINE (1:1 MOLAR RATIO)

This reaction was carried out twice as follows.

Reaction (a): Bistrifluoromethylamino-oxyl (0.17 g, 1.01 mmoles) and N-isobutylideneisobutylamine (0.13 g, 1.01 mmoles) were reacted in a 300 cm^3 sealed tube using the same method as that described for the last reaction. The reaction was complete within 10 minutes giving a colourless liquid which turned pale yellow on exposure to the air.

G.l.c. analysis (2m SE30, 70 to 100°C) of the products showed peaks for compounds which were identified from their retention times as N,N-bistrifluoromethylhydroxylamine,

unreacted N-isobutylideneisobutylamine,

N-(1-hydroxy-2-methylpropylidene)-isobutylamine,

N-[2-(bistrifluoromethylamino-oxy)-2-methylpropylidene]-

isobutylamine.

The ^{1}H n.m.r. spectrum of a sample of the products showed a

mixture of peaks due to the 4 main products named above plus a very minor

peak at -2.2 ppm from ext. DCB due to the -CHO of isobutyraldehyde.

The ^{19}F n.m.r. spectrum (ref. ext. TFA) showed 3 main peaks

having areas in the following proportions:

-8.7 ppm	...	$(CF_3)_2NOH$	.....	40%
-9.8 ppm	...	$(CF_3)_2NON(CF_3)_2$..		34%
-10.7 ppm	...	$Me_2CCH=NCH_2CHMe_2$ ...		23%
		$\quad\quad|$		
		$\quad\quad R$		

Reaction (b):

The reaction was repeated in order to examine the more volatile

products. 0.45 g $(CF_3)_2NO^\bullet$ (2.68 mmoles) and 0.34 g N-isobutylidene-

isobutylamine (2.68 mmoles) were caused to react in a 25 cm^3 sealed tube.

The reaction was complete on reaching room temperature, within about 5

minutes. The reaction tube was attached to the system and heated. The

volatiles were stripped off gradually and condensed at -196°C. The i.r.

spectrum of the vapour was examined for each fraction using a gas cell.

The i.r. spectrum of the first 0.01 g showed peaks for 2-(bistrifluoro-

methylamino-oxycarbonyl)propane, $Me_2CHCOON(CF_3)_2$ at 1830 cm^{-1} (C=O str.),

1310, 1275 and 1215 cm^{-1} (C-F str.), 1040 cm^{-1} (N-O str.), 965 cm^{-1}

(C-N str.) and for isobutyraldehyde as 1740 cm^{-1} (C=O str.), 2960 cm^{-1}

(C-H str.).

The i.r. spectrum of the next 0.23 g (gas cell pressures of 0.5,

1.5, 3.0, 4.0 and 5.0 cm Hg) showed very strong peaks for perfluoro-

(2,4-dimethyl-3-oxa-2,4-diazapentane), $(CF_3)_2NON(CF_3)_2$ at 1350, 1305,

1275, 1260, 1230, 1210, 1192, 1176, 1015, 960 and 700 cm^{-1}, weaker peaks due to isobutyraldehyde at 2960, 2860, 2775, 2670 cm^{-1} (C-H str.), 1740 cm^{-1} (C=O str.) and 1470 cm^{-1}, and peaks due to $Me_2CHCOON(CF_3)_2$ at higher gas cell pressures. The next 0.24 g consisted of a fairly involatile liquid, the i.r. spectrum of the vapour of which showed only weak to medium peaks due to a $(CF_3)_2NO-$ group at pressures of 0.5, 2.0 and 3.0 cm Hg. No peaks attributable to $(CF_3)_2NOH$ were observed in any of the spectra.

The yields shown below are based on a combination of n.m.r. peak areas (yields of $(CF_3)_2NOH$, $(CF_3)_2NON(CF_3)_2$ and $Me_2CRCH=NCH_2CHMe_2$ being based on the relative integrations in the ^{19}F n.m.r. spectrum already quoted) and g.l.c. peak areas (for yields of the other products; the yield of $Me_2CRCH=NCH_2CHMe_2$ calculated from its g.l.c. peak area correlated fairly well with that calculated from the ^{19}F n.m.r. peak area).

Reaction summary

Reactants:	Reaction (a)	Reaction (b)
$(CF_3)_2NO^\bullet$	0.17 g, 1.01 mmoles	0.45 g, 2.68 mmoles
$Me_2CHCH=NCH_2CHMe_2$	0.13 g, 1.01 mmoles	0.34 g, 2.68 mmoles
Products:		
$Me_2CHCH=NCH_2CHMe_2$	0.08 g, 0.59 mmoles, 58%	0.20 g, 1.55 mmoles, 58%
$(CF_3)_2NOH$	0.07 g, 0.40 mmoles, 40%	0.18 g, 1.07 mmoles, 40%
$(CF_3)_2NON(CF_3)_2$	0.05 g, 0.17 mmoles, 34%	0.15 g, 0.46 mmoles, 34%
$Me_2\overset{\text{R}}{\underset{}{C}}CH=NCH_2CHMe_2$	0.07 g, 0.23 mmoles, 55%	0.18 g, 0.62 mmoles, 55%
$Me_2CH\overset{}{\underset{\text{OH}}{C}}=NCH_2CHMe_2$	0.02 g, 0.17 mmoles, 40%	0.06 g, 0.45 mmoles, 40%
Me_2CHCHO	0.001 g, 0.01 mmoles, 2%	0.0014 g, 0.02 mmoles, 2%
Me_2CHCOR	0.001 g, 0.004 mmoles, 1%	0.002 g, 0.01 mmoles, 1%

5.   REACTION OF $(CF_3)_2NO^{\bullet}$ WITH BENZYLAMINE (1:1 MOLAR RATIO)

This reaction was carried out three times as described below.

Reaction (a):   Bistrifluoromethylamino-oxyl (0.46 g, 2.74 mmoles) was condensed, in vacuo, into a 25 cm^3 Pyrex reaction tube containing benzylamine (0.29 g, 2.74 mmoles) cooled to -196°C. The reaction was complete within 20 to 30 minutes giving pale yellow liquid and some whitish solid.

The volatile products (0.39 g) were condensed into the vacuum system. An i.r. spectrum of the vapour showed peaks for $(CF_3)_2NOH$ and ammonia, the spectrum being identical to that for the $(CF_3)_2NOH.NH_3$ adduct. A molecular weight determination on the vapour using a molecular weight bulb gave a mean value of 123.3 ± 0.8 (the expected value for the 1:1 $(CF_3)_2NOH.NH_3$ adduct, being about 50% dissociated at room temperature, would be 124; however, the volatiles from this reaction would be expected to contain a 2:1 molar ratio of $(CF_3)_2NOH$ to NH_3 which would give a mean value of 142 for the molecular weight on the basis of a 1:1 mixture of $(CF_3)_2NOH.NH_3$ and free $(CF_3)_2NOH$. The molecular weight might be expected to be still higher if the adduct were less than 50% dissociated in the presence of excess $(CF_3)_2NOH$).

The involatile liquid and the solid were separated. Their i.r. spectra (20) were identical. Both were dissolved in CDCl$_3$ and shown by n.m.r. spectroscopy to consist of the same compound, namely N-benzylidene-benzylamine (n.m.r. 24). The n.m.r. and i.r. spectra were identical to that of a sample of N-benzylidenebenzylamine prepared from benzaldehyde and benzylamine.

The yield of $C_6H_5CH=NCH_2C_6H_5$ was at least 95% (0.25 g, 1.30 mmoles).

Reaction (b):   The reaction was repeated using 1.12 g $(CF_3)_2NO^{\bullet}$ (6.67 mmoles) and 0.72 g benzylamine (6.73 mmoles). The products, which

consisted of yellowish liquid and some whitish solid were dissolved in
$CDCl_3$. G.l.c. of the resulting solution (2m SE30, 200-230°C) showed
peaks for $(CF_3)_2NOH$, $CDCl_3$, benzylamine (approximately 5% unreacted),
N-benzylidenebenzylamine and several very minor products.

The ^1H n.m.r. spectrum of the solution showed peaks for
$C_6H_5CH=NCH_2C_6H_5$ plus a broad peak for $(CF_3)_2NOH$ plus NH_3 at 3.40 τ
and an additional small unidentified peak at 6.56 τ.

The ^{19}F n.m.r. of the solution showed one singlet only, at
-9.1 ppm from TFA, for $(CF_3)_2NOH$. No other peaks, even minor ones, were
present.

Reaction summary

Reactants:

$(CF_3)_2NO^\bullet$	.....	1.12 g, 6.67 mmoles
$C_6H_5CH_2NH_2$	.....	0.72 g, 6.73 mmoles

Products:

$C_6H_5CH_2NH_2$	.....	0.04 g, 0.34 mmoles, 5% unreacted
$(CF_3)_2NOH$	.....	1.13 g, 6.67 mmoles, 100%
$C_6H_5CH=NCH_2C_6H_5$	...	0.59 g, 3.04 mmoles, 95%
NH_3	....	not determined
unidentified	.....	5%

Reaction (c): The reaction was repeated, using 1.37 g $(CF_3)_2NO^\bullet$
(8.15 mmoles) and 0.87 g benzylamine (8.15 mmoles), in order to examine
the volatiles. After completion the reaction tube was attached to the
vacuum system and heated, using a hair dryer, to constant weight. The
volatiles (1.42 g) were passed through -78°C and -196°C traps. The -78°C
trap contained white solid which melted to a colourless liquid on warming.
An i.r. spectrum of the vapour showed peaks for $(CF_3)_2NOH$ and ammonia.

Presuming the maximum amount of ammonia formed to be approximately 4 mmoles (0.07 g) this leaves 1.35 g $(CF_3)_2NOH$ ... 8.00 mmoles, 98% of $(CF_3)_2NO^{\bullet}$ used.

The involatiles remaining in the reaction tube consisted of a whitish-yellow crystalline solid (0.26 g) and an amber liquid (0.55 g). The liquid was shown by g.l.c. and i.r. spectroscopy to consist of N-benzylidenebenzylamine plus traces of $(CF_3)_2NOH$ and three very minor products. The solid proved insoluble in both CCl_4 and $CHCl_3$ and was not investigated further.

6.   REACTION OF $(CF_3)_2NO^{\bullet}$ WITH BENZYLAMINE (2:1 MOLAR RATIO)

This reaction was carried out 4 times in all. The method used was exactly the same as that used in the 1:1 molar ratio reactions. Reaction (a):   The reaction was carried out using 2.72 g $(CF_3)_2NO^{\bullet}$ (16.19 mmoles) and 0.87 g benzylamine (8.10 mmoles) in a 50 cm^3 sealed tube. The reaction was complete within about 30 minutes giving a pale yellow solid in a colourless liquid. There was much more solid than in the case where equimolar amounts of reactants were used.

The volatiles were removed by heating the reaction tube to constant weight under vacuum using a hair dryer, and the collected volatile fraction was separated by trap-to-trap fractionation.

-78°C trap: 2.56 g, shown by i.r. spectroscopy to consist of $(CF_3)_2NOH$ plus some ammonia.

-196°C trap: traces of $(CF_3)_2NO^{\bullet}$ ... approximately 0.01 mmoles, 0.02 g.

The involatiles consisted of a yellow crystalline solid. Chloroform was added forming a yellow solution and leaving a white solid. The solution was filtered and the chloroform was removed from the filtrate leaving 0.56 g of an amber liquid which deposited orange-yellow crystals on cooling. This residue was redissolved in deuterochloroform. The i.r.

spectrum was virtually identical to that of N-benzylidenebenzylamine, although it showed a small sharp peak at 1700 cm^{-1} attributed to benzaldehyde.

The ^{1}H n.m.r. spectrum of this solution (ref. int. TMS) showed:

Band	Int.	Chemical shift	Band structure	Assignment
1	∿0.1	0.12 τ	singlet	PhCHO
2	1.0	1.45 τ	broad singlet	(PhCH=N)$_2$CHPh
3	2.0	1.74 τ	singlet	PhCH=NCH$_2$Ph
4	40	2.05 to 2.50 τ	complex	
		2.50 to 2.90 τ	complex	C$_6$H$_5$ groups
		(including a singlet at 2.68 τ)		
5	0.5	4.05 τ	broad singlet	(PhCH=N)$_2$CHPh
6	4.0	5.30 τ	singlet	PhCH=NCH$_2$Ph

plus very minor unidentified peaks at 4.73 and 8.70 τ

The peaks for N-benzylidenebenzylamine were identified by comparison of their chemical shifts with those of a previously isolated sample of this compound (n.m.r. 24). The peaks due to hydrobenzamide, (PhCH=N)$_2$CHPh were identified by comparison of their chemical shifts with those of a sample (n.m.r. 25) prepared by leaving benzaldehyde to stand in an excess of ammonia for two days and recrystallising the solid hydrobenzamide from ethanol.

The residue from the filtration consisted of 0.26 g of a white solid. This solid was identified as probably an adduct between 1,2,3,4-tetrahydro-2,4,6-triphenyl-1,3,5-triazine and (CF$_3$)$_2$NOH. The evidence on which this identification is based is given below.

(i)   The white solid dissolved in acetone on heating. On removing the acetone a yellowish-white solid remained which gave an i.r. spectrum

identical to that of 2,4,6-triphenyl-1,3,5-triazine[154], having peaks at 1590 (w), 1524 (v.s.), 1454 (m), 1368 (s), 1296, 1170, 1062, 1022, 834 (all weak), 735 (m), 672 (m), 634 (w). The melting point of this yellowish-white solid was 228-232°C (lit. melting point for 2,4,6-triphenyl-1,3,5-triazine is 232°C[141]).

(ii)   Heating the original solid, in vacuo, with the tube attached to a -196°C trap, for 1 hour, resulted in 0.055 g of solid losing approximately 0.015 g. On warming the contents of the trap to room temperature they were shown by vapour i.r. spectroscopy to consist of $(CF_3)_2NOH$. The residue consisted of a yellow solid, the i.r. spectrum of which was identical to that of 2,4,6-triphenyl-1,3,5-triazine.

(iii)   A melting point determination was carried out on the white solid. It appeared to undergo decomposition between 135 and 140°C leaving a fragmented white solid which did not change further until about 185°C. It then slowly melted between 185° and 220°C. The residue in the tube was shown by its i.r. spectrum to consist of 2,4,6-triphenyl-1,3,5-triazine.

(iv)   The i.r. spectrum of the white solid (Fig. 9) shows C=N stretching
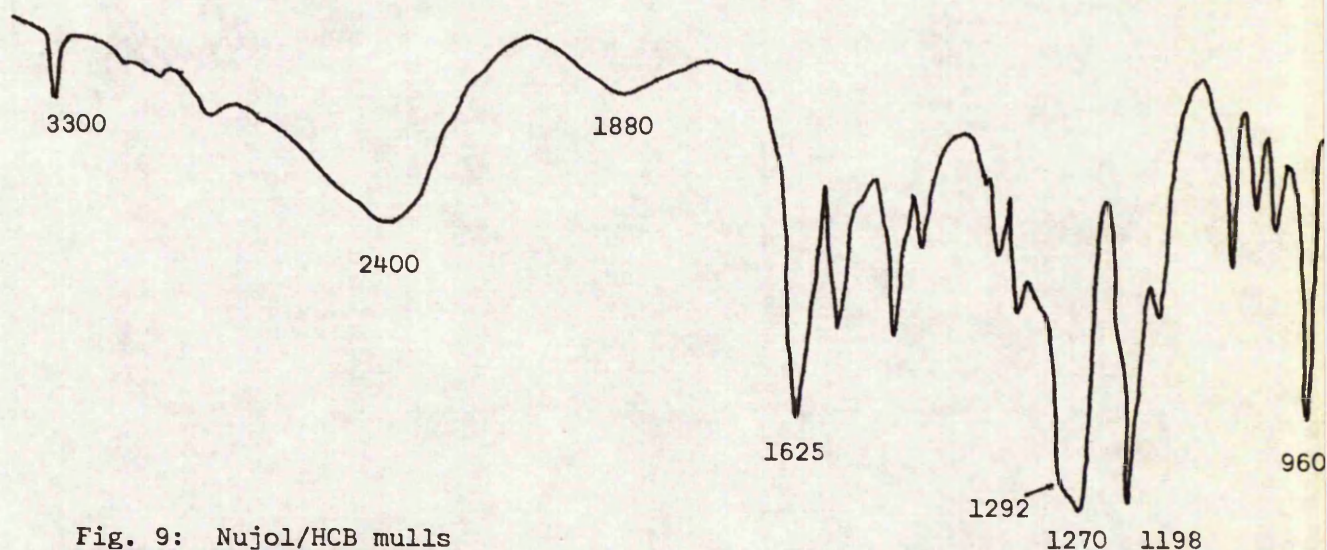
Fig. 9: Nujol/HCB mulls

at 1625 cm^{-1} (strong), N-H stretching at 3300 cm^{-1} (weak, sharp), C-F str. at 1292, 1270, 1198 cm^{-1} (v. strong), C-N str. at 960 cm^{-1} (s) and a broad band between 3100 and 2100 cm^{-1} (medium). Secondary amine -(CF$_3$)$_2$NOH adducts give similar bands.[132]

(v)   Analysis of the white solid.

	Required for the proposed adduct	Found 1.	2.	3.
% C	57.3	55.1	57.8	56.7
% H	4.1	4.3	4.3	4.5
% N	11.6	11.7	11.8	11.5
% F	23.7	26.3	24.6	

Analysis 3 was carried out on a portion of the same sample as analysis 2 after the analysis for fluorine had been carried out. The adduct appears to decompose slowly at room temperature.

(vi)   1,2-Dihydro-2,4,6-triphenyl-1,3,5-triazine is well known. Its i.r. spectrum[140] shows C=N at 1605 cm^{-1} and N-H at 3200 cm^{-1}. Its n.m.r. spectrum shows multiplets at 1.96 and 2.50 τ (aromatic Hs), a singlet at 3.75 τ (benzyl) and a broad band at 4.80 τ (amino).[140,155] It seems unlikely that the presence of (CF$_3$)$_2$NOH would affect the position of the C=N stretching frequency. Furthermore a 1:1 adduct would not be expected to show a free N-H stretching band. This compound can therefore be ruled out.

As the tetrahydro-compound has only one C=N bond the C=N stretching frequency would be expected to be higher than in the case of the dihydro-compound which has two conjugated C=N bonds.

(vii)   1,2-Dihydro-2,4,6-triphenyl-1,3,5-triazine can be easily converted to the aromatic 1,3,5-triazine by heating in refluxing nitrobenzene or xylene.[156]
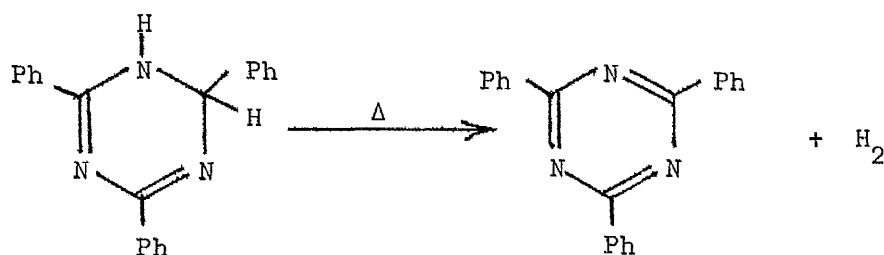
Presumably a similar reaction is possible with the tetrahydro compound.

(viii) No references to 1,2,3,4-tetrahydro-2,4,6-triphenyl-1,3,5-triazine could be found in the literature, other than as an intermediate in the hydrogenation of 2,4,6-triphenyl-1,3,5-triazine:
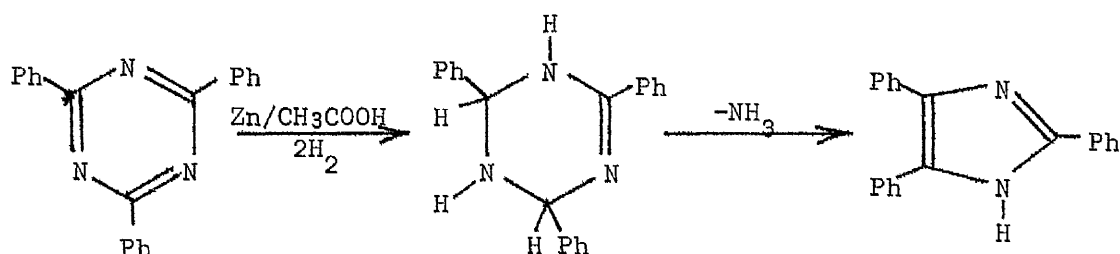
(ix)   Another structure considered as a possibility was the adduct PhCH=NCHNHCHNH$_2$·HON(CF$_3$)$_2$ which would be an intermediate in both the
         Ph Ph
condensation of 3 moles of PhCH=NH to hydrobenzamide and the trimerisation of 3 moles of PhCH=NH to the hexahydro-2,4,6-triphenyl-1,3,5-triazine. This was rejected on the grounds that on removal of $(CF_3)_2NOH$ the compound would be more likely to lose ammonia to give hydrobenzamide than to cyclise.

Reaction summary

Reactants:

$(CF_3)_2NO^•$ ....   2.72 g, 16.19 mmoles

$PhCH_2NH_2$ ....   0.87 g, 8.10 mmoles

Products:

$(CF_3)_2NOH$ .... 2.54 g, 15.06 mmoles, 93%

$(CF_3)_2NO^\bullet$ .... 0.02 g, 0.10 mmoles, 0.6% unreacted

$PhCH=NCH_2Ph$ .... 0.40 g, 2.05 mmoles, 51%

$(PhCH=N)_2CHPh$ .. 0.15 g, 0.50 mmoles, 19%

probably
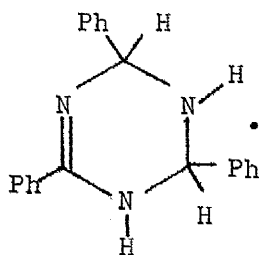
$\cdot(CF_3)_2NOH$ .... 0.26 g, 0.54 mmoles, 20% of $PhCH_2NH_2$ used, 3.3% of $(CF_3)_2NO^\bullet$ used.

PhCHO .... trace

NH_3 .... not determined

unaccounted for .... 0.20 g, 6% total reactants.

Reaction (b):

The reaction was repeated using 1.19 g (7.08 mmoles) $(CF_3)_2NO^\bullet$ and 0.38 g (3.54 mmoles) benzylamine. The products consisted of a white solid and a yellowish liquid. CCl_4 was added to the products dissolving some of the solid. The ^1H n.m.r. spectrum of the resulting mixture showed peaks for benzaldehyde, N-benzylidenebenzylamine and hydrobenzamide. From the relative integrations of the n.m.r. peaks these compounds were calculated to be present in molar ratios of 2.5:10:1 respectively.

The ^{19}F n.m.r. spectrum showed two singlets at -9.0 ppm from TFA (int. 36) for $(CF_3)_2NOH$ and at -10.7 ppm for possibly $PhCOON(CF_3)_2$ (int. 1).

The i.r. spectrum of the products showed peaks at 1795 cm^{-1} for the C=O stretch of $PhCOON(CF_3)_2$, 1700 cm^{-1} for the C=O stretch of PhCHO and 1640 cm^{-1} for the C=N stretch of $PhCH=NCH_2Ph$ and $(PhCH=N)_2CHPh$.

Reaction (c):

The reactants were thoroughly dried, as described below, in order

to eliminate any water which could be a possible source of the benzaldehyde

observed in the products, formed by hydrolysis of either N-benzylidene-

benzylamine or hydrobenzamide.

(i)   The benzylamine was distilled roughly and then fractionated

immediately before use.

(ii)   The $(CF_3)_2NO^{\bullet}$ was dried by passing through a P_2O_5 tube.

(iii)   The CCl_4 used for preparation of the n.m.r. sample was dried

by distillation, the first 10% of the distillate being discarded.

The reaction was then repeated using 1.54 g $(CF_3)_2NO^{\bullet}$ (9.17

mmoles) and 0.50 g benzylamine (4.70 mmoles). The reaction was complete

within 40 minutes giving a yellow solid in a colourless liquid. Some of

the volatiles were condensed into the system. CCl_4 was added to the

remaining products which were filtered to remove insoluble white solid

(0.13 g).

The ^{1}H n.m.r. spectrum (ref. ext. DCB) of the filtrate showed:

Band	Int.	Chemical shift	Band structure	Assignment
1	<0.1	−2.34 ppm	singlet	PhC$\underline{H}$O
2	5.3	−1.20 ppm	sharp singlet on top of a broad singlet	$(PhC\underline{H}=N)_2$C$\underline{H}$Ph $(CF_3)_2NOH$
3	0.5	−0.92 ppm	triplet, J ∿ 2 Hz	PhC$\underline{H}$=NCH$_2$Ph
4	12.0	−0.56 to +0.24 ppm	complex	C_6H_5 groups
5	0.3	+1.32 ppm	broad singlet	$(PhCH=N)_2$C$\underline{H}$Ph
6	1.0	+2.55 ppm	doublet, J ∿ 2 Hz	PhCH=NC$\underline{H}_2$Ph

plus minor unidentified peaks at +1.78, +1.98, +2.08 ppm

The i.r. spectrum of the solution in CCl_4 showed a strong peak at 1640 cm^{-1} (C=N stretch of $PhCH=NCH_2Ph$ and $(PhCH=N)_2CHPh$) and very weak peaks at 1700 cm^{-1} (PhCHO, C=O str.) and 1800 cm^{-1} ($PhCOON(CF_3)_2$, C=O str.).

Reaction summary

Reactants:

$(CF_3)_2NO^\bullet$ ...... 1.54 g, 9.17 mmoles

$PhCH_2NH_2$ ...... 0.50 g, 4.70 mmoles

The percentages shown below are calculated from the n.m.r. integrations.

Products:

$PhCH=NCH_2Ph$ ...... 0.19 g, 0.99 mmoles, 42%

$(PhCH=N)_2CHPh$ .... 0.17 g, 0.58 mmoles, 37%

PhCHO ...... 0.01 g, 0.12 mmoles, 2.5%

$PhCOON(CF_3)_2$ ..... 0.01 g, 0.05 mmoles, 1%

probably
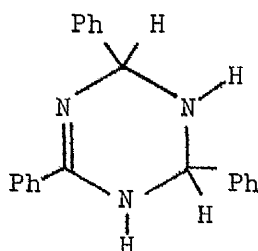
$\bullet(CF_3)_2NOH$ ... 0.13 g, 0.27 mmoles, 17% of $PhCH_2NH_2$ used, 3% of $(CF_3)_2NO^\bullet$ used.

$(CF_3)_2NOH$ ...... not determined

NH_3 .... not determined

Reaction (d):

The reaction was repeated using 2.27 g $(CF_3)_2NO^\bullet$ (13.51 mmoles) and 0.72 g benzylamine (6.73 mmoles). After completion the reaction tube was attached to the system and heated strongly using a hair dryer until it reached constant weight. An i.r. spectrum of the vapour from the volatiles showed peaks for $(CF_3)_2NOH$ and NH_3. The involatiles were heated further, converting them to a yellowish solid mixed with a viscous liquid. On addition of chloroform all the solid dissolved giving

a yellow solution. The chloroform was removed and CCl_4 added to the residue giving a yellow solution and an orange-buff solid which was separated by filtration. This solid melted gradually over a temperature range of 70° to 280°C.

The weight of volatiles was consistent with 100% $(CF_3)_2NOH$ (13.51 mmoles, 2.28 g) plus ammonia (0.04 g, 2.25 mmoles).

7.   REACTION OF $(CF_3)_2NO^\bullet$ WITH BENZYLAMINE (3:1 MOLAR RATIO)

This reaction, between 2.04 g $(CF_3)_2NO^\bullet$ (12.14 mmoles) and 0.43 g benzylamine (4.04 mmoles) was carried out using the same method employed in the 1:1 and 2:1 molar ratio reactions. The reaction was complete within about 25 minutes giving a lot of yellow-white solid and some liquid. Most of the volatiles (1.68 g) were removed into the system and condensed at -196°C. The reaction tube was not warmed. The i.r. spectrum of the vapour showed peaks for $(CF_3)_2NOH$.

The involatiles were dissolved as far as possible in CCl_4 and filtered giving 0.37 g of a whitish solid and a yellow solution. The i.r. spectrum of the solid showed the peaks previously found for the 1,2,3,4-tetrahydro-2,4,6-triphenyl-1,3,5-triazine-$(CF_3)_2NOH$ adduct plus peaks due to 2,4,6-triphenyl-1,3,5-triazine at 1595 (w), 1522 (s), 1363 (s), 734 (m), 672 (m) and 632 cm^{-1} (m) in the same positions as in 2,4,6-triphenyl-1,3,5-triazine previously isolated.

Analysis of this solid gave 65.1% C, 4.6% H, 13.1% N and 16.5% F. A mixture of 70% of the 1,2,3,4-tetrahydro-2,4,6-triphenyl-1,3,5-triazine -$(CF_3)_2NOH$ adduct and 30% of 2,4,6-triphenyl-1,3,5-triazine requires analysis figures of 64.6% C, 4.4% H, 12.2% N and 16.6% F.

i.e.   The 0.37 g of solid consisted of 0.08 g, 0.26 mmoles 2,4,6-triphenyl-1,3,5-triazine and 0.29 g, 0.60 mmoles 1,2,3,4-tetrahydro-2,4,6-triphenyl-1,3,5-triazine-$(CF_3)_2NOH$.

The i.r. spectrum of the solution in CCl_4 showed a strong peak at 1640 cm^{-1}, a weak peak at 1800 cm^{-1} probably due to PhCOON(CF$_3$)$_2$ plus peaks at 1522 and 1363 cm^{-1} due to 2,4,6-triphenyl-1,3,5-triazine.

The ^{1}H n.m.r. spectrum (ref. ext. DCB) of the solution in CCl_4 showed:

Band	Int.	Chemical shift	Band structure	Assignment
1	trace	-2.65 ppm	singlet	PhCHO
2	2.0	-1.65 to -1.35 ppm	complex	ortho H's of 2,4,6-triphenyl-1,3,5-triazine
3	0.5	-1.30 ppm	singlet	(PhCH=N)$_2$CHPh
4	0.5	-1.02 ppm	singlet	PhCH=NCH$_2$Ph
5	16	-0.7 to +0.4 ppm	complex	meta- and para- H's of 2,4,6-triphenyl-1,3,5-triazine/C$_6$H$_5$ groups.
6	0.3	+1.24 ppm	broad singlet	(PhCH=N)$_2$CHPh
7	1.0	+2.40 ppm	singlet	PhCH=NCH$_2$Ph

From the integrations the molar ratio of N-benzylidenebenzylamine : hydrobenzamide : 2,4,6-triphenyl-1,3,5-triazine is 44% : 27% : 29%.

i.e. The solution contained, on the basis of 1.46 mmoles of benzylamine unaccounted for:

N-benzylidenebenzylamine ... 0.32 mmoles, 0.06 g,

hydrobenzamide ... 0.13 mmoles, 0.04 g,

2,4,6-triphenyl-1,3,5-triazine ... 0.14 mmoles, 0.04 g.

Reaction summary

Reactants:

(CF$_3$)$_2$NO$^\bullet$ ...... 2.04 g, 12.14 mmoles

PhCH$_2$NH$_2$ ...... 0.43 g, 4.04 mmoles

Products:

PhCH=NCH$_2$Ph .... 0.06 g, 0.32 mmoles, 16%

(PhCH=N)$_2$CHPh .... 0.04 g, 0.13 mmoles, 10%

PhCHO .... trace

PhCOON(CF$_3$)$_2$ .... trace
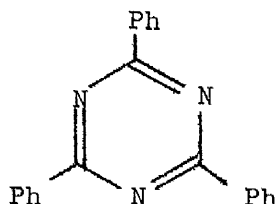
.... 0.12 g, 0.40 mmoles, 30%
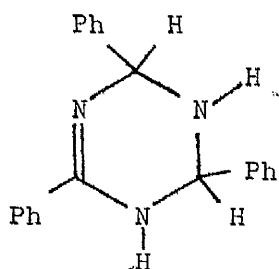
. (CF$_3$)$_2$NOH .... 0.29 g, 0.60 mmoles, 45%

based on PhCH$_2$NH$_2$ used.

(CF$_3$)$_2$NOH .... yield not determined.

8. REACTION OF (CF$_3$)$_2$NO$^{\bullet}$ WITH N-BENZYLIDENEBENZYLAMINE

N-benzylidenebenzylamine was prepared by slowly adding benzaldehyde (16.51 g, 0.156 moles) to benzylamine (16.76 g, 0.156 moles) at 0°C with shaking. It was dried over MgSO$_4$ and distilled under reduced pressure (120-152°C at 10 mmHg) immediately before being used.

The reaction, between 1.34 g (CF$_3$)$_2$NO$^{\bullet}$ (7.98 mmoles) and 0.88 g N-benzylidenebenzylamine (4.51 mmoles) was carried out using the same method as used in the (CF$_3$)$_2$NO$^{\bullet}$-benzylamine reactions. The reaction was complete within about 30 minutes giving pale yellow liquid products.

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The volatile products (0.66 g) were condensed into a trap in the vacuum system. From the vapour i.r. spectrum they appeared to consist exclusively of $(CF_3)_2NOH$.

The involatiles were dissolved in CCl_4. The ^1H n.m.r. spectrum of this solution showed (ref. ext. DCB) peaks for N-benzylidenebenzylamine and N-benzylidene-1-(bistrifluoromethylamino-oxy)benzylamine.

Band	Int.	Chemical shift	Band structure	Assignment
1	approx. 1.3	-0.86 ppm	singlet	PhCH=NCHRPh
2	approx. 0.3	-0.76 ppm	triplet, J ∿ 1 Hz	PhCH=NCH$_2$Ph
3	18	-0.5 to +0.3 ppm	complex	C_6H_5 groups
4	1.1	+1.53 ppm	singlet	PhCH=NCHRPh
5	0.5	+2.72 ppm	doublet, J ∿ 1 Hz	PhCH=NCH$_2$Ph

The ^{19}F n.m.r. spectrum (ref. ext. TFA) of the solution showed (Fig. 10):

Band	Int.	Chemical shift	Band structure	Assignment
1	55	-11.80 ppm	very broad singlet	PhCH=NCHRPh
2	1	-11.10 ppm	sharp singlet	-
3	0.2	-10.56 ppm	doublet, J ∿ 4 Hz	-
4	8	-9.75 ppm	singlet	$(CF_3)_2NOH$

210
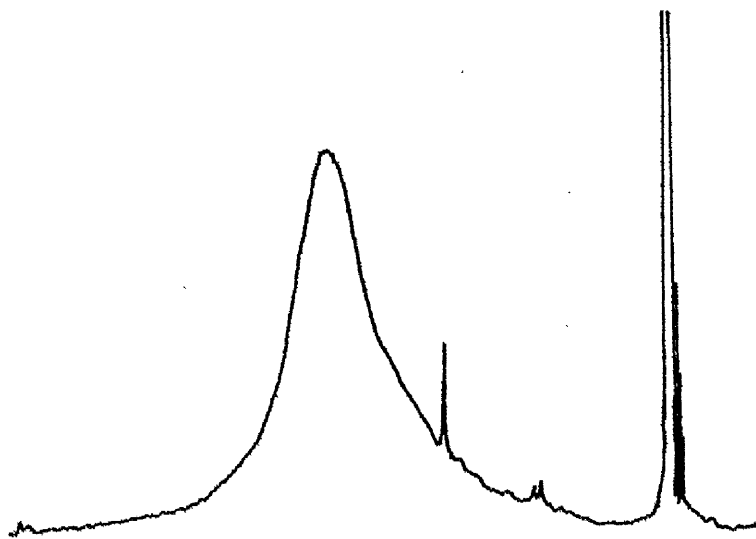
Fig. 10:   Products of $(CF_3)_2NO^{\bullet}$ + $PhCH=NCH_2Ph$ (involatiles) in CCl_4.
^{19}F spectrum at room temperature.

The ^{19}F spectrum was rerun at +60°C and -10°C with the following results.
^{19}F spectrum at +60°C (ref. ext. TFA):

Band	Int.	Chemical shift	Band structure	Assignment
1	23	-11.98 ppm	slightly broadened singlet	PhCH=NC$\underline{H}$RPh
2	1.0	-11.50 ppm	singlet	—
3	0.5	-11.24 ppm	singlet	—
4	0.1	-10.70 ppm	doublet, J ∿ 4 Hz	—
5	3.4	-9.85 ppm	singlet	$(CF_3)_2NOH$

^{19}F spectrum at -10°C (Fig. 11).

Band	Int.	Chemical shift	Band structure	Assignment
1	14.8	-11.95 ppm	quartet, J ∿ 9.5 Hz	PhCH=NCHPh
2	16.4	-10.91 ppm	quartet, J ∿ 9.5 Hz	$\overset{\mid}{R}$
3	3.5	-9.55 ppm	singlet	

The two quartets in fact constitute a doublet of quartets, $\Delta\nu$ being 90 Hz and J 9.5 Hz.
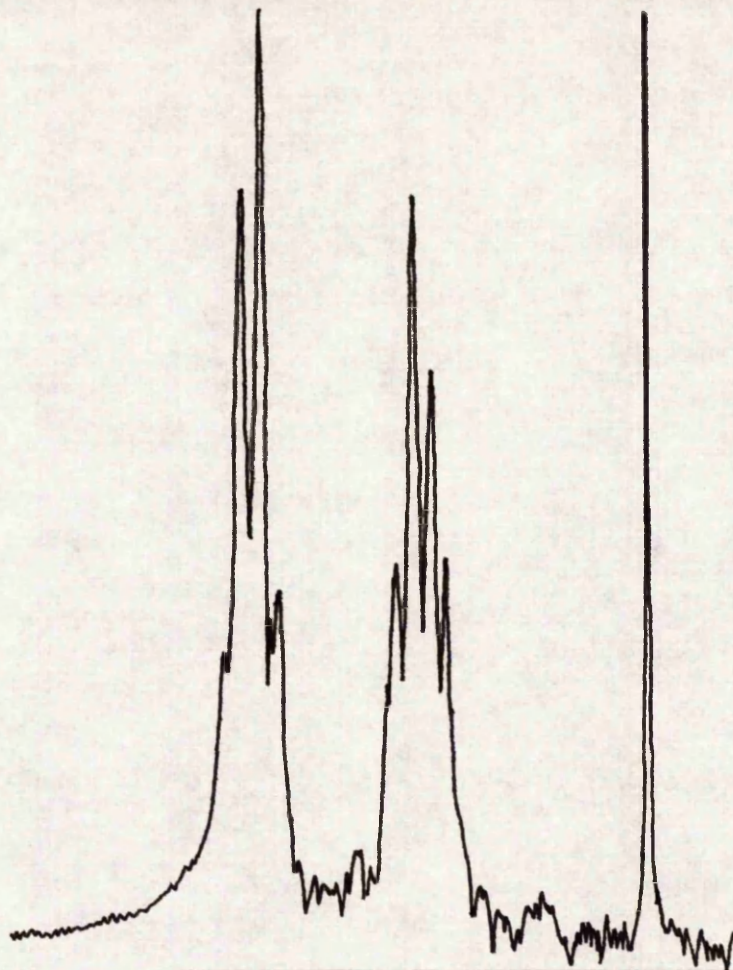
Fig. 11: Products of $(CF_3)_2NO^{\cdot}$ + $PhCH=NCH_2Ph$ (involatiles) in CCl_4. ^{19}F Spectrum at $-10^{\circ}C$.

The broad peak at room temperature changing to a doublet of quartets is attributed to magnetic non-equivalence of the CF_3 groups in

$$PhCH=NCHPh.$$
$$\quad\quad\quad\quad | $$
$$\quad\quad\quad ON(CF_3)_2$$

At $-10^{\circ}C$ the fluorines of the CF_3 groups are coupling to give quartets.

Reaction summary   (percentages of $PhCH=NCH_2Ph$ and $PhCH=NCHRPh$ being based on n.m.r. peak integrations)

Reactants:

$(CF_3)_2NO^{\cdot}$ ...... 1.34 g, 7.98 mmoles

$PhCH=NCH_2Ph$ ..... 0.88 g, 4.51 mmoles

Products:

$(CF_3)_2NOH$ ..... 0.71 g, 4.23 mmoles, 53%

$PhCH=NCH_2Ph$ ..... 0.15 g, 0.77 mmoles, 17% unreacted

PhCH=NCHPh   ....   1.33 g, 3.68 mmoles, 99%
       |
       R

unidentified 1%

9.   <u>REACTION OF $(CF_3)_2NO^\bullet$ WITH N-METHYLANILINE (2:1 MOLAR RATIO)</u>

This reaction was carried out four times in all using the
following amounts of reactants.

	$(CF_3)_2NO^\bullet$	PhNHMe
(a)	0.42 g, 2.50 mmoles	0.12 g, 1.25 mmoles
(b)	0.70 g, 4.17 mmoles	0.22 g, 2.06 mmoles
(c)	0.59 g, 3.51 mmoles	0.21 g, 1.96 mmoles
(d)	2.00 g, 11.90 mmoles	0.64 g, 5.98 mmoles

The reactions were all carried out using the same method. Reaction (d)
is taken as a typical example and is described below.

Bistrifluoromethylamino-oxyl was condensed, <u>in vacuo</u>, onto
N-methylaniline in a 25 cm^3 Pyrex reaction tube at -196°C. The tube
was sealed and allowed to warm to room temperature. The reactants quickly
turned red-purple, then thick white fumes were evolved which settled
down giving dark wine-red viscous liquid products. The reaction took
about 3 minutes after removal of the tube from the liquid nitrogen.

The volatile products were condensed into the vacuum system
leaving a brown-black tarry residue. The tube was heated using a hair
dryer until it reached constant weight. The volatiles were separated
by trap-to-trap fractionation and identified as follows.

-78°C trap: A white solid giving a colourless liquid and vapour on
warming. G.l.c. (2m SE30 at 50°C) showed the liquid to be N,N-
bistrifluoromethylhydroxylamine. A vapour phase i.r. spectrum showed
mainly $(CF_3)_2NOH$ with traces of bistrifluoromethylamine, $(CF_3)_2NH$.

-196°C trap: A white solid giving a colourless gas on warming to room temperature. The i.r. spectrum of this gas showed it to consist of mainly bistrifluoromethylamine[157] [peaks at 3442 (m, N-H str.), 1608 (w), 1500 (s, N-H bend), 1352, 1312, 1266, 1202, 1142 (v.s., C-F str.), 1044 (w), 946 (s, C-N str.), 890 (m), 732 (m), 707 (m), 667 cm^{-1} (m)] with some $(CF_3)_2NOH$.

The presence of a weak to medium band at 1805 cm^{-1} indicated the probably presence of traces of perfluoro(methylenemethylamine), $CF_3N=CF_2$.[158]

The involatile residue was dissolved as far as possible in chloroform and filtered giving a black insoluble solid (melting point >300°C) and a red-brown solution. G.l.c. analysis of this solution (2m SE30 at 200°) showed it to contain only one product with retention time greater than that for N-methylaniline. The solution slowly deposited more brown insoluble solid over a period of several days. The solution was refiltered and the chloroform was removed leaving a pale, red-brown, viscous liquid. This was identified from its n.m.r. (26), i.r. (21) and mass (42) spectra as N^1-methyl-N^1-phenyl-N^2-(trifluoromethyl)-fluoro-formamidine, $Ph(Me)NCF=NCF_3$.

The conclusion that the spectra produced are those of the above named compound is based on the following reasoning.

(i)   The ^{1}H n.m.r. spectrum shows peaks for C_6H_5 (2.3 to 3.6 τ, complex, int. 5) and CH_3 (6.65 τ, singlet, int. 3) only.

(ii)   The ^{19}F n.m.r. shows a doublet (int. 3, J ∿ 12.4 Hz) at about -28.0 ppm from external TFA and a quartet (int. 1, J ∿ 12.4 Hz) at about -34.5 ppm, attributed to a CF_3 group and a single F atom respectively.

The chemical shift of the CF_3N group is normally in the range -10 to -30 ppm from TFA.[159] Values for a number of examples of compounds containing $CF_3-N=C$ groups fall within the range -16 to -29 ppm from TFA.[160]

These values compare with a normal range of -18 to +12 ppm for the CF_3-C group.[159] Values for a number of examples of compounds containing CF_3-C=N fall within the range -8 to -15 ppm from TFA.[160] It was concluded that the compound under consideration contains the group CF_3-N=C rather than CF_3-C=N.

The chemical shift of the group F-N=C usually falls in the range -87 to -126 ppm. Typical shifts for the group F-C=N (with C branch) fall in the range -50 to -74 ppm.[160]

However a number of compounds containing the group F-C=N (with N branch) have chemical shifts for F in the range -28 to -43 ppm.[160] It was concluded that the compound being considered contains the group F-C=N-CF$_3$ (with N branch).

It can be seen from the examples given below[160] that the coupling between the fluorines in the present compound (12.4 Hz) is typical of the group F-C=N-CF$_3$.

$$CF_3N=CFCF \overline{\quad\quad} NCF_3$$
$$\lfloor 14.2 Hz \rfloor$$

┌── 14.3Hz ──┐
F_3C \   / F
      \   /
       N=C
          \
           $C(CF_3)=NCF_3$

┌── 13.3Hz ──┐
F_3C \   / F
      \   /
       N=C
          \
           $CF(CF_3)N=CF_2$

┌──── 6 Hz ──┐
              / F
             /
          N=C
     /   \
F_3C $CF(CF_3)N=CF_2$
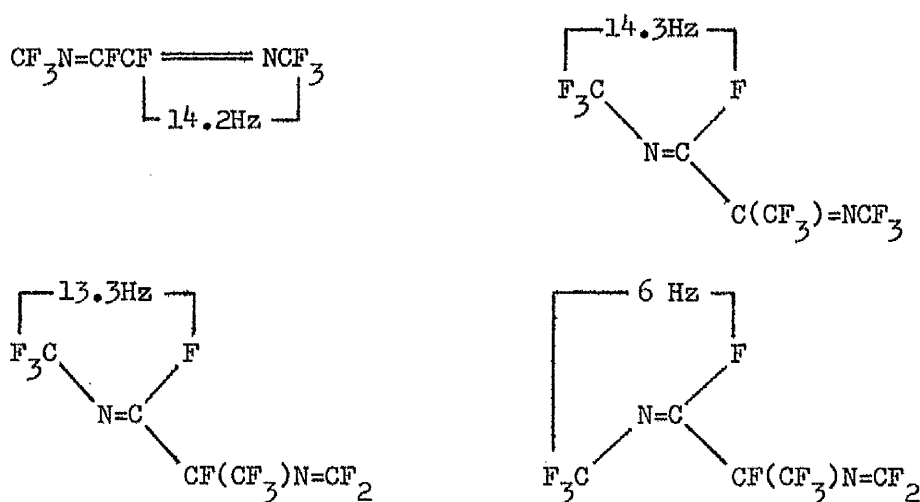
(iii)   The i.r. spectrum has a very strong absorption at 1690 cm^{-1} (5.92 μ) which is approximately as expected from comparison with values for the C=N stretching frequency in other compounds,

e.g.   alkyl-CH=N-alkyl ...   1665-1674 cm^{-1},[130]

and perfluoroalkyl-CF=N-perfluoroalkyl ... 1770-1790 cm^{-1}.^{159}

(iv)   The mass spectrum shows the following main peaks at m/e values 220 (parent ion, $C_9H_8N_2F_6^+$), 201 (M-F), 151 (M-CF$_3$), 106 ($C_6H_5NCH_3^+$), 91 ($C_6H_5N^+$), 83 (CF$_3$N$^+$), 77 ($C_6H_5^+$) and 69 (CF$_3^+$).

Reaction summary

Reactants:

(CF$_3$)$_2$NO$^•$ ......   2.00 g, 11.90 mmoles

PhNHMe   ....   0.64 g, 5.98 mmoles

Products:

(CF$_3$)$_2$NOH   ......   1.28 g, 7.57 mmoles, 64%

(CF$_3$)$_2$NH   ......   0.29 g, 1.90 mmoles, 16%

CF$_3$N=CF$_2$ ......   traces

PhNCF=NCF$_3$ ......   0.47 g, 2.14 mmoles, 36% of PhNHMe used.
|
Me

insoluble tarry solid .... 0.59 g, 27% of total weight reactants

unaccounted for   ....   0.07 g, 3% of total weight reactants.

10.   REACTION OF (CF$_3$)$_2$NO$^•$ WITH N-ETHYLANILINE (2:1 MOLAR RATIO)

This reaction was carried out four times in all using the following amounts of reactants.

	(CF$_3$)$_2$NO$^•$	PhNHEt
(a)	0.89 g, 5.95 mmoles	0.36 g, 2.97 mmoles
(b)	0.60 g, 3.57 mmoles	0.23 g, 1.90 mmoles
(c)	1.14 g, 6.79 mmoles	0.44 g, 3.64 mmoles
(d)	1.30 g, 7.74 mmoles	0.41 g, 3.39 mmoles

These reactions were carried out using exactly the same method as that used for the reactions of (CF$_3$)$_2$NO$^•$ with N-methylaniline. The reactions were complete within three minutes of removing the reaction tubes from

liquid nitrogen giving very dark red, liquid products. The products were treated in the same way as those from the N-methylaniline reactions. Taking reaction (d) as a typical example, the volatiles were separated by trap-to-trap fractionation.

$-78^{\circ}C$ trap: Mainly $(CF_3)_2NOH$ with traces of $(CF_3)_2NH$.

$-196^{\circ}C$ trap: The vapour phase i.r. spectrum showed mainly $(CF_3)_2NH$ with traces of $(CF_3)_2NOH$ and $CF_3N=CF_2$. The contents of the trap were condensed onto excess N-ethylaniline at $-196^{\circ}C$ and allowed to warm up. The volatiles left after this reaction were shown by vapour phase i.r. spectroscopy to consist of perfluoro-(2,4-dimethyl-3-oxa-2,4-diazapentane), $(CF_3)_2NON(CF_3)_2$. It was presumed that the i.r. peaks of this compound had been previously obscured by those of $(CF_3)_2NH$.

The involatiles from the original reaction were found to consist of 0.33 g of a black tarry insoluble solid and 0.25 g of a red-brown viscous liquid which was identified by its n.m.r. (27), i.r. (22) and mass (43) spectra as N^1-ethyl-N^1-phenyl-N^2-(trifluoromethyl)-fluoro-formamidine, $Ph(Et)NCF=NCF_3$.

Reaction summary

Reactants:

$(CF_3)_2NO^{\bullet}$ .....   1.30 g, 7.74 mmoles

PhNHEt   ....   0.41 g, 3.39 mmoles

Products:

$(CF_3)_2NOH$ ......   0.78 g, 4.62 mmoles, 60%

$(CF_3)_2NH$ ......   0.24 g, 1.55 mmoles, 20%

$(CF_3)_2NON(CF_3)_2$ ..   0.07 g, 0.23 mmoles, 3%

$CF_3N=CF_2$ .....   trace

$\underset{Et}{PhNCF=NCF_3}$ ......   0.25 g, 0.87 mmoles, 26% of PhNHEt used.

insoluble tarry solid   ..... 0.33 g, 19% total weight reactants

unaccounted for   ..... 0.08 g, 5% total weight reactants

11.   <u>REACTION OF $(CF_3)_2NO\cdot$ WITH N-ETHYLANILINE (1:4 MOLAR RATIO)</u>

This reaction was carried out twice, as described below.

<u>Reaction (a):</u>   Bistrifluoromethylamino-oxyl (0.38 g, 2.26 mmoles) was condensed, <u>in vacuo,</u> onto <u>N</u>-ethylaniline (1.10 g, 9.09 mmoles) at -196°C in a 50 cm^3 reaction tube. The tube was sealed and removed from the liquid nitrogen. Reaction was complete within about 3 minutes, before the tube had reached room temperature, giving very dark red, almost black, liquid products. The products gradually resolved into a dark red-brown liquid and a tarry black solid.

G.l.c. of the liquid products (2m SE30) showed three main peaks, for $(CF_3)_2NOH$, unreacted <u>N</u>-ethylaniline and $\underline{N}^1$-ethyl-$\underline{N}^1$-phenyl-$\underline{N}^2$-(trifluoromethyl)-fluoroformamidine.

<u>Reaction (b):</u>   The reaction was repeated using 1.34 g $(CF_3)_2NO\cdot$ (7.98 mmoles) and 3.91 g <u>N</u>-ethylaniline (32.31 mmoles). After completion the tube was attached to the system and the volatiles were condensed through two -78°C traps and one -196°C trap. Initial heating of the reaction tube produced only 0.02 g loss in weight rather than the large initial loss usually found with the products of the 2:1 molar ratio reactions. Heating the tube strongly for an hour resulted in a weight loss of 0.80 g after which the weight of the tube remained constant.

<u>-78°C traps:</u>   Approximately 0.77 g of $(CF_3)_2NOH$ (4.56 mmoles, 57%).

<u>-196°C trap:</u>   0.03 g of $(CF_3)_2NON(CF_3)_2$ (0.08 mmoles, 2%).

No bistrifluoromethylamine was detectable in the products.

12.   REACTION OF BISTRIFLUOROMETHYLAMINE, $(CF_3)_2NH$, WITH N-ETHYLANILINE

Bistrifluoromethylamine, obtained from the products of reactions of N-methyl- and N-ethylaniline with $(CF_3)_2NO^{\bullet}$, was purified by passing it through two $-78°C$ traps into a $-196°C$ trap.

Bistrifluoromethylamine (0.41 g, 2.68 mmoles) was condensed, in vacuo, into a 25 cm^3 reaction tube containing N-ethylaniline (0.33 g, 2.73 mmoles) at $-196°C$. The tube was sealed and allowed to warm to room temperature. After 30 minutes the initial pale yellow colour of the N-ethylaniline had disappeared and the liquid was slightly darkened by traces of fine solid. After 45 minutes whitish-grey crystals started to deposit on the tube sides. Over the next 10 minutes the whole of the liquid appeared to crystallise on the sides of the tube to give wettish looking grey-white crystals.

The volatiles from the reaction (0.18 g) were condensed into a $-196°C$ trap. Gas phase i.r. spectroscopy showed only $(CF_3)_2NH$.

Tests on the crystals showed them to be soluble in water but insoluble in chloroform. Accordingly chloroform was added to the involatiles and the resulting mixture filtered. Removal of chloroform from the solution left 0.34 g of a colourless viscous liquid, the i.r. spectrum of which was identical to that of N^1-ethyl-N^1-phenyl-N^2-(trifluoromethyl)-fluoroformamidine (i.r. 22).

The residue from the filtration consisted of 0.17 g of fine, needle-like, greyish-white crystals. The i.r. spectrum of these crystals showed multiple bands over the whole region of 3300 to 2300 cm^{-1} with a very strong broad band at 3080 cm^{-1} (N-H str.), a strong band at 1600 cm^{-1} (N-H bend), other strong bands at 1450 cm^{-1} and from 780 to 690 cm^{-1}. The spectrum showed a marked similarity to that of a prepared sample of N-ethylaniline hydrochloride, $PhNH_2^+Et\,\overline{Cl}$, and it was concluded that the crystalline product was a salt from reaction of N-ethylaniline with HF.

Analysis of the crystals gave the following percentages: 47.8% C, 6.0% H, 7.3% N, 29.1% F. These figures are a fairly good fit for the formula $C_6H_5\overset{+}{N}H_2CH_2CH_3\ \overset{=}{H}_2F_3\cdot H_2O$ which requires 48.2% C, 8.0% H, 7.0% N, 28.6% F.

Reaction summary

Reactants:

(CF$_3$)$_2$NH   .....   0.41 g, 2.68 mmoles

PhNHEt   ......   0.33 g, 2.73 mmoles

Products:

(CF$_3$)$_2$NH   ......   0.18 g, 1.18 mmoles, 44% unreacted

Ph(Et)NCF=NCF$_3$ ...   0.34 g, 1.45 mmoles, 53%

PhN$\overset{+}{H}_2$Et $\overset{=}{H}_2F_3$ ....   0.17 g, 0.94 mmoles, 34%

unaccounted for   ...   0.05 g, 7% total weight reactants

13.   REACTION OF (CF$_3$)$_2$NO$^\bullet$ WITH 2-CHLORO-4-(N-PROPYLAMINO)-TOLUENE

2-Chloro-4-(N-propylamino)-toluene was prepared from 4-amino-2-chlorotoluene and n-propyl bromide. Its identity was confirmed by its i.r. and n.m.r. (28) spectra.

The reaction with (CF$_3$)$_2$NO$^\bullet$ was carried out three times using the quantities of reactants shown below. The method used was exactly the same as previously described for reactions of (CF$_3$)$_2$NO$^\bullet$ with the other N-alkylanilines.
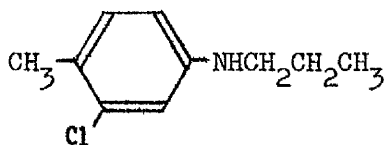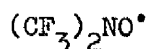
	(CF$_3$)$_2$NO$^\bullet$	CH$_3$—⟨ ⟩—NHCH$_2$CH$_2$CH$_3$ (Cl)
(a)	1.73 g, 10.30 mmoles	0.93 g, 5.15 mmoles
(b)	1.47 g, 8.75 mmoles	0.80 g, 4.38 mmoles
(c)	0.99 g, 5.89 mmoles	0.55 g, 3.00 mmoles

The reactions were complete within 3-5 minutes of removing the reaction tubes from liquid nitrogen, giving dark red liquid products. The volatiles were condensed over into the system, the reaction tube being heated with a hair dryer until there was no further loss in weight. The volatiles were separated by trap-to-trap fractionation and the components identified by their vapour phase i.r. spectra.

The involatile residue, a brown-black tarry liquid, was found to be completely soluble in chloroform giving a dark brown solution. G.l.c. analysis (2m SE30, 180-200°C) of this solution showed one major peak, a small peak for unreacted amine and 3 other minor peaks. The chloroform solution was poured into 30/40 pet. ether depositing a brown-black residue which was filtered off. The solvents were then removed leaving a reddish-brown viscous liquid which was identified by its n.m.r., i.r. and mass spectra as N^1-(3-chloro-4-methylphenyl)-N^1-propyl-N^2-(trifluoromethyl)-fluoroformamidine,

(n.m.r. 29, i.r. 23, m.s. 44).
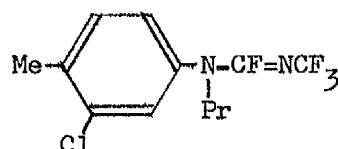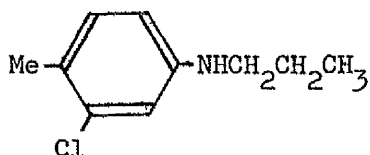
Taking reaction (c) as a typical example the yields of the products were as shown below.

Reaction summary

Reactants:

$(CF_3)_2NO^•$ ....   0.99 g, 5.89 mmoles

    ....   0.55 g, 3.00 mmoles
0.55 g, 3.00 mmoles

Products:

$(CF_3)_2NOH$ ....   0.62 g, 3.67 mmoles, 62%

$(CF_3)_2NH$ ....   0.13 g, 0.86 mmoles, 15%

unreacted amine   ....   0.006 g, 0.03 mmoles, 1%

Me—⟨ring⟩—NCF=NCF$_3$ ....   0.22 g, 0.71 mmoles, 24%
with Cl and Pr substituents
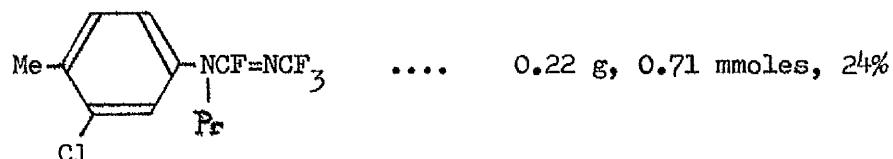
solid, tarry residue   ....   0.44 g, 29% total weight reactants

unidentified   ....   0.12 g

14.   REACTION OF $(CF_3)_2NO^\bullet$ WITH 4-CHLORO-2-(N-PROPYLAMINO)-TOLUENE

4-Chloro-2-(N-propylamino)-toluene was prepared from 2-amino-4-chlorotoluene and n-propyl bromide. Its identity was confirmed by its i.r. and n.m.r. (30) spectra.

The reaction with $(CF_3)_2NO^\bullet$ was carried out once using 0.27 g $(CF_3)_2NO^\bullet$ (1.61 mmoles) and 0.15 g 4-chloro-2-(N-propylamino)-toluene (0.82 mmoles). The method used and the treatment of the products were exactly the same as in the last reaction.

The main product was identified by its n.m.r. (31) and i.r. (virtually identical to that of the corresponding compound in the previous reaction) spectra as $\underline{N}^1$-(5-chloro-2-methylphenyl)-$\underline{N}^1$-propyl-$\underline{N}^2$-(trifluoromethyl)-fluoroformamidine.

Reaction summary

Reactants:

$(CF_3)_2NO^\bullet$ ....   0.27 g, 1.61 mmoles

⟨ring with Cl and Me⟩—NHCH$_2$CH$_2$CH$_3$ ....   0.15 g, 0.82 mmoles
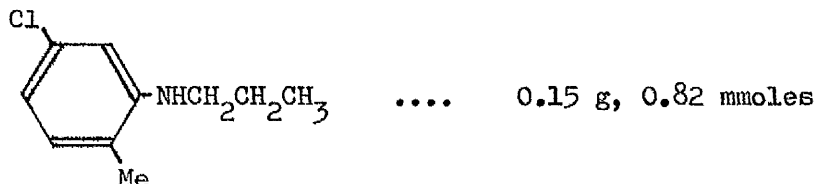
Products:

$(CF_3)_2NOH$ ....   0.12 g, 0.71 mmoles, 44%

$(CF_3)_2NH$ ....   0.09 g, 0.56 mmoles, 35%

....   0.10 g, 0.34 mmoles, 41%
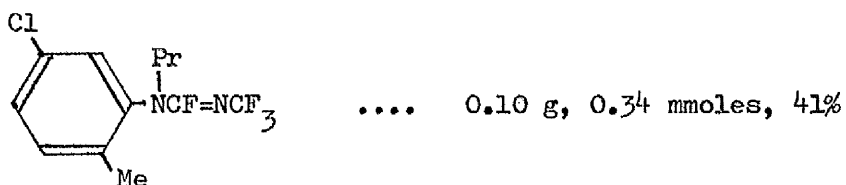
solid, tarry residue   ....   0.09 g, 21% total weight reactants

unaccounted for   ....   0.02 g, 5% total weight reactants

15.   REACTION OF $(CF_3)_2NO^\bullet$ WITH N-BENZYLANILINE

This reaction was carried out three times as described below.

Reaction (a):   Bistrifluoromethylamino-oxyl (2.27 g, 13.51 mmoles) was condensed, in vacuo, into a 25 cm^3 reaction tube containing N-benzylaniline (1.24 g, 6.78 mmoles) dissolved in carbon tetrachloride (4.73 g) at -196°C. The reaction tube was sealed and removed from liquid nitrogen. Reaction was complete within 3 minutes giving dark red liquid products.

The volatile products (6.51 g) were condensed over into the system and separated by trap-to-trap fractionation. The reaction tube was heated to constant weight using a hair dryer.

-78°C trap: Shown by i.r. spectroscopy and g.l.c. to contain CCl_4 and $(CF_3)_2NOH$, total 6.17 g; presumably 4.73 g CCl_4 and 1.44 g $(CF_3)_2NOH$ (8.52 mmoles).

-196°C trap: Shown by i.r. spectroscopy to contain $(CF_3)_2NH$ and $(CF_3)_2NOH$, in an approximately 4:1 ratio, i.e. 0.27 g, 1.78 mmoles $(CF_3)_2NH$ and 0.07 g, 0.44 mmoles $(CF_3)_2NOH$.

The involatile residue was dissolved as far as possible in chloroform and filtered giving a brown-black tarry residue and a brown solution. G.l.c. of the solution showed peaks for chloroform and 3 other compounds, the peak areas of which were in the ratio 22:56:21 respectively. The first two of these compounds were identified as follows.

(i)   Benzaldehyde, by comparison of its g.l.c. retention time (2m
and 4m SE30, 200 to 230°C) with that of an authentic sample. It was
separated by preparative g.l.c. (4m SE30 at 230°C) and its identity
confirmed by its n.m.r. and i.r. spectra.

(ii) N^1-benzyl-N^1-phenyl-N^2-(trifluoromethyl)-fluoroformamidine by
comparison of its g.l.c. retention time with that of this compound
produced by reaction of bistrifluoromethylamine with N-benzylaniline,
and by the presence in the i.r. spectrum of the involatile products of
a very strong peak due to C=N stretching at 1690 cm^{-1}.
The third compound remained unidentified.

Reaction (b):   The reaction was repeated using 1.38 g $(CF_3)_2NO^{\bullet}$
(8.21 mmoles) and 0.44 g N-benzylaniline (4.11 mmoles) but no solvent.
The reaction was much slower, being complete within 10 to 15 minutes.

The volatiles (1.10 g) were separated by trap-to-trap fraction-
ation and shown to consist of

1.90 mmoles $(CF_3)_2NH$ ....   0.29 g, 23%

4.79 mmoles $(CF_3)_2NOH$ ....   0.81 g, 58%

The involatile residue was dissolved as far as possible in
chloroform and filtered giving 0.17 g of a black tarry solid and a dark
brown solution. G.l.c. analysis (2m SE30 at 230°C) of this solution
showed the same peaks as in reaction (a): chloroform, benzaldehyde,
N^1-benzyl-N^1-phenyl-N^2-(trifluoromethyl)-fluoroformamidine and one
unidentified compound, the last three having peak areas in the ratio of
40:52:8 respectively.

A ^{19}F n.m.r. spectrum of the involatiles in CDCl$_3$ showed:

Band	Int.	Chemical shift	Band structure	Assignment
1	1	-36.2 ppm	broad singlet	F-C=N
2	3	-29.2 ppm	broad singlet	CF_3-N=C
3	approx. 5	-10.2 ppm	broad, complex	$(CF_3)_2$NOH plus other $(CF_3)_2$NO-compounds

Reaction (c): The reaction was repeated using 1.20 g $(CF_3)_2$NO$^\bullet$ (7.14 mmoles) and 0.65 g N-benzylaniline (3.55 mmoles). Some of the volatiles were condensed into the system. The remaining products were dissolved as far as possible in CCl_4 and filtered giving 0.30 g black tarry solid.

An n.m.r. spectrum of a sample of the resulting solution showed:

^{1}H (ext. DCB)

Band	Int.	Chemical shift	Band structure	Assignment
1	0.5	-2.62 ppm	singlet	PhCHO
2	26.3	-0.7 to +0.25 ppm	complex	C_6H_5 groups
3	2.5	+2.38 ppm	singlet	CH_2 of $PhCH_2$(Ph)NCF=NCF_3

^{19}F (ext. TFA)

Band	Int.	Chemical shift	Band structure	Assignment
1	1-2	-36.5 ppm	multiplet	F-C=N
2	5.3	-29.0 ppm	doublet, J ∿ 13 Hz	CF_3-N=C
3	4.7	-12.3 to -10.3 ppm	complex series of bands	$(CF_3)_2$NO groups
4	7.3	-9.8 ppm	singlet	$(CF_3)_2$NOH

The reaction summary given below takes reaction (c) as an example. Percentage yields are based on ^{1}H n.m.r. peak areas, the

yield of unidentified $(CF_3)_2NO$-compounds being based on the C_6H_5 group

integration unaccounted for by PhCHO and $PhCH_2(Ph)NCF=NCF_3$.

Reaction summary

Reactants:

$(CF_3)_2NO^{\bullet}$ .... 1.20 g, 7.14 mmoles

$PhCH_2NHPh$ ..... 0.65 g, 3.55 mmoles

Products:

$(CF_3)_2NOH$ .... 0.70 g, 4.14 mmoles, 58%

$(CF_3)_2NH$ .... 0.25 g, 1.64 mmoles, 23%

$PhCH_2\underset{\underset{Ph}{|}}{N}CF=NCF_3$ .... 0.23 g, 0.78 mmoles, 22%

PhCHO .... 0.03 g, 0.32 mmoles, 9%

unidentified $(CF_3)_2NO$-compounds .... approximately 0.34 g, 19% based

on $PhCH_2NHPh$ used

black tarry solid .... 0.30 g, 18% total weight reactants

16. ___REACTION OF BISTRIFLUOROMETHYLAMINE, $(CF_3)_2NH$, WITH N-BENZYLANILINE___

Bistrifluoromethylamine (0.56 g, 3.66 mmoles) was condensed,

in vacuo, into a tube containing N-benzylaniline (1.38 g, 7.54 mmoles)

and 5.05 g CCl_4 at -196°C. The tube was sealed and allowed to warm to

room temperature. Within 5 minutes of the tube reaching room temperature

the products consisted of a white crystalline solid and a colourless

liquid. The products were filtered and the white crystals washed several

times with CCl_4.

The ^1H n.m.r. spectrum of the CCl_4 solution showed (ref. ext.

DCB):

Band	Int.	Chemical shift	Band structure	Assignment
1	approx. 27	+ 0.05 ppm	singlet }	C_6H_5 groups
2	approx. 9	0 to +0.8 ppm	complex }	
3	3.6	+2.43 ppm	singlet	$PhCH_2(Ph)NCF=NCF_3$
4	0.4	+2.66 ppm	singlet	
5	1.8	+3.02 ppm	singlet	$PhCH_2NHPh$
6	0.9	+3.49 ppm	broad singlet	$PhCH_2NHPh$

The ^{19}F n.m.r. (ext. TFA) spectrum showed:

Band	Int.	Chemical shift	Band structure	Assignment
1	1	-36.5 ppm	broad singlet	$F-C=N-$
2	3	-29.3 ppm	broad singlet	$CF_3-N=C$

From the integrations the solution consisted of a mixture of $PhCH_2(Ph)NCF=NCF_3$ and $PhCH_2NHPh$ in a 2:1 molar ratio.

The i.r. spectrum of the solution showed a very strong band at 1690 cm^{-1} for C=N stretching and strong bands for C-F stretching between 1300 and 1100 cm^{-1}.

The i.r. spectrum of the crystalline solid showed a series of medium to strong bands between 3100 cm^{-1} and 2100 cm^{-1}, medium broad absorptions at 2050 and 1850 cm^{-1}, strong sharp peaks at 1600, 1490, 1480 and 1450 cm^{-1}, medium peaks at 1205 and 1195 cm^{-1}, a series of medium peaks between 1100 and 900 cm^{-1} and strong peaks at 780, 750 and 690 cm^{-1}.

Two samples of the crystalline solid were analysed.

(i)   The first sample was dried for several hours in an oven at 40°C

to ensure it contained no solvent, but appeared to undergo decomposition although the residue was still white and crystalline. It analysed as 76.1% C, 7.3% H, 7.6% N, 9.0% F. These figures are a reasonable fit for $C_6H_5CH_2\overset{+}{N}H_2C_6H_5\ \bar{F}$ which requires 76.8% C, 6.9% H, 6.9% N, 9.4% F.

(ii)   A second sample was submitted a week later, without drying. It had become slightly discoloured, turning slightly greenish. It analysed as 69.7% C, 6.5% H, 6.3% N, 13.4% F (a repeat of the fluorine analysis gave 13.3%). $C_6H_5CH_2\overset{+}{N}H_2C_6H_5\ \overline{HF}_2$ would require 70.0% C, 6.7% H, 6.2% N but 17.0% F. The analysis figures fit reasonably with those of the mixed salt $(C_6H_5CH_2\overset{+}{N}H_2C_6H_5)_2\ \bar{F}.\overline{HF}_2.H_2O$ which requires 70.1% C, 7.2% H, 6.3% N, 12.8% F. It is possible that the original salt is of this mixed formula although the weight of the salt produced in the reaction would agree with a formula of $C_6H_5CH_2\overset{+}{N}H_2C_6H_5\ \overline{HF}_2$; it can be seen from the analysis figures in (i) that loss of HF is extremely facile and it seems likely that HF has been lost in the second case also. The H_2O is included to bring the analysis figures up to 100%. Another possibility which could account for the discrepancy would be if the crystals had retained some of the CCl_4 with which they were washed.

Reaction summary

Reactants:

$(CF_3)_2NH$ ....   0.56 g, 3.66 mmoles

$PhCH_2NHPh$ ....   1.38 g, 7.54 mmoles

CCl_4 ....   5.05 g

Products:

$PhCH_2NHPh$ ....   0.28 g, 1.51 mmoles, 20% unreacted

$(CF_3)_2NH$ ....   not determined

$PhCH_2NCF=NCF_3$ (Ph)   ...   0.89 g, 3.02 mmoles, 40%

probably $PhCH_2\overset{+}{N}H_2Ph\ \overline{HF}_2$ ....   0.67 g, 3.02 mmoles, 40%

17.   REACTION OF $(CF_3)_2NO^\bullet$ WITH N-BENZYLIDENEANILINE (1:1 MOLAR RATIO)

N-benzylideneaniline was prepared in 85% yield by adding aniline to stirred benzaldehyde and recrystallising from ethanol.[161] Its identity was confirmed by its n.m.r. spectrum (32), its i.r. spectrum (C=N stretching at 1630 cm^{-1}) and its melting point (51-52°C).

Bistrifluoromethylamino-oxyl (1.30 g, 7.74 mmoles) was condensed, in vacuo, into a 25 cm^3 reaction tube containing N-benzylideneaniline (1.40 g, 7.74 mmoles) and 6.73 g CCl$_4$ at -196°C. The tube was sealed and allowed to warm to room temperature. Reaction was complete within 30 to 40 minutes giving dark red-brown liquid products.

The volatiles were condensed into the vacuum system, the reaction tube being warmed until it reached constant weight, and separated by trap-to-trap fractionation. They were shown to consist of $(CF_3)_2NH$ (0.24 g, 1.58 mmoles), $(CF_3)_2NOH$ (0.42 g, 2.49 mmoles), $CF_3N=CF_2$ (trace) and CCl$_4$.

The involatile residue consisted of a red-brown viscous liquid which solidified to a dark tarry crystalline solid on cooling. It was dissolved as far as possible in CCl$_4$ and filtered giving 0.20 g of a black solid and a dark red-brown solution. G.l.c. of this solution (2m SE30, 230°C) showed peaks for CCl$_4$, benzaldehyde, N-benzylideneaniline and 4 very minor products.

The i.r. spectrum of this solution showed peaks for N-benzylidene-aniline, benzaldehyde (C=O stretching at 1705 cm^{-1}) and for $(CF_3)_2NO-$ groups.

The ^1H n.m.r. spectrum of the solution showed (ref. ext. DCB):

Band	Int.	Chemical shift	Band structure	Assignment
1	0.4	-2.33 ppm	singlet	PhC<u>H</u>O
2	2.6	-0.83 ppm	singlet	PhC<u>H</u>=NPh
3	39	-0.52 to -0.18 ppm and -0.07 to +0.63 ppm	complex	C_6H_5 groups

The ^{19}F n.m.r. spectrum of the solution showed:

Band	Int.	Chemical shift	Band structure	Assignment
1	1.3	-11.50 ppm	singlet	
2	18.4	-11.25 to -9.65 ppm	complex series of peaks	$(CF_3)_2NO$-compounds
3	5.5	-9.76 ppm	singlet	$(CF_3)_2NOH$

In the ^{1}H n.m.r. spectrum the integration of the C_6H_5 groups is too great to be due only to PhCHO and PhCH=NPh, the excess being attributed to the unidentified $(CF_3)_2NO$-compounds shown to be present by ^{19}F n.m.r. spectroscopy. From the ^{1}H integrations the molar ratios of products in the CCl_4 solution were calculated to be:

PhCHO 10%

PhCH=NPh ... 63%

unidentified compounds 27%

Reaction summary

Reactants:

$(CF_3)_2NO^•$ .... 1.30 g, 7.74 mmoles

PhCH=NPh .... 1.40 g, 7.74 mmoles

Products:

$(CF_3)_2NOH$ .... 0.42 g, 2.49 mmoles, 32%

$(CF_3)_2NH$ .... 0.24 g, 1.58 mmoles, 20%

$CF_3N=CF_2$ ....   trace

black tarry solid   ....   0.20 g, 7% total weight reactants

unreacted PhCH=NPh   ....   63% ⎫
                                 ⎪
PhCHO   ....   10%   ⎬ of soluble involatile products
                                 ⎪ which total approx. 1.84 g,
unidentified compounds containing ⎪ 68% of total weight reactants
                                 ⎪
phenyl and $(CF_3)_2$NO-groups .. 27% ⎭

18.   **REACTION OF $(CF_3)_2$NO· WITH N-BENZYLIDENEANILINE (2:1 MOLAR RATIO)**

This reaction was carried out using the same method as for the

1:1 molar ratio reaction. The products were treated in the same way.

The reactants used were 1.85 g $(CF_3)_2$NO· (11.01 mmoles), 1.00 g

N-benzylideneaniline (5.52 mmoles) and 3.47 g CCl_4. The reaction was

complete within 30 to 40 minutes giving dark red liquid products.

The volatiles from the products were found to consist of 0.62 g

(3.67 mmoles) $(CF_3)_2$NOH, 0.28 g (1.83 mmoles) $(CF_3)_2$NH and a trace of

$CF_3N=CF_2$·

The involatiles were dissolved as far as possible in CCl_4 and

filtered giving 0.51 g of a black-brown tarry residue and a red-brown

solution. G.l.c. of the solution showed peaks for benzaldehyde, unreacted

N-benzylideneaniline and 3 minor products. An i.r. spectrum of the

solution showed peaks for benzaldehyde, PhCH=NPh and $(CF_3)_2$NO- groups.

The ^{1}H n.m.r. spectrum (ref. ext. DCB) of the solution showed:

Band	Int.	Chemical shift	Band structure	Assignment
1	0.6	-2.55 ppm	singlet	PhC<u>H</u>O
2	1.8	-1.04 ppm	singlet	PhC<u>H</u>=NPh
3	31	-0.65 to -0.38 ppm and -0.30 to +0.55 ppm	complex	C_6H_5 groups

In the ^{1}H n.m.r. spectrum the integration of the C_6H_5 groups is too great to be due only to benzaldehyde and PhCH=NPh; the molar ratios in the CCl_4 solution were calculated to be:

PhCHO 18%

PhCH=NPh 53%

unidentified phenyl compounds 29%

The ^{19}F n.m.r. spectrum (ext. TFA) of the solution showed:

Band	Int.	Chemical shift	Band structure	Assignment
1	0.6	-27.3 ppm	doublet, J ~ 17 Hz	possibly $CF_3N=CF$
2	2.7	-23.5 to -21.5 ppm	complex, including singlets at -22.8 -22.4 and -22.0 ppm	$(CF_3)_2N-$ groups
3	8.3	-12.0 to -9.7 ppm	complex series of peaks	$(CF_3)_2NO-$ groups
4	0.8	-9.4 ppm	singlet	$(CF_3)_2NOH$

Reaction summary

Reactants:

$(CF_3)_2NO^\bullet$ ....   1.85 g, 11.01 mmoles

PhCH=NPh   ....   1.00 g, 5.52 mmoles

Products:

$(CF_3)_2NOH$ ....   0.62 g, 3.67 mmoles, 33%

$(CF_3)_2NH$ ....   0.28 g, 1.83 mmoles, 17%

$CF_3N=CF_2$ ....   trace

black tarry solid ... 0.51 g, 18% total weight of reactants

PhCHO 18%

PhCH=NPh ... 53%

unidentified compounds containing

phenyl groups and one $CF_3N=CF$

group, approx. 5 $(CF_3)_2N-$ groups, ⎫ ... 29%   ⎫ of soluble involatile products which total approx. 1.44 g, 51% total weight of reactants

approx. 6 $(CF_3)_2NO-$ groups

(ratio of $CF_3N=CF$: total $(CF_3)_2N$: total $(CF_3)_2NO$ = 1 : 2.2 : 6.8)

19. REACTION OF $(CF_3)_2NO^•$ WITH N-METHYLBENZYLAMINE (2:1 MOLAR RATIO)

This reaction was carried out 6 times in all using exactly the same method as used for previous amine-$(CF_3)_2NO^•$ reactions. The quantities of reactants used were as shown below.

	$(CF_3)_2NO^•$	$PhCH_2NHCH_3$
(a)	1.48 g, 8.76 mmoles	0.53 g, 4.38 mmoles
(b)	1.65 g, 9.82 mmoles	0.57 g, 4.91 mmoles
(c)	2.56 g, 15.24 mmoles	0.92 g, 7.62 mmoles
(d)	2.20 g, 13.09 mmoles	0.80 g, 6.61 mmoles
(e)	0.82 g, 4.88 mmoles	0.30 g, 2.48 mmoles
(f)	0.53 g, 3.17 mmoles	0.19 g, 1.57 mmoles

The reactions were complete within 45 to 50 minutes giving golden-yellow liquid products. In two of the reactions, (b) and (d), the volatiles were condensed from the reaction tube into a $-196°C$ trap, the reaction tube being warmed until it reached constant weight. In the case of reaction (b) the volatiles (1.49 g) were separated by trap-to-trap fractionation.

$-78°C$ trap: An i.r. spectrum of the vapour showed $(CF_3)_2NOH$.

$-196°C$ trap: Traces of $(CF_3)_2NO^•$ and $(CF_3)_2NOH$.

In the case of reaction (d) the liquid volatiles (1.85 g) were examined by g.l.c. (2m SE30, 160°C). This showed peaks for, in order of increasing retention time:
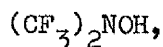
$(CF_3)_2NOH$,

3 very minor products,

one other major product shown to be $PhCOON(CF_3)_2$, as described below,

benzaldehyde (comparatively minor peak, approximately 10%)

A vapour phase i.r. spectrum of the volatiles showed only $(CF_3)_2NOH$. An i.r. spectrum of the liquid, after the $(CF_3)_2NOH$ had been allowed to evaporate leaving a comparatively involatile liquid, showed peaks for (bistrifluoromethylamino-oxy)carbonylbenzene, $PhCOON(CF_3)_2$, (C=O str., 1800 cm^{-1}, strong) and some benzaldehyde (C=O str., 1700 cm^{-1}, medium).

The n.m.r. spectra of the liquid showed:

^1H (ext. DCB)

Band	Int.	Chemical shift	Band structure	Assignment
1	1	-2.47 ppm	singlet	PhCHO
2	<1	-0.98 ppm	broad peak	
3	80	-0.8 to +0.3 ppm	complex	C_6H_5 groups, mainly $PhCOON(CF_3)_2$
4	2	+3.80 ppm	doublet, J ∿ 1 Hz	
5	5	+4.15 to +4.75 ppm	complex	

^{19}F (ext. TFA)

Band	Int.	Chemical shift	Band structure	Assignment
1	1	-9.8 ppm	singlet	$PhCOON(CF_3)_2$
2	7	-8.1 ppm	singlet	$(CF_3)_2NOH$

The identity of (bistrifluoromethylamino-oxy)carbonyl benzene was confirmed by comparing its g.l.c. retention time with that of a sample of this compound prepared by reacting $(CF_3)_2NO^\bullet$ with benzaldehyde.

The products of the other reactions, (a), (c), (e) and (f), were examined by g.l.c. (2m and 4m SE30, 180° to 230°C) without the volatiles being removed. The g.l.c. trace showed the following peaks; the percentages give the relative g.l.c. peak areas:

N,N-bistrifluoromethylhydroxylamine,

(bistrifluoromethylamino-oxy)carbonylbenzene, $PhCOON(CF_3)_2$ .. 7%,

benzaldehyde 21%,

N-benzylidenemethylamine, $PhCH=NCH_3$ 32%,

N^1-benzyl-N^1-methyl-N^2-(trifluoromethyl)-fluoroformamidine,

$PhCH_2(Me)NCF=NCF_3$ 29%,

(4 minor peaks .... total 11%).

The $(CF_3)_2NOH$, $PhCOON(CF_3)_2$, benzaldehyde and N-benzylidenemethylamine were identified by comparative g.l.c. (the last of these being compared with a sample of N-benzylidenemethylamine prepared from benzaldehyde and methylamine).

The N^1-benzyl-N^1-methyl-N^2-(trifluoromethyl)-fluoroformamidine was separated by preparative g.l.c. and identified by its n.m.r. (33), i.r. (24) and mass (45) spectra. Further confirmation of its identity was given by its g.l.c. retention time and i.r. spectrum which were identical to the product of the reaction between N-methylbenzylamine and bistrifluoromethylamine.

The ^1H n.m.r. spectrum (ref. ext. DCB) of a sample of the products of reaction (f) in CCl_4 showed the following:

Band	Int.	Chemical shift	Band structure	Assignment
1	0.3	~2.43 ppm	singlet	$PhC\underline{H}O$
2	1.0	−0.95 ppm	multiplet, $J \sim 1$ Hz	$PhC\underline{H}{=}NCH_3$
3	37	−0.75 to +0.50 ppm	complex	C_6H_5 groups
4	0.4	+2.10 ppm	singlet	
5	0.5	+2.50 ppm	complex	
6	2.0	+2.86 ppm	singlet	$PhC\underline{H}_2(Me)NCF{=}NCF_3$
7	2.0	+3.42 ppm	singlet	$PhC\underline{H}_2\overset{+}{N}H_2CH_3$
8	2.7	+3.83 ppm	doublet, $J \sim 1$ Hz	$PhCH{=}NC\underline{H}_3$
9	2.0	+4.33 ppm	singlet	
10	3.0	+4.37 ppm	singlet	$PhCH_2(C\underline{H}_3)NCF{=}NCF_3$
11	0.4	+4.54 ppm	singlet	
12	0.2	+4.70 ppm	singlet	
13	3.2	+4.76 ppm	singlet	$PhCH_2\overset{+}{N}H_2C\underline{H}_3$
14	0.1	+5.10 ppm	singlet	

It was presumed that the peaks at +3.42 and +4.76 ppm were due to the CH_2 and CH_3 groups respectively of $PhCH_2\overset{+}{N}H_2CH_3$. No peak was observed for the amine salt in the g.l.c. trace but its presence was confirmed by the singlet for $\overline{H}F_2$ in the ^{19}F n.m.r. spectrum.

The ^{19}F n.m.r. spectrum (ext. TFA) showed:

Band	Int.	Chemical shift	Band structure	Assignment
1	1.5	−29.2 ppm	broad peak	$PhCH_2(Me)NCF=NCF_3$
2	1.0	−10.5 ppm	singlet	$PhCOON(CF_3)_2$
3	15.0	−8.8 ppm	singlet	$(CF_3)_2NOH$
4	0.5	+58.2 ppm*	singlet	$\overline{HF}_2$

(* The chemical shift is in fact −26.2 ppm from ext. C_6F_6 which

converts to +58.2 ppm from ext. TFA.)

The i.r. spectrum of the products showed peaks at 1795 cm^{-1} (medium, C=O str. of $PhCOON(CF_3)_2$), 1690-1700 cm^{-1} (very strong, C=O str. of PhCHO and C=N str. of $PhCH_2(Me)NCF=NCF_3$) and 1650 cm^{-1} (medium, C=N str. of PhCH=NMe).

The following were shown to be absent from the products.

(i)   Cyanide ion. A "Prussian blue" test on a sample of the products gave a negative result.

(ii)   Hexamethylenetetramine. The [1]H n.m.r. spectrum (ext. DCB) of a sample of this compound showed a singlet at +2.55 ppm.

A summary of the reaction is given below using reaction (c) as the example. The yields are calculated from the mean values derived from the g.l.c. peak areas and n.m.r. integrations.

Reaction summary

Reactants:

$(CF_3)_2NO^{\bullet}$ ....   2.56 g, 15.24 mmoles

$PhCH_2NHCH_3$ ....   0.92 g, 7.62 mmoles

Products:

$(CF_3)_2NOH$ ....   2.14 g, 12.65 mmoles, 83%

PhCHO   ......   0.10 g, 0.91 mmoles, 12%

PhCOON(CF$_3$)$_2$ .... 0.19 g, 0.69 mmoles, 9%

PhCH=NCH$_3$ ...... 0.22 g, 1.83 mmoles, 24%

PhCH$_2$NCF=NCF$_3$ .... 0.39 g, 1.68 mmoles, 22%

CH$_3$

PhCH$_2\overset{+}{N}$H$_2$CH$_3$ $\overline{\text{HF}}_2$ ... 0.28 g, 1.75 mmoles, 23%

unidentified 10%

20. **REACTION OF BISTRIFLUOROMETHYLAMINE, (CF$_3$)$_2$NH, WITH N-METHYLBENZYL-AMINE**

Bistrifluoromethylamine (0.10 g, 0.65 mmoles) was condensed, *in vacuo*, into a 50 cm^3 reaction tube containing N-methylbenzylamine (0.25 g, 2.07 mmoles) at -196°C. The tube was sealed and allowed to warm to room temperature. It was left for one hour; the products consisted of colourless liquid. There were no volatile products. Chloroform was added to the products giving a colourless solution. Water was added to this, shaken up and the two layers separated. The chloroform layer was dried with MgSO$_4$ and filtered. The i.r. spectrum of the chloroform layer showed peaks for N^1-benzyl-N^1-methyl-N^2-(trifluoromethyl)-fluoro-formamidine. G.l.c. of the chloroform layer showed peaks for N-methylbenzylamine and PhCH$_2$(Me)NCF=NCF$_3$.

The aqueous layer was evaporated leaving a colourless gummy residue. The i.r. spectrum indicated a probable amine salt. It was presumed that this was PhCH$_2\overset{+}{N}$H$_2$Me $\overline{\text{HF}}_2$ as indicated by the n.m.r. spectra of the products of the reaction of (CF$_3$)$_2$NO° with N-methylbenzylamine.

Reaction summary

Reactants:

(CF$_3$)$_2$NH .... 0.10 g, 0.65 mmoles

PhCH$_2$NHCH$_3$ .... 0.25 g, 2.07 mmoles

Products:

PhCH$_2$NHCH$_3$ ....   0.10 g, 0.79 mmoles, 38% unreacted

PhCH$_2$NCF=NCF$_3$ ...   0.15 g, 0.65 mmoles, 51%
      |
      CH$_3$
      +
PhCH$_2$NH$_2$CH$_3$ $\overline{HF}_2$ ...   0.10 g, 0.62 mmoles, 48%

21.   <u>REACTION OF $(CF_3)_2$NO$^{\bullet}$ WITH N-BENZYLIDENEMETHYLAMINE</u>

N-benzylidenemethylamine was prepared by slowly adding benzaldehyde to a stirred solution of methylamine in ethanol. The reaction was monitored by i.r. spectroscopy and the addition stopped when the C=O stretch of benzaldehyde at 1700 cm^{-1} appeared. A slight excess of methylamine solution was then added. Distillation under reduced pressure removed first the methylamine and the ethanol. The N-benzylidenemethyl-amine was dried over MgSO$_4$ and then distilled under reduced pressure. The distillate was shown to be pure by g.l.c. and identified by its i.r. (C=N stretch at 1650-1655 cm^{-1}) and n.m.r. (34) spectra.

The reaction of $(CF_3)_2$NO$^{\bullet}$ with N-benzylidenemethylamine was carried out twice using the same method as with the other amines and Schiff's bases.

Reaction (a): 1.34 g bistrifluoromethylamino-oxyl (7.98 mmoles) and 0.49 g of N-benzylidenemethylamine (4.12 mmoles) were reacted. The reaction was complete after about 50 minutes giving a clear yellow liquid. G.l.c. analysis (4m SE30, 185-230°C) of the products showed peaks, identified by comparative g.l.c., for the following compounds, in order of increasing retention time.

       $(CF_3)_2$NOH
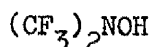
       PhCOON$(CF_3)_2$ 7%

       PhCHO 15%

       PhCH=NCH$_3$ 48%

two unidentified products   ....   10% and 12%

(4 very minor products   ....   total 8%).

The percentages give the relative g.l.c. peak areas.

An i.r. spectrum of the products showed peaks for $PhCOON(CF_3)_2$ (C=O str. at 1800 cm^{-1}, weak), PhCHO (C=O str. at 1700 cm^{-1}, strong), $PhCH=NCH_3$ (C=N str. at 1650 cm^{-1}, strong).

The [1]H n.m.r. spectrum (ref. ext. DCB) showed peaks for PhCHO and $PhCH=NCH_3$ and a number of unidentified singlets at +4.12 ppm (int. 2.8), +4.30, +4.39, +4.54, +4.68 ppm (all about equal int. of 0.6) compared with the integration of the peak for the CH_3 of $PhCH=NCH_3$ of 2.1. A number of very minor peaks were also present in the spectrum.

The [19]F n.m.r. spectrum of the products (ref. ext. TFA) showed:

Band	Int.	Chemical shift	Band structure	Assignment
1	1.5	-10.5 ppm	singlet	prob. $PhCOON(CF_3)_2$
2	3.7	-10.2 ppm	singlet	prob. $(CF_3)_2NON(CF_3)_2$
3	13.1	-8.9 ppm	singlet	$(CF_3)_2NOH$

The region from -13.3 to -9.3 ppm showed 10 other very minor singlets superimposed on what appeared to be several broad peaks, as well as the other more prominent singlets at -10.5 and -10.2 ppm. The total integration for the region was 11.8. From the [19]F n.m.r. integrations the molar ratios of the $(CF_3)_2NO$-compounds were calculated to be:

     $(CF_3)_2NOH$ 52%

     $(CF_3)_2NON(CF_3)_2$ ... 15%

     $PhCOON(CF_3)_2$ 6%

     unidentified $(CF_3)_2NO$-compounds   ... 27%

Reaction (b):   The reaction was repeated using 1.26 g $(CF_3)_2NO^{\cdot}$ (7.50 mmoles) and 0.46 g N-benzylidenemethylamine (3.87 mmoles). The tube was

attached to the vacuum system and warmed to almost constant weight. The volatiles (0.66 g) were separated by passing through -78°C and -196°C traps.

Vapour phase i.r. spectra of the contents of the -78°C trap showed the following:

at 1 cm Hg pressure: peaks for $(CF_3)_2NON(CF_3)_2$ at 1342 (w), 1308 (v.s.), 1278 (v.s.), 1230 (s), 1194 (s), 1180 (s), 960 (m) and 707 cm^{-1} (s),

at 2 cm Hg pressure: peaks for a mixture of $(CF_3)_2NON(CF_3)_2$ and $(CF_3)_2NOH$,

at 4 cm Hg pressure: peaks for $(CF_3)_2NOH$ masking those for $(CF_3)_2NON(CF_3)_2$.

The n.m.r.spectra of the volatiles showed the following.

^1H (ext. DCB)

Band	Int.	Chemical shift	Band structure	Assignment
1	4.2	+0.97 ppm	singlet	$(CF_3)_2NO\underline{H}$
2	0.2	+2.15 ppm	broad singlet	
3	0.1	+4.17 ppm	broad singlet	
4	0.6	+4.92 ppm	broad singlet	possibly CH_3-N

^{19}F (ext. TFA)

Band	Int.	Chemical shift	Band structure	Assignment
1	0.4	-12.4 ppm	singlet	
2	0.9	-10.4 ppm	singlet	$(CF_3)_2NON(CF_3)_2$
3	18.5	-8.9 ppm	singlet	$(CF_3)_2NOH$

A summary of the reaction, using (a) as an example is given below; yields are based on g.l.c. peak areas and ^{19}F n.m.r. peak integrations.

Reaction summary

Reactants:

$(CF_3)_2NO^{\bullet}$ .... 1.34 g, 7.98 mmoles

$PhCH=NCH_3$ .... 0.49 g, 4.12 mmoles

Products:

$(CF_3)_2NOH$ .... 0.70 g, 4.15 mmoles, 52%

$(CF_3)_2NON(CF_3)_2$ ... 0.19 g, 0.60 mmoles, 15%

$PhCH=NCH_3$ .... 0.24 g, 1.98 mmoles, 48% unreacted

PhCHO ...... 0.07 g, 0.62 mmoles, 29% of $PhCH=NCH_3$ reacted

$PhCOON(CF_3)_2$ ... 0.08 g, 0.29 mmoles, 14%

unidentified .... 57% based on $PhCH=NCH_3$ reacted and 27% of

$(CF_3)_2NO^{\bullet}$ used.

APPENDICES

APPENDIX 1:   NUCLEAR MAGNETIC RESONANCE SPECTRA

The following reference standards were used.

^{1}H spectra: internal tetramethylsilane (TMS), external para̲dichloro-
benzene (DCB), external benzene.

^{19}F spectra: external trifluoroacetic acid (TFA).

Absorption bands are numbered in order of increasing τ value or increasing
ppm relative to an external standard. Peaks to high field of external
references are given positive values; those to low field are given
negative values.

Relative intensities and suggested assignments (Assign.) are given.
The chemical shifts of simple multiplets are quoted as the centre of
the multiplet.

The ^{19}F n.m.r. spectra of a number of bis(bistrifluoromethylamino-
oxy) compounds of general formula $CH_2-C(CH_3)CH_2X$ show a singlet for the
$\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\ |\ \ \ \ |$
$\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad R\ \ \ R$

terminal $(CF_3)_2NO$ group and a slightly broadened singlet, which appears
complex on expansion, for the other $(CF_3)_2NO$ group. The complexity of
this peak is attributable[143] to magnetic non-equivalence of the CF_3
groups due to the asymmetry of the C atom to which the $(CF_3)_2NO$ group
is attached.

A variable temperature study of a solution of one of these compounds,
1,2-bis(bistrifluoromethylamino-oxy)-4-bromo-2-methylbutane (n.m.r. 12)
in CCl_4 was carried out. At -10°C considerable broadening of both peaks
in the spectrum was observed but no splitting. At lower temperatures
the solution solidified. This may be compared with the ^{19}F n.m.r.
spectrum of the compound PhCH=NCHRPh which at room temperature shows a
very broad singlet which splits into a doublet of quartets at -10°C
(see Figures 10 and 11, Experimental Section V, Reaction 8).

N.M.R. 1:   1,2-Bis(bistrifluoromethylamino-oxy)-2-methylpentane,

$$\underset{\substack{| \\ R}}{CH_2}-\underset{\substack{| \\ R}}{C}(CH_3)CH_2CH_2CH_3 \qquad\qquad \text{neat liquid}$$

(A) (B)

^{1}H (int. TMS)

Band	Int.	Chemical shift	Band structure	Assign.	J
1	2	5.95 τ	singlet	CH_2-R	-
2	7	8.1 to 9.1 τ	complex, including a singlet at	CH_2CH_2	-
			8.60 τ	CH_3-C-R	-
3	3	9.10 τ	triplet	CH_3	6 Hz

^{19}F (ext. TFA)

Band	Int.	Chemical shift	Band structure	Assign.
1	1	-10.4 ppm	slightly broadened singlet	$(CF_3)_2$NO- (B)
2	1	-8.2 ppm	singlet	$(CF_3)_2$NO- (A)

N.M.R. 2:   2-(Bistrifluoromethylamino-oxy)-2,4,4-trimethylpentane,

$(CH_3)_2CCH_2C(CH_3)_3$
$\quad\quad\quad |$
$\quad\quad\quad R$
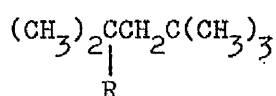
approx. 20% in CCl_4

^1H (ext. DCB)

Band	Int.	Chemical shift	Band structure	Assign.
1	2	+5.64 ppm	singlet	CH_2
2	6	+5.92 ppm	singlet	$(CH_3)_2C$
3	9	+6.24 ppm	singlet	$(CH_3)_3C$

^{19}F (ext. TFA)

Band	Int.	Chemical shift	Band structure	Assign.
1	-	-12.7 ppm	singlet	$(CF_3)_2NO-$

N.M.R. 3:   1,2-Bis(bistrifluoromethylamino-oxy)-2,4,4-trimethylpentane

$$CH_2-C(CH_3)CH_2C(CH_3)_3$$

R   R
(A)   (B)
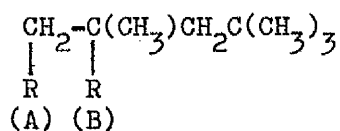
approx. 20% in CCl_4

^{1}H (ext. DCB)

Band	Int.	Chemical shift	Band structure	Assign.
1	2	+3.19 ppm	singlet	CH_2-R
2	2	+5.63 ppm	singlet	CH_2-C-R
3	3	+5.67 ppm	singlet	CH_3-C-R
4	9	+6.27 ppm	singlet	$(CH_3)_3C$

^{19}F (ext. TFA)

Band	Int.	Chemical shift	Band structure	Assign.
1	1	-12.3 ppm	slightly broadened singlet which on expansion shows a multiplet.	$(CF_3)_2NO-$ (B)
2	1	-10.2 ppm	singlet	$(CF_3)_2NO-$ (A)

N.M.R. 4:   1,2-Bis(bistrifluoromethylamino-oxy)-2-(bistrifluoromethyl-

amino-oxymethyl)-4,4-dimethylpentane,

$(RCH_2)_2CCH_2C(CH_3)_3$ approx. 20% in CCl_4
$\quad\quad\ |$
$\quad\quad R$
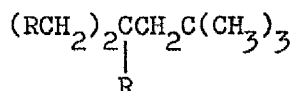
^1H (ext. DCB)

Band	Int.	Chemical shift	Band structure	Assign.
1	4	+2.83 and +2.90 ppm	At low sensitivity appears to consist of 2 singlets. At higher sensitivity appears as a broad singlet with a shoulder.	2 CH_2R groups
2	2	+5.37 ppm	singlet	CH_2
3	9	+6.12 ppm	singlet	$(CH_3)_3C$

^{19}F (ext. TFA)

Band	Int.	Chemical shift	Band structure	Assign.
1	1	-11.7 ppm	singlet	$(CF_3)_2NO-C$
2	2	-10.0 ppm	singlet	2 $(CF_3)_2NO-CH_2$ groups

N.M.R. 5: 2-(Bistrifluoromethylamino-oxy)-1-chloro-2-methylpropane,
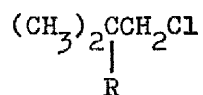
$(CH_3)_2CCH_2Cl$ (with R below)   neat liquid

^1H (ext. benzene)

Band	Int.	Chemical shift	Band structure	Assign.
1	1	+3.18 ppm	singlet	CH_2
2	3	+5.24 ppm	singlet	$(CH_3)_2C$

^{19}F (ext. TFA)

Band	Int.	Chemical shift	Band structure	Assign.
1	-	-11.0 ppm	singlet	$(CF_3)_2NO-$

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N.M.R. 6:   2-(Bistrifluoromethylamino-oxy)-2-methylpentan-4-one,

$(CH_3)_2CCH_2COCH_3$
|
R
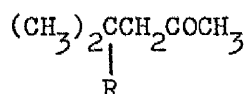
approx. 20% in CCl_4

^1H (int. TMS)

Band	Int.	Chemical shift	Band structure	Assign.
1	2	7.36 τ	singlet	CH_2
2	3	7.92 τ	singlet	CH_3CO
3	6	8.63 τ	singlet	$(CH_3)_2CO$

^{19}F (ext. TFA)

Band	Int.	Chemical shift	Band structure	Assign.
1	-	-11.8 ppm	singlet	$(CF_3)_2NO-$

N.M.R. 7:   2-(Bistrifluoromethylamino-oxy)-2-methylpropyl acetate,

$(CH_3)_2CCH_2OOCCH_3$
          |
          R
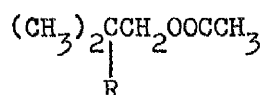
approx. 20% in CCl_4

^1H (ext. DCB)

Band	Int.	Chemical shift	Band structure	Assign.
1	2	+3.20 ppm	singlet	CH_2
2	3	+5.17 ppm	singlet	CH_3COO
3	6	+5.86 ppm	singlet	$(CH_3)_2C$

^{19}F (ext. TFA)

Band	Int.	Chemical shift	Band structure	Assign.
1	-	-12.0 ppm	singlet	$(CF_3)_2NO-$

<u>N.M.R. 8</u>:   <u>1,2-Bis(bistrifluoromethylamino-oxy)-2-methylpropyl acetate</u>,
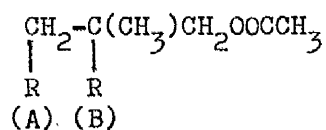
CH_2-$C(CH_3)CH_2OOCCH_3$
  | |
  R R
(A) (B)

approx. 20% in CCl_4

^1H (ext. DCB)

Band	Int.	Chemical shift	Band structure	Assign.
1		+3.05 ppm	overlapping	CH_2OOC
2	4	+3.10 ppm	singlets	and CH_2R
3	3	+5.23 ppm	singlet	CH_3-COO
4	3	+5.84 ppm	singlet	CH_3-C-R

^{19}F (ext. TFA)

Band	Int.	Chemical shift	Band structure	Assign.
1	1	-11.5 ppm	singlet	$(CF_3)_2NO-$ (B)
2	1	-9.6 ppm	singlet	$(CF_3)_2NO-$ (A)

N.M.R. 9:   2-(Bistrifluoromethylamino-oxy)-2-methyl-1-nitropropane,

$(CH_3)_2CCH_2NO_2$
         |
         R
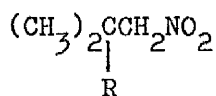
approx. 20% in CCl_4

^1H (ext. DCB)

Band	Int.	Chemical shift	Band structure	Assign.
1	1	+2.86 ppm	singlet	CH_2
2	3	+5.92 ppm	singlet	$(CH_3)_2C$

^{19}F (ext. TFA)

Band	Int.	Chemical shift	Band structure	Assign.
1	-	-10.4 ppm	singlet	$(CF_3)_2NO-$

N.M.R. 10:   2-(Bistrifluoromethylamino-oxy)-1-iodo-2-methylpropane,

$(CH_3)_2CCH_2I$
      |
      R
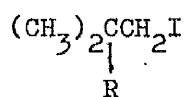
approx. 20% in CCl_4

^1H (int. TMS)

Band	Int.	Chemical shift	Band structure	Assign.
1	1	6.72 τ	singlet	CH_2
2	3	8.50 τ	singlet	$(CH_3)_2C$

^{19}F (ext. TFA)

Band	Int.	Chemical shift	Band structure	Assign.
1	-	-12.0 ppm	singlet	$(CF_3)_2NO-$

N.M.R. 11:   3-(Bistrifluoromethylamino-oxy)-1-bromo-3-methylbutane,

$(CH_3)_2CCH_2CH_2Br$
     |
     R
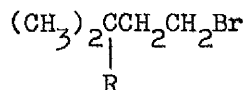
approx. 20% in CCl_4

^1H (int. TMS)

Band	Int.	Chemical shift	Band structure	Assign.	J
1	1	6.60 τ	AA'XX' splitting pattern	CH_2Br	8.4 Hz
2	1	7.81 τ	AA'XX' splitting pattern (see Fig. 12, below)	CH_2	8.4 Hz
3	3	8.65 τ	singlet	$(CH_3)_2C$	-

^{19}F (ext. TFA)

Band	Int.	Chemical shift	Band structure	Assign.
1	-	-12.2 ppm	singlet	$(CF_3)_2NO-$
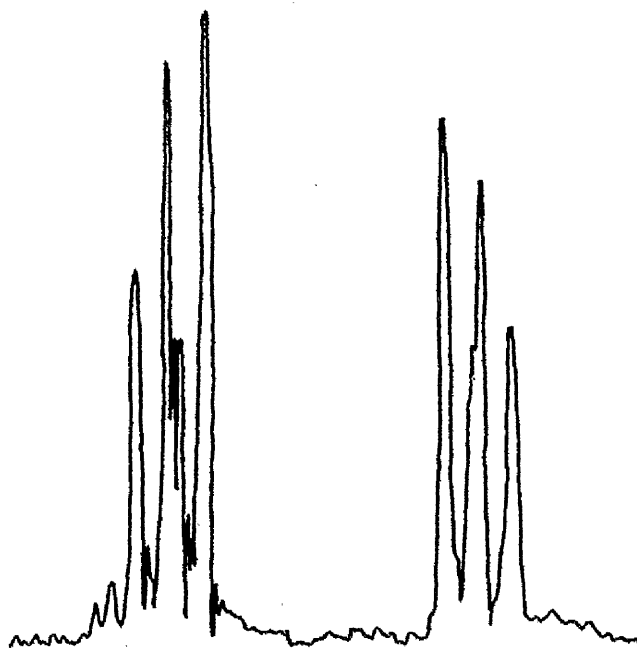
Fig. 12: AA'XX' splitting pattern for CH_2CH_2 in $(CH_3)_2CCH_2CH_2Br$.
                             |
                             R
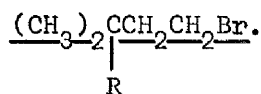
N.M.R. 12:   1,2-Bis(bistrifluoromethylamino-oxy)-4-bromo-2-methylbutane,

$$\underset{\underset{(A)\ (B)}{R\quad R}}{\overset{}{CH_2-C(CH_3)CH_2CH_2Br}}$$
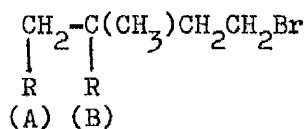
approx. 20% in CCl_4

^{1}H (int. TMS)

Band	Int.	Chemical shift	Band structure	Assign.	J
1	2	5.92 τ	singlet	CH_2-R	—
2	2	6.65 τ	AA'XX' splitting pattern	CH_2Br	8.1 Hz
3	2	7.75 τ	AA'XX' splitting pattern	CH_2	8.1 Hz
4	3	8.60 τ	singlet	CH_3	—

^{19}F (ext. TFA)

Band	Int.	Chemical shift	Band structure	Assign.
1	1	−11.8 ppm	broadened singlet, complex on expansion	$(CF_3)_2NO-$ (B)
2	1	−9.7 ppm	singlet	$(CF_3)_2NO-$ (A)

N.M.R. 13:   3-(Bistrifluoromethylamino-oxy)-3-methyl-l-nitrobutane,
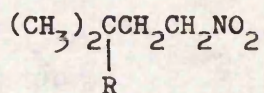
$(CH_3)_2CCH_2CH_2NO_2$
     |
     R

10-20% in CCl_4, capillary sample

^1H (ext. DCB)

Band	Int.	Chemical shift	Band structure	Assign.	J
1	1	+2.70 ppm	AA'XX' splitting pattern	CH_2NO_2	7.5 Hz
2	1	+4.79 ppm	AA'XX' splitting pattern (see Fig. 13, below)	CH_2	7.5 Hz
3	3	+5.77 ppm	singlet	$(CH_3)_2C$	-

^{19}F (ext. TFA)

Band	Int.	Chemical shift	Band structure	Assign.
1	-	-12.5 ppm	singlet	$(CF_3)_2NO-$
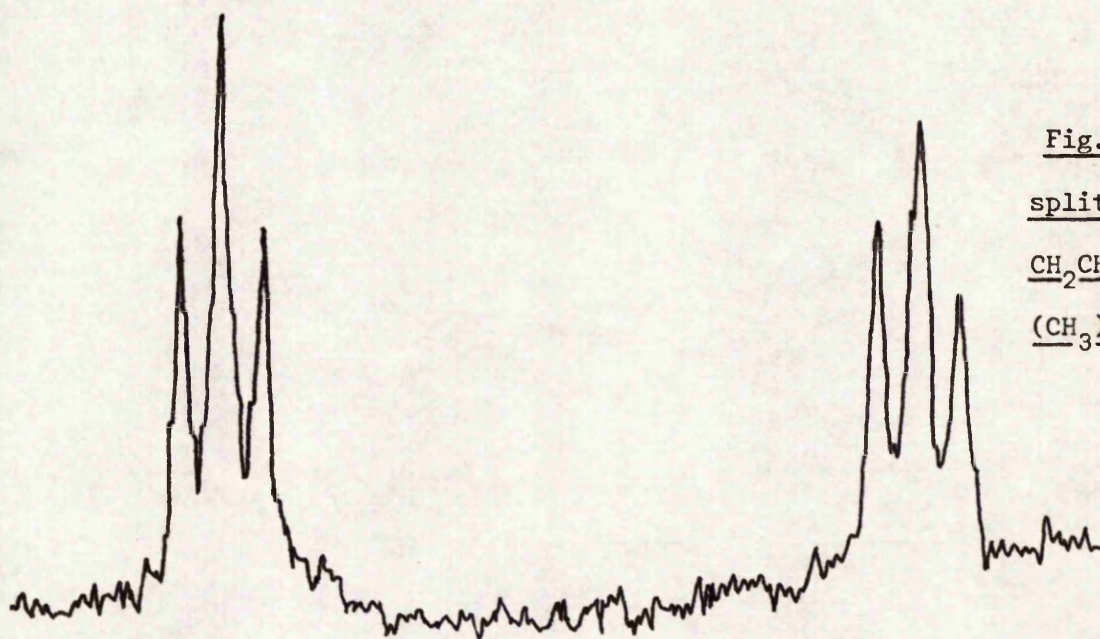
Fig. 13: AA'XX' splitting pattern for CH_2CH_2 in $(CH_3)_2CCH_2CH_2NO_2$. R
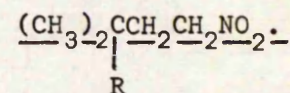
N.M.R. 14:   1,2-Bis(bistrifluoromethylamino-oxy)-2-methyl-4-nitrobutane,

$$CH_2-C(CH_3)CH_2CH_2NO_2$$
$$\;\;\;|\;\;\;\;\;|$$
$$\;\;\;R\;\;\;\;R$$
(A) (B)
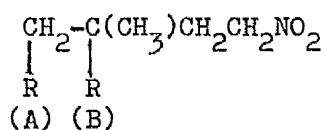
10-20% in CCl_4, capillary sample.

^{1}H (ext. DCB)

Band	Int.	Chemical shift	Band structure	Assign.	J
1	2	+2.70 ppm	AA'XX' splitting pattern	CH_2NO_2	7.5 Hz
2	2	+3.03 ppm	singlet	CH_2R	-
3	2	+4.65 ppm	AA'XX' splitting pattern	CH_2	7.5 Hz
4	3	+5.72 ppm	singlet	CH_3	-

^{19}F (ext. TFA)

Band	Int.	Chemical shift	Band structure	Assign.
1	1	-12.1 ppm	slightly broadened singlet, complex on expansion	$(CF_3)_2NO-$ (B)
2	1	-10.1 ppm	singlet	$(CF_3)_2NO-$ (A)

N.M.R. 15:   3-(Bistrifluoromethylamino-oxy)-1-iodo-3-methylbutane,

$(CH_3)_2CCH_2CH_2I$ approx. 10% in CCl_4
$\qquad\quad |$
$\qquad\quad R$

^1H (ext. DCB)

Band	Int.	Chemical shift	Band structure	Assign.	J
1	1	+3.91 ppm	AA'XX' splitting pattern	CH_2I	8 Hz
2	1	+4.90 ppm	AA'XX' splitting pattern	CH_2	8 Hz
3	3	+5.80 ppm	singlet	$(CH_3)_2C$	

^{19}F (xt. TFA)

Band	Int.	Chemical shift	Band structure	Assign.
1	--	-12.5 ppm	singlet	$(CF_3)_2NO-$

N.M.R. 16:   1,2-Bis(bistrifluoromethylamino-oxy)-4-iodo-2-methylbutane,

$$\underset{\underset{(A)\ (B)}{R\quad R}}{CH_2-C(CH_3)CH_2CH_2I}$$
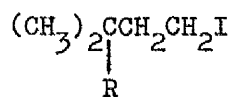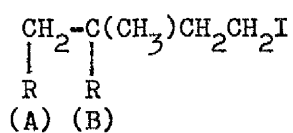
approx. 10% in CCl_4

^1H (ext. DCB)

Band	Int.	Chemical shift	Band structure	Assign.	J
1	2	+3.06 ppm	singlet	CH_2R	–
2	2	+4.00 ppm	AA'XX' splitting pattern	CH_2I	8.4 Hz
3	2	+4.82 ppm	AA'XX' splitting pattern	CH_2	8.4 Hz
4	3	+5.76 ppm	singlet	CH_3	–

^{19}F (ext. TFA)

Band	Int.	Chemical shift	Band structure	Assign.
1	1	–12.2 ppm	slightly broadened singlet, complex on expansion	$(CF_3)_2NO-$ (B)
2	1	–10.2 ppm	singlet	$(CF_3)_2NO-$ (A)

N.M.R. 17:   2-(Bistrifluoromethylamino-oxy)-5-bromo-2-methylpentane,
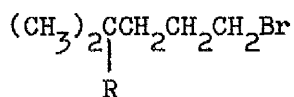
$(CH_3)_2CCH_2CH_2CH_2Br$ approx. 20% in CCl_4, capillary sample
$\overset{|}{R}$

^1H (ext. DCB)

Band	Int.	Chemical shift	Band structure	Assign.	J
1	1	+3.85 ppm	distorted triplet	CH_2-Br	6-7 Hz
2	2	+5.2 to +5.6 ppm	complex	CH_2CH_2	-
3	3	+5.93 ppm	singlet	$(CH_3)_2C$	-

(The $CH_2CH_2CH_2Br$ group would be expected to give an AA'BB'XX' splitting pattern.)

^{19}F (ext. TFA)

Band	Int.	Chemical shift	Band structure	Assign.
1	-	-12.4 ppm	singlet	$(CF_3)_2NO-$

N.M.R. 18:   1,2-Bis(bistrifluoromethylamino-oxy)-5-bromo-2-methylpentane,
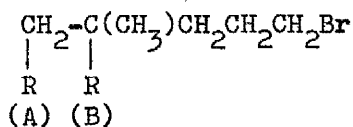
$$CH_2-C(CH_3)CH_2CH_2CH_2Br$$
$$\;\;|\;\;\;\;\;|$$
$$\;\;R\;\;\;\;R$$
$$(A)\;(B)$$

approx. 20% in CCl_4, capillary sample.

^1H (ext. DCB)

Band	Int.	Chemical shift	Band structure	Assign.
1	2	+3.12 ppm	singlet	CH_2R
2	2	+3.81 ppm	distorted triplet	CH_2Br
3	4	+5.29 and +5.34 ppm	complex	CH_2CH_2
4	3	+5.80 ppm	singlet	CH_3

(The $CH_2CH_2CH_2Br$ group would be expected to give an AA'BB'XX'
splitting pattern.)

^{19}F (ext. TFA)

Band	Int.	Chemical shift	Band structure	Assign.
1	1	-12.0 ppm	slightly broadened singlet, complex on expansion	$(CF_3)_2NO-$ (B)
2	1	-10.0 ppm	singlet	$(CF_3)_2NO-$ (A)

N.M.R. 19:   1-(Bistrifluoromethylamino-oxycarbonyl)-2-methylpropane,
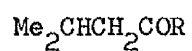
Me_2CHCH_2COR approx. 5-10% in CCl_4, capillary sample

^1H (ext. DCB)

Band	Int.	Chemical shift	Band structure	Assign.	J
1	1	+4.75 to +5.05 ppm	complex	$CHCH_2$	-
3	2	+6.16 ppm	doublet	$(CH_3)_2C$	6-7 Hz

^{19}F (ext. TFA)

Band	Int.	Chemical shift	Band structure	Assign.
1	-	-11.0 ppm	singlet	$(CF_3)_2NO-$

<u>N.M.R. 20:</u> <u>N-[2-(bistrifluoromethylamino-oxy)-2-methylpropylidene]-</u>
<u>-isobutylamine</u>, $(CH_3)_2CCH=NCH_2CH(CH_3)_2$ approx. 20% in CCl_4

with R below the central C.

^{1}H (int. TMS)

Band	Int.	Chemical shift	Band structure	Assign.	J
1	1	2.39 τ	broad singlet	CH=N	-
2	2	6.77 τ	doublet of doublets	-CH$_2$-	6.7 and ∿1 Hz
3	1	8.22 τ	multiplet	Me$_2$C$\underline{H}$	6.7 Hz
4	6	8.58 τ	singlet	(CH$_3$)$_2$CR	-
5	6	9.11 τ	doublet	(C$\underline{H_3}$)$_2$CH	6.7 Hz

^{19}F (ext. TFA)

Band	Int.	Chemical shift	Band structure	Assign.
1	-	-11.7 ppm	singlet	(CF$_3$)$_2$NO-

N.M.R. 21: N-isobutylideneisobutylamine,

$(CH_3)_2CHCH=NCH_2CH(CH_3)_2$ neat liquid

(A)   (B)
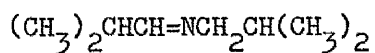
^1H (int. TMS)

Band	Int.	Chemical shift	Band structure	Assign.	J
1	1	2.53 τ	doublet of triplets	CH=N	4 Hz/1 Hz
2	2	6.88 τ	doublet of doublets	CH_2	6 Hz/1 Hz
3	2	7.70 τ	complex multiplet	$Me_2C\underline{H}-(A)$	—
4		8.20 τ	multiplet	$Me_2C\underline{H}$ (B)	6-7 Hz
5	6	8.93 τ	doublet	$(CH_3)_2C-(A)$	7 Hz
6	6	9.08 τ	doublet	$(CH_3)_2C-(B)$	7 Hz

N.M.R. 22:   N-(1-hydroxy-2-methylpropylidene)-isobutylamine,
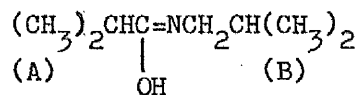
$(CH_3)_2CHC=NCH_2CH(CH_3)_2$ approx. 20% in CCl_4, capillary sample.
(A) | (B)
             OH

^1H (ext. DCB)

Band	Int.	Chemical shift	Band structure	Assign.	J
1	1	-1.24 ppm	broad singlet	OH	-
2	3	+3.94 ppm	doublet, overlying	CH_2	7 Hz
			a multiplet	Me_2CH (A)	7 Hz
3	12-13	+5.81 ppm	doublet	$(CH_3)_2C$ (A)	7 Hz
4		+6.14 ppm	doublet	$(CH_3)_2C$ (B)	7 Hz

The multiplet from the second -CH- was presumed to be hidden by

spinning side-bands from the methyl groups and the baseline "noise".

N.M.R. 23:   N-isobutyl-2-methylpropanamide,

$(CH_3)_2CHCONHCH_2CH(CH_3)_2$ approx. 20% in CCl_4
(A)   (B)
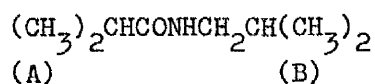
^1H (ext. DCB)

Band	Int.	Chemical shift	Band structure	Assign.	J
1	1	-0.36 ppm	broad singlet	NH	-
2	2	+4.17 ppm	triplet	CH_2	6-7 Hz
3	1	+4.63 ppm	multiplet	CHCO	7 Hz
4	1	+5.43 ppm	multiplet	$Me_2\underline{CH}CH_2$	7 Hz
5	6	+5.96 ppm	doublet	$(CH_3)_2C-(A)$	7 Hz
6	6	+6.16 ppm	doublet	$(CH_3)_2C-(B)$	7 Hz

N.M.R. 24: N-benzylidenebenzylamine, $C_6H_5CH=NCH_2C_6H_5$

(A)   (B)

approx. 10% in $CDCl_3$

^1H (int. TMS)

Band	Int.	Chemical shift	Band structure	Assign.	J
1	1	1.65 τ	triplet	CH=N	1 Hz
2	2	2.1-2.4 τ	complex	orth-H's from C_6H_5 - (A)	
3	8	2.5-2.9 τ	complex including a singlet at 2.69 τ	meta- and para- H's from C_6H_5-(A) C_6H_5-(B)	
4	2	5.20 τ	doublet	CH_2	1 Hz

[literature[130] parameters for $\overset{c}{C_6H_5}-\overset{a}{CH}=N-\overset{b}{CH_2}-\overset{d}{C_6H_5}$:

a ... 1.98 τ, tr, J 1.4 Hz,   b ... 5.41 τ, doublet, J 1.4 Hz,

c and d ... 2.15-2.38 and 2.65-2.95 τ, complex]

N.M.R. 25: Hydrobenzamide, $(C_6H_5CH=N)_2CHC_6H_5$

approx. 30% in $CDCl_3$

^1H (int. TMS)

Band	Int.	Chemical shift	Band structure	Assign.
1	2	1.46 τ	singlet	CH=N
2	4	2.05 to 2.30 τ	complex	ortho H's of $C_6H_5C=N$
3	11	2.38 to 2.90 τ	complex	other C_6H_5 H's
4	1	4.04 τ	singlet	N-CH-N Ph

[literature[162] parameters for $(C_6H_5CH=N)_2CHC_6H_5$: (c a b d)

a ... 1.6 τ, s, b ... 4.1 τ, s, c and d ... 2.3 τ, 4 H multiplet, 2.7 τ, 11 H multiplet]

N.M.R. 26: N^1-methyl-N^1-phenyl-N^2-(trifluoromethyl)-fluoroformamidine,

$C_6H_5NCF=NCF_3$, approx. 20% in $CDCl_3$

|
CH_3
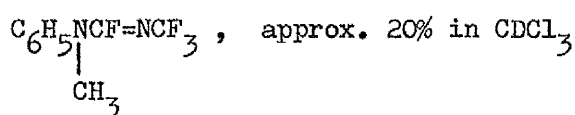
^1H (ext. DCB)

Band	Int.	Chemical shift	Band structure	Assign.
1	5	-0.5 to +0.8 ppm	complex	C_6H_5
2	3	+3.80 ppm	singlet	CH_3

^{19}F (ext. TFA)

Band	Int.	Chemical shift	Band structure	Assign.	J
1	1	-32.5, -35.8, -35.4 ppm	quartet	C-F	12.4, -, 11.3 Hz
2	3	-26.7, -28.6 -29.0 ppm	doublet	CF_3-N	12.4, 13.6, 11.3 Hz

[slightly different values from 3 different solutions]

N.M.R. 27: $\underline{N^1\text{-ethyl-}N^1\text{-phenyl-}N^2\text{-(trifluoromethyl)-fluoroformamidine,}}$

$C_6H_5NCF=NCF_3$,   10-20% in $CDCl_3$
|
CH_2CH_3
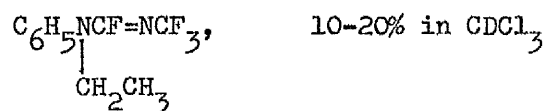
^1H (ext. DCB)

Band	Int.	Chemical shift	Band structure	Assign.	J
1	5	-0.5 to +0.1 ppm	complex	C_6H_5	-
2	2	+3.35 ppm	quartet	CH_2	7.2 Hz
3	3	+5.87 ppm	triplet	CH_3	7.2 Hz

^{19}F (ext. TFA)

Band	Int.	Chemical shift	Band structure	Assign.	J
1	-	-26.95 ppm	doublet	CF_3N	12.4 Hz

The expected quartet for C-F was not observed.

N.M.R. 28:   2-chloro-4-(N-propylamino)-toluene,

CH$_3$CH$_2$CH$_2$—N—H

H$_c$ H$_a$

H$_b$ Cl

CH$_3$

^{1}H (int. TMS)
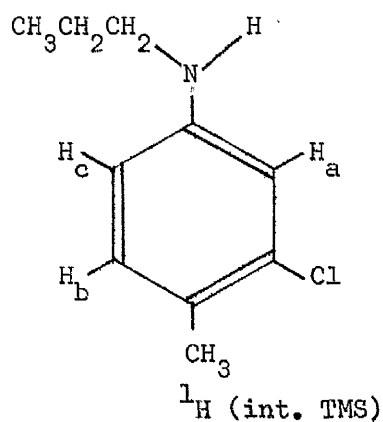
approx. 20% in CCl$_4$

Band	Int.	Chemical shift	Band structure	Assign.	J
1	1	3.10 τ	doublet	H$_b$	9 Hz
2	1	3.50 τ	doublet	H$_a$	3 Hz
3	1	3.74 τ	doublet of doublets	H$_c$	3 Hz/9 Hz
4	1	6.53 τ	singlet	N-H	-
5	2	7.05 τ	triplet	N-CH$_2$	7 Hz
6	3	7.76 τ	singlet	CH$_3$-ring	-
7	2	8.52 τ	multiplet	CH$_2$	7 Hz
8	3	9.07 τ	triplet	CH$_3$	7 Hz

N.M.R. 29: N^1-(3-chloro-4-methylphenyl)-N^1-propyl-N^2-(trifluoromethyl)-fluoroformamidine,

approx. 20% in $CDCl_3$
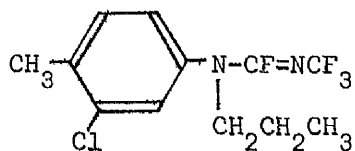
^{1}H (int. TMS)

Band	Int.	Chemical shift	Band structure	Assign.	J
1	3	2.3 to 3.5 τ	complex	C_6H_3	–
2	2	6.35 τ	triplet	CH_2-N	8 Hz
3	3	7.65 τ	singlet	CH_3-ring	–
4	∿2	8.44 τ	multiplet	$-CH_2-$	8 Hz
5	3	9.10 τ	triplet	CH_3	8 Hz

^{19}F (ext. TFA)

Band	Int.	Chemical shift	Band structure	Assign.	J
1	–	-29.3 ppm	doublet	CF_3-N	∿ 12 Hz

The expected quartet for C-F was not observed.

N.M.R. 30:   4-chloro-2-(N-propylamino)-toluene,

$CH_3CH_2CH_2$—N—H

CH$_3$

Cl
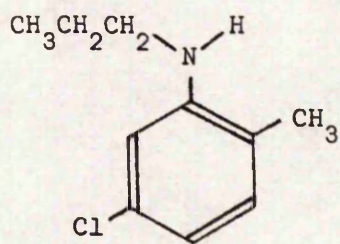
approx. 20% in CCl_4

^1H (int. TMS)

Band	Int.	Chemical shift	Band structure	Assign.	J
1	3	2.9-3.8 τ	complex	C_6H_3	-
2	1	6.75 τ	broad singlet	NH	-
3	2	7.03 τ	triplet	CH_2-N	7 Hz
4	3	8.03 τ	singlet	CH_3-ring	-
5	2	8.46 τ	multiplet	CH_2	7 Hz
6	3	9.03 τ	triplet	CH_3	7 Hz

N.M.R. 31: N^1-(5-chloro-2-methylphenyl)-N^1-propyl-N^2-(trifluoromethyl)-fluoroformamidine,

approx. 20% in $CDCl_3$
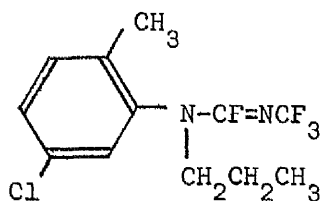
^1H (int. TMS)

Band	Int.	Chemical shift	Band structure	Assign.	J
1	3	2.6 to 3.4 τ	complex	C_6H_3	–
2	2	6.25 τ	triplet	CH_2-N	7 Hz
3	3	7.77 τ	singlet	CH_3-ring	–
4	2	8.34 τ	multiplet	CH_2	7 Hz
5	3	9.08 τ	triplet	CH_3	7 Hz

^{19}F (ext. TFA)

Band	Int.	Chemical shift	Band structure	Assign.	J
1	1	-37.5 ppm	multiplet	F-C	–
2	3	-29.5 ppm	doublet	CF_3-N	11.8 Hz

N.M.R. 32: <u>N-benzylideneaniline</u>, $C_6H_5CH=NC_6H_5$

(A)   (B)

approx. 20% in CCl_4

^1H (int. TMS)

Band	Int.	Chemical shift	Band structure	Assign.
1	1	1.72 τ	singlet	CH=N
2	2	2.05 to 2.30 τ	complex	ortho — H's of C_6H_5 (A)
3	8	2.40 to 3.03 τ	complex	other C_6H_5 hydrogens

N.M.R. 33: N^1-benzyl-N^1-methyl-N^2-(trifluoromethyl)-fluoroformamidine,

$PhCH_2NCF=NCF_3$, approx. 30% in CCl_4

|
CH_3
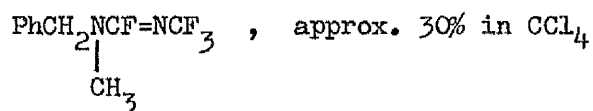
^1H (ext. DCB)

Band	Int.	Chemical shift	Band structure	Assign.
1	5	+0.07 ppm	broad singlet	C_6H_5
2	2	+2.97 ppm	broad singlet	CH_2
3	3	+4.57 ppm	broad singlet	CH_3

^{19}F (ext. TFA)

Band	Int.	Chemical shift	Band structure	Assign.	J
1	-	-30.4 ppm	doublet	CF_3-N	10.2 Hz

The expected quartet for C-F was not observed. A complex band was present at -28.9 ppm but its integration was only about 10% of that of the CF_3N doublet.

N.M.R. 34:   N-benzylidenemethylamine, $C_6H_5CH=NCH_3$

neat liquid.

^1H (ext. DCB)

Band	Int.	Chemical shift	Band structure	Assign.	J
1	1	-0.14 ppm	quartet	CH=N	1-2 Hz
2	2	+0.05 to +0.25 ppm	complex	ortho - H's of C_6H_5	
3	3	+0.5 to +0.7 ppm	complex	meta and para H's of C_6H_5	
4	3	+4.52 ppm	doublet	CH_3	1-2 Hz

APPENDIX 2:   INFRARED SPECTRA

Band positions in the spectra are presented in order of decreasing wavenumber. Band intensities are classified as very strong (vs), strong (s), medium (m), weak (w) or very weak (vw).

In general $(CF_3)_2NO$-compounds are characterised by having bands in their i.r. spectra at about the following positions.

$1320\text{-}1160$ cm^{-1} (7.6-8.6 μ) ... C-F stretching

1075 cm^{-1} (9.3 μ)   ...   N-O stretching

970 cm^{-1} (10.3 μ)   ...   C-N stretching

714 cm^{-1} (14.0 μ)   ... CF_3 deformation

These characteristic absorptions are frequently the strongest bands of the spectrum.[17]

I.R. 1:   2-(Bistrifluoromethylamino-oxy)-2,4,4-trimethylpentane,

$Me_2CCH_2CMe_3$, neat liquid film,
R

2942 cm^{-1} s, 2915 m, 2880 m, 1480 m, 1390 m, 1370 m, 1295 vs, 1250 vs,

1196 vs, 1118 m, 1042 m, 1020 m, 957 s, 805 w, 700 m.

I.R. 2:   1,2-Bis(bistrifluoromethylamino-oxy)-2,4,4-trimethylpentane,

CH_2-C(Me)CH$_2$CMe$_3$, neat liquid film,
R   R

2942 cm^{-1} s, 2915 m, 2880 m, 1480 m, 1390 m, 1370 m, 1295 vs, 1250 vs,

1196 vs, 1055 s, 1030 m, 1012 m, 963 vs, 870 w, 810 w, 700 w.

I.R. 3:   2-(Bistrifluoromethylamino-oxy)-1-chloro-2-methylpropane,

Me_2CCH_2Cl , neat liquid film,
R

3030 cm^{-1} m, 2940 m, 2880 w, 1480 w, 1450 w, 1398 m, 1385 m, 1315 s,

1307 vs, 1242 vs, 1197 vs, 1132 m, 1129 m, 1063 m, 1054 m, 1036 m, 962 s,

888 w, 847 w, 813 w, 784 w, 704 s.

I.R. 4:   2-(Bistrifluoromethylamino-oxy)-2-methylpentan-4-one,

Me_2CCH_2COMe , neat liquid film,
R

3355 cm^{-1} w, 2976 m, 2906 m, 2824 w, 1724 s, 1461 m, 1416 m, 1381 m,

1356 s, 1290 s, 1250 s, 1197 s, 1121 s, 1042 m, 1026 s, 960 s, 945 m,

840-810 m (broad), 704 s.

I.R. 5:   2-(Bistrifluoromethylamino-oxy)-2-methylpropyl acetate

Me_2CCH_2OOCMe , neat liquid film,
R

3470 cm^{-1} w, 2990 m, 2950 m, 2910 w, 2400 w, 2110 w, 1754 s, 1470 m,

1438 m, 1395 m, 1381 s, 1364 m, 1342 m, 1295 m, 1250 s, 1200 s, 1163 s, 1064 s, 1055 s, 990 w, 974 s, 968 s, 956 w, 926 m, 873 m, 865 m, 858 w, 824 m, 781 w, 714 s.

I.R. 6: 1,2-Bis(bistrifluoromethylamino-oxy)-2-methylpropyl acetate,

$\text{CH}_2\text{-C(Me)CH}_2\text{OOCMe}$, neat liquid film,
| |
R   R

3495 cm^{-1} w, 2995 m, 2957 m, 2904 w, 1760 s, 1480 m, 1461 m, 1400 m, 1381 m, 1295 s, 1250 s, 1200 s, 1136 m, 1055 s, 972 s, 965 s, 954 w, 920 w, 903 w, 820 w, 744 w, 708 s.

I.R. 7: 2-(Bistrifluoromethylamino-oxy)-1-iodo-2-methylpropane,

$\text{Me}_2\text{CCH}_2\text{I}$, neat liquid film,
    |
    R

2990 cm^{-1} m, 2960 w, 2940 w, 1465 m, 1457 m, 1426 w, 1414 w, 1388 m, 1375 m, 1295 s, 1250 s, 1200 s, 1155 m, 1112 s, 1077 m, 1060 s, 1047 s, 1032 s, 965 s, 958 s, 865 w, 825 m, 810 m, 765 w, 704 s.

I.R. 8: 3-(Bistrifluoromethylamino-oxy)-1-bromo-3-methylbutane,

$\text{Me}_2\text{CCH}_2\text{CH}_2\text{Br}$, neat liquid film
    |
    R

2985 cm^{-1} m, 2960 m, 2890 w, 1480 m, 1470 m, 1455 m, 1397 m, 1380 m, 1350 m, 1300 s, 1255 s, 1200 s, 1175 m, 1135 m, 1105 m, 1060 m, 1035 s, 969 s, 960 s, 922 w, 864 m, 820 m, 707 s, 663 m.

I.R. 9: 1,2-Bis(bistrifluoromethylamino-oxy)-4-bromo-2-methylbutane,

$\text{CH}_2\text{-C(Me)CH}_2\text{CH}_2\text{Br}$, neat liquid film,
| |
R   R

3000 cm^{-1} m, 2970 m, 2930 w, 1490 m, 1470 m, 1455 m, 1445 m, 1396 m, 1383 m, 1300 s, 1255 s, 1206 s, 1170 s, 1058 s, 1047 m, 970 s, 966 s, 870 w, 822 m, 744 w, 708 s.

I.R. 10:   3-(Bistrifluoromethylamino-oxy)-3-methyl-1-nitrobutane,

$Me_2CCH_2CH_2NO_2$, solution in CCl_4,
|
R

3030 to 2700 cm^{-1} w, 1558 s, 1377 m, 1351 w, 1295 vs, 1250 vs, 1205 vs,

1142 m, 1053 w, 1031 m, 960 s, 820 to 730 s (broad, CCl_4), 706 s.

I.R. 11:   1,2-Bis(bistrifluoromethylamino-oxy)-2-methyl-4-nitrobutane,

CH_2-C(Me)$CH_2CH_2NO_2$, solution in CCl_4,
| |
R   R

1558 cm^{-1} s, 1370 w, 1291 vs, 1245 vs, 1207 vs, 1053 m, 1027 w, 963 s,

820 to 730 s (broad, CCl_4), 706 s.

I.R. 12:   3-(Bistrifluoromethylamino-oxy)-1-iodo-3-methylbutane,

$Me_2CCH_2CH_2I$, neat liquid film,
|
R

2949 cm^{-1} m, 2906 m, 1464 m, 1438 m, 1383 m, 1369 m, 1333 m, 1291 s,

1243 s, 1197 s, 1156 m, 1124 m, 1077 m, 1058 s, 1036 s, 965 s, 959 s,

853 m, 814 m, 735 to 667 m (broad), 709 s.

I.R. 13:   1,2-Bis(bistrifluoromethylamino-oxy)-4-iodo-2-methylbutane,

$CH_2C(Me)CH_2CH_2I$, neat liquid film,
| |
R R

2906 cm^{-1} m, 2801 w, 1461 m, 1432 m, 1370 m, 1290 s, 1245 s, 1199 s,

1170 m, 1149 m, 1058 s, 1031 m, 965 s, 949 w, 866 w, 851 w, 817 m,

738 to 667 m (broad), 708 s.

I.R. 14:   2-(Bistrifluoromethylamino-oxy)-5-bromo-2-methylpentane,

$Me_2CCH_2CH_2Br$, neat liquid film,
|
R

2944 cm^{-1} m, 2870 w, 1464 m, 1440 m, 1390 m, 1374 m, 1298 vs, 1254 vs,

1200 vs, 1040 s, 960 s, 884 w, 865 w, 804 w, 782 w, 702 m.

I.R. 15:   1,2-Bis(bistrifluoromethylamino-oxy)-5-bromo-2-methylpentane,

CH_2-C(Me)$CH_2CH_2CH_2$Br , neat liquid film,
| |
R   R
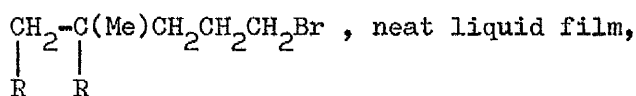
2942 cm^{-1} m, 2870 w, 1484 w, 1466 m, 1440 m, 1390 m, 1375 m, 1296 vs,

1254 vs, 1204 vs, 1056 s, 1030 w, 962 s, 885 w, 802 w, 700 m.

I.R. 16:   1-(Bistrifluoromethylamino-oxycarbonyl)-2-methylpropane,

Me_2CHCH$_2$COR, neat liquid film,
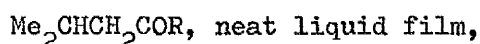
2924 cm^{-1} s, 2857 m, 1824 s, 1461 m, 1381 m, 1362 m, 1299 vs, 1257 vs,

1205 vs, 1036 s, 974 s, 965 s, 713 m, 706 m.

I.R. 17:   3-(Bistrifluoromethylamino-oxy)-3-methylpentan-1-ol,

Me_2CCH$_2$CH$_2$OH , neat liquid film
      |
      R
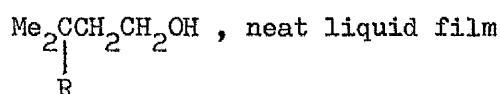
3246 s (broad), 2906 s, 1457 m, 1381 s, 1370 s, 1291 vs, 1245 vs, 1199 vs,

1131 m, 1055 s, 1028 s, 963 s, 708 s.

I.R. 18:   N-[2-(bistrifluoromethylamino-oxy)-2-methylpropylidene]-

-isobutylamine, Me_2CCH=NCH$_2$CHMe$_2$, neat liquid film,
                        |
                        R
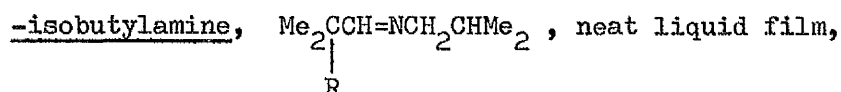
3500 cm^{-1} w, 3330 to 3080 w, 2965 s, 2940 s, 2906 s, 2878 s, 2830 m,

1742 w, 1675 s, 1466 s, 1453 m, 1385 s, 1366 s, 1292 vs, 1252 vs,

1196 vs, 1135 s, 1055 s, 1032 s, 995 m, 960 s, 920 w, 860 m, 812 m, 786 m,

703 s.

I.R. 19:   N-isobutylideneisobutylamine, Me_2CHCH=NCH$_2$CHMe$_2$, neat

liquid film,

2945 cm^{-1} s, 2925 s, 2870 s, 2825 s, 1675 s, 1470 s, 1450 m, 1388 s,

1368 s, 1350 w, 1290 m, 1240 vw, 1195 w, 1165 m, 1108 s, 1075 w, 1030 m,

970 w, 952 w, 920 w, 850 vw, 810 vw.

I.R. 20:   <u>N-benzylidenebenzylamine</u>, $C_6H_5CH=NCH_2C_6H_5$, neat liquid film,

3065 cm^{-1} m, 3045 s, 3010 s, 2855 s, 2820 s, 1952 w, 1880 w, 1808 w,

1640 vs, 1598 m, 1575 s, 1490 s, 1445 s, 1370 m, 1335 m, 1320 w, 1305 m,

1285 m, 1214 m, 1162 m, 1150 w, 1068 w, 1018 s, 990 w, 950 w, 900 w,

848 w, 800 w, 742 s, 720 s, 682 s.

I.R. 21:   <u>N^1-methyl-N^1-phenyl-N^2-(trifluoromethyl)-fluoroformamidine</u>,

C_6H_5(Me)NCF=NCF$_3$, solution in chloroform,

2940 cm^{-1} m (broad), 1690 vs, 1600 s, 1545 m, 1540 m, 1520 m, 1500 m,

1440 m, 1305 s, 1250 vs, 1180 s, 1117 s, 1043 w, 1025 w, 970 s, 930 w,

850 w, 690 m.

I.R. 22:   <u>N^1-ethyl-N^1-phenyl-N^2-(trifluoromethyl)-fluoroformamidine</u>,

C_6H_5(CH$_3$CH$_2$)NCF=NCF$_3$, solution in chloroform,

2965 cm^{-1} m, 2915 w, 1690 vs, 1600 m, 1500 m, 1470 m, 1450 m, 1432 m,

1390 w, 1305 s, 1290 s, 1260 s, 1230 s, 1180 m, 1120 m, 1100 m, 1040 w,

1025 w, 980 m, 960 w, 845 w, 690 m.

I.R. 23:   <u>N^1-(3-chloro-4-methylphenyl)-N^1-propyl-N^2-(trifluoromethyl)-</u>

<u>fluoroformamidine</u> , Me(Cl)C$_6$H$_3$N(CH$_2$CH$_2$CH$_3$)CF=NCF$_3$, neat liquid film,

2965 cm^{-1} s, 2930 s, 2890 m, 1692 vs, 1610 s, 1580 m, 1505 s, 1465 s,

1385 m, 1370 m, 1302 vs, 1265 vs, 1235 vs, 1210 s, 1175 s, 1120 s,

1052 m, 1040 m, 1005 s, 980 m, 968 m, 900 m, 880 m, 870 m, 840 m, 820 m,

750 m, 720 m, 705 m.

I.R. 24:   <u>N^1-benzyl-N^1-methyl-N^2-(trifluoromethyl)-fluoroformamidine</u>,

PhCH$_2$(Me)NCF=NCF$_3$, solution in CCl$_4$,

3570 cm^{-1} w, 3350 w, 3150 w, 3100 w, 3075 w, 3050 m, 3020 m, 2925 m,

2860 w, 2800 w, 2505 w, 2195 w, 1952 w, 1780 w, 1690 vs, 1670 m, 1602 w,

1582 w, 1495 s, 1452 s, 1424 m, 1420 m, 1390 m, 1358 m, 1290 vs, 1260 s,

1220 vs, 1197 s, 1160 vs, 1102 vs, 1020 m, 1004 s, 955 s, 895 s, 870 m,

827 m, 783 m, 750 s, 740 s, 718 s, 697 s, 690 s, 635 m.

APPENDIX 3:   MASS SPECTRA

The mass spectra of the compounds studied are given as tables of m/e values. Suggested assignments (Assign.) are given, along with the abundance of the ion expressed as a percentage of the most abundant peak.

Peaks of abundance less than 4.0% are only quoted where they are of diagnostic importance, or where similar spectra are compared side by side.

Where the ions are considered to contain unfragmented $(CF_3)_2NO$ groups, for the sake of clarity these are given as R rather than being included in the formulae as C_2F_6NO,

> e.g. in mass spectrum 1 the M-CH$_3$ (15) peak is given as
>
> $C_5H_{10}R^+$ rather than as $C_7H_{10}F_6NO^+$,
>
> and in mass spectrum 11 the peak at m/e 598 is given as
>
> $C_7H_{10}R_3^+$ rather than as $C_{13}H_{10}F_{18}N_3O_3^+$.

Most of the $(CF_3)_2NO$-compounds studied were of general formula $(CH_3)_2\underset{R}{C}CH_2X$ or $CH_2-\underset{R}{C}(CH_3)\underset{}{C}H_2X$.

Almost all of these compounds showed prominent peaks for the following m/e values.

M-R (168)

$$
\begin{array}{lll}
150 & \ldots\ldots & C_2F_5NOH^+ \\
69 & \ldots\ldots & CF_3^+ \\
43 & \ldots\ldots & C_2H_3O^+ \text{ (frequently the base peak)}
\end{array}
$$

None of these compounds showed a molecular ion peak; a few showed low abundance M-1 peaks.

For the mono-amino-oxy compounds of general formula $(CH_3)_2\underset{R}{C}CH_2X$ the following m/e values are also characteristic.

M-CH$_3$ (15)

$M-CH_2X$ ...... i.e. m/e 210, $C_3H_6R^+$

For the di-amino-oxy compounds of general formula

$$CH_2-C(CH_3)CH_2X$$
$$\;\;|\;\;\;\;\;|$$
$$\;\;R\;\;\;\;R$$

the following m/e value is also characteristic.

$M-CH_2R$

Many of these compounds also show peaks at m/e values 376 ($C_3H_4R_2^+$), 377 ($C_3H_5R_2^+$) or 378 ($C_3H_6R_2^+$).

Mass Spectrum 1: 2-(Bistrifluoromethylamino-oxy)-2-methylpentane

$(CH_3)_2\overset{|}{C}CH_2CH_2CH_3$, $C_6H_{13}R$, $\underline{M} = 253$
$ON(CF_3)_2$
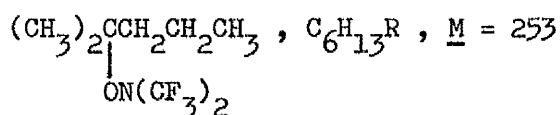
m/e	%	Ion	m/e	%	Ion
238	8.7	$C_5H_{10}R^+$	55	13.1	$C_4H_7^+$
210	33.2	$C_3H_6R^+$	44	4.9	
150	4.8	$C_2F_5NOH^+$	43	100.0	$C_2H_3O^+/C_3H_7^+$
86	7.7		41	26.2	$C_3H_5^+$
85	33.1	$C_6H_{13}^+$	39	6.4	
71	4.5		32	10.2	
69	15.0	CF_3^+	29	9.9	
58	24.7	$C_3H_6O^+$	28	52.3	
57	8.2				

Mass Spectrum 2: Probably 2-(bistrifluoromethylamino-oxy)-4-methyl-

pentane, $(CH_3)_2CHCH_2\overset{|}{C}HCH_3$, $C_6H_{13}R$; $\underline{M} = 253$
$ON(CF_3)_2$
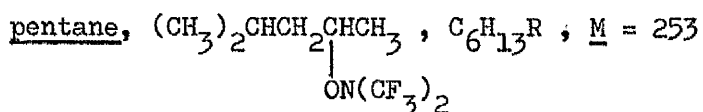
m/e	%	Ion	m/e	%	Ion
238	0.4	$C_5H_{10}R^+$	43	100.0	$C_2H_3O^+/C_3H_7^+$
196	5.3	$C_2H_4R^+$	42	9.5	
150	5.7	$C_2F_5NOH^+$	41	48.6	$C_3H_5^+$
85	41.1	$C_6H_{13}^+$	40	5.6	
83	33.8	$C_6H_{11}^+$	39	13.2	
69	24.1	CF_3^+	32	31.9	
57	16.4	$C_4H_9^+$	29	17.4	
55	56.5	$C_4H_7^+$	28	98.5	
44	11.9				

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Mass Spectrum 3: 1,2-Bis(bistrifluoromethylamino-oxy)-2-methylpentane

$$\underset{\substack{| \\ (CF_3)_2NO}}{CH_2}-\underset{\substack{| \\ ON(CF_3)_2}}{C}(CH_3)CH_2CH_2CH_3 \ , \ C_6H_{12}R_2 \ , \ \underline{M} = 420$$
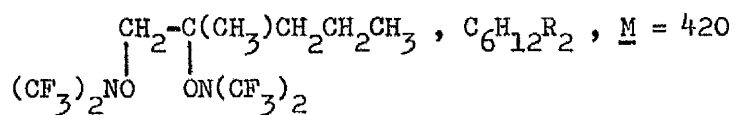
m/e	%	Ion	m/e	%	Ion
404	0.2	$C_5H_8R_2^+$	69	34.1	CF_3^+
376	4.4	$C_3H_4R_2^+$	58	36.7	
252	15.1	$C_6H_{12}R^+$	57	26.8	
238	35.9	$C_5H_{10}R^+$	56	7.2	
210	10.5		55	45.3	$C_4H_7^+/C_3H_3O^+$
196	17.1		44	9.1	
166	5.3		43	100.0	$C_2H_3O^+/C_3H_7^+$
150	22.2	$C_2F_5NOH^+$	42	5.9	
100	8.4	$C_6H_{12}O^+$	41	36.7	$C_3H_5^+$
86	11.5	$C_5H_{10}O^+$	39	6.4	
84	5.1	$C_6H_{12}^+$	32	14.4	
83	61.3	$C_6H_{11}^+$	29	19.4	
71	31.7		28	68.1	

Mass Spectrum 4:   2,3-Bis(bistrifluoromethylamino-oxy)-2-methylpentane,

$(CH_3)_2C$—$CHCH_2CH_3$, $C_6H_{12}R_2$, $\underline{M} = 420$
$(CF_3)_2NO$ $ON(CF_3)_2$
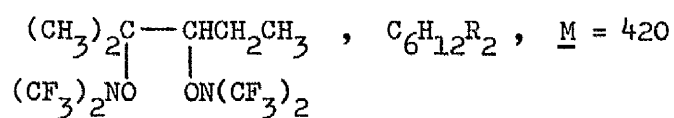
m/e	%	Ion	m/e	%	Ion
344.5	0.9		58	41.4	
252	19.2	$C_6H_{12}R^+$	57	42.1	
210	43.6	$C_3H_6R^+$	56	10.5	
196	15.0		55	18.9	$C_4H_7^+$
150	11.3	$C_2F_5NOH^+$	44	18.0	
100	8.7		43	100.0	$C_2H_3O^+$
85	4.9		42	5.0	
84	4.5	$C_6H_{12}^+$	41	21.8	$C_3H_5^+$
83	19.8	$C_6H_{11}^+$	40	9.3	
72	24.6		39	5.8	
71	16.7		32	94.4	
69	41.4	CF_3^+	29	23.4	
59	5.5				

Mass Spectra 5-8:   Bistrifluoromethylamino-oxy substituted 2-methylpent-
-1-enes, $C_6H_{11}ON(CF_3)_2$, $\underline{M}$ = 251

m/e	m.s. 5 %	m.s. 6 %	m.s. 7 %	m.s. 8 %	Ion
251			0.2	0.3	$C_6H_{11}R^+$
222	1.2	0.1			$C_4H_6R^+$
166	1.3				
150	1.2	0.8	1.2	1.0	$C_2F_5NOH^+$
91			1.7	2.2	
84	4.8	3.3	4.8	5.6	
83	73.3	47.4	65.9	74.3	$C_6H_{11}^+$
79		1.6	1.3	1.2	
71			0.5	1.9	
70	2.4				
69	13.3	11.8	13.2	13.1	CF_3^+
68	1.0		2.3	2.7	
67	6.2	7.9	7.5	7.8	
61	2.8				
57	5.0		1.4	6.4	
56	4.8	5.5	5.0	6.0	
55	100.0	100.0	100.0	100.0	$C_3H_3O^+$
53	3.9	5.2	5.0	5.2	
44	1.9	1.6	3.9	5.1	
43	14.4	14.0	20.2	28.2	$C_2H_3O^+$
42	8.3	5.5	4.0	4.7	
41	51.3	49.7	41.6	46.0	$C_3H_5^+$
40	5.4	4.3	5.3	5.5	
39	14.2	12.0	10.1	11.7	
32	24.1	10.4	27.7	27.4	
29	14.5	12.9	10.5	14.0	

Mass Spectrum 9: 2-(Bistrifluoromethylamino-oxy)-2,4,4-trimethylpentane,

$(CH_3)_2CCH_2C(CH_3)_3$, $C_8H_{17}R$, $\underline{M} = 281$
|
$ON(CF_3)_2$
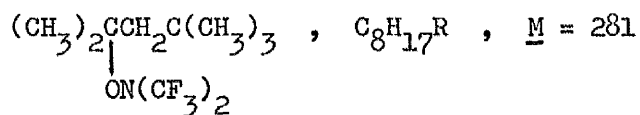
m/e	%	Ion	m/e	%	Ion
266	0.7	$C_7H_{14}R^+$	57	100.0	$C_4H_9^+$
238	1.0		56	6.7	
210	45.4	$C_3H_6R^+$	55	6.5	
150	2.1	$C_2F_5NOH^+$	43	23.5	$C_2H_3O^+$
113	4.1	$C_8H_{17}^+$	41	18.6	$C_3H_5^+$
71	2.8	$C_5H_{11}^+$	32	5.2	
69	8.0	CF_3^+	29	9.2	
58	20.7		28	31.8	

Mass Spectrum 10: 1,2-Bis(bistrifluoromethylamino-oxy)-2,4,4-

trimethylpentane, CH_2——$C(CH_3)CH_2C(CH_3)_3$, $C_8H_{16}R_2$, $\underline{M} = 448$
| |
$(CF_3)_3NO$ $ON(CF_3)_2$
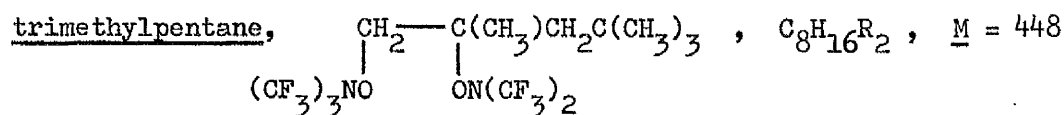
m/e	%	Ion	m/e	%	Ion
432	0.1	$C_7H_{12}R_2^+$	69	7.9	CF_3^+
376	1.6	$C_3H_4R_2^+$	58	6.8	
266	1.3	$C_7H_{14}R^+$	57	100.0	$C_4H_9^+$
210	6.8		56	4.3	
150	4.1	$C_2F_5NOH^+$	55	6.0	
112	1.9	$C_8H_{16}^+$	43	29.7	
71	4.4	$C_5H_{11}^+$	41	16.1	$C_3H_5^+$

Mass Spectrum 11:   1,2-Bis(bistrifluoromethylamino-oxy)-2-
(bistrifluoromethylamino-oxymethyl)-4,4-dimethylpentane,

$[(CF_3)_2NOCH_2]_2CCH_2C(CH_3)_3$, $C_8H_{15}R_3$, $\underline{M} = 615$
with $ON(CF_3)_2$
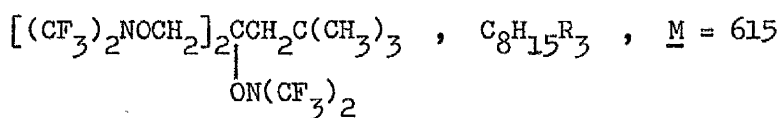
m/e	%	Ion	m/e	%	Ion
598	0.5	$C_7H_{10}R_3^+$	71	7.7	$C_5H_{11}^+$
46	0.1	$C_8H_{14}R_2^+$	69	12.3	CF_3^+
430	0.7		58	6.4	
376.5	0.4	$376 = C_3H_4R_2^+$	57	100.0	$C_4H_9^+$
210	5.4		55	7.1	
182	2.7	CH_2R^+	43	18.6	
150	4.3	$C_2F_5NOH^+$	41	14.0	$C_3H_5^+$
111	1.3	$C_8H_{15}^+$	32	10.1	
109	4.3		29	8.8	
95	4.2		28	57.7	
94	4.0				

Mass Spectrum 12:   Probably 2-(bistrifluoromethylamino-oxy)-3-methylbutane,

$(CH_3)_2CHCHCH_3$, $C_5H_{11}R$, $\underline{M} = 239$
with $ON(CF_3)_2$
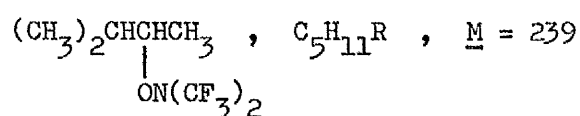
m/e	%	Ion	m/e	%	Ion
238	0.1	$C_5H_{10}R^+$	55	9.0	
224	1.1	$C_4H_8R^+$	44	7.9	
196	3.2	$C_2H_4R^+$	43	100.0	$C_2H_3O^+/C_3H_7^+$
150	5.6	$C_2F_5NOH^+$	41	21.5	$C_3H_5^+$
72	6.5		39	4.9	
71	44.7	$C_5H_{11}^+$	29	12.8	
69	8.8	CF_3^+	28	19.2	

Mass Spectrum 13:   2-(Bistrifluoromethylamino-oxy)-1-chloro-2-methyl-

propane , $(CH_3)_2CCH_2Cl$, C_4H_8ClR , $\underline{M}$ = 261(^{37}Cl)/259(^{35}Cl)

$ON(CF_3)_2$

m/e	%	Ion	m/e	%	Ion
246	2.1	$C_3H_5{}^{37}ClR^+$	55	66.9	$C_4H_7{}^+/C_3H_3O^+$
244	7.1	$C_3H_5{}^{35}ClR^+$	49	6.9	
210	43.3	$C_3H_6R^+$	43	100.0	$C_2H_3O^+$
150	18.2	$C_2F_5NOH^+$	41	15.0	$C_3H_5{}^+$
93	13.2	$C_4H_8{}^{37}Cl^+$	39	16.0	
92	5.2		32	8.2	
91	42.7	$C_4H_8{}^{35}Cl^+$	29	31.8	
69	12.2	$CF_3{}^+$	28	45.2	
63	11.6				
58	41.6	$C_3H_6O^+$			

Mass Spectrum 14:   1,2-Bis(bistrifluoromethylamino-oxy)-3-chloro-2-

methylpropane,

$$\begin{array}{cc} CH_2 & C(CH_3)CH_2Cl, \quad C_4H_7ClR_2 , \\ | & | \\ (CF_3)_2NO & ON(CF_3)_2 \end{array}$$
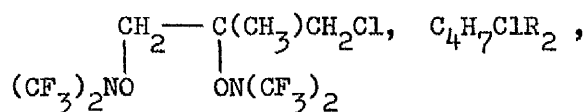
$$\underline{M} = 428(^{37}Cl)/426(^{35}Cl)$$

m/e	%	Ion	m/e	%	Ion
377	8.3	$C_3H_5R_2^+$	69	23.5	CF_3^+
260	2.9	$C_4H_7{}^{37}ClR^+$	63	5.7	
258	9.5	$C_4H_7{}^{35}ClR^+$	57	33.9	$C_3H_5O^+$
246	2.5	$C_3H_5{}^{37}ClR^+$	55	10.4	$C_4H_7^+$
244	8.8	$C_3H_6{}^{35}ClR^+$	53	6.7	
222	4.3		49	6.1	
196	4.5		44	6.5	
182	4.7	CH_2R^+	43	100.0	$C_2H_3O^+$
166	7.4		42	22.5	
150	15.4	$C_2F_5NOH^+$	41	34.7	$C_3H_5^+$
94	6.3		39	9.2	
78	5.6		32	15.1	
77	5.9		29	16.2	
75	5.7		28	71.8	
71	5.5				

Mass Spectra 15 and 16:   Bistrifluoromethylamino-oxy substituted

3-chloro-2-methylprop-1-enes, $C_4H_6ClON(CF_3)_2$, $\underline{M} = 259(^{37}Cl)/257(^{35}Cl)$

m/e	m.s. 15 %	m.s. 16 %	Ion
259	0.4		$C_4H_6{}^{37}ClR^+$
257	1.5	0.1	$C_4H_6{}^{35}ClR^+$
222		5.7	$C_4H_6R^+$
91	33.0	34.0	$C_4H_6{}^{37}Cl^+$
90	4.8	4.6	
89	<u>100.0</u>	<u>100.0</u>	$C_4H_6{}^{35}Cl^+$
77	1.4	1.9	$C_3H_4{}^{37}Cl$
75	4.2	3.6	$C_3H_4{}^{35}Cl$
69	11.6	13.4	$CF_3{}^+$
54	3.8	7.0	
53	77.0	81.1	$C_4H_5{}^+$
51	4.5	5.0	
49	4.3	5.8	
43	6.3	3.1	
41	10.9	11.9	$C_3H_5{}^+$
40	2.8	5.4	
39	17.6	21.7	
32	5.0	7.4	
29	4.7	5.9	

Mass Spectrum 17:   2-(Bistrifluoromethylamino-oxy)-1-bromo-2-methylpropane, $(CH_3)_2CCH_2Br$, C_4H_8BrR , $\underline{M}$ = 305(^{81}Br)/303(^{79}Br)

$\overset{|}{ON(CF_3)_2}$

m/e	%	Ion	m/e	%	Ion
304	0.1	$C_4H_7{}^{81}BrR^+$	93	4.4	
302	0.2	$C_4H_7{}^{79}BrR^+$	69	29.2	$CF_3{}^+$
290	12.7	$C_3H_5{}^{81}BrR^+$	58	35.6	$C_3H_6O^+$
288	13.1	$C_3H_5{}^{79}BrR^+$	57	5.8	
211	9.2		56	9.2	
210	<u>100.0</u>	$C_3H_6R^+$	55	74.0	$C_4H_7{}^+/C_3H_3O^+$
150	47.6	$C_2F_5NOH^+$	53	10.9	
138	7.4		43	81.2	$C_2H_3O^+$
137	66.9	$C_4H_8{}^{81}Br^+$	42	5.9	
136	8.2		41	25.2	$C_3H_5{}^+$
135	70.1	$C_4H_8{}^{79}Br^+$	39	19.5	
133	4.6		32	13.4	
109	6.4		29	25.3	
107	6.6		28	71.8	

Mass Spectrum 18: 1,2-Bis(bistrifluoromethylamino-oxy)-3-bromo-2-methylpropane,

$$CH_2-C(CH_3)CH_2Br \quad , \quad C_4H_7BrR_2 ,$$
$$(CF_3)_2NO \qquad ON(CF_3)_2$$
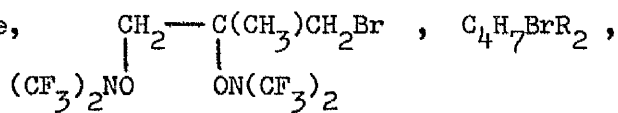
$$\underline{M} = 472(^{81}Br)/470(^{79}Br)$$

m/e	%	Ion	m/e	%	Ion
377	12.3	$C_3H_5R_2^+$	133	5.6	
305	4.1		121	8.2	
304	66.6	$C_4H_7{}^{81}BrR^+$	71	25.3	
303	4.6		69	45.3	CF_3^+
302	68.2	$C_4H_7{}^{79}BrR^+$	57	54.5	$C_3H_5O^+$
290	13.7	$C_3H_5{}^{81}BrR^+$	55	37.2	$C_4H_7^+$
288	14.0	$C_3H_5{}^{79}BrR^+$	53	8.8	
222	8.6		44	6.8	
196	6.7		43	100.0	$C_2H_3O^+$
182	6.2	CH_2R^+	42	28.3	
166	6.3		41	37.6	$C_3H_5^+$
152	8.7		39	15.0	
150	38.6	$C_2F_5NOH^+$	32	28.7	
136	5.2		29	24.0	

Mass spectrum 19:   2-(Bistrifluoromethylamino-oxy)-2-methylpentan-4-one,

$(CH_3)_2\overset{\underset{|}{ON(CF_3)_2}}{C}CH_2COCH_3$, $C_6H_{11}OR$, $\underline{M} = 267$
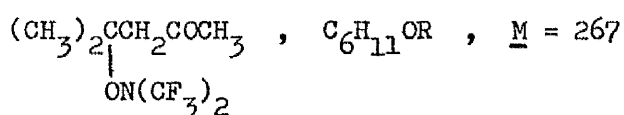
m/e	%	Ion	m/e	%	Ion
252	0.1	$C_5H_8OR^+$	69	7.5	CF_3^+
211	0.2		58	5.8	$C_3H_6O^+$
210	4.0	$C_3H_6R^+$	43	100.0	$C_2H_3O^+$
150	2.7	$C_2F_5NOH^+$	41	6.0	$C_3H_5^+$
99	13.9	$C_6H_{11}O^+$	28	11.8	
83	1.4	$C_6H_{11}^+$			

Mass spectrum 20:   1,2-Bis(bistrifluoromethylamino-oxy)-2-methylpentan-4-one,

$\underset{(CF_3)_2NO}{CH_2}\text{—}\underset{ON(CF_3)_2}{C}(CH_3)CH_2COCH_3$, $C_6H_{10}OR_2$, $\underline{M} = 434$
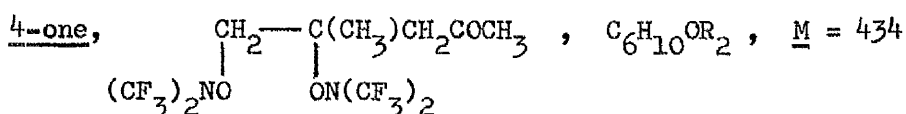
m/e	%	Ion	m/e	%	Ion
349	0.3		97	8.0	
282	0.5	$C_6H_{10}O_2R^+$	69	11.6	CF_3^+
266	0.9	$C_6H_{10}OR^+$	43	100.0	$C_2H_3O^+$
182	0.4	CH_2R^+	41	5.2	$C_3H_5^+$
150	1.7	$C_2F_5NOH^+$	29	4.2	

Mass spectrum 21:   2-(Bistrifluoromethylamino-oxy)-2-methylpropyl acetate,

$(CH_3)_2CCH_2COCCH_3$, $C_6H_{11}O_2R$, $\underline{M} = 283$
$\quad\quad |$
$\quad ON(CF_3)_2$
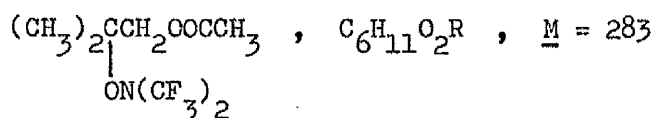
m/e	%	Ion	m/e	%	Ion
268	1.2	$C_5H_8O_2R^+$	55	9.1	$C_4H_7^+/C_3H_3O^+$
210	25.8	$C_3H_6R^+$	43	100.0	$C_2H_3O^+$
115	15.0	$C_6H_{11}O_2^+$	41	6.1	$C_3H_5^+$
69	6.5	CF_3^+	29	4.6	
58	15.5	$C_3H_6O^+$	28	14.4	

Mass spectrum 22:   1,2-Bis(bistrifluoromethylamino-oxy)-2-methylpropyl

acetate, $CH_2 \!\!-\!\! C(CH_3)CH_2COCCH_3$, $C_6H_{10}O_2R_2$, $\underline{M} = 450$
$\quad\quad\quad\quad\quad |\quad\quad\quad |$
$\quad\quad (CF_3)_2NO\quad ON(CF_3)_2$
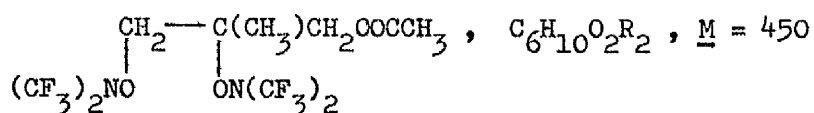
m/e	%	Ion	m/e	%	Ion
376.5	0.3	$377 = C_3H_5R_2^+$			
282	7.4	$C_6H_{10}O_2R^+$	41	8.3	$C_3H_5^+$
268	2.3	$C_5H_8O_2R^+$	32	5.4	
113	1.1	$C_6H_9O_2^+$	29	4.3	
69	8.2	CF_3^+	28	22.3	
43	100.0	$C_2H_3O^+$			

Mass Spectrum 23: Probably 3-(bistrifluoromethylamino-oxy)-2-methylpropyl

acetate , $(CH_3)_2CHCHOOCCH_3$, $C_6H_{11}O_2R$, $\underline{M} = 283$

$\quad\quad\quad\quad\quad$ |
$\quad\quad\quad\quad ON(CF_3)_2$

m/e	%	Ion	m/e	%	Ion
224	0.5	$C_4H_8R^+$	44	6.5	
115	1.4	$C_6H_{11}O_2^+$	43	100.0	$C_2H_3O^+$
73	13.1	$C_3H_5O_2^+$	41	14.6	$C_3H_5^+$
69	4.2	CF_3^+	40	6.2	
61	10.9		32	68.4	
56	38.1	$C_4H_8^+$	29	9.4	
55	7.3				

Mass Spectrum 24: 2-(Bistrifluoromethylamino-oxy)-2-methyl-1-

-nitropropane , $(CH_3)_2CCH_2NO_2$, $C_4H_8NO_2R$, $\underline{M} = 270$

$\quad\quad\quad\quad\quad$ |
$\quad\quad\quad\quad ON(CF_3)_2$

m/e	%	Ion	m/e	%	Ion
255	0.1	$C_3H_5NO_2R^+$	55	100.0	$C_3H_5N^+/C_4H_7^+$
224	1.9	$C_4H_8R^+$	53	5.1	
210	6.7	$C_3H_6R^+$	44	6.9	
150	13.8	$C_2F_5NOH^+$	43	74.4	$C_2H_3O^+$
102	1.6	$C_4H_8NO_2^+$	42	8.5	
72	17.3		41	61.7	$C_3H_5^+$
71	30.4		39	18.5	
69	25.6	CF_3^+	32	8.5	
58	13.8		30	17.3	
57	23.8		29	34.5	
56	36.8	$C_4H_8^+$	28	62.8	

Mass Spectrum 25:   Probably 1,2-bis(bistrifluoromethylamino-oxy)-2-

methyl-1-nitropropane , CH_2—$C(CH_3)CH_2NO_2$, $C_4H_7NO_2R_2$, $\underline{M}$ = 437

$(CF_3)_2NO$ $ON(CF_3)_2$

m/e	%	Ion	m/e	%	Ion
281	0.5		69	100.0	$CF_3^+/C_4H_7N^+$
269	1.9	$C_4H_7NO_2R^+$	61	11.4	
222	23.4		57	16.3	
182	7.0	CH_2R^+	56	4.9	
166	15.5		55	38.2	$C_4H_7^+/C_3H_3O^+$
150	12.7	$C_2F_5NOH^+$	53	5.2	
131	5.3		44	17.8	
114	4.7		43	61.2	$C_2H_3O^+$
100	18.5	$C_4H_6NO_2^+$	42	21.4	
96	9.4		41	62.8	$C_3H_5^+$
94	6.6		40	14.6	
81	4.4		39	19.4	
78	6.1		31	5.6	
72	8.2		30	36.7	
70	10.1		29	34.7	

<u>Mass Spectrum 26:</u>   <u>2-(Bistrifluoromethylamino-oxy)-1-iodo-2-methylpropane,</u>

$(CH_3)_2CCH_2I$, C_4H_8IR , $\underline{M} = 351$

$ON(CF_3)_2$
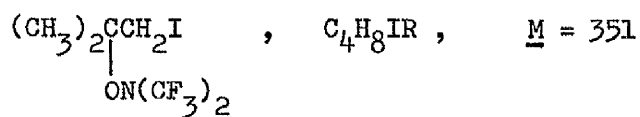
m/e	%	Ion	m/e	%	Ion
335.5	0.4	$336 = C_3H_5IR^+$	55	<u>100.0</u>	$C_4H_7^+/C_3H_3O^+$
303.5	1.1		53	8.1	
301.5	1.1		44	5.8	
210	1.4	$C_3H_6R^+$	43	27.4	$C_2H_3O^+$
183	39.3	$C_4H_8I^+$	42	5.7	
150	10.3	$C_2F_5NOH^+$	41	31.8	$C_3H_5^+$
81	6.8		40	6.2	
69	62.1	CF_3^+	39	23.9	
58	4.6		32	26.4	
57	5.4		29	34.5	
56	21.4	$C_4H_8^+$			

Mass Spectrum 27:   3-(Bistrifluoromethylamino-oxy)-1-bromo-3-

methylbutane, $(CH_3)_2CCH_2CH_2Br$, $C_5H_{10}BrR$, $\underline{M} = 319(^{81}Br)/317(^{79}Br)$

$ON(CF_3)_2$ (attached below the C)

m/e	%	Ion	m/e	%	Ion
318	1.6	$C_5H_9{}^{81}BrR^+$	69	87.5	$CF_3{}^+$
316	1.7	$C_5H_9{}^{79}BrR^+$	67	6.9	
304	2.6	$C_4H_7{}^{81}BrR^+$	58	33.8	$C_3H_6O^+$
302	2.7	$C_4H_7{}^{79}BrR^+$	55	10.4	
210	44.7	$C_3H_6R^+$	53	8.9	
151	27.5	$C_5H_{10}{}^{81}Br^+$	44	7.0	
150	22.1	$C_2F_5NOH^+$	43	100.0	$C_2H_3O^+$
149	28.6	$C_5H_{10}{}^{79}Br^+$	42	8.9	
109	6.0	$C_2H_4{}^{81}Br^+$	41	56.0	$C_3H_5{}^+$
107	6.8	$C_2H_4{}^{79}Br^+$	39	14.8	
85	4.6		32	6.2	
71	15.9		29	15.7	
70	6.6		28	40.4	

Mass Spectrum 28:   1,2-Bis(bistrifluoromethylamino-oxy)-4-bromo-2-

-methylbutane, CH_2—$C(CH_3)CH_2CH_2Br$, $C_5H_9BrR_2$,

(with substituents $(CF_3)_2NO$ and $ON(CF_3)_2$) $\underline{m}$ = 486(^{81}Br)/484(^{79}Br)
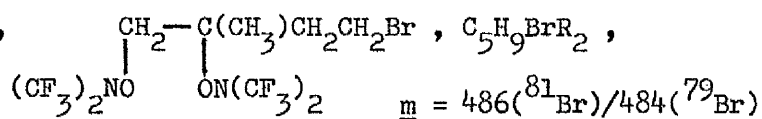
m/e	%	Ion	m/e	%	Ion
485	4.8	$C_5H_8{}^{81}BrR_2{}^+$	83	14.9	
483	5.3	$C_5H_8{}^{79}BrR_2{}^+$	82	7.0	
318	3.9	$C_5H_9{}^{81}BrR^+$	81	6.6	
316	5.1	$C_5H_9{}^{79}BrR^+$	78	9.0	
304	8.5	$C_4H_7{}^{81}BrR^+$	73	5.3	
302	9.3	$C_4H_7{}^{79}BrR^+$	71	12.9	
276	5.0		70	8.0	
274	5.1		69	100.0	$CF_3{}^+/C_5H_9{}^+$
206	6.2		67	20.5	
196	5.0		65	4.6	
182	30.0	CH_2R^+	59	11.8	
166	62.7		58	10.4	
151	6.0		57	19.9	
150	30.5	$C_2F_5NOH^+$	56	5.9	
149	7.4		55	51.3	$C_4H_7{}^+/C_3H_3O^+$
137	14.6		54	5.6	
135	20.4		53	22.2	
133	9.6		44	29.2	
123	6.4		43	86.5	$C_2H_3O^+$
121	8.0		42	12.6	
114	5.2		41	41.2	$C_3H_5{}^+$
109	22.7		40	9.0	
107	23.0		39	11.4	

Mass Spectrum 28 continued:

m/e	%	Ion	m/e	%	Ion
94	11.1		36	7.7	
91	5.2		32	81.7	
85	8.3				

Mass Spectrum 29:   3-(Bistrifluoromethylamino-oxy)-1-chloro-3-

-methylbutane, $(CH_3)_2CCH_2CH_2Cl$, $C_5H_{10}ClR$, $\underline{M}$ = 275(^{37}Cl)/273(^{35}Cl)

$\quad\quad\quad\quad\quad\quad\quad$ $ON(CF_3)_2$

m/e	%	Ion	m/e	%	Ion
272	0.4	$C_5H_9{}^{35}ClR^+$	58	19.8	$C_3H_6O^+$
260	2.2	$C_4H_7{}^{37}ClR^+$	55	7.9	
258	7.5	$C_4H_7{}^{35}ClR^+$	53	6.9	
210	28.1	$C_3H_6R^+$	44	8.3	
150	13.1	$C_2F_5NOH^+$	43	100.0	$C_2H_3O^+$
107	4.2	$C_5H_{10}{}^{37}Cl^+$	42	8.7	
105	13.6	$C_5H_{10}{}^{35}Cl$	41	51.1	$C_3H_5{}^+$
71	9.6		39	10.6	
69	84.1	$CF_3{}^+$	32	14.8	
67	9.7		29	11.3	
63	7.3		28	63.5	

Mass Spectrum 30:   1,2-Bis(bistrifluoromethylamino-oxy)-4-chloro-2-

-methylbutane, $CH_2-C(CH_3)CH_2CH_2Cl$, $C_5H_9ClR_2$,

$(CF_3)_2NO$ $ON(CF_3)_2$
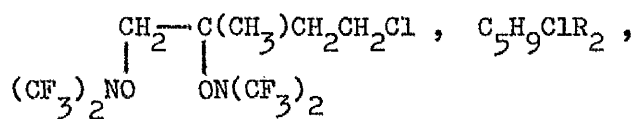
$\underline{M} = 442(^{37}Cl)/440(^{35}Cl)$

m/e	%	Ion	m/e	%	Ion
378	2.2	$C_3H_6R_2^+$	65	4.4	
274	3.3	$C_5H_9{}^{37}ClR^+$	63	8.5	
272	10.6	$C_5H_9{}^{35}ClR^+$	58	25.7	
260	4.3	$C_4H_7{}^{37}ClR^+$	57	38.9	$C_3H_5O^+$
258	13.8	$C_4H_7{}^{35}ClR^+$	56	8.3	
196	5.7		55	28.6	$C_4H_7^+$
166	4.6		53	9.0	
150	16.1	$C_2F_5NOH^+$	44	12.6	
120	5.8		43	100.0	$C_2H_3O^+$
91	7.7		42	4.9	
85	7.9		41	24.8	$C_3H_5^+$
84	5.5		39	8.4	
71	12.6		32	23.6	
69	40.8	CF_3^+	29	17.4	
67	11.0		28	99.5	

Mass Spectrum 31:   3-(Bistrifluoromethylamino-oxy)-1-iodo-3-methylbutane

$(CH_3)_2CCH_2CH_2I$, $C_5H_{10}IR$, $\underline{M} = 365$

$\overset{|}{O}N(CF_3)_2$
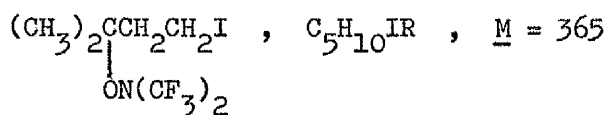
m/e	%	Ion	m/e	%	Ion
364	1.6	$C_5H_9IR^+$	67	7.6	
362	3.3		58	18.8	$C_3H_6O^+$
210	24.4	$C_3H_6R^+$	55	14.5	
197	27.0	$C_5H_{10}I^+$	53	6.8	
155	5.1	C_2H_4I	43	98.3	$C_2H_3O^+$
151	10.8		42	7.6	
150	12.4	C_2F_5NOH	41	70.3	$C_3H_5^+$
149	11.3		39	13.5	
105	4.5		32	17.7	
71	7.9		29	13.8	
70	6.0		28	83.7	
69	100.0	CF_3^+			

Mass Spectrum 32:   1,2-Bis(bistrifluoromethylamino-oxy)-4-iodo-2-

-methylbutane, CH_2—$C(CH_3)CH_2CH_2I$, $C_5H_9IR_2$, $\underline{M}$ = 532

$(CF_3)_2NO$ $ON(CF_3)_2$
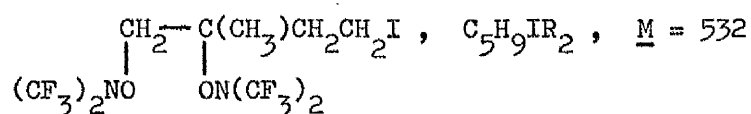
m/e	%	Ion	m/e	%	Ion
406	1.7		69	44.7	CF_3^+
405	18.0	$C_5H_9R_2^+$	67	17.6	
364	5.9	$C_5H_9IR^+$	58	16.6	
318	11.9		57	32.1	$C_3H_5O^+$
316	12.3		56	6.7	
304	5.3		55	30.4	$C_4H_7^+$
302	5.3		53	9.9	
272	5.2		44	7.0	
236	7.6		43	100.0	$C_2H_3O^+$
196	9.1	$C_5H_9I^+$	42	4.7	
182	4.0	CH_2R^+	41	32.6	$C_3H_5^+$
166	8.1		40	4.8	
155	16.8	$C_2H_4I^+$	39	10.0	
150	17.9	$C_2F_5NOH^+$	32	36.2	
85	12.0		29	19.0	
84	7.3				
71	13.0				

Mass Spectrum 33:   2-(Bistrifluoromethylamino-oxycarbonyl)propane,

$(CH_3)_2CHC=O$, C_4H_7OR , $\underline{M} = 239$
　　　|
　　$ON(CF_3)_2$
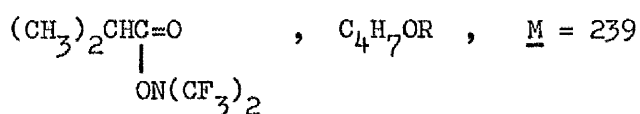
m/e	%	Ion	m/e	%	Ion
220	0.7	$C_6H_7F_5NO_2{}^+$(M-F)	43	<u>100.0</u>	$C_2H_3O^+/C_3H_7{}^+$
150	3.4	$C_2F_5NOH^+$	42	6.6	
133	1.6	$C_2F_5N^+$	41	35.3	$C_3H_5{}^+$
114	2.4	$C_2F_4N^+$	39	8.6	
71	58.9	$C_4H_7O^+$	32	11.9	
69	40.9	$CF_3{}^+$	29	5.1	
44	7.2		28	61.0	

Mass Spectrum 34:   2-(Bistrifluoromethylamino-oxy)-2-methylpropan-1-ol,

$(CH_3)_2CCH_2OH$, $C_4H_8(OH)R$, $\underline{M} = 241$
　　　|
　　$ON(CF_3)_2$
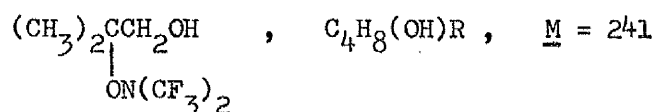
m/e	%	Ion	m/e	%	Ion
226	1.1	$C_3H_5(OH)R^+$	44	7.1	
210	50.8	$C_3H_6R^+$	43	<u>100.0</u>	$C_2H_3O^+$
150	20.8	$C_2F_5NOH^+$	42	6.9	
73	36.2	$C_4H_8OH^+$	41	20.8	$C_3H_5{}^+$
69	35.7	$CF_3{}^+$	39	10.0	
58	39.7	$C_3H_6O^+$	32	26.3	
57	7.9		31	23.9	
55	22.6	$C_4H_7{}^+/C_3H_3O^+$	29	24.0	
45	11.1				

Mass Spectrum 35:   1-(Bistrifluoromethylamino-oxycarbonyl)-2--methylpropane, $(CH_3)_2CHCH_2\underset{\underset{ON(CF_3)_2}{|}}{C}=O$, C_5H_9OR, $\underline{M} = 253$

m/e	%	Ion	m/e	%	Ion
238	0.6	$C_4H_6OR^+$	58	6.5	
211	8.0		57	92.7	$C_4H_9^+$
196	8.4	COR^+	56	7.8	
191	4.7		55	15.2	
150	2.6	$C_2F_5NOH^+$	44	12.5	
86	5.3		43	97.2	$C_3H_7^+$
85	100.0	$C_5H_9O^+$	42	17.0	
83	5.6		41	80.8	$C_3H_5^+$
72	7.8		40	5.8	
69	44.3	CF_3^+	39	21.1	
59	17.9		32	25.1	

Mass Spectrum 36:   3-(Bistrifluoromethylamino-oxy)-3-methylpentan-1-ol,

$(CH_3)_2CCH_2CH_2OH$, $C_5H_{10}(OH)R$, $\underline{M}$ = 255

$\overset{|}{O}N(CF_3)_2$
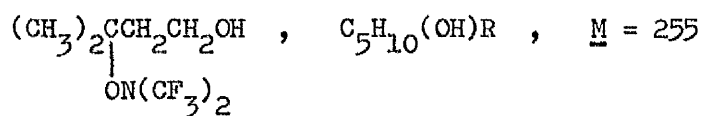
m/e	%	Ion	m/e	%	Ion
254	0.2	$C_5H_{10}OR^+$	56	7.9	
240	1.5	$C_4H_7(OH)R^+$	55	11.5	
210	23.6	$C_3H_6R^+$	45	12.4	
150	7.5	$C_2F_5NOH^+$	44	5.8	
87	10.6	$C_5H_{10}OH^+$	43	92.1	$C_2H_3O^+$
85	7.5		42	11.0	
71	7.7		41	84.0	$C_3H_5^+$
70	10.0	$C_5H_{10}^+$	39	10.7	
69	100.0	$CF_3^+/C_5H_9^+$	32	15.4	
59	4.5		31	53.2	
58	27.7	$C_3H_6O^+$	29	28.9	
57	18.8		28	75.7	

Mass Spectrum 37:   1-(Bistrifluoromethylamino-oxy)-3-methyl-1-

-phenylbutane, $(CH_3)_2CHCH_2CHC_6H_5$, $C_{11}H_{15}R$, $\underline{M}$ = 315

$\qquad\qquad\qquad\qquad\quad \overset{|}{O}N(CF_3)_2$

The spectrum also shows peaks for isopentylbenzene ($C_{11}H_{16}$, $\underline{M}$ = 148);

the two peaks overlap in the g.l.c. trace.

m/e	%	Ion	m/e	%	Ion
314	1.5	$C_{11}H_{14}R^+$	79	7.6	
258	15.2	$C_7H_6R^+$	78	12.1	
148	17.1		77	23.2	$C_6H_5^+$
147	54.3	$C_{11}H_{15}^+$	69	19.2	CF_3^+
131	12.3	$C_{10}H_{11}^+$	65	15.2	
106	15.7		57	18.5	
105	76.9	$C_8H_9^+$	51	12.5	
104	15.9		43	32.5	$C_2H_3O^+$
103	8.3		41	30.4	
93	7.0		39	16.4	
92	65.0		32	8.0	
91	100.0	$C_7H_7^+$			

Mass Spectrum 38:   N-[2-(bistrifluoromethylamino-oxy)-2-methylpropylidene]
-isobutylamine, $(CH_3)_2CCH=NCH_2CH(CH_3)_2$, $C_8H_{16}NR$, $\underline{M} = 294$
$\quad\quad\quad\quad\quad\quad\quad\quad |$
$\quad\quad\quad\quad\quad\quad ON(CF_3)_2$

m/e	%	Ion	m/e	%	Ion
251	1.5	$C_5H_9NR^+$	58	23.0	
210	14.1	$C_3H_6R^+$	57	100.0	$C_4H_9^+$
126	10.7	$C_8H_{16}N^+$	55	8.3	
86	8.5		44	12.0	
84	36.2	$C_5H_{10}N^+$	43	35.8	$C_2H_3O^+/C_3H_7^+$
83	14.6		42	9.8	
82	9.4		41	36.4	$C_3H_5^+$
70	11.0		39	7.6	
69	16.7	CF_3^+	32	22.2	
68	5.1		29	22.6	
59	4.6		28	96.2	

Mass Spectrum 39:   2-(Bistrifluoromethylamino-oxy)-2-methylpropylamine,

$(CH_3)_2CCH_2NH_2$, $C_4H_{10}NR$, $\underline{M} = 240$
$\quad\quad |$
$\quad\;\; ON(CF_3)_2$
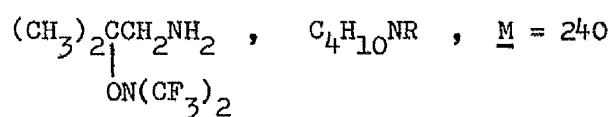
m/e	%	Ion	m/e	%	Ion
225	1.9		56	27.1	
224	27.2	$C_4H_8R^+$	55	27.4	
210	1.7	$C_3H_6R^+$	44	33.9	
150	3.6	$C_2F_5NOH^+$	43	77.9	$C_2H_3O^+$
81	7.3		42	18.5	
72	34.8	$C_4H_{10}N^+$	41	100.0	$C_3H_5^+$
69	62.5	CF_3^+	40	25.0	
68	4.5		39	30.5	
58	11.1		30	58.7	
57	82.7		29	76.1	

Mass Spectrum 40: N-[2-(bistrifluoromethylamino-oxy)-2-methylpropylidene]-2'-(bistrifluoromethylamino-oxy)-2'-methylpropylamine,

$(CH_3)_2CCH=\!\!=\!\!NCH_2C(CH_3)_2$, $C_8H_{15}NR_2$, $\underline{M} = 461$
with $ON(CF_3)_2$ $ON(CF_3)_2$
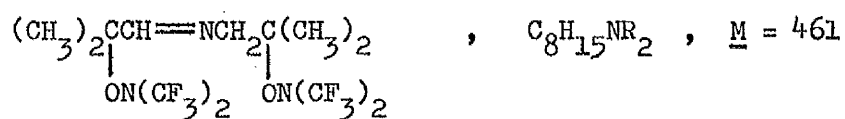
m/e	%	Ion	m/e	%	Ion
446	0.4	$C_7H_{12}NR_2{}^+$	71	37.7	$C_4H_7O^+$
294	2.2		70	27.0	
293	16.5	$C_8H_{15}NR^+$	69	29.9	$CF_3{}^+$
274	4.9		68	7.4	
251	48.7	$C_5H_9NR^+$	59	7.0	
224	7.1		58	33.0	$C_3H_6O^+$
210	27.7	$C_3H_6R^+$	57	19.5	
140	11.6		56	11.8	
125	31.6	$C_8H_{15}N^+$	55	23.3	
124	5.0		44	10.6	
110	6.4		43	100.0	$C_2H_3O^+$
99	33.2		42	12.1	
98	25.2		41	23.7	$C_3H_5{}^+$
84	28.0		40	6.9	
83	45.8		39	8.8	
82	38.0		32	54.0	
72	28.8		29	14.1	

Mass Spectra 41(a) and (b):

(a) <u>N-(1-hydroxy-2-methylpropylidene)-isobutylamine</u>,

$(CH_3)_2CHC = NCH_2CH(CH_3)_2$, $C_8H_{17}NO$, $\underline{M} = 143$
|
OH
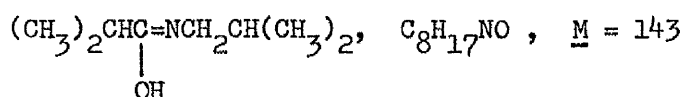
(b) <u>N-isobutyl-2-methylpropanamide</u>, $(CH_3)_2CHCONHCH_2CHMe_2$,

$C_8H_{17}NO$, $\underline{M} = 143$

m/e	% (a)	% (b)	Ion	m/e	% (a)	% (b)	Ion
144	3.8	5.7		68	6.5	1.5	
143	34.5	35.8	$C_8H_{17}NO^+$	58	30.1	35.5	
128	20.8	16.9	$C_7H_{14}NO^+$	57	62.4	79.9	$C_4H_9^+$
101	4.7	6.7		56	19.8	18.2	
100	19.1	26.4	$C_5H_{10}NO^+$	55	18.3	11.2	
98	5.5			44	35.1	17.8	
97	5.1			43	<u>100.0</u>	<u>100.0</u>	$C_3H_7^+$
95	5.6			42	21.2	18.2	
88	46.1	63.5		41	63.5	67.8	$C_3H_5^+$
86	6.1	5.4		40	12.3	5.7	
83	4.3			39	17.0	22.9	
81	7.0			32	66.5	5.0	
73	9.4	9.3		30	59.8	82.9	
72	64.4	74.0	$C_4H_{10}N^+$	29	29.4	40.6	
71	82.3	94.8	$C_4H_7O^+$				
70	9.4	6.5					
69	28.1	2.7					

Mass Spectrum 42: N^1-methyl-N^1-phenyl-N^2-(trifluoromethyl)-

-fluoroformamidine, $C_6H_5(CH_3)NCF=NCF_3$, $C_9H_8N_2F_4$, $\underline{M} = 220$

m/e	%	Ion	m/e	%	Ion
221	4.1		69	25.0	CF_3^+
220	50.5	$C_9H_8N_2F_4^+$	65	4.9	
219	73.6	$C_9H_7N_2F_4^+$	64	5.1	
201	8.0	$C_9H_8N_2F_3^+$	60	57.4	
181	5.8		52	5.9	
150	6.5		51	28.0	
106	19.7	$C_7H_8N^+$	50	9.4	
105	14.2		44	100.0	$C_2H_6N^+$
104	17.2		40	20.3	
96	9.9		39	9.4	
91	14.5	$C_6H_5N^+$	38	10.8	
85	6.8		36	29.2	
83	10.1	CF_3N^+	31	5.5	
78	9.2		29	11.2	
77	40.9	$C_6H_5^+$			

Mass Spectrum 43: N^1-ethyl-N^1-phenyl-N^2-(trifluoromethyl)--fluoroformamidine, $C_6H_5(CH_3CH_2)NCF=NCF_3$, $C_{10}H_{10}N_2F_4$, $\underline{M} = 234$

m/e	%	Ion	m/e	%	Ion
235	9.0		85	7.9	
234	84.3	$C_{10}H_{10}N_2F_4^+$	83	9.9	CF_3N^+
233	42.8	$C_{10}H_9N_2F_4^+$	78	11.9	
219	30.5	$C_9H_7N_2F_4^+$	77	100.0	$C_6H_5^+$
215	14.3	$C_{10}H_{10}N_2F_3^+$	74	21.5	
207	6.5		69	36.2	CF_3^+
206	27.4		65	12.0	
205	12.8	$C_8H_5N_2F_4^+$	64	9.6	
199	9.2		63	5.5	
186	34.2	$C_8H_5N_2F_3^+$	52	6.4	
167	7.2		51	37.0	
136	8.8		50	10.8	
123	7.3		46	7.8	
122	74.6		44	94.9	
120	33.0	$C_8H_{10}N^+$	42	7.9	
119	30.2		41	6.4	
118	13.6		40	18.6	
117	6.2		39	10.4	
105	11.4		38	13.4	
104	33.2		36	36.6	
96	13.0		31	7.2	
91	11.4	$C_6H_5N^+$	29	38.6	

Mass Spectrum 45: N^1-benzyl-N^1-methyl-N^2-(trifluoromethyl)-
-fluoroformamidine , $C_6H_5CH_2(CH_3)NCF=NCF_3$, $C_{10}H_{10}N_2F_4$, $\underline{M} = 234$

m/e	%	Ion	m/e	%	Ion
235	8.7		92	10.7	
234	70.2	$C_{10}H_{10}N_2F_4{}^+$	91	100.0	$C_7H_7{}^+$
233	11.6		90	5.0	
219	28.9	$C_9H_7N_2F_4{}^+$	89	9.1	
215	3.3	$C_{10}H_{10}N_2F_3{}^+$	78	3.9	
213	6.3		77	8.4	$C_6H_5{}^+$
199	9.2		69	8.7	$CF_3{}^+$
165	4.0	$C_9H_{10}N_2F^+$	65	20.6	
150	4.4		63	5.9	
149	11.3		60	13.5	
120	34.1	$C_8H_{10}N^+$	51	8.5	
118	7.0		42	9.1	
109	7.0		39	8.8	
105	5.7		28	22.2	
104	7.1				

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