POLYFLUOROAROMATIC AZO-COMPOUNDS

AND SOME RELATED HETEROCYCLES

by

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This thesis is submitted in part fulfilment of the requirements for the degree of Doctor of Philosophy in the University of Manchester.

Unless otherwise stated, the work described is that of the author, and has not been previously submitted, in whole or in part, at this or any other University.

(J.E.G. Kemp)

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The author studied at the University of Bristol from 1960 until 1963, graduating in the Honours School of Chemistry [Class II, Division (ii)].

Between October 1963 and October 1966 the author has been carrying out research in the Department of Chemistry of the Faculty of Technology in the University of Manchester, under the direction of Prof. R.N. Haszeldine and Dr. J.M. Birchall.

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SUMMARY

Decafluoroazobenzene and related compounds have been prepared by the oxidation of highly fluorinated anilines with either bleaching powder in refluxing carbon tetrachloride (yields 17-51%) or lead tetra-acetate in refluxing benzene (yields 42-48%); the latter procedure yielded fluorinated phenazines (18-28%) as by-products. The azo-compounds are oxidized quantitatively to azoxy-compounds by peroxytrifluoroacetic acid; the phenazines with the same reagent give tars. Hydriodic acid cleaves the azoxy- and azo-compounds to anilines in good yields, and reduces the phenazines to very readily-oxidized dihydro-derivatives. Decafluoroazobenzene and the azoxy-compound are reduced in good yields by zinc and ammonium chloride to the hydrazo-compound.

Decafluoroazobenzene reacts easily with nucleophiles in the 4- and 4'-positions; the 4H,4'H-compound reacts in the 2-position. Hydroxide ion and ammonia give only mono-substituted products, and there is some evidence that a little 2-substitution occurs also in the reaction between decafluoroazobenzene and ammonia. Decafluoro-azobenzene reacts with methoxide and ethoxide ions to give both mono- and di-substituted products, which can be separated easily by chromatography on alumina; the decafluoro-azo-compound reacts with one mole of thiophenoxide ion to give mainly the 4,4'-di-substituted product and starting material - the mono-substituted product can be isolated, but only in low yield. Decafluoroazobenzene is reduced by hydrosulphide ion and by hydrazine, but substitution occurs as well,

and no products have been characterized from these complex reactions.

The substituted azo-compounds are cleaved more readily by hydriodic acid than is the parent decafluoroazobenzene; the dialkoxy--derivatives give almost quantitative yields of alkyl iodide and 4-aminotetrafluorophenol - this amino-phenol is produced also, along with pentafluoroaniline, on reduction of the monohydroxy-azo-compound. 4-Aminononafluoroazobenzene may be reduced to pentafluoroaniline and tetrafluoro-p-phenylenediamine. This diamine, and the aforementioned amino-phenol, are oxidized by warm nitric acid to give good yields of tetrafluorobenzoquinone.

4,4'-Dithiophenoxyoctafluoroazobenzene, in contrast with the alkoxy-azo-compounds, is cleaved by hydriodic acid to give fair yields of diphenyl disulphide and 4H-tetrafluoroaniline, rather than the amino-thiol.

The reactions of the azoxy-compounds with nucleophiles parallel closely those of pentafluoronitrobenzene; that is, substitution occurs in the ring adjacent to the nitrogen bearing the oxygen atom, and is ortho-para; in the reaction with ethanolic ammonia the ortho/para ratio is 2. The azoxy-compounds give 1-(phenylamino)-benzotriazoles with hydrazine in yields of 9-37%, and this reaction has been used to establish the position of the oxygen atom in the asymmetric azoxy-compounds. Perfluoro-1-(phenylamino)benzotriazole reacts with lead tetra-acetate to give an unresolved mixture of azo-compounds, and is cleaved slowly by hydriodic acid to give pentafluoroaniline (84%) and tetrafluorobenzotriazole (4%).

This last compound may also be obtained by diazotization of the o-diamine, and (quantitatively) by hydriodic acid reduction of tetrafluorobenzotriazol-1-ol, which has been made (14% yield) by the reaction of pentafluoronitrobenzene with hydrazine. Tetrafluorobenzotriazole may be acetylated in the 1-position, but is otherwise resistant to electrophilic substitution.

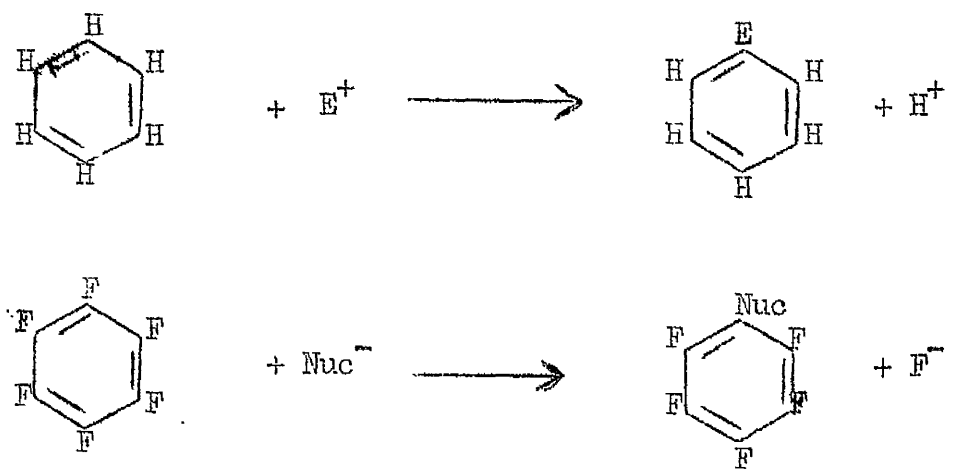
Diazotization of tetrafluoroanthranilic acid leads to loss of fluorine to give trifluorobenzenediazonium-2-oxide-6-carboxylic acid, which on reduction gives 2,3,4-trifluoro-5-hydroxybenzoic acid.

Thirty three new polyfluoroaromatic compounds have been fully characterized.

CONTENTS

INTRODUCTION

The general chemistry of azo-compounds has not proved to be very relevant to the work described in this thesis and will not be discussed in this introduction, which is concerned solely with the chemistry of aromatic fluorine compounds. A brief survey is presented of the more important aspects of the field; in addition, most of the reported reactions of polyfluoro-aromatic compounds with nucleophiles are presented in tabular form, and a brief discussion of the theoretical aspects of these reactions is also included. Nucleophilic reactions are as important to hexafluorobenzene as electrophilic reactions are in the benzene series, and represent a large proportion of the work described in this thesis:



Now that many highly fluorinated aromatic compounds (including all but one of the starting materials for the research described in this thesis) are available commercially, a satisfactory background to this work need not include an account

of their preparation. Several reviews are available, and the preparation of polyfluoroaromatic compounds has been summarized in several recent theses produced in this Department.[1-5]

The Physical Properties of Polyfluoroaromatic Compounds.

Perfluoroaromatic compounds have molecular weights and specific gravities of about twice those of their hydrocarbon analogues, yet in some of their physical properties they resemble closely the corresponding hydrocarbons. For example, they often have closely similar boiling points - the higher molecular weights being offset by extremely low van der Waals interactions. However, the partially fluorinated benzenes are all less volatile, presumably owing to the relatively strong interactions between hydrogen and the strongly electronegative fluorine. Benzene and hexafluorobenzene are compared in Table 1.

The Reactions of Highly Fluorinated Aromatic Compounds with Electrophiles.

No-one has yet succeeded in displacing an F^+ cation from hexafluorobenzene. The displacement of H^+ from pentafluorobenzene can be achieved by sulphonation[7] in oleum at 15°, and by bromination[8] or iodination[8] in oleum at 60°. The nitration of pentafluorobenzene takes place only in the most reactive medium known, nitric acid in anhydrous hydrogen fluoride, and proceeds at room temperature[9]. Nitration of 1,2,3,4-tetrafluorobenzene followed by reduction provides the best route to 2H-tetrafluoroaniline and related compounds.[10]

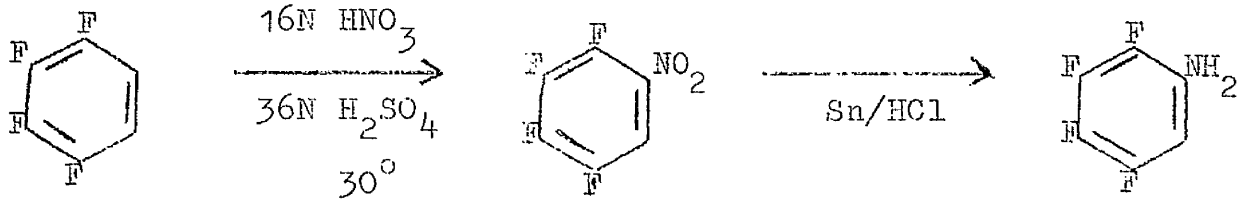
(to p.4)

Table 1

Comparison of Benzene and Hexafluorobenzene.[2]

Property	Benzene, C_6H_6	C_6F_6
Molecular weight	78.1	186.1
Boiling point, °C.	80.10	80.26
Melting point, °C.	5.51	5.2
Specific gravity	0.879	1.613
Viscosity at 25° in C.P.	0.608	0.903
Surface tension, dyne/cm.	28.88	22.6
Dielectric constant	2.28	2.07
Ultra-violet spectrum[6], mμ/EtOH		λ_{max} 230, ε 770
	λ_{max} 255, ε 160	λ_{inf} 250-255
Refractive index[6], n_D^{18}	1.5014 (n_D^{20})	1.3746
Susceptibility to substitution	Electrophiles	Nucleophiles
Flammability	Yes	No
Radiation stability	Good	Good
Thermal stability T_D, °C.	600	>650, <850

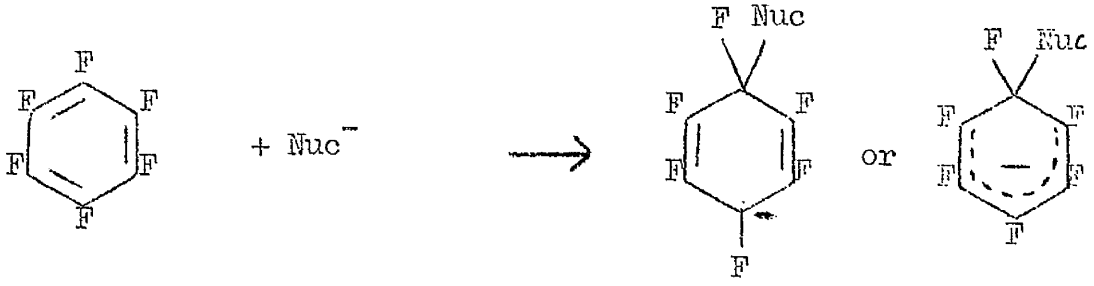
(from p.2)



Bromination and nitration of the tetrafluoroanilines is achieved more easily[11] (see also p. 47).

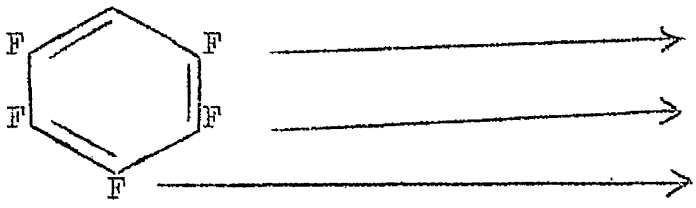
The Reactions of Highly Fluorinated Aromatic Compounds with Nucleophiles.

Aromatic nucleophilic substitution reactions may proceed via any of three mechanisms: a few are unimolecular and show first-order kinetics, the best-known examples being the decompositions of diazonium ions, and some (again, relatively few) nucleophilic reactions proceed via a benzyne intermediate.[12] The great majority, however, show second order kinetics, and only these reactions, which are bimolecular, are discussed here, for there is no reason to believe that any other mechanisms were involved in any of the nucleophilic reactions described herein. These bimolecular reactions are generally believed to proceed by the addition of the nucleophile across a π-bond to form an intermediate of the following type.[12]



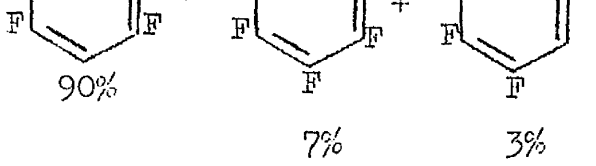
Fluorine as a substituent on the benzene ring is classified as a -I + M group, which means that it withdraws electrons inductively, but donates them mesomerically. The two effects are superimposed, and the expectation (based partly on simple electronic theory, partly by analogy with chlorine, and, increasingly, on experimental evidence) is that in nucleophilic substitution reactions, fluorine has little effect on the rate of displacement of a substituent *para* to it, is moderately activating from the *ortho* position, andis relatively highly activating from the *meta* position (where the +M effect does not operate).[13]

The activation pattern in highly fluorinated benzenes can be predicted by assuming that the electronic effects of successive replacement of hydrogen by fluorine are additive, and the justification for this assumption is provided by the accuracy of the predictions that follow. Consider pentafluorobenzene. Each fluorine atom is potentially capable of being displaced as the anion, and each fluorine atom will have an activating effect on every other fluorine atom in the molecule - the extent of this activation depending on the particular *ortho*, *meta*, or *para* relationship. These effects may be shown as follows:



Activation by:	meta-F	ortho-F	para-F
→	2	1	1
→	1	2	1
→	2	2	

Assuming that activation is in the expected order meta > > ortho > para, it is seen that the fluorine atom para to the hydrogen atom is not only the most labile one in the molecule, but is highly activated compared to that in fluorobenzene. The ortho position will be only slightly less activated, and some ortho substitution is observed in most of the nucleophilic reactions of pentafluorobenzene, for example:[14]

$C_6F_5H + H^-$ (i.e. $LiAlH_4$) ⟶  + +

90% 7% 3%

A similar pattern is observed for most pentafluorophenyl compounds, and is altered only by those substituents (e.g. NH_2)[15] whose deactivating effect is sufficiently strong to overcome the activating effect of 2 meta + 2 ortho fluorine atoms, or by those substituents (e.g. NO_2)[16] which exert a powerful activating effect on a position other than the para position:

$$C_6F_5.NH_2 \xrightarrow{NaOMe} \begin{cases} o\text{-}MeO.C_6F_4.NH_2 & (5\%) \\ m\text{-}MeO.C_6F_4.NH_2 & (79\%) \\ p\text{-}MeO.C_6F_4.NH_2 & (16\%) \end{cases}$$

$$C_6F_5.NO_2 \xrightarrow[ether]{NaOMe} o\text{-}MeO.C_6F_4.NO_2 (50\%) + p\text{-}MeO.C_6F_4.NO_2 (50\%)$$

Substituent effects on orientation in fluoroaromatic compounds are illustrated in the table below; the discussion section includes also several references to reaction rates and solvent effects.

A very recent paper by Ho and Miller discusses the reactivity of highly fluorinated compounds in the same way as the above pages,[13] and includes much kinetic data on all the important pentafluorophenyl derivatives except the very interesting nitro-compound. A slightly earlier paper by Burdon[17] on reactivity and orientation in pentafluorophenyl compounds is somewhat unorthodox, but is important in making a clear distinction between effects due to variations in ground state stabilities and those in the transition states of nucleophilic reactions.

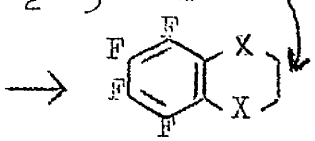
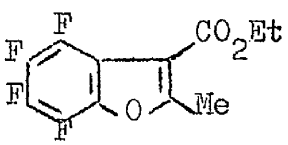
Table 2.

Nucleophilic Substition in Aromatic Fluorocarbons.

Substrate	Nucleophile	o	m	p	Reference
C_6F_6*	NH_3;$NaNH_2$;$MeNH_2$	monosubstitution			18, 19
"	C_6F_5.NHNa	"			20, 21
"	$N_2H_4.H_2O$	"			22
"	NaOMe	"			19, 33
"	NH_4OH	"			23
"	NaSH/py	"			24, 25
"	C_6F_5.SK	polymer			24
"	n-BuLi,MeLi	monosubstitution			26
"	CH_3.CH:CHLi	"			27

* Reactions in which disubstitution occurs readily are listed under C_6F_6; where forcing conditions are required, under C_6F_5.Nuc.

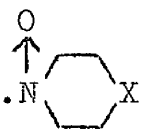
(continued)

Substrate	Nucleophile	o	m	p	Reference
C_6F_6	EtOK;KOH/t-BuOH	monosubstitution			28
"	$LiAlH_4$(replaces F by H); C_6F_5OK		"		19
"	$C_6H_5.CH_2.ONa$/t-BuOH; $C_6H_5.ONa$/DMF		"		19
"	KOH aq.; RLi; Alkenyl Li		"		19
"	$HO.CH_2.CH_2.ONa$; $HO.CH_2.CH_2.NH_2$	" then K_2CO_3/DMF			29
"	$H_2N.CH_2.CH_2.NH_2$	→			29
"	$HO.CH_2.CH_2.SNa$	1,4-disubstitution			29
"	$HO.CH_2.CH_2.ONa$		"		30
		mono-	m-di	p-di	
"	N_2H_4 anhydrous/dioxan	24	12.5	12.5	31
"	" /THF	32	0	35	31
"	$CH_3.CO.CHNa.CO_2Et$				32
		o	m	p	
C_6F_5H	NH_3; $N_2H_4.H_2O$			+	18
"	$LiAlH_4$	7	3	90	14
"	NaSH			+	24, 25
"	NaOMe			+	7
"	C_6F_5SK; p-HC_6F_4SK			+	24

(continued)

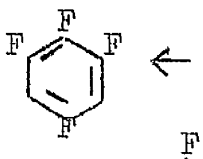
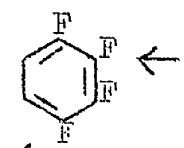
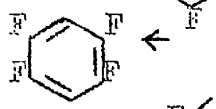
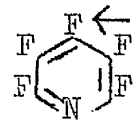
Substrate	Nucleophile	o	m	p	Reference
C_6F_5X					
X = Cl, Br, I	KOH/t-BuOH; KOH/py.			+	19, 34
Br, I	$NaNH_2$			+	19
I	$N_2H_4.H_2O$			+	35
Cl	$LiAlH_4$; NH_3; $N_2H_4.H_2O$	~25	~5	~70	36
Cl	CsF/sulfolan	replacement of Cl by F			37
Br	CuCN; CuCl; $CuSC_6F_5$/DMF	" " " by nucleophile			38
		o	m	p	
$C_6F_5.NH_2$	NH_3		+		39
"	$N_2H_4.H_2O$		+		1
"	NH_3; $MeNH_2$; Me_2NH	~0	~88	~12	15
"	NaOMe	5	79	16	15
$C_6F_5.NHMe$	NH_3	0	40	60	15
"	$MeNH_2$	0	60	40	15
"	Me_2NH	0	52	48	15
"	NaOMe	5	43	52	15
$C_6F_5.NMe_2$	NH_3	0	7	93	15
"	$MeNH_2$	0	6	94	15
"	Me_2NH	3	5	92	15
"	NaOMe	1	2	97	15
$C_6F_5.OMe$	NaOMe; NaNHMe	40	40	10	17

(continued)

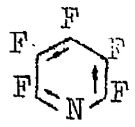
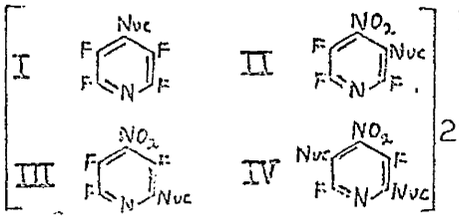
Substrate	Nucleophile	o	m	p	Reference
$C_6F_5.OH$	KOH aq., autoclave		+		40
$C_6F_5CO_2H$	NaOMe; NaSMe			+	41
"	$MeNH_2$*	40		60	41
"	Me_2NH*	57		43	41
$C_6F_5.NO_2$	NaOMe/MeOH	8		92	16
"	" /MeOH, 3.8% + Et_2O, 96.2%	50		50	16
"	NH_3/Et_2O	70		30	42
"	$MeNH_2$	65		35	43
"	Me_2NH	19		81	43
"	$C_6F_5.MgBr$	9		91	44
	NaOMe			+	45
(X = CH_2 or O)	Me_2NH(2 equivalents)		+ (both positions)		45
$C_6F_5.N_2H_3$	(see under C_6F_6)				
$C_6F_5.C_6H_5$	C_6H_5Li; N_2H_4; NH_3; NaSH			+	46
"	KOH/t-BuOH; NaOMe			+	35
C_6F_5Me	KOH/t-BuOH			+	19
"	MeLi			+	47
$C_6F_5.CF_3$	$LiAlH_4$; MeLi; NH_4OH; NaOEt			+	48
"	N_2H_4; C_6H_5SK			+	48

*Competitive decarboxylation reduces yields: ratios are thus approximate.

(continued)

Substrate	Nucleophile	o	m	p	Reference
$C_6F_5.C_2F_5$	N_2H_4;NH_3;MeLi;$LiAlH_4$; NaOMe			+	50
$C_6F_5.C_6F_5$	NH_3;N_2H_4;Me_2NH;KOH;NaOMe	(both pos.)+			51
$C_6F_5.Hg.C_6F_5$	KOH;NaOMe;N_2H_4		"	+	52
		o	m	p	
$C_6F_5.CH:CHMe$	MeCH:CHLi			+	27
$C_6F_5.SMe$	NH_3;NaOMe			+	1
$C_6F_5.SO_2Me$	NH_3;NaOMe			+	1
$C_6F_5.NHCOMe$	NaSH			+	1
$C_6F_5.N_2^{+1}SO_4^{--}$	NaOH			+	1
o-$C_6F_4(CF_3)_2$	$N_2H_4.H_2O$;NH_3;NaSH	4-position			53
p-$C_6F_4(CF_3)_2$	NH_3	2-position			53
"	NaOMe	2,5-disubstitution			53
m-$C_6F_4(CF_3)_2$	$N_2H_4.H_2O$;MeLi;NaOMe	4,6-disubstitution			54
"	NaSH	4 + trace 2			54
		arrowed position			17, 55
		"			17, 55
		"			17, 55
	NH_3;NaOH;N_2H_4;$LiAlH_4$	"			56
"	MeCH:CHLi;Me_2NH	4,2-disubstitution			56

(continued)

Substrate	Nucleophile	o	m	p	Reference
	NaOMe	4,2,6-trisubs.			56
"	aq.40%NaOH at 80°	4,2 di-(20%)+ NH_3;CO_3^{--};F^-			56
"	$F_3C.CF:CF_2$ + KF/sulfolan, 120°	4(90%)+4,2 di-(5%)			57
	(i.e.$(F_3C)_2CF^-$; nucleophilic equiv. of Friedel-Crafts reaction)				
	NH_3/Et_2O 	I 27	II 48	III 25 IV tr	58
"	NaOMe/EtOH	70	7	23 -	58
"	$NaOMe/Et_2O$, 90% + EtOH, 10%	70	12	18 -	58

Other Reactions of Polyfluorobenzenes.

The reactions of hexafluorobenzene with free radicals and the reactions of the pentafluorophenyl radical have little relevance to the present work and have been reviewed in a recent thesis prepared in this Department.[3]

Very recently reported reactions include the oxidation of hexafluorobenzene and of chloropolyfluorobenzenes to benzoquinones[59] with nitric acid at 80°, and the photoisomerization of hexafluorobenzene and of octafluorotoluene to perfluoro--Dewar-benzenes.[60,61]

Substituted Polyfluorobenzenes.

(a) Halogenopolyfluorobenzenes.

Iodopentafluorobenzene is prepared from pentafluorobenzene by treatment with iodine in oleum[8] (p.2). The bromo-compound may be prepared analogously,[8] or by halogen exchange from hexabromobenzene.[62] Halogen exchange is likely to become the standard method of preparation of chloropentafluorobenzene (a useful intermediate, participating, unusually for a chloro--compound, in Grignard and Ullmann reactions) and also of hexafluorobenzene.[63]

$$C_6Cl_6 \xrightarrow[450^o]{KF} \underset{(21\%)}{C_6F_6} + \underset{(20\%)}{C_6ClF_5} + \underset{(14\%)}{C_6Cl_2F_4} \text{ (Chiefly } \underline{\text{meta}}\text{)}$$

The ortho and para dihalogenotetrafluorobenzenes, which are not available from the halogen exchange reactions, are prepared by the halogenation of the appropriate tetrafluorobenzenes.[64-5]

All three halogenopentafluorobenzenes (chloro[51,66], bromo[67], iodo[46,68]) yield Grignard reagents and undergo Ullmann reactions on heating with copper to yield decafluorobiphenyl. Ullmann reactions on the p-dibromo and di-iodo compounds,[65,69] and on the readily available m-dichloro-compound,[70] have been used to obtain polymers.

(b) Organometallic Compounds of Polyfluorobenzenes.

The Grignard compounds and lithium derivatives of polyfluoroaromatic compounds are easy to prepare, but

conventional reactions of Ar^- have to be carried out at low temperatures; at room temperature benzyne formation occurs. Solvent effects are often important (one example is given in the chart on p.15).

Much work has been done on polyfluoroaromatic derivatives of other metals, but these compounds will not be discussed here.

(c) Alkyl- and Alkenyl-polyfluorobenzenes.

Compounds of the type $C_6F_5.C_xH_y$ are prepared by the reaction of alkyl- or alkenyl-lithiums with hexafluorobenzene (p. 7) or by the reaction of pentafluorophenyl Grignard reagents with alkyl halides. The simplest of these compounds, pentafluorotoluene, reacts typically; it can be oxidized (albeit in low yield) to pentafluorobenzoic acid with chromium trioxide,[26] and one, two, or three chlorine atoms may be introduced into the side-chain by free-radical chlorination.[26,47] Compounds with fluorinated side chains are best prepared by the defluorination of aliphatic compounds, for example:[77]

$$\text{cyclo-}C_6F_{11}.CF_2.CF_3 \xrightarrow[490^\circ]{Fe} C_6F_5.CF_2.CF_3\ (15\%) \xrightarrow[600^\circ]{Fe} C_6F_5.CF{:}CF_2\ (13\%)$$

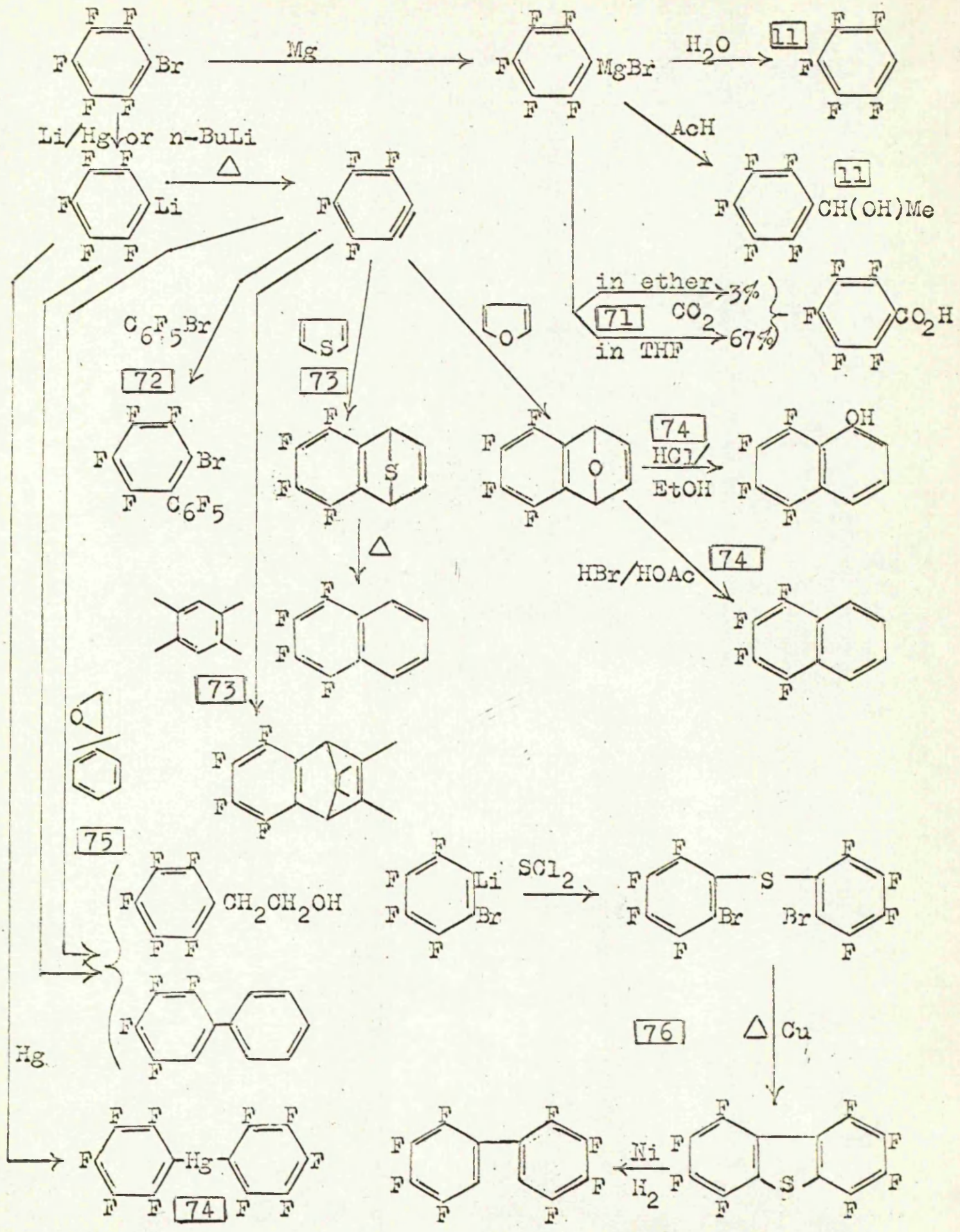
This last compound, octafluorostyrene, can be polymerized only at high pressures under γ-ray irradiation.[78]

(d) Highly Fluorinated Aromatic Compounds with Functional Groups derived from Oxygen.

Pentafluoro- phenol, -anisole, and -phenetole are prepared by nucleophilic replacement reactions (p.7):

(to p.16)

Polyfluoro-aryl Grignard and Lithium Reagents



$C_6F_6 + {}^{-}OR \longrightarrow C_6F_5.OR$ (R = H, Me, Et etc.)

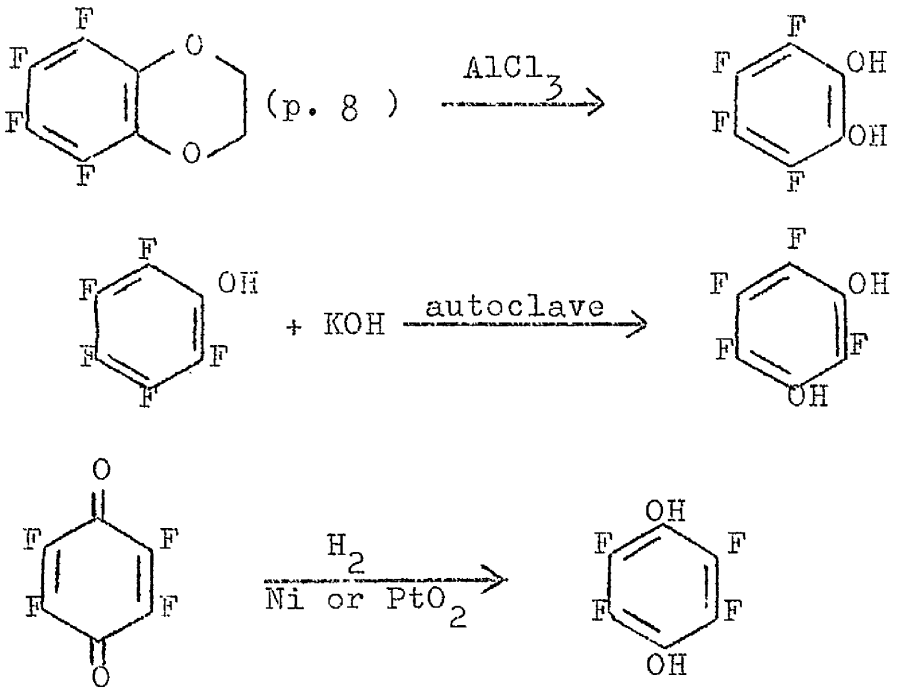
The ethers are cleaved to pentafluorophenol by anhydrous aluminium chloride,[33] hydriodic acid (see discussion, p.50), hydrobromic acid, and, surprisingly, by acids and alkalis; in these hydrolytic reactions the ethers show similarity to esters. The phenol is also obtained by oxidative cleavage of pentafluorophenylboronic acid (or its esters):[79]

$$C_6F_5.OCH_3 \xrightarrow{AlCl_3} C_6F_5.OH \quad (60\%)$$

$$C_6F_5.BCl_2 \xrightarrow{H_2O} C_6F_5.B(OH)_2 \xrightarrow{H_2O_2} H_3BO_3 + C_6F_5.OH \ (91\%)$$

Pentafluorophenol ($K_a = 3 \times 10^{-6}$) is much more acidic than phenol.[28]

Tetrafluoro-derivatives of catechol[29], resorcinol[40], and hydroquinone[80,81] are prepared thus:



Pentafluorobenzyl alcohol[47] is prepared by the reduction of pentafluorobenzaldehyde, which in turn is prepared by a Grignard synthesis:

$$C_6F_5.Br \longrightarrow C_6F_5.MgBr \xrightarrow{Ph.NMe.CHO} C_6F_5.CHO$$

Ethyl formate can react further with the pentafluorophenylmagnesium halide, giving bispentafluorophenylmethanol, which can be oxidized to decafluorobenzophenone:[47]

$$2C_6F_5.MgI + HCO_2Et \longrightarrow (C_6F_5)_2CH.OH \xrightarrow[AcOH]{CrO_3} (C_6F_5)_2CO$$

Pentafluorobenzaldehyde undergoes the usual transformations of an aromatic aldehyde, and in addition undergoes a haloform-type cleavage in alkali to form pentafluorobenzene and formic acid:

$$C_6F_5.CHO \xrightarrow{OH^-} C_6F_5H + HCO_2H$$

The carbonyl group in decafluorobenzophenone is very inert, and will not condense with the usual reagents.

Pentafluorobenzoic acid and the tetrafluorophthalic acids have been prepared by some or all of the following routes:*

(i) $ArLi \text{ or } ArMgX \xrightarrow{CO_2} ArCO_2H$

(ii) $ArCN \xrightarrow{H_2SO_4} ArCO_2H$

---

* $C_6F_5.CO_2H$, method (i) [71], (iii)[27], (iv)[82]; ortho-$C_6F_4(CO_2H)_2$, (ii)[3], (iv)[49]; meta-$C_6F_4(CO_2H)_2$, (iv)[83]; para-$C_6F_4(CO_2H)_2$, (ii)[3,38], (iii)[27], (iv)[49].

(iii) $ArR \text{ or } ArCH{=}CHR \xrightarrow{[O]} ArCO_2H$

(iv) $ArCF_3 \xrightarrow{H_2SO_4} ArCO_2H$

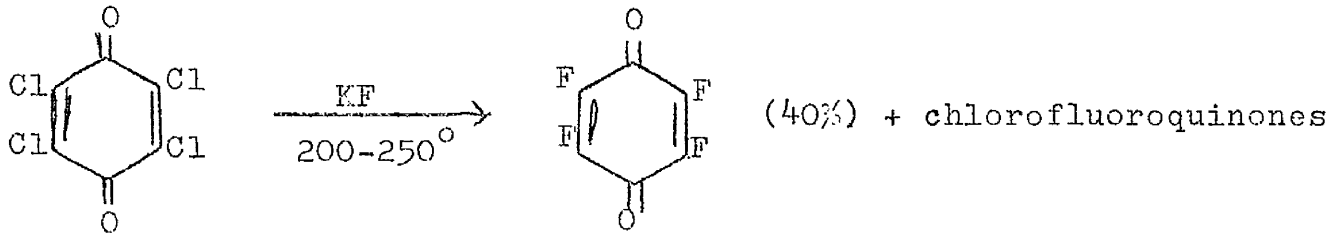
As expected, the acids are stronger than their hydrocarbon analogues. Some reactions of compounds derived from pentafluorobenzoic acid are shown below:[27,84]

$$C_6F_5.CO_2Ag \xrightarrow{I_2} C_6F_5I + AgI$$

$$C_6F_5.CO_2Ag + NOCl \longrightarrow C_6F_5.CO.ONO \xrightarrow{\Delta} C_6F_5.NO + CO_2$$

$$(C_6F_5.CO_2)_2Hg \xrightarrow{\Delta} (C_6F_5)_2Hg + 2CO_2$$

Tetrafluorobenzoquinone (fluoranil) is made by halogen exchange:[80]



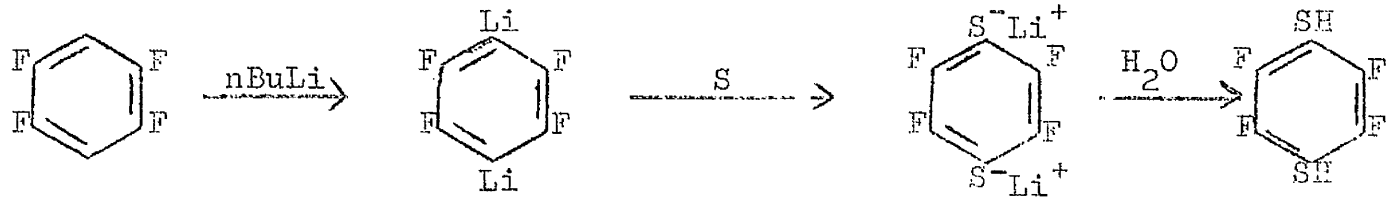
(40%) + chlorofluoroquinones

(e) Aromatic Fluorine Compounds containing Sulphur.

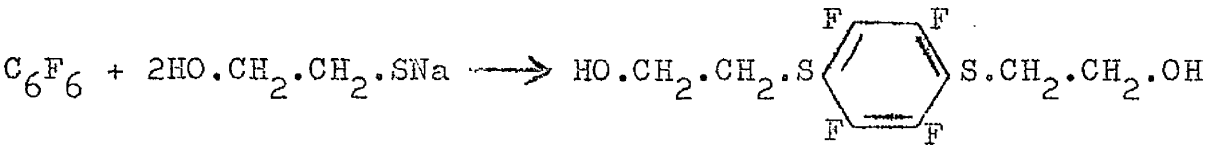
Pentafluorothiophenol and 4H-tetrafluorothiophenol are made by nucleophilic elimination of fluorine by the hydrosulphide anion (p. 7):

$$XC_6F_5 + {}^-SH \longrightarrow p\text{-}XC_6F_4.SH \qquad (X = F \text{ or } H)$$

Tetrafluorobenzene-1,4-dithiol cannot be made similarly, for the $-S^-$ group (necessarily anionic in the reaction medium) is deactivating towards further attack; the compound is made thus:[85]



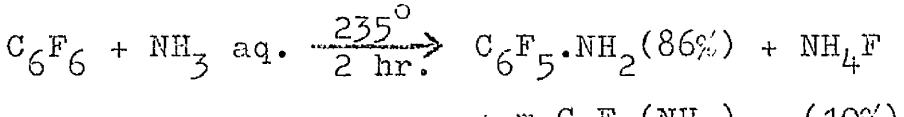
Thio-ethers (p. 7) can be made either from hexafluorobenzene and the RS^- anion, or by the specific replacement of bromine (rather than fluorine) by the action of the copper derivatives of thiols on bromopolyfluorobenzenes:

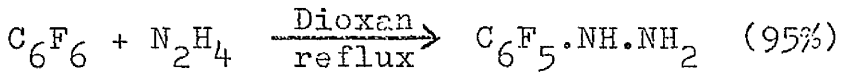


The fluorinated thiophenols have been converted by standard procedures into disulphides, sulphonic acids, and sulphonyl chlorides, and the sulphides into sulphones,[24,25] and a sulphur heterocycle has been reported recently (p. 15).[76]

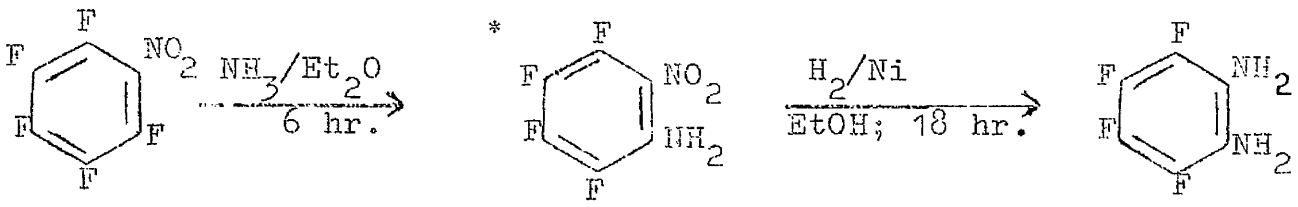
(f) Aromatic Fluorine Compounds containing Nitrogen.

The preparations of pentafluoroaniline[19] and the hydrazine[35] are simple nucleophilic substitution reactions (p.7):



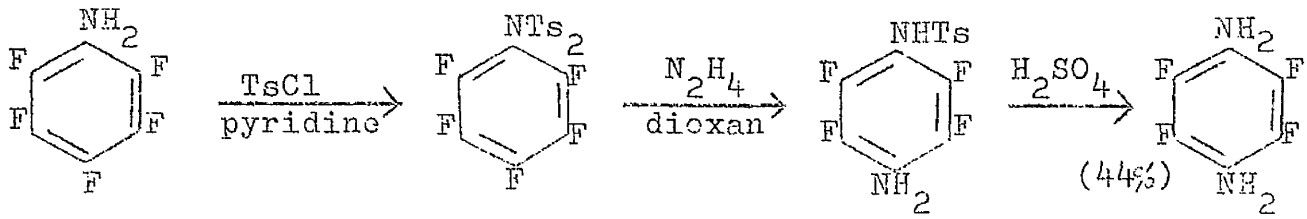


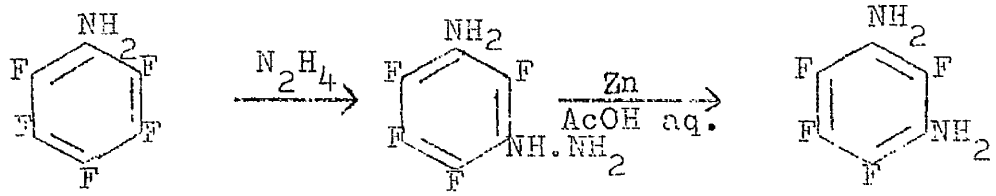
Tetrafluoro-o-phenylene diamine is made by reduction of the ortho-nitroamine:[42,43]



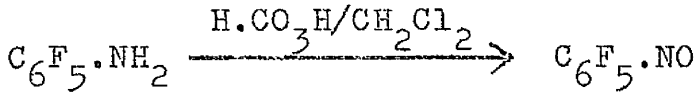
*major product: other amines also formed

Good routes to the other two diamines have been provided recently by Wilks:[4]





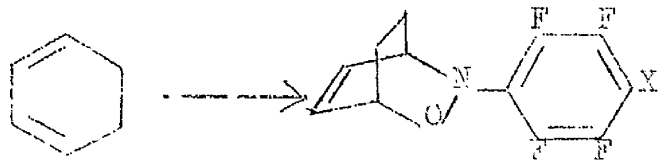
Pentafluoroaniline, owing to the inductive effect of the fluorine atoms, is a weaker base than aniline, though it can still be extracted from solution in light petroleum by concentrated hydrochloric acid. This amine, unlike aniline, is not oxidized on exposure to air, and remains colourless indefinitely. Oxidation of pentafluoroaniline with performic acid gives pentafluoronitrosobenzene, which is green and monomeric:[86]



Oxidation with peroxytrifluoroacetic acid gives the nitro--compound:[43]

$$C_6F_5\cdot NH_2 \xrightarrow[CH_2Cl_2]{CF_3\cdot CO_3H} C_6F_5\cdot NO_2$$

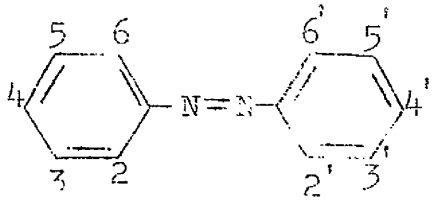
The nitroso-compounds have been studied by Castellano and his co-workers,[11] who report Diels-Alder additions of cyclohexadiene to the nitroso-group:



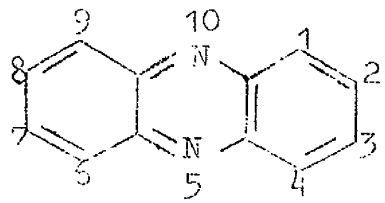
Pentafluorophenylhydrazine reacts somewhat differently to the unfluorinated compounds; the most important differences (its reactions with base and with hydriodic acid) are discussed in the main section of this thesis.

The purpose of this project was to investigate the chemistry of decafluoroazobenzene. Some related heterocycles were also investigated, and the following nomenclature is used:

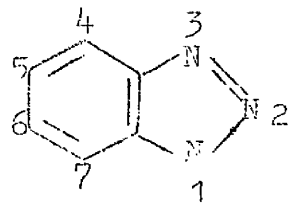
Ring systems.- Standard numberings are used, thus:



azobenzene



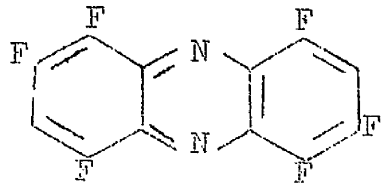
phenazine



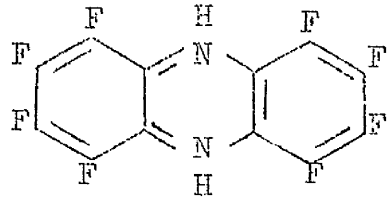
benzotriazole

The prefix H-. Until recently, this prefix has been used to indicate the position of hydrogen in either partially hydrogenated compounds or in tautomeric compounds

(e.g. benzotriazole). This latter usage is extended to indicate the placing of hydrogen in polyfluoro-compounds; partially hydrogenated derivatives are indicated by writing out the prefix in full, thus:

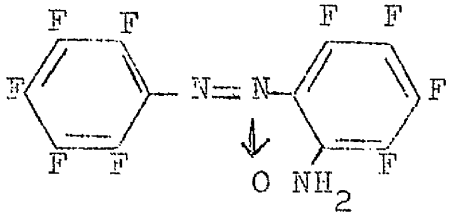


2H,7H-hexafluorophenazine.

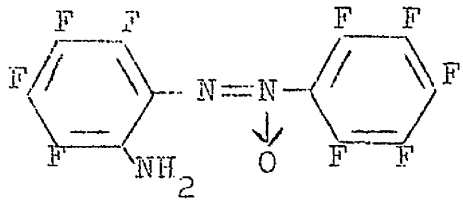


5,10-dihydro-octafluorophenazine.

Azoxy-compounds. - Symmetrically substituted compounds, and asymmetric compounds whose isomerism is not known, are named similarly to the related azo-compounds. Specific isomers of unsymmetrical azoxy-compounds are named by the following procedure (Handbook for Chemical Society Authors, 1961,195): The compound RH is regarded as the parent, into which the R.N=N(O)- group is substituted, thus:-



2-(pentafluorophenylazoxy)-tetrafluoroaniline.



(2-aminotetrafluorophenylazoxy)-pentafluorobenzene.

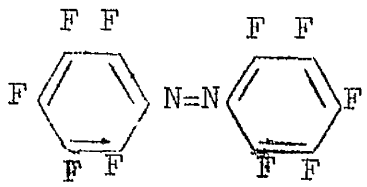
In view of the inter-relation of all parts of this work, the discussion is divided not into sections dealing with classes of compounds, but into two sections only, the first describing the reactions, and the second section consisting of the detailed arguments pertaining to the identification of new compounds.

SECTION I. THE REACTIONS.

The Oxidation of Highly Fluorinated Anilines with Lead Tetra-acetate.

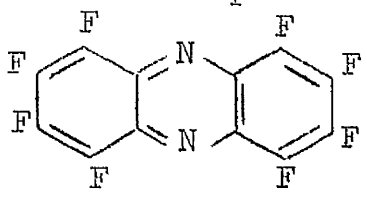
The use of lead tetra-acetate for the preparation of symmetrical azo-compounds from amines was first reported by Baer and Tosoni,[87] who used the lead salt in benzene at room temperature as oxidant for several mono- and di- halogenated amines, and obtained azo-compounds in yields approaching 50%. The preparation of decafluoroazobenzene by this procedure was first achieved by Wilkinson in this Department;[88] his work was repeated and extended by the present author, and decafluoroazobenzene and octafluorophenazine were obtained in yields of 50% and 2%, respectively. The latter compound had not been identified by Wilkinson.

decafluoroazobenzene



orange-red, m.p. 143°

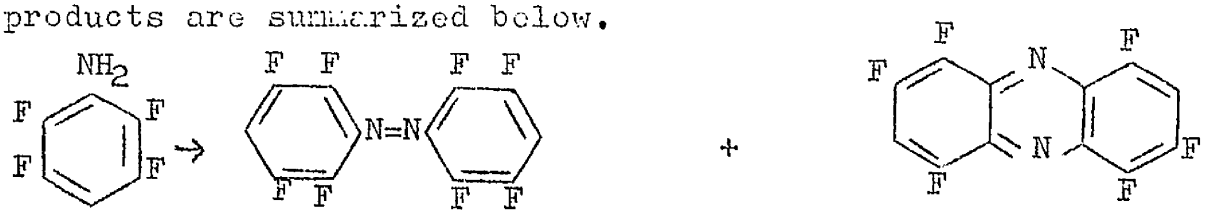
octafluorophenazine



yellow, with blue-green fluorescence m.p. 239°

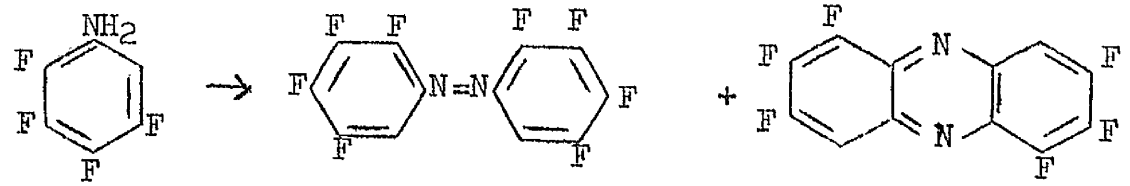
The reaction was repeated at reflux temperature in an attempt to improve the yield of the azo-compound, for lead tetra-acetate is much more soluble in benzene at 80° than at 20°, and a more concentrated solution could be used. The yield of azo-compound (48%) was almost unchanged, but the yield of phenazine rose to 28% and the amount of tarry residue was reduced; thus three-quarters of the pentafluoroaniline had been converted into tractable products in this reaction compared with only half at room temperature.

The reaction involving the tetra-acetate in refluxing benzene was applied to two other anilines, enabling new azo-compounds and phenazines to be prepared. The characterization of these products, in which ultra-violet spectroscopy was of considerable importance, is described on pp.100,102 , and the reactions and products are summarized below.



(42%) (23%)

4H,4H-octafluoroazobenzene 2H,7H-hexafluorophenazine



(43%) (18%)

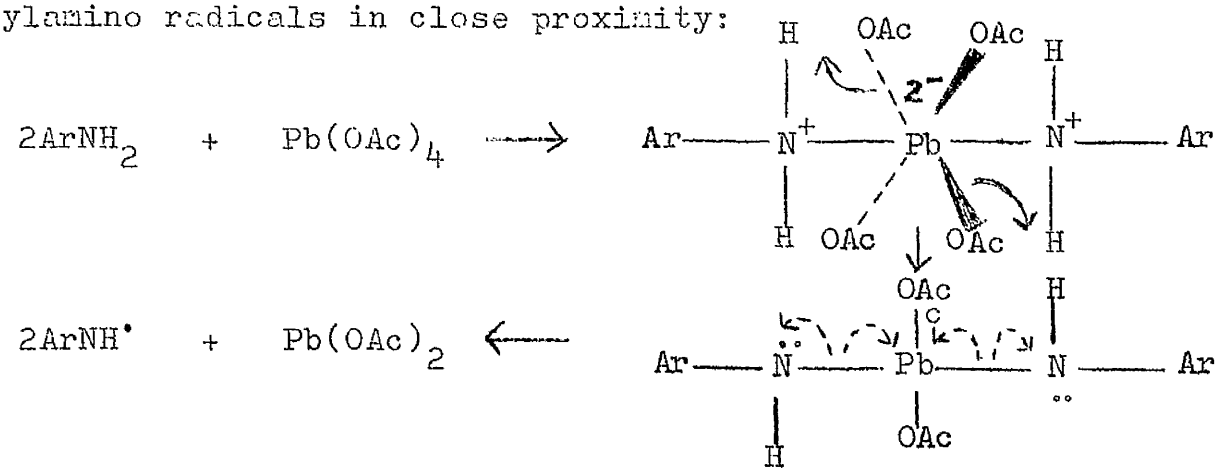
2H,2H-octafluoroazobenzene 1H,6H-hexafluorophenazine

The S- (as opposed to M-) symmetry of the two hexafluorophenazines follows from their mode of production.

Several facts have to be explained by any proposed mechanism for these reactions: (i) the formation of the azo-compound, (ii) the formation of the phenazine - in low yield at 20° but fair yield at 80°, (iii) in the oxidation of 2H-tetrafluoroaniline, the formation of only that phenazine produced by elimination of the fluorine atom (not hydrogen) ortho to the amino-group.

Baer and Tosoni [87] suggest that the oxidation of anilines by lead tetra-acetate proceeds by a free-radical mechanism; however, although lead tetra-acetate does decompose homolytically on heating,

it is stable at room temperature, and Baer and Tosoni do not explain the occurrence of a reaction at room temperature. It may be that the oxidation is aided by complex formation, in which case decomposition of the complex is likely to generate two arylamino radicals in close proximity:



In reactions carried out in refluxing benzene the normal mode of decomposition will also occur:

$$Pb(OAc)_4 \xrightarrow{\Delta} Pb(OAc)_2 + 2AcO^{\bullet}$$

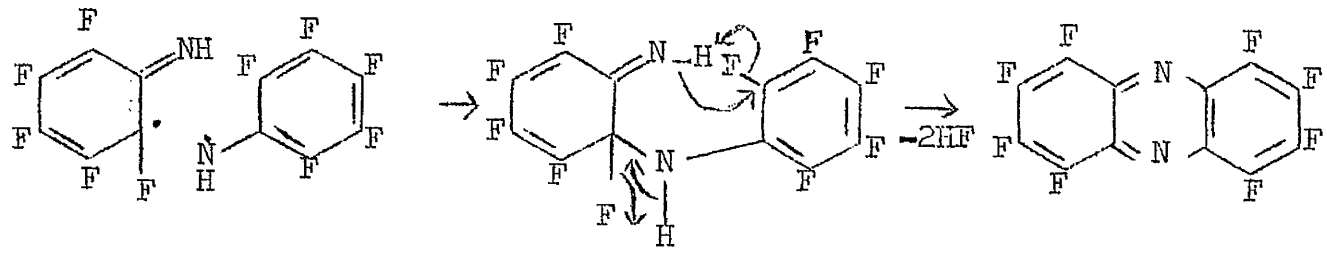
$$AcO^{\bullet} + ArNH_2 \longrightarrow AcOH + ArNH^{\bullet}$$

With pentafluoroaniline;

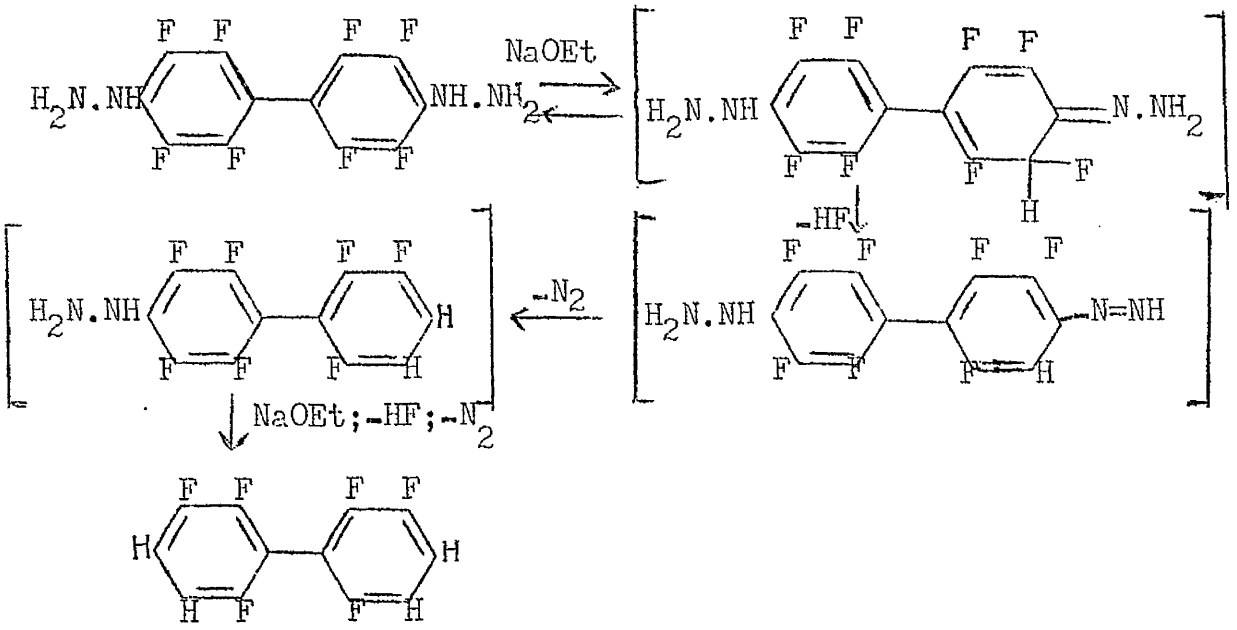
$$2C_6F_5 \cdot NH^{\bullet} \longrightarrow C_6F_5 \cdot NH \cdot NH \cdot C_6F_5 \xrightarrow{R^{\bullet}}$$

$$C_6F_5 \cdot NH \cdot \dot{N} \cdot C_6F_5 \longrightarrow C_6F_5 \cdot N{=}N \cdot C_6F_5$$

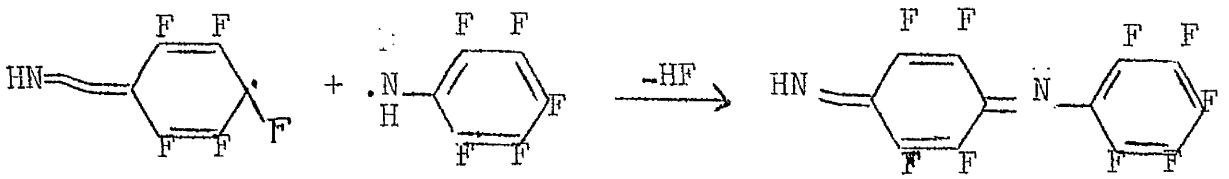
Reaction at the ortho position on one of the pentafluorophenylamino radicals would explain the production of the phenazine:



Loss of hydrogen fluoride from quinonoid intermediates has been postulated before in the polyfluoro-aromatic field:[89]



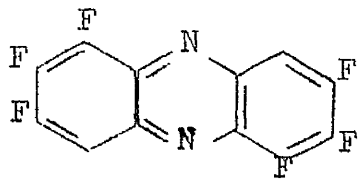
The phenylamino radical may also react at the para position, but the resulting intermediate can eliminate only one molecule of hydrogen fluoride:



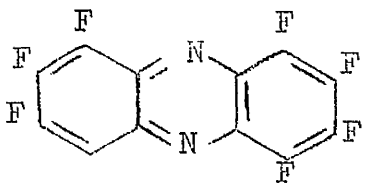
This last compound would almost certainly be destroyed in the reaction mixture, since quinones are very susceptible to homolytic reactions, and fluorinated quinones are also extremely susceptible to nucleophilic attack, even by unionized ethanol;[90] reaction with pentafluoroaniline is clearly possible.

The reaction of 4H-tetrafluoroaniline with lead tetra-acetate to yield the azo-compound and the phenazine calls for no special comment; it can be explained by a mechanism exactly comparable to that given for the oxidation of pentafluoroaniline. Furthermore

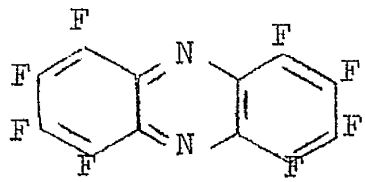
it is seen that in this reaction too, only one possible phenazine can be formed, since there must be a hydrogen atom *para* to each of the nitrogen atoms. However, from the oxidation of 2H-tetrafluoroaniline one might expect a mixture of three phenazines, depending on whether F or H is eliminated from the *ortho* positions:



(2 *ortho* F's eliminated)



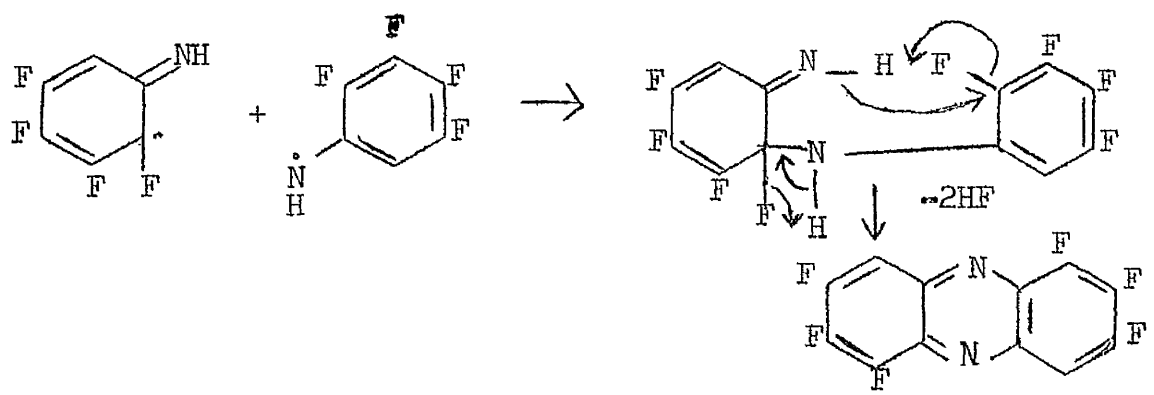
(1F & 1H eliminated)



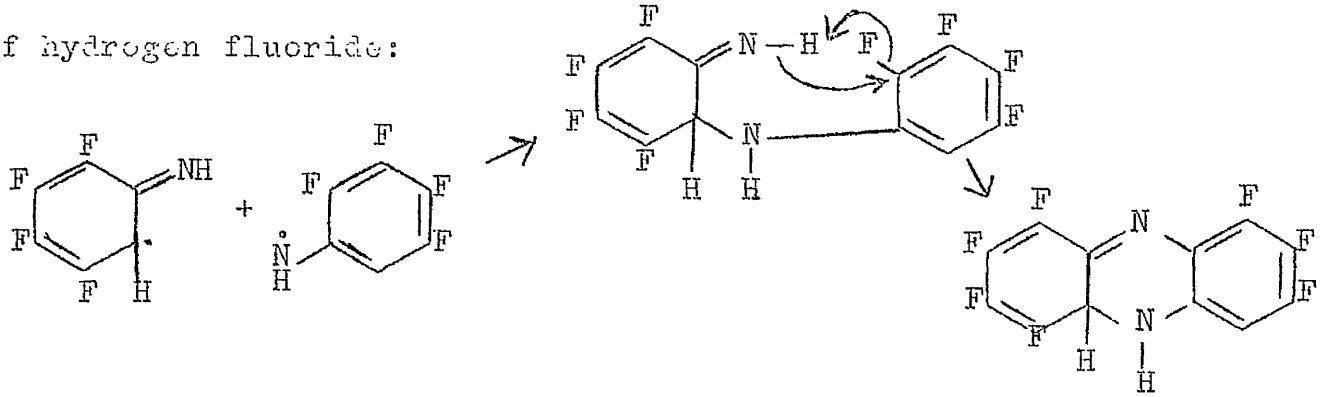
(2 *ortho* H's eliminated)

The phenazine fraction obtained by chromatographic separation of the reaction mixture consisted of the pure hexafluoro-compound, formed by the elimination of *two ortho* fluorine atoms, and the possibility that other phenazines were separated and lost during the chromatography seems remote; octafluorophenazine (and also the 2H,7H-compound) has chromatographic characteristics which are almost identical with those of 1H,6H-hexafluorophenazine, and one would expect the 1H-heptafluoro-compound also to be similar.

The two *ortho* positions in 2H-tetrafluoroaniline are not equivalent. Attack at the *ortho* position bearing a fluorine atom will give the hexafluorophenazine in the normal way by elimination of two molecules of hydrogen fluoride:



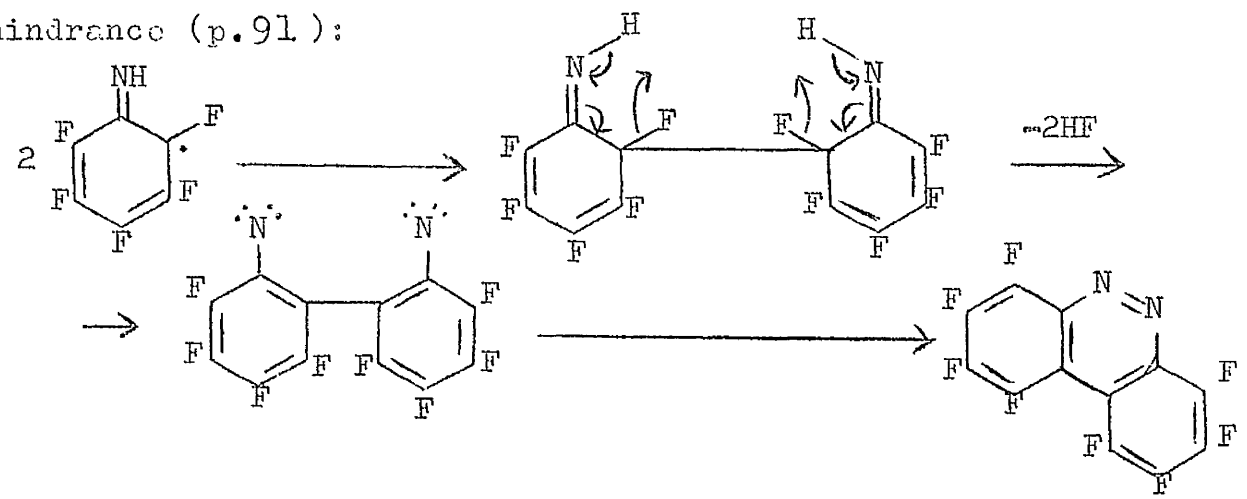
The other intermediate compound can eliminate only one molecule of hydrogen fluoride:



The resulting compound could, of course, be oxidised to a phenazine, and it can only be assumed that if it is formed at all, it reacts in other ways.

One might surmise that the production of a single phenazine from the oxidation of 2H-tetrafluoroaniline could be explained by a mechanism involving nucleophilic elimination of fluorine. However, attempts to formulate such a mechanism failed, firstly, because pentafluoroaniline is both a very weak nucleophile and is deactivated towards nucleophilic attack itself, and secondly, because it was not possible to account for the cyclization stage if initial oxidation of the amino-group (which would facilitate subsequent nucleophilic attack) were assumed.

Finally, the non-formation of benzocinnolines (for which the following route would appear possible) can be attributed to steric hindrance (p.91):

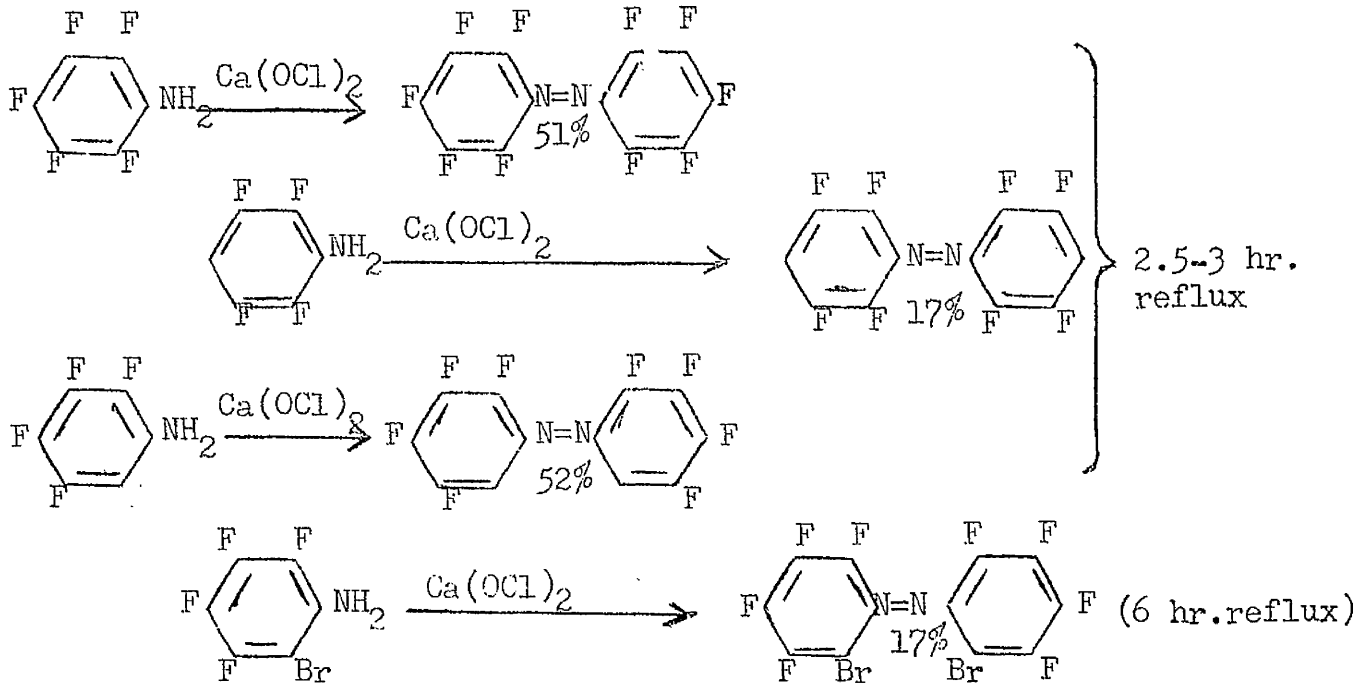


The Oxidation of Highly Fluorinated Anilines with Bleaching Powder.

Wilkinson[88] oxidized pentafluorophenylhydrazine with bleaching powder in refluxing carbon tetrachloride:

$$C_6F_5{\cdot}NH{\cdot}NH_2 \xrightarrow{Ca(OCl)_2} C_6F_5{\cdot}N{=}N{\cdot}C_6F_5\ (20\%) + C_6F_5H\ (9\%)$$

Although in this reaction formation of the azo-compound is unlikely to proceed *via* pentafluoroaniline (reaction *via* species such as $C_6F_5{\cdot}N{=}N^{\cdot}$ is more probable), it seemed reasonable to attempt the oxidation of the aniline with bleaching powder during the present work. The reaction was successful, and furthermore, the product (decafluoroazobenzene) was much easier to isolate from the reaction mixture than was the case with the oxidation involving lead tetra-acetate. Octafluorophenazine was not formed - quite a small amount would have been detected because of its low solubility in the solvent, carbon tetrachloride. This reaction too was extended to other anilines, and the results are summarized below, the solvent in each case being refluxing carbon tetrachloride.



The initial stage in the oxidation of pentafluoroaniline can be assumed to be chlorination:

$$C_6F_5.NH_2 \xrightarrow{Ca(OCl)_2} C_6F_5.NHCl$$

Arylchloramines are unstable at room temperature and above, and the decomposition will give a nitrene intermediate:

$$C_6F_5.NHCl \longrightarrow C_6F_5.\ddot{N}: + HCl$$

$$C_6F_5.\ddot{N}: + C_6F_5.NH_2 \longrightarrow C_6F_5.NH.NH.C_6F_5 \xrightarrow{Ca(OCl)_2}$$

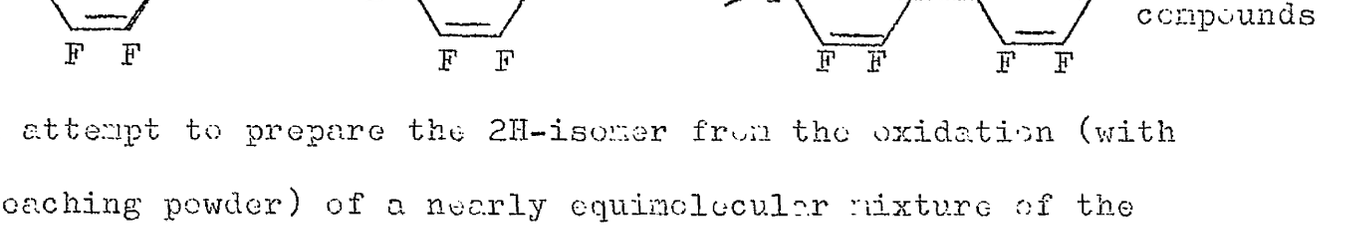
$$C_6F_5.NCl.NH.C_6F_5 \xrightarrow{-HCl} C_6F_5.N{=}N.C_6F_5$$

The non-formation of phenazines in these reactions may be due to the difference in the nature of the intermediates (nitrene rather than free radical) in the oxidation with bleaching powder. The oxidations of the other anilines probably proceed by similar routes. Furthermore, it is easier to explain the variations in yield for the oxidations with bleaching powder than for those with lead tetra-acetate.

4H-Tetrafluoroaniline gave a much poorer yield (17%) of azo-compound than did pentafluoroaniline (51%). The former amine is just as sterically hindered in the two ortho positions as is pentafluoroaniline, and the hydrogen at the para position will make it much more susceptible to oxidation to quinonoid products, which cannot yield the azo-compound. The higher yield from the 2H-isomer can be explained by the position of the nuclear hydrogen atom; in the 2-position it provides less steric hindrance than does fluorine. The low yield of azo-compound from the 2-bromo-aniline can be attributed to steric hindrance by bromine.

The Oxidation of Mixtures of Highly Fluorinated Anilines.

Two such oxidations were carried out, one with lead tetra-acetate, and the other with bleaching powder. To a first approximation, an equimolecular mixture of two anilines would be expected to give the two symmetrical azo-compounds and the unsymmetrical compound in the ratio 1:1:2, respectively. Alternatively, the use of a large excess of one aniline should lead to a mixture consisting largely of two compounds, with only a minute proportion of the symmetrical compound derived from the minor component - this latter procedure * was used for the preparation of 4H-nonafluoroazobenzene:



An attempt to prepare the 2H-isomer from the oxidation (with bleaching powder) of a nearly equimolecular mixture of the 2H-aniline and pentafluoroaniline failed because the mixture of azo-compounds could not be separated.

Exploratory Experiments on the Oxidation of Anilines.

Although the lead tetra-acetate and bleaching powder procedures were available early in the course of this project, a number of exploratory experiments were carried out with readily available oxidants, with the intention of finding a procedure which would give better yields of the azo-compounds. Oxidants used were Br_2, $KMnO_4$, $Ce(SO_4)_2$, ICl, chloramine-T, $C_2H_4(CO)_2NBr$,

* Lead tetra-acetate was used as oxidant, because of the low yield of 4H,4H-octafluoroazobenzene obtained by the use of the bleaching powder procedure.

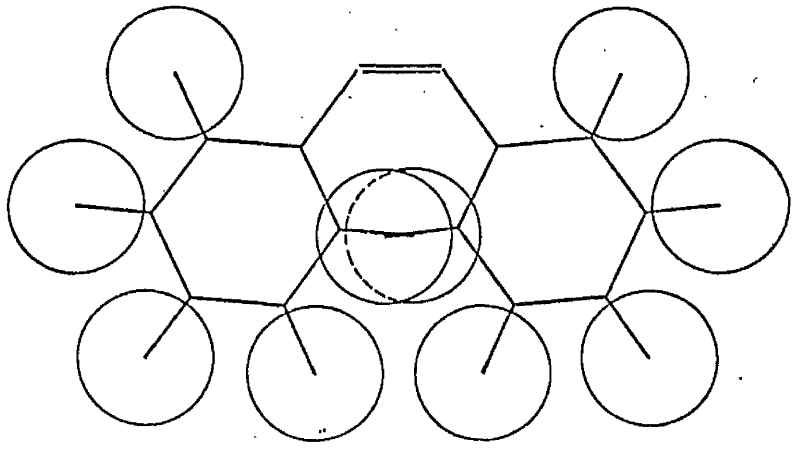
Bz_2O_2, O_2/CuCl/pyridine, and MnO_2. All experiments were more or less unsuccessful in that only a small yield, or with some reagents none at all, of the azo-compound was produced.

The Attempted Preparation of cis-Decafluoroazobenzene.

cis-Azobenzene was reported first by Hartley,[91] who prepared it by irradiation of the ordinary (trans) isomer. The product was isolated by extraction into water and recrystallization at low temperature to constant m.p. Recently Badger and his co-workers[92] have described a simple procedure in which they repeatedly irradiated azobenzene in 20% benzene/light petroleum, and removed the cis-isomer between irradiations by passing this solution through alumina. Their procedure was applied to decafluoroazobenzene by the present author, but the fraction removed last from the chromatography column showed no increase in the intensity of the -N=N- absorption band (presumed to be in the 1400-1630 cm^{-1} region)[93] nor the appearance of a band[94] in the 720-760 cm^{-1} region - both effects characteristic of cis-azo-compounds.

Even cis-azobenzene, with four hydrogen atoms ortho to the azo-group, has been shown[95] (by X-ray diffraction) to be much distorted from planarity. The reason is clear if one draws the cis-isomer in a hypothetical planar form; the diagram overleaf is from Pauling.[96] cis-Decafluoroazobenzene, owing to the larger size of fluorine, would be even more distorted than cis-azobenzene. In view of the above considerations, no further attempts were made to prepare cis-decafluoroazobenzene.

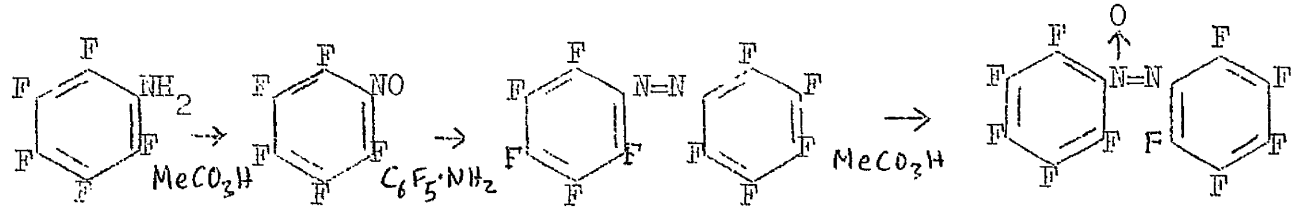
Hypothetical planar form of cis-azobenzene.



A Re-examination of Other Authors' Work on Decafluoroazoxybenzene.

Shortly after this project was begun, a report appeared from Wall, Pummer, Fearn, and Antonucci[19] of the preparation of decafluoroazoxybenzene, and its subsequent reduction to decafluoroazobenzene. The former reaction was repeated and confirmed during the present work, but the reduction product from decafluoroazoxybenzene was shown to be the hydrazo-compound.

Decafluoroazoxybenzene was prepared in a crude yield of 23% (cf. Wall et al., 22%) by the oxidation of pentafluoroaniline with peracetic acid at room temperature. The reaction mixture turned successively blue, green, brown, yellow, red, and orange, and these colour changes were interpreted by Wall and his colleagues as supporting the following mechanism:



However, pentafluoronitrosobenzene and pentafluoroaniline cannot be condensed to give the azo-compound;[59] the classical condensation would appear to be more probable (though this still leaves the

colour changes unexplained):

$$ArNH.OH + ArNO \xrightarrow{-H_2O} ArN{=}NAr^{O}$$

The present author attempted the condensation of pentafluoronitrobenzene and pentafluoroaniline, but the reaction did not occur under the conditions used for the preparation of decafluoroazobenzene. The reaction occurs in the hydrocarbon series only in the presence of sodium:[97]

$$PhNH_2 + O_2NPh \xrightarrow{Na} PhN(Na^+)-NPh(O^-Na^+) \xrightarrow{H_2O} PhN{=}NPh^{O}$$

The reduction of the azoxy-compound was also carried out by the procedure of Wall and his colleagues.[19] Decafluoroazoxybenzene was reduced with zinc and ammonium chloride to give decafluorohydrazobenzene, m.p. 62-3°, in 33% yield (cf. Wall: "decafluoroazobenzene", m.p. 57-9°, 41%). The characterization of this compound is described on p.101; of great significance also is the experiment discussed on p.39, in which decafluoroazobenzene was shown to be unstable in the above reaction mixture, changing instantaneously on dissolution into the hydrazo-compound.

The reduction of decafluoroazoxybenzene to the hydrazo-compound parallels closely the reduction of nitrobenzene to phenylhydroxylamine, and other examples of the very close similarity between nitro-compounds and azoxy-compounds are described in this thesis (pp.79,84):

$$C_6H_5\overset{\downarrow}{N}{=}O \xrightarrow[60\text{-}65^\circ]{Zn/NH_4Cl} C_6H_5\underset{H}{\overset{|}{N}}\text{-}\underset{H}{\overset{|}{O}}$$

$$C_6F_5\overset{\downarrow}{N}{=}NC_6F_5 \xrightarrow[80^\circ]{Zn/NH_4Cl} C_6F_5\underset{H}{\overset{|}{N}}\text{-}\underset{H}{\overset{|}{N}}C_6F_5$$

The Oxidation of Highly Fluorinated Azo-compounds.

Burdon, Morton, and Thomas [98] describe the preparation of decafluoroazoxybenzene by three methods:* (i) it was isolated in 17% yield from the high-boiling residue from the preparation of pentafluoronitrosobenzene [86], by the oxidation of pentafluoroaniline with performic acid, (ii) in 53% yield by the pyrolysis at 60° of the nitroso-compound, and (iii) in 80% yield by the action of triethyl phosphite on the nitroso-compound in benzene at 60°.

$$C_6F_5{\cdot}NO + P(OEt)_3 \longrightarrow C_6F_5{\cdot}\dot{N}\!:\; + PO(OEt)_3$$

$$C_6F_5{\cdot}NO + C_6F_5\dot{N}\!:\; \longrightarrow C_6F_5{\cdot}\overset{\downarrow}{N}{=}N{\cdot}C_6F_5$$

Burdon et al. attempted to prepare decafluoroazoxybenzene by the oxidation of decafluoroazobenzene with peroxytrifluoroacetic acid in dichloromethane, but the azo-compound was recovered in 90% yield even after refluxing for 72 hr. They also obtained starting material in high recovery on attempting to oxidize decafluoroazobenzene with performic, peracetic, and fuming nitric acids.

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* This paper appeared after the present author's re-investigation of Wall's work (p.33), but before the experiments discussed below on the oxidation of highly fluorinated azo-compounds were carried out.

Other azo-compounds were oxidized, however, by peroxytrifluoroacetic acid, and since a sample of 4H,4'H-octafluoroazoxybenzene was required for the reaction described on p.80 ,it was decided to attempt to find an improved route to this compound by following up the preparation given by Burdon and his co-workers.

Burdon and his co-workers made 4H,4'H-octafluoroazoxybenzene in 57% yield by treating the azo-compound with aqueous 90% hydrogen peroxide and trifluoroacetic anhydride in refluxing dichloromethane for 50 hr. They also isolated starting material in 32% recovery. With this in mind their procedure was modified by the present author; further portions of peroxide and anhydride were added during the reflux. The azoxy-compound was isolated chromatographically in 44% yield, and no starting material was recovered. The literature method was then repeated almost exactly, the chief difference in the procedure being that the reaction was stopped after only 1 hr., since it was noticed that the orange colour due to the azo-compound had disappeared by this time. The azoxy--compound was isolated in 98% yield, and no starting material was recovered. 2H,2'H-Octafluoroazobenzene was then oxidized to the (new) azoxy-compound by a similar procedure, and the yield was quantitative. These two reactions may be formulated thus:

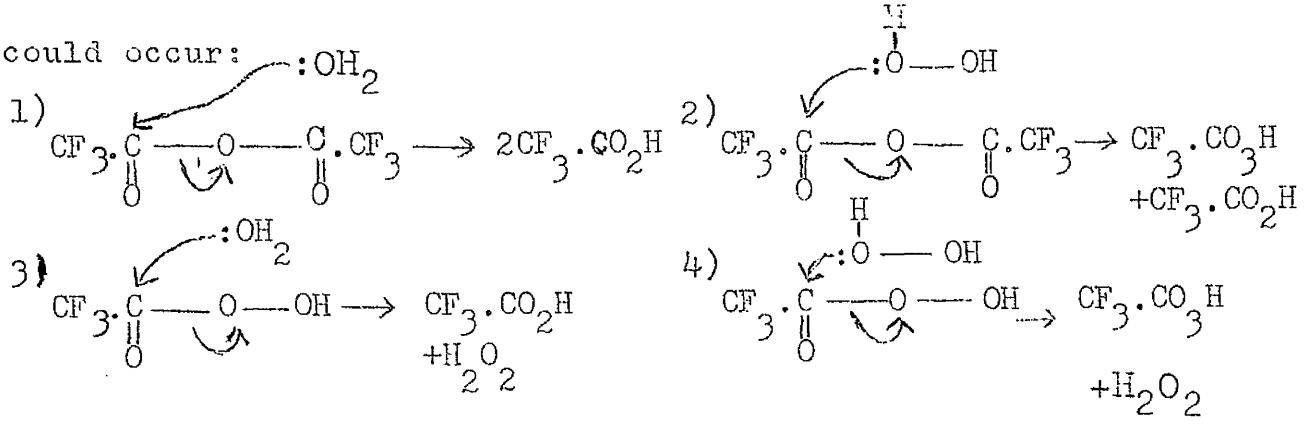
$$H.C_6F_4.N{=}N.C_6F_4.H \xrightarrow[CH_2Cl_2;\ 1\ hr.]{CF_3.CO_3H} H.C_6F_4.\overset{\uparrow O}{N}{=}N.C_6F_4.H \ + \ CF_3.CO_2H$$

After these successes, the oxidation of decafluoroazobenzene to the azoxy-compound was also achieved by the use of peroxytri-

fluoroacetic acid in dichloromethane.

$$C_6F_5.N{=}N.C_6F_5 \xrightarrow[CH_2Cl_2;\,4\ hr.]{CF_3.CO_3H} C_6F_5.\overset{O}{\overset{\uparrow}{N}}{=}N.C_6F_5 \quad (94\%)$$

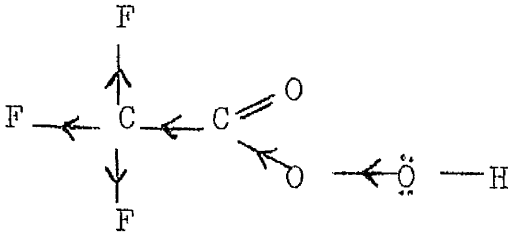
The chief difference in the procedure used, compared with the unsuccessful attempt by other workers, [98] was that the present author used an excess of trifluoroacetic anhydride, sufficient to react with all the hydroxylic species (i.e. H_2O and H_2O_2) present in the reaction mixture. The peroxide/anhydride ratio used earlier was such that sufficient water was introduced into the reaction mixture to hydrolyse all the trifluoroacetic anhydride. Since in both experiments, the peroxide/water ratio was high (85-90% peroxide was used), it must be assumed that the anhydride is solvolysed preferentially by water. The following reactions could occur:

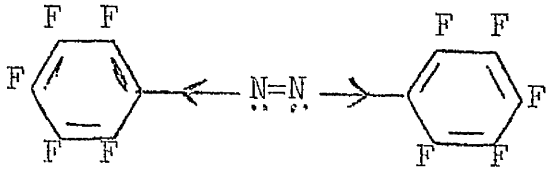


Water is probably a stronger nucleophile than is hydrogen peroxide, and reactions (1) and (3) will be favoured relative to reactions (2) and (4); in any case, the last reaction is trivial, and has no net effect on the system.

The strong oxidizing power of peroxytrifluoroacetic acid is

due to the inductive effect of the trifluoromethyl group, which renders the terminal oxygen atom more susceptible to nucleophilic attack; the resistance to oxidation shown by the fluorinated azo-compounds is also due to the inductive effect of fluorine:





The Oxidation of Highly Fluorinated Phenazines.

Since it has not been found possible to prepare the N-oxide of pentafluoropyridine,[99] it was decided to use peroxytrifluoroacetic acid, already shown to be a strong oxidant, in an attempt to oxidize the fluorinated phenazines.

An initial experiment was carried out on the readily available 2H,7H-hexafluorophenazine. The phenazine was heated under reflux for 50 hr. with hydrogen peroxide and an excess of trifluoroacetic anhydride in dichloromethane. Work-up yielded a pale brown gum, from which some starting material (13%) was recovered; no other product could be removed from the chromatography column.

Attention was now turned to the oxidation of octafluorophenazine. Hydrogen peroxide in a large excess of trifluoroacetic anhydride was used with no additional solvent. The reactions were carried out at reflux temperature (ca. 40°); the first one (30 min. duration) gave a 60% yield of an intractable brown gum. In a second experiment, starting material

was obtained quantitatively after 1 min., and a third experiment (5 min. reflux) gave a product (80%) similar to that from the first reaction, except that it was yellow and probably contained some starting material.

These reactions were not followed up further, so nothing can be said yet about their course. It may be significant, however, that half the fluorine atoms in the monoxide and all eight in the hypothetical dioxide of octafluorophenazine are situated ortho or para to positive nitrogen, and will be highly activated towards nucleophilic attack.

Decafluorohydrazobenzene.

It was shown earlier (p. 34) that decafluoroazoxybenzene is reduced by zinc and ammonium chloride to the hydrazo-compound, and not (as previously reported) to the azo-compound; it was clearly of interest to investigate the reaction of authentic decafluoroazobenzene with the same reductant. A mixture of zinc dust, ammonium chloride, water, and ethanol was prepared in the same proportions as were used earlier (p. 34) for the reduction of decafluoroazoxybenzene. Decafluoroazobenzene was added and dissolved rapidly to give a colourless solution; it was therefore pointless to heat the mixture under reflux as had been done with the azoxy-compound. A simple work-up gave pure decafluorohydrazobenzene in 80% yield.

A second efficient reductant, sodium hydrosulphite (dithionite) was also found; five equivalents gave the hydrazo-compound in 85% yield.

$$C_6F_5.N{=}N.C_6F_5 \xrightarrow[\text{or } Na_2S_2O_4/\text{aq. MeOH}]{Zn/NH_4Cl/\text{aq.EtOH}} C_6F_5.NH.NH.C_6F_5$$

The relative stability of the hydrazo-compound to further reduction is discussed later (p.42).

Reductive Cleavage of Decafluoro-azo,-azoxy-, and -hydrazobenzenes.

In 1962, Birchall, Haszeldine, and Parkinson [22] reported an attempt to prepare pentafluoroiodobenzene from pentafluorophenylhydrazine by the reaction of the hydrazine with iodine in refluxing aqueous hydriodic acid. In the hydrocarbon series, the following sequence occurs:[100]

$$C_6H_5.NH.NH_2 + 2I_2 \xrightarrow{-3HI} C_6H_5.N_2^+I^- \longrightarrow C_6H_5I + N_2$$

However, with the pentafluoro-compound, reduction to pentafluoroaniline occurred with the generation of further iodine:

$$C_6F_5.NH.NH_2 + 3HI \longrightarrow C_6F_5.NH_2 + NH_4I + I_2$$

It seemed probable that decafluorohydrazobenzene could be reduced similarly to pentafluoroaniline by refluxing hydriodic acid. This was achieved, and the reaction was later extended to the reduction of both the azo- and the azoxy-compound; pentafluoroaniline was obtained also in both these reactions. The reactions are summarized below; the reducing agent was refluxing aqueous 55% hydriodic acid in each case:

Table 3

Pentafluoroaniline from the Reaction of Related Compounds with Hydriodic Acid.

Compound	Yield of $C_6F_5.NH_2$
$C_6F_5.NH.NH_2$ (Birchall et al.[22])	75%
$C_6F_5.NH.NH.C_6F_5$	63%
$C_6F_5.N=N.C_6F_5$	57%
$C_6F_5.N(O)=N.C_6F_5$	33%

Two points arise from the above table. Firstly, the isolation of the aniline in yields of greater than 50% from the azo- and hydrazo-compounds supports the suggestion[22] that the terminal nitrogen atom from pentafluorophenylhydrazine is converted into ammonia (which was not isolated) by the cleavage reaction. Secondly, the lower yield of pentafluoroaniline obtained from the azoxy-compound may be due in part to incomplete reaction, for in an early experiment on the cleavage of the azoxy-compound, in which half the quantity of hydriodic acid was used, starting material (74%) was recovered after a reaction period of 2.5 hr.

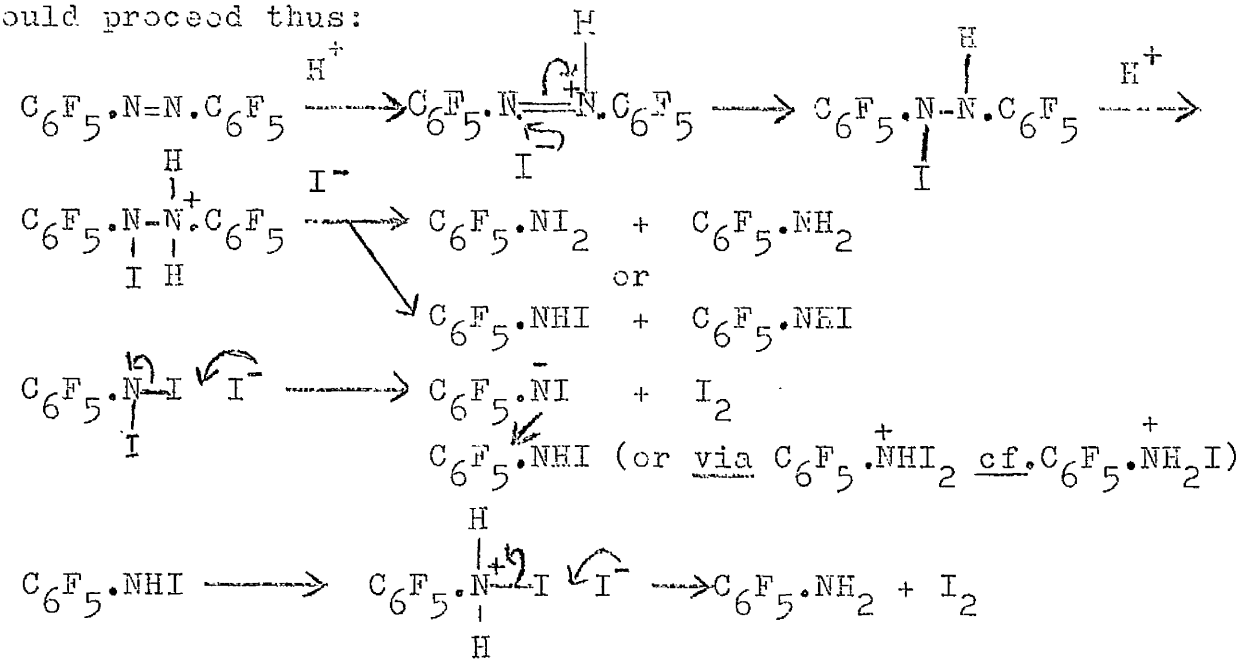
Earlier attempts to cleave decafluoroazobenzene gave the hydrazo-compound (tin and hydrochloric acid) or a tar (triethanolamine); the product in both cases had an odour of pentafluoroaniline. Decafluoroazobenzene did not react with zinc and alkali; this reagent usually gives hydrazo-compounds.

Discussion: The Reduction of Azo- Azoxy- and Hydrazo-compounds.

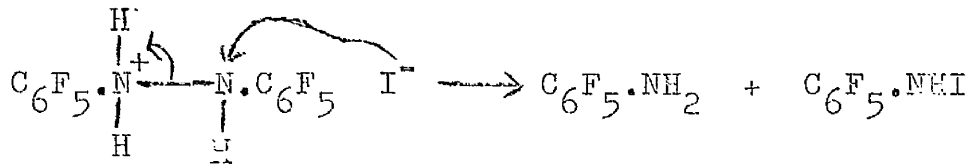
Two contrasting observations can be made in relation to the above experiments on the reduction of decafluoroazobenzene. Firstly, reduction to decafluorohydrazobenzene is accomplished quickly and easily; to the reagents described so far (Zn/NH_4Cl; $Na_2S_2O_4$; Sn/HCl) can be added hydrazine (p.62) and hydrosulphide ion (p.61), though it is probable that in the latter two cases, the reduction stage occurred on products formed during initial substitution reactions. Secondly, it is extremely difficult to cleave decafluorohydrazobenzene to pentafluoroaniline - the only really satisfactory reagent (HI) being an unorthodox one. Both the above observations are in accord with recent investigations by other workers on substituent effects in the reduction of (non-fluorinated) azo-compounds. Thus, the results of Khalifa[101] (on the products of reduction) and of Warwick[102] (on the rates of reduction) can be summarized as follows (both workers used a wide variety of azo-compounds and reducing agents). The relevant variable in all the reaction series is the electron density on the azo-group. Compounds containing electron-withdrawing substituents are reduced faster than the parent azobenzene to the hydrazo-compound, but are not readily cleaved to amines. Conversely, compounds containing substituents which increase the electron density on the azo-group are reduced more slowly than the parent compound, but the resulting hydrazo-compounds are readily reduced further. In polysubstituted compounds, substituent effects are

approximately additive. The collective effect of ten fluorine atoms will be powerfully electron-withdrawing (the C_6F_5-group has about the same electronegativity as a bromine atom)[103], and decafluoroazobenzene is clearly in the former category.

The reduction of decafluoroazobenzene by hydriodic acid could proceed thus:



Reduction of the hydrazo-compound probably proceeds *via* a comparable mechanism:



Reduction of azoxy-compounds includes two distinct types of reaction. The first, deoxygenation, occurs with strong Lewis bases, *e.g.* $P(OEt)_3$:

$$Ar_2N_2O + :Base \rightarrow Ar_2N_2 + O{\leftarrow\!\!-}Base$$

The above reaction will not be discussed. Secondly, more conventional reducing agents can give the azo- or the hydrazo-compound, or cleavage to amines can occur. It is to be noted

that the initial stage is not necessarily reduction to the azo-compound, for 4,4'-diethoxyazoxybenzene is reduced to the hydrazo-compound twice as fast as is the azo-compound under identical conditions (Zn/KOH/EtOH).[104]

Very few reports of the use of hydriodic acid as a reducing agent for compounds containing N-N bonds have appeared. Presumably this is because both azoxy- and hydrazo-compounds usually rearrange under strongly acidic conditions. There is, however, one report of the reduction of azoxybenzene with hydriodic acid; benzidine was produced, presumably by rearrangement of the hydrazo-compound:[105]

$$Ph.N(O)=N.Ph \xrightarrow{HI} [Ph.NH.NH.Ph] \xrightarrow{H^+} H_2N\text{-}C_6H_4\text{-}C_6H_4\text{-}NH_2$$

The mechanism of this reaction can be inferred from the work of Shemyakin, Maimind, and Agadzhanyan,[106] who were interested primarily in the Wallach rearrangement (the acid-catalysed rearrangement of azoxybenzene to 4-hydroxyazobenzene). These workers found that azoxybenzene rearranged in cold chlorosulphonic acid under conditions in which sulphuric acid was ineffective:

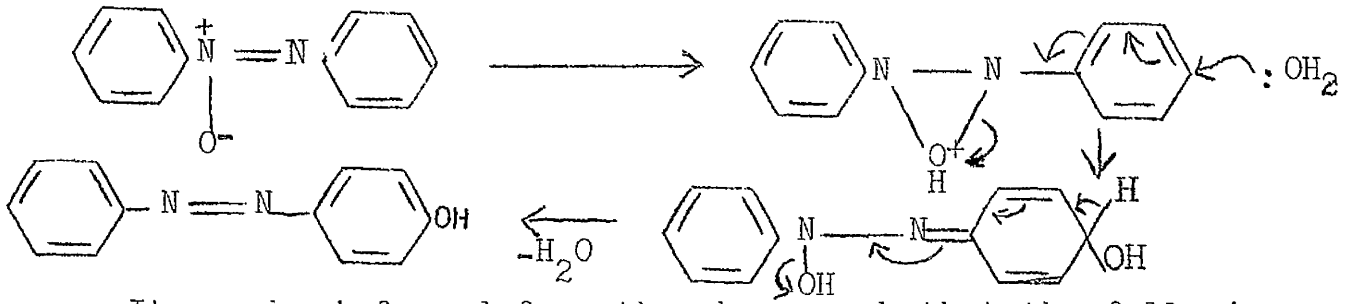
$$C_6H_5\text{-}N=N^+(O^-)\text{-}C_6H_5 \xrightarrow{ClSO_3H} C_6H_5\text{-}N=N\text{-}C_6H_4\text{-}OH$$

Furthermore, if the reaction was done in the presence of iodide ion, azobenzene was produced:

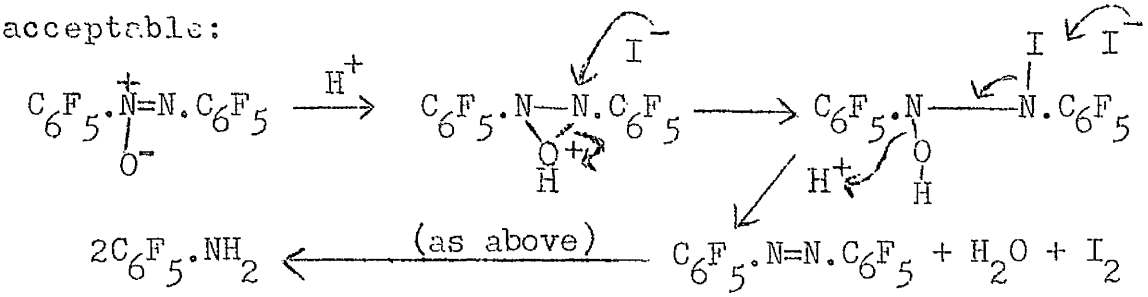
$$PhN(O)=NPh \xrightarrow{KI/ClSO_3H} PhN{=}{=}NPh + I_2$$

Azoxybenzene was not reduced by potassium iodide in sulphuric acid. These observations were interpreted thus. In chlorosulphonic acid a cyclic intermediate is formed; this can react either with

water, or with iodide ion, and the following mechanism for the Wallach rearrangement may apply:



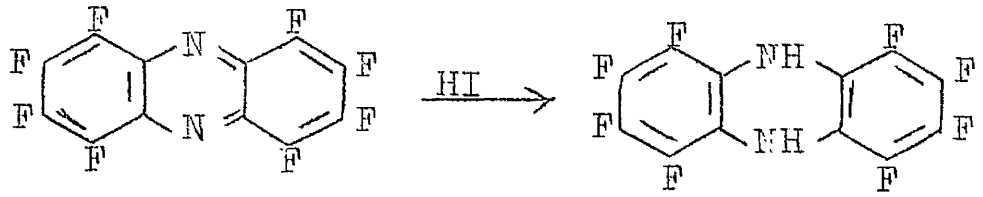
It can be inferred from the above work that the following mechanism for the reduction of decafluoroazoxybenzene would be acceptable:



Finally, it may be noted that a benzidine rearrangement (p.44) is not possible with decafluorohydrazobenzene, for there are no protons in any nuclear position in the molecule.

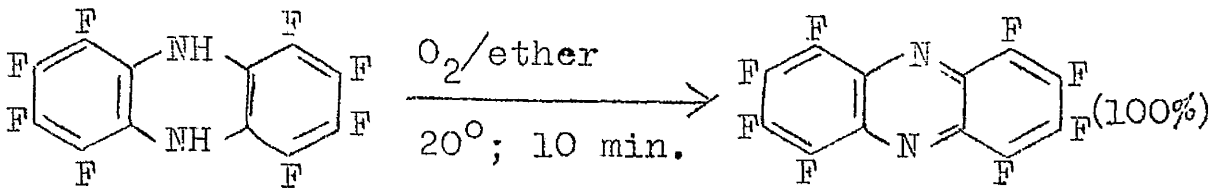
Fluorinated Dihydrophenazines.

Octafluorophenazine was immediately reduced by aqueous hydriodic acid at room temperature:



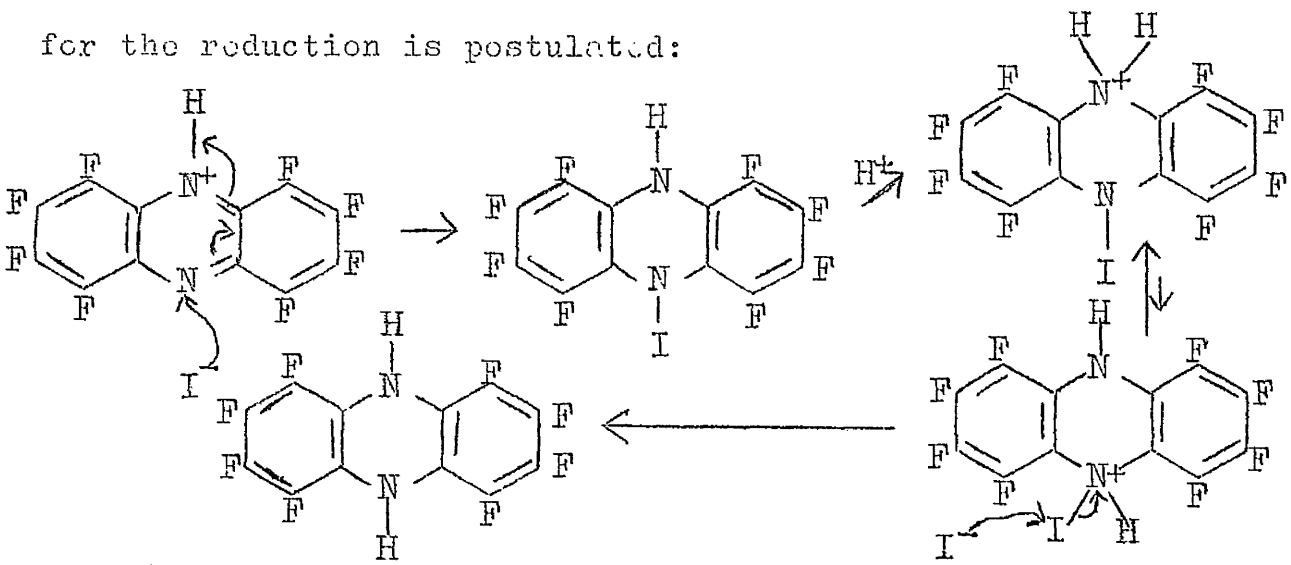
Similar dihydro-derivatives were made from the two hexafluorophenazines. None of the compounds was obtained pure, but their identities are not in doubt (the spectroscopic characterizations are given on p.103). On exposure to air, all the compounds

(momentarily colourless when first isolated) were spontaneously oxidized, giving a series of green, blue, or violet molecular complexes ("phenazhydrins"). The octafluoro-compound was aerated in ether for 10 min., and was completely and quantitatively oxidized back to the starting material:



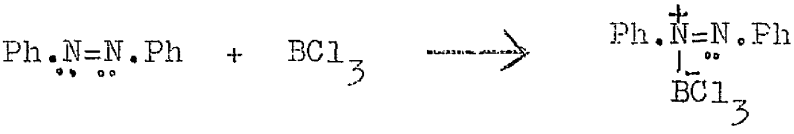
Dihydrophenazine itself is also readily oxidized at room temperature, and gives similar coloured complexes with its oxidation product.[107]

The azine group $-N=C-C=N-$ can be considered to be a vinylogue of the azo-group $-N=N-$, and the following mechanism for the reduction is postulated:



Attempted Preparation of a Decafluoroazobenzene - Boron Trifluoride Complex.

Azobenzene is a Lewis base, and combines with boron trichloride to form a complex; this reaction is used for the removal of the latter from silicon tetrachloride, for most other bases (e.g. aniline) react with the silicon compound also:[108]

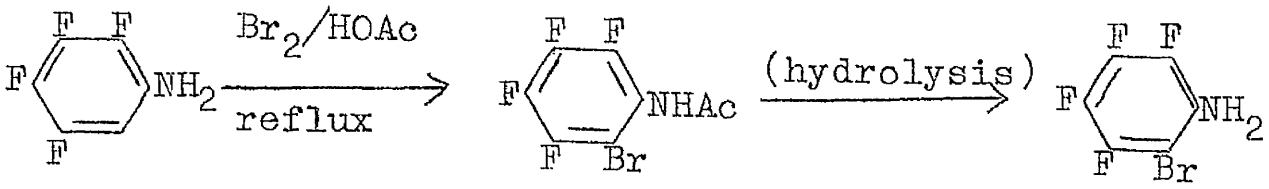


In the present work boron trifluoride was used in an attempt to make a similar complex from decafluoroazobenzene. No reaction occurred. This is probably because of the same electronic factors which make oxidation to the azoxy-compound difficult (p. 37), together with steric hindrance involving the ortho fluorine atoms and the boron trifluoride molecule.

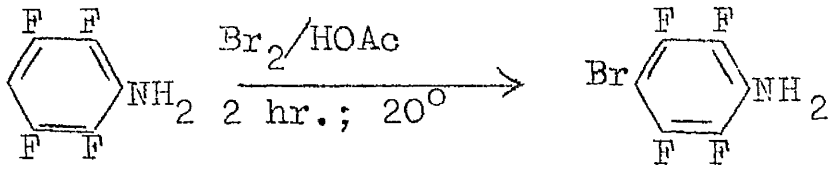
2,2'-Dibromo-octafluoroazobenzene.

Two attempts to brominate 2H,2'H-octafluoroazobenzene failed. In the first experiment, bromine in oleum was used under conditions which have been used before in the polyfluoroaromatic field,[8] and in the second, bromine in refluxing acetic acid was used. Starting material was recovered almost quantitatively in both experiments. The 2-position in the octafluoroazo-compound is deactivated towards electrophilic substitution by one ortho and two meta fluorine atoms, but the ortho phenylazo-group should have little net electronic effect on the electrophilic replacement of hydrogen. The hydrogen atoms will be very sterically hindered, and this may explain the lack of success of the reaction.

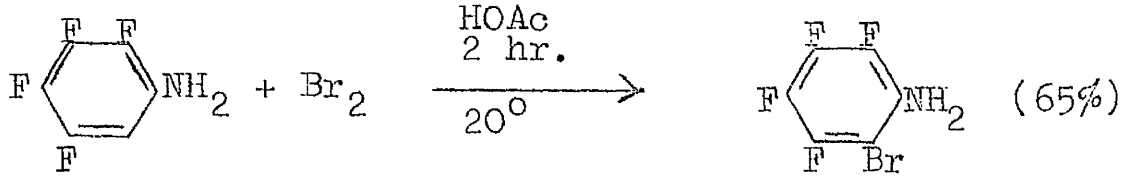
The dibromo-azo-compound was prepared by the oxidation of 2-bromotetrafluoroaniline (p. 29), and an improved route to this aniline was found. The first report of the compound gave the following route:[10]



Castellano and his co-workers [11] reported a direct synthesis of the 4-Br isomer in glacial acetic acid at room temperature:

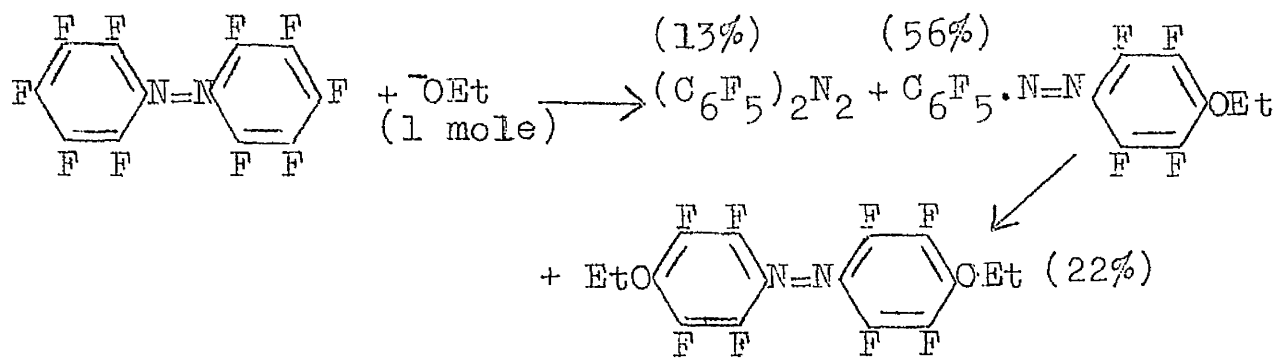


An identical procedure was applied to 2H-tetrafluoroaniline by the present author, and gave the 2-bromo-compound in 65% yield:



The reaction of Decafluoroazobenzene with Ethoxide Ion.

Decafluoroazobenzene reacted with two moles of ethoxide ion in refluxing ethanol to give a quantitative yield of crude 4,4'-diethoxyoctafluoroazobenzene; one recrystallization gave the pure sample in 59% recovery. Decafluoroazobenzene reacted with one mole of ethoxide ion to give recovered starting material and mono- and di-substituted products:

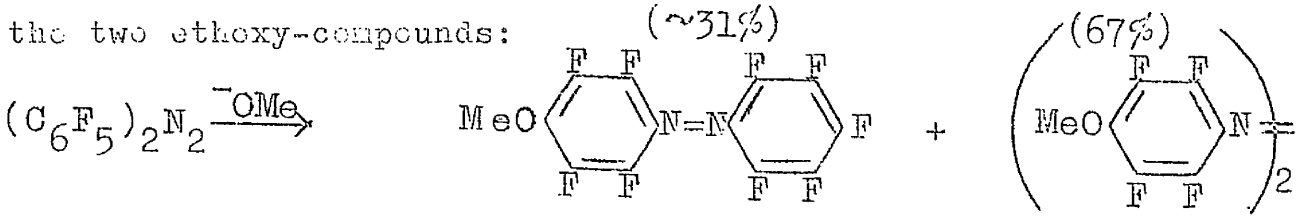


The products were separated chromatographically and identified by their melting points and infra-red spectra. The monoethoxy-compound was characterized by its elemental analysis and by conversion to the 4,4'-diethoxy-compound by reaction with a further mole of ethoxide ion. The recrystallized compounds were shown to be single isomers by their n.m.r. spectra and by the quantitative

yield of 4-aminotetrafluorophenol obtained on reductive cleavage (p.50).

The reaction of Decafluoroazobenzene with Methoxide Ion.

An early reaction of one third the duration of the above reactions with ethoxide ion gave only a low conversion of the decafluoroazobenzene. The reaction was therefore repeated over an extended period of reflux, and gave the methoxy-analogues of the two ethoxy-compounds:



The activation pattern of the polyfluorophenylazo-group is discussed later (p.60).

The reaction of Decafluoroazobenzene with Thiophenoxide Ion.

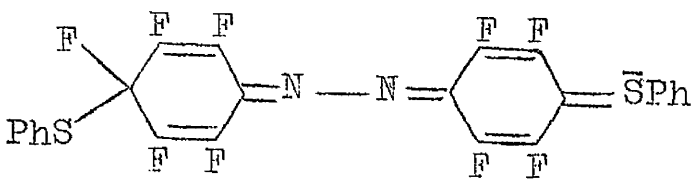
Decafluoroazobenzene reacted quickly with two moles of sodium thiophenoxide in methanol, and a quantitative yield of almost pure 4,4'-dithiophenoxyoctafluoroazobenzene was obtained. One recrystallization gave the pure compound (81% recovery), which was characterized by reductive cleavage (p.51).

Less thiophenoxide (0.7 mole) reacted with decafluoroazobenzene to give a mixture consisting largely of unreacted starting material and disubstituted product, but the monosubstituted product could also be isolated in 6% yield.

The success of the first experiment can be ascribed to the high nucleophilicity of the thiophenoxide ion, and to the relatively high acidity of thiophenol, which would ensure that the following equilibrium would lie far to the right:

$$MeONa + PhSH \rightleftharpoons MeOH + PhSNa$$

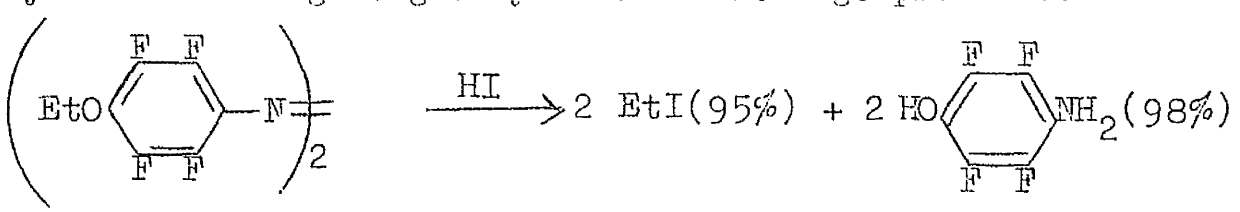
The high isomeric purity of the crude disubstituted product can be ascribed to steric hindrance to substitution in the 2-position, and the low yield of monosubstituted product in the second reaction is due to the activating influence of the first thiophenoxy-substituent. This influence will be transmitted through the azo-linkage to the second ring, since ultra-violet spectroscopy showed that decafluoroazobenzene is (like azobenzene) planar. Accordingly, stabilization of the intermediate should occur as follows:



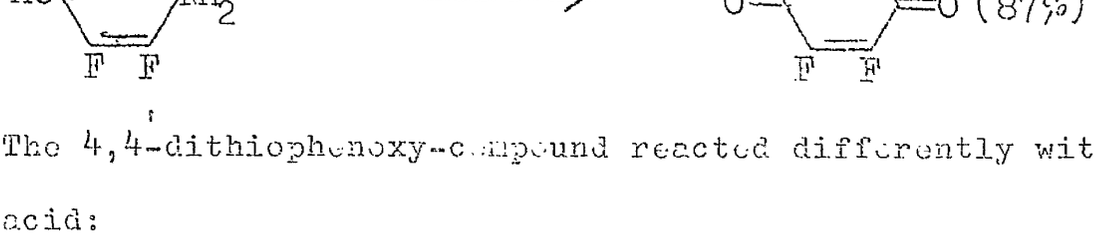
The n.m.r. spectrum of the monothiophenoxy-compound was exceptionally well resolved, and confirmed the orientation and isomeric purity of the compound. 4-Thiophenoxynonafluoroazobenzene also gave the 4,4'-disubstituted compound on reaction with a further mole of thiophenoxide ion.

The Reductive Cleavage of the Dialkoxy- and Dithiophenoxy--derivatives of Decafluoroazobenzene.

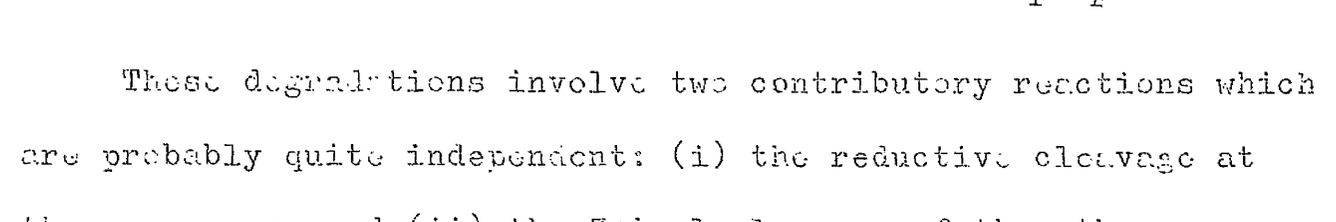
The reaction of 4,4'-diethoxyoctafluoroazobenzene with hydriodic acid gave good yields of cleavage products:



The 4,4'-dimethoxy-compound reacted similarly to give the aminophenol in 100% yield, but no attempt was made to isolate iodomethane. The aminophenol was characterized by oxidation to fluoranil:



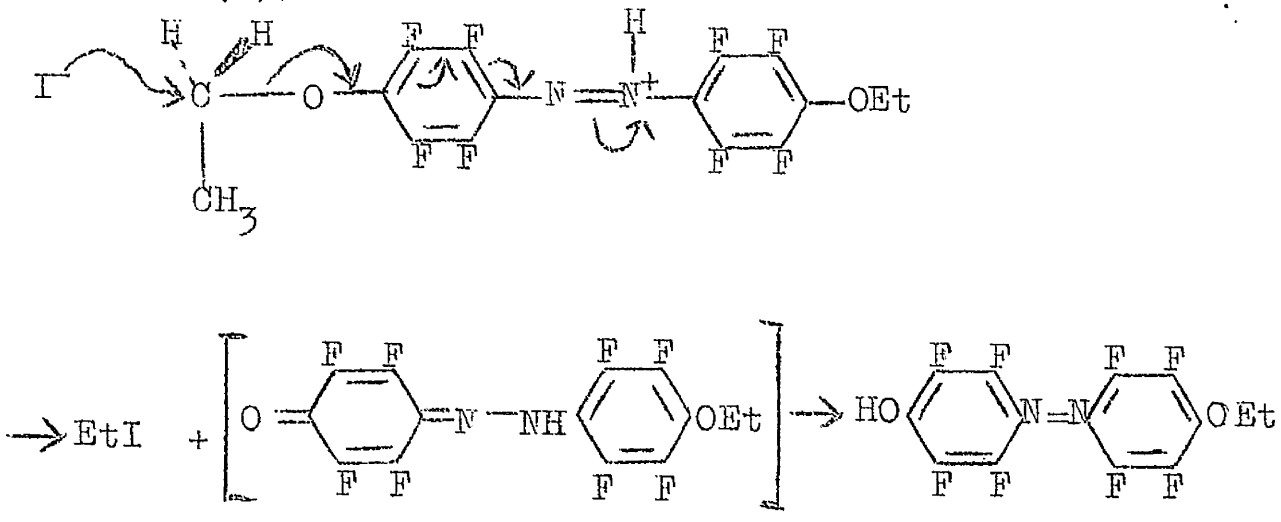
The 4,4'-dithiophenoxy-compound reacted differently with hydriodic acid:



These degradations involve two contributory reactions which are probably quite independent: (i) the reductive cleavage at the azo-group, and (ii) the Zeisel cleavage of the ether group. The order in which these reactions occur - or more accurately, the proportion of each occurring first - cannot be determined in the absence of any definitive mechanism for the reduction of the azo-group. The azo-compound, in solution, will exist largely as the conjugate acid, which will be a mixture of two tautomeric forms:

Form (a) must be capable of undergoing reaction with hydriodic acid,

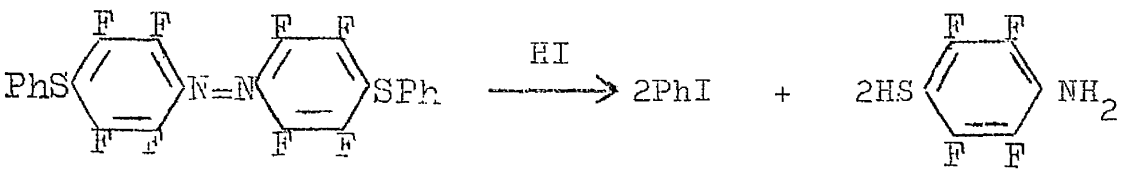
since decafluoroazobenzene, which has only the azo site of protonation, can be reduced (unless, of course, the reduction proceeds only via the neutral molecule in both cases), and by an analogous argument, form (b) must be capable of Zeisel cleavage. However, both forms can probably undergo both reactions, thus with form (a):



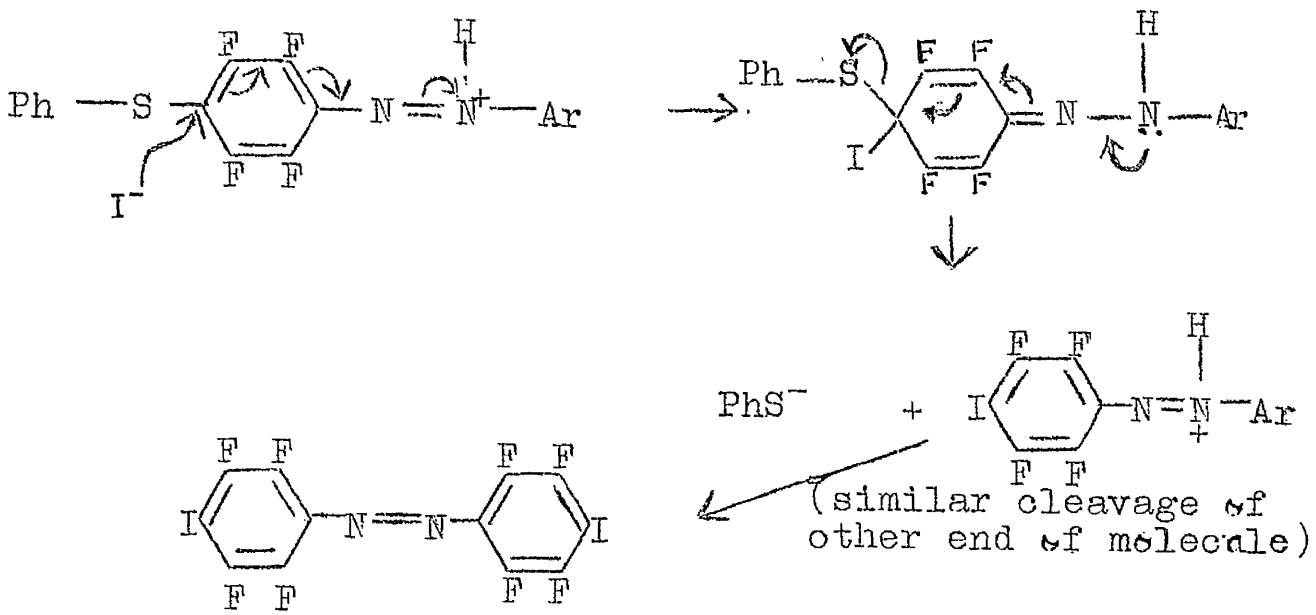
Repetition of the cleavage and reduction reactions would give the products observed, and cleavage of the dimethoxy-compound undoubtedly takes a similar course. An attempted de-ethylation of the diethoxy-compound with hydrobromic acid was unsuccessful, perhaps because the acid was not sufficiently strong.

The path taken during the reaction of 4,4'-dithiophenoxyoctafluoroazobenzene requires further discussion. Thioanisole[109] is stable to conditions (HI; 2 hr.; 230°) under which anisole is cleaved quantitatively; the thio-compound is, however, cleaved by other standard reagents ($AlCl_3$; Na/pyridine; Na/liquid NH_3), but much more slowly than is anisole. The failure of thioanisole

to react with hydriodic acid can be ascribed in part to the low basicity of the thioether, and cleavage of the azo-compound discussed here is probably due to activation by formation of the N-conjugate acid. A reaction analogous to the cleavage of the alkoxy-azo-compounds would give iodobenzene and the fluorinated amino-thiol:



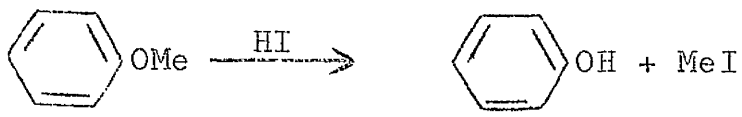
However, from the products observed it is seen that in the Zeisel cleavage it is the C-S bond to the fluoroaromatic ring which is broken; it will be assumed for convenience that the cleavage reaction occurs before the reduction stage, but this order is not essential to the argument:



The following reaction is well known, and accounts for the diphenyl disulphide obtained:

$$PhSH + HSPh + I_2 \longrightarrow PhS.SPh + 2HI$$

To account for the different positions of cleavage found in the ethers and the thio-ethers is not as difficult as might be expected. The alkoxy-compounds are alkyl aryl ethers, and the cleavage to the iodoalkane and the phenol parallels the cleavage of better-known compounds such as anisole:



The dithiophenoxy-compound is a diaryl ether, and the relative susceptibilities of the two aryl groups to nucleophilic attack have to be considered. Each of the carbon atoms para to the azo-group in the dithiophenoxy-compound is activated by the inductive effects of the eight fluorine atoms, the phenylazo--group, and the other phenylthio-group, and in addition, activation is likely to be increased due to formation of the N-conjugate acid.

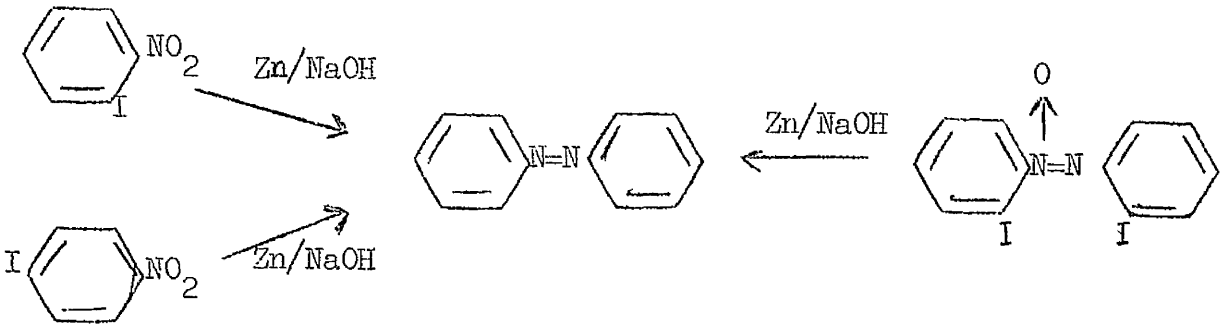
The C-S bonds of the terminal phenyl groups are unactivated, and the production of thiophenol in the cleavage reaction is thus rationalized; the probable mechanism is given above.

The production of 4H- (rather than 4-iodo-) tetrafluoroaniline now has to be explained. The preparation of iodobenzene from iodine and benzene is usually carried out in the presence of an

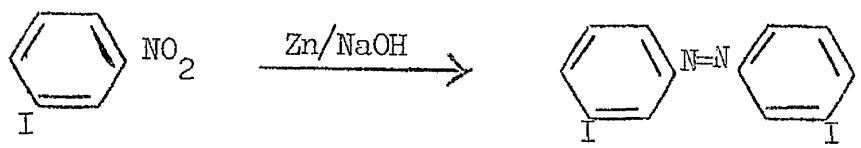
oxidizing agent, whose function is generally believed to be to drive the following equilibrium to the right:

$$PhH + I_2 \rightleftharpoons PhI + HI \quad (\xrightarrow{HNO_3} I_2)$$

There is some evidence that electron-withdrawing substituents favour the reduction of aryl iodides, thus Newbold[110] reduced the 2- and 4-iodonitrobenzenes and also 2,2'-di-iodoazoxybenzene to azobenzene:



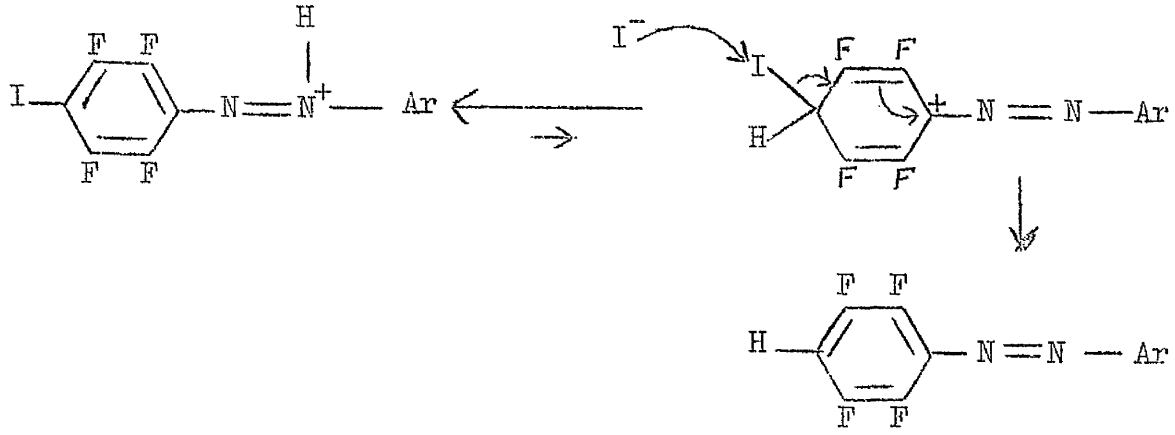
But:



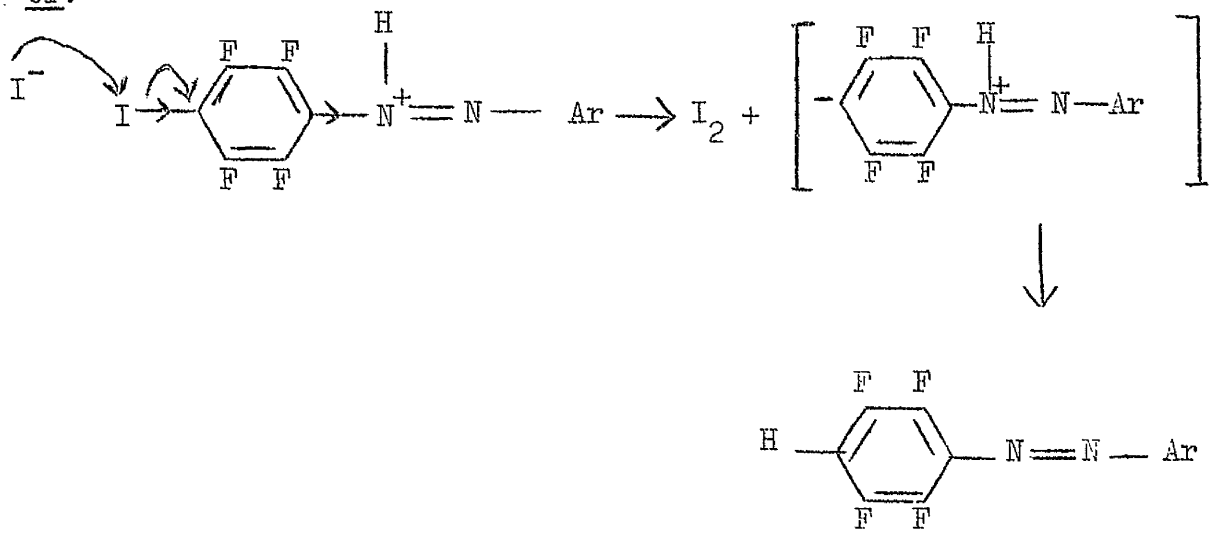
The last compound (3-iodonitrobenzene) and its reduction product, are the only compounds in the above series in which the iodine atom is not conjugated with an electron-withdrawing group (the nitro-, azoxy- or azo-group).

It has been assumed that at some stage of the reaction of 4,4'-dithiophenoxyoctafluoroazobenzene with hydriodic acid, the thiophenoxy-groups are replaced by iodine. The removal of these iodine atoms could occur in either the azo-compound, or in the hydrazo-compound, or in the aniline, for each of these

species will be activated in the strongly acidic medium used, owing to formation of their conjugate acids. The mechanism (given only for the azo-compound) requires either protonation at carbon or the elimination of a carbanion:

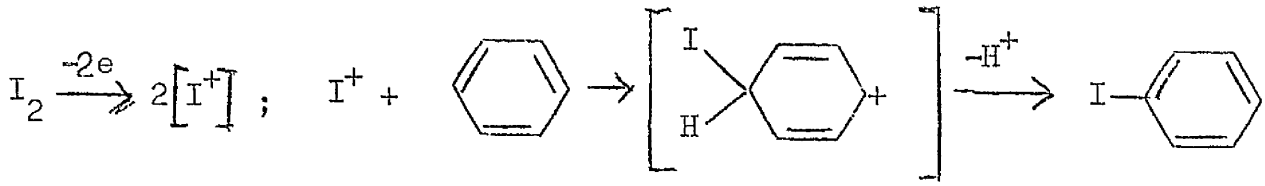


Or:



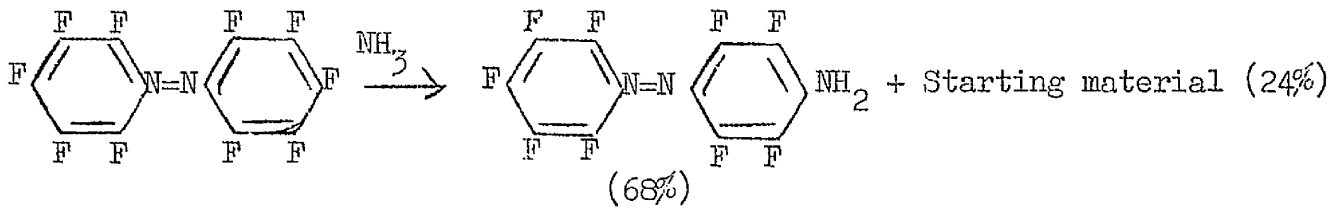
To the present author the second possibility appears quite acceptable, for the electronegativity of the pentafluorophenyl group has been given as about the same as that of a bromine atom (p.43),[103] and in the present case the polarity of the C-I bond will be further enhanced by the protonation of the azo-group.

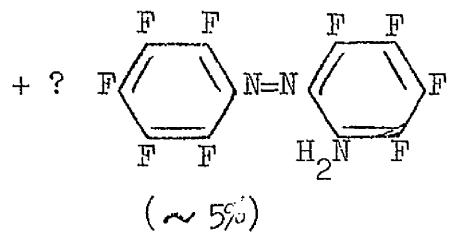
Incidentally, both the above mechanisms appear unconvincing to the present author when applied to the alleged reaction of iodobenzene with hydrogen iodide. It seems more likely that the function of the oxidizing agent in the preparation of iodobenzene is to provide an effective source of iodine cations (either free or complexed) so that the expected electrophilic reaction can take place:



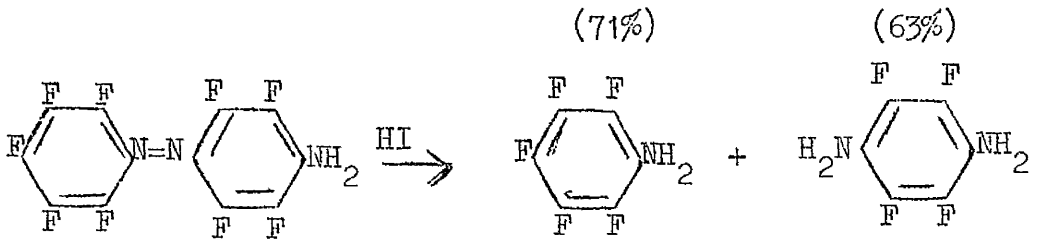
The Reaction of Decafluoroazobenzene with Ammonia

The reaction of decafluoroazobenzene with ammonia in refluxing aqueous ethanol gave the following products:

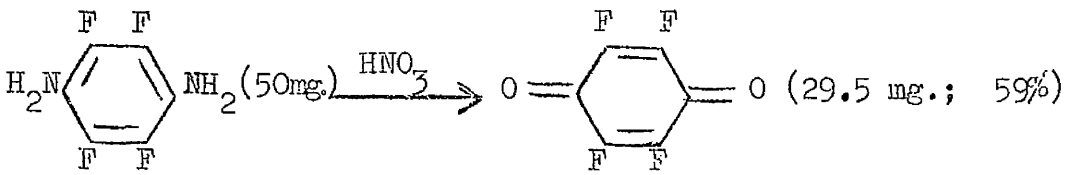




The 4-amino-compound was shown tc be isomerically pure by n.m.r. spectroscopy, and was cleaved by hydriodic acid to tetrafluoro-p-pheaylenediamine and pentafluoroaniline:



The diamine was, like the aminophenol (p.51), oxidized to fluoranil by nitric acid:

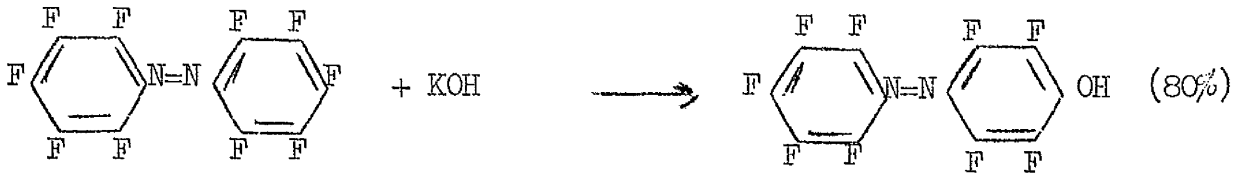


The suspected 2-amino-compound could not be isolated, owing to the small yield and the similarity of its chromatographic characteristics to those of decafluoroazobenzene. Its low polarity suggests that the compound is a monosubstituted derivative, and the 2-isomer can be inferred from its colour, and from the position of the N-H absorptions in the infra-red spectrum - indentical with those of 2-amino-4H,4H-heptafluoroazobenzene.

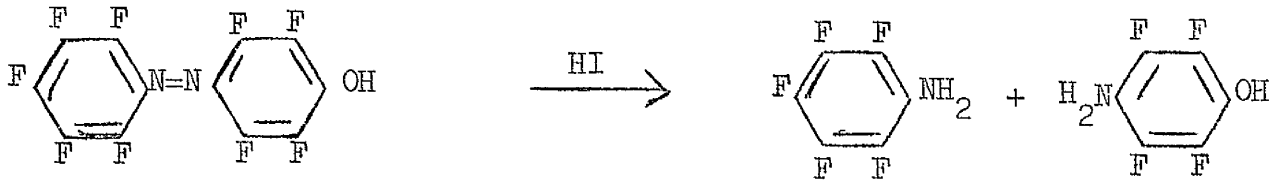
The absence of a disubstituted product is presumably due to the deactivating influence of the first amino-group.

4-Hydroxynonafluoroazobenzene.

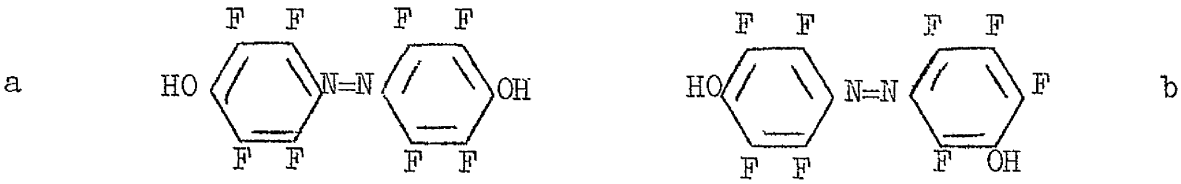
Potassium hydroxide (1.3 mole) in refluxing t-butanol reacted with decafluoroazobenzene to give the 4-hydroxy--derivative in 80% yield based on starting material consumed (50%):



The procedure was adapted from Birchall's[28] preparation of pentafluorophenol, and the work-up was by chromatography. The major product was recrystallized with very little effect on its melting point, and the resulting product was shown to be pure by n.m.r. spectroscopy; it was identified by reductive cleavage:



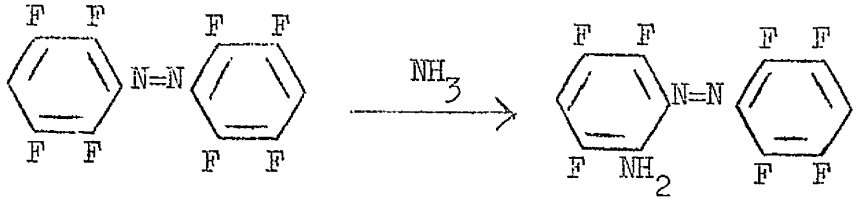
A small quantity of a more polar product, m.p. 208-210°, was obtained, but could not be purified. It was presumably a disubstituted compound, (a) or (b)



- depending on whether the O^- group partially or completely destroys the activating influence of the ArN_2 group. The fact that further reaction occurred at all suggests that compound (a) is the more likely product.

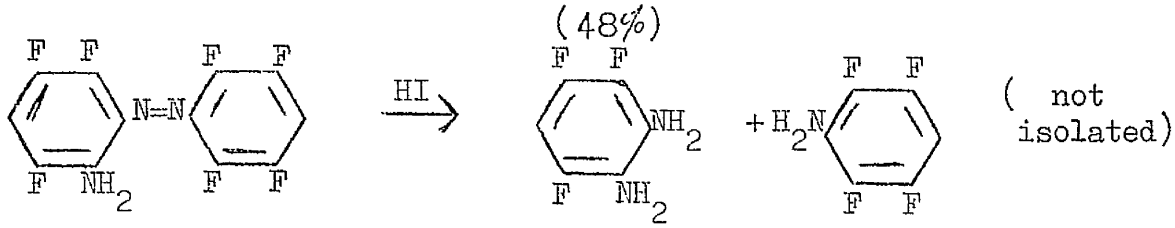
2-Amino-4H,4'H-heptafluoroazobenzene.

4H,4'H-Octafluoroazobenzene, treated with refluxing aqueous ethanolic ammonia as for the reaction with decafluoroazobenzene, gave, after an extended reaction time, 2-amino-4H,4'H-heptafluoroazobenzene in 78% yield:



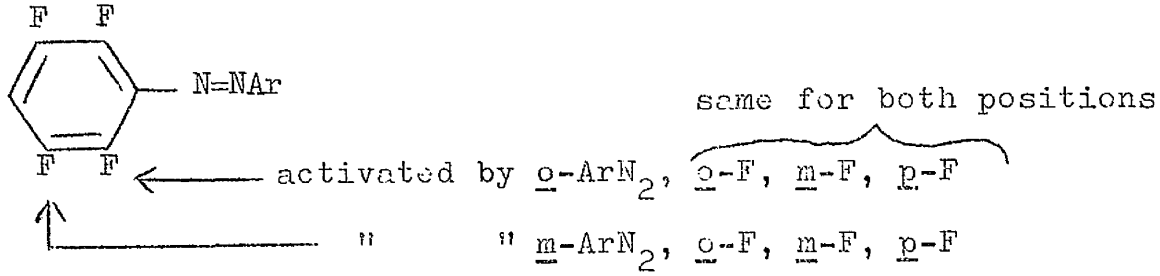
The crude product (isolated by chromatography) was of high purity; recrystallization raised the m.p. slightly, and the resulting product was shown to be pure by its n.m.r. spectrum and by elemental analysis.

Reductive cleavage gave the expected mixture of amines:



The diamine was characterized as its benzil derivative.

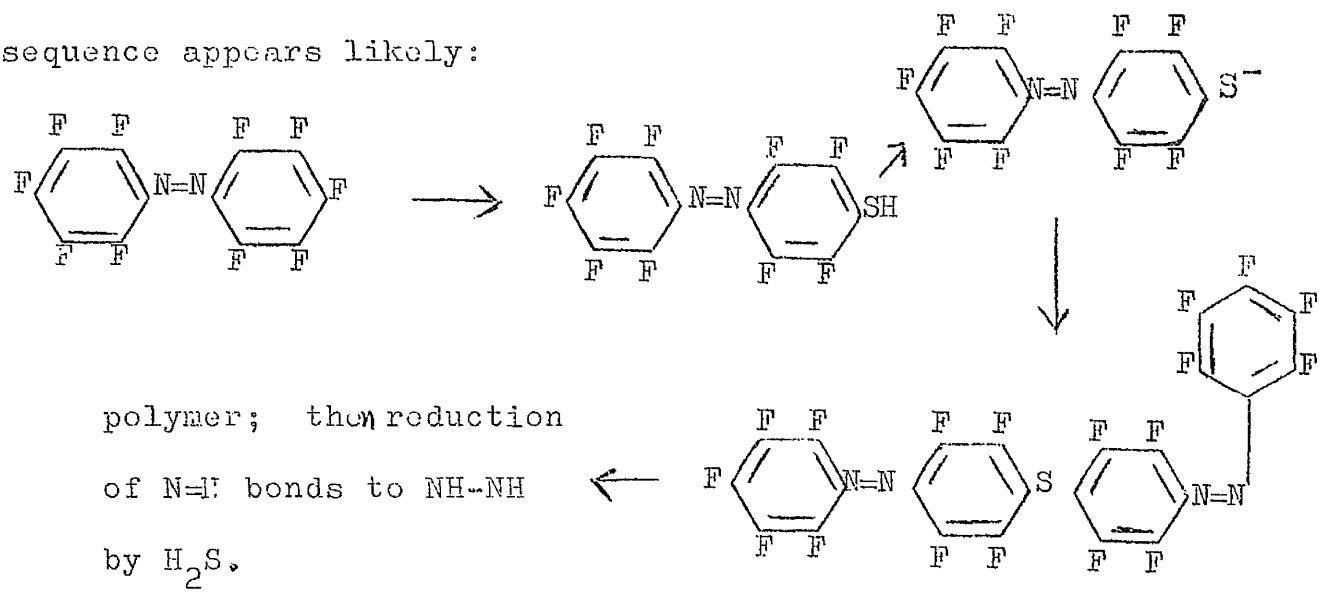
The initial nucleophilic substitution reaction was carried out to obtain some indication of the activating pattern of the fluorinated phenylazo-group. In the octafluoro-azo-compound, the 2- and 3-positions are activated thus:



The experiment shows that the ArN_2-group is much more activating in the ortho than in the meta position and this implies that the polyfluorophenylazo-group is (as expected) activating in nucleophilic substitution, since deactivating groups are generally meta-directing.

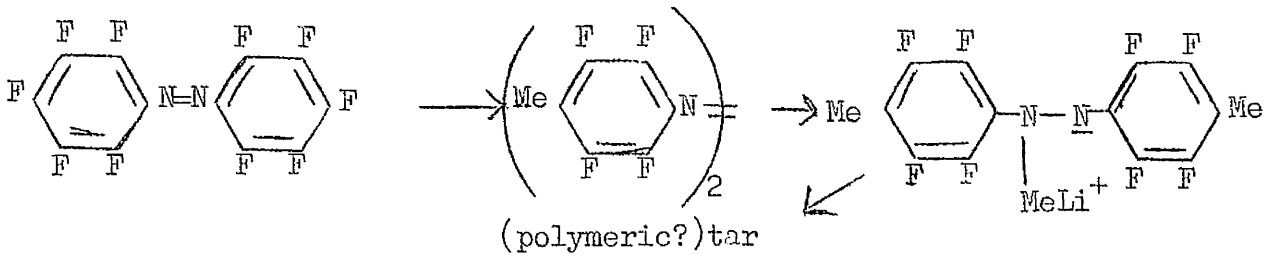
The Reactions of Decafluoroazobenzene with Other Nucleophiles.

The reaction of decafluoroazobenzene with sodium hydrosulphide in refluxing methanol yielded an intractable gummy solid showing N-H but no S-H in the infra-red spectrum. The following sequence appears likely:



polymer; then reduction of N=N bonds to NH-NH by H_2S.

Methyl-lithium in ether reacted with decafluoroazobenzene at 0-5° to give a tar. Polysubstitution is likely to have occurred, and reaction at the azo-group is also possible, since Grignard reagents are known to add to azo-compounds:[111]



A similar experiment with phenyl-lithium gave an equally intractable product.

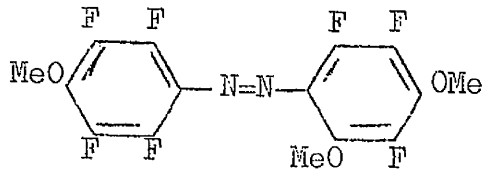
Several experiments were carried out on the reaction of decafluoroazobenzene with hydrazine hydrate. Methanol, ethanol, ether, dioxan, and pyridine were used as solvents, and the reactions at room temperature or under reflux were investigated. The products were colourless or pale brown, suggesting that reduction of the azo-group as well as substitution had occurred. All the products were intractable.

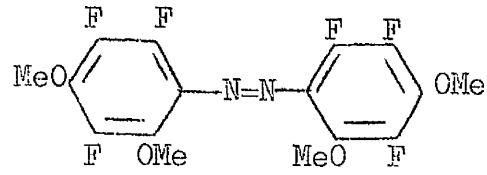
A clue to possible complicating factors is given by Holland and Tamborski's observation of the base-catalysed defluorination of the polyfluorophenylhydrazines; one example is illustrated on p.26 . The defluorination requires the abstraction of a proton from the hydrazine group as the initial step in the reaction, and this normally requires hydroxide or ethoxide ion. The hydrogen atoms in decafluorohydrazobenzene are likely to be more acidic than those in the phenylhydrazine, owing to the inductive effect of the additional pentafluorophenyl group. It is therefore possible that comparable defluorinations could occur also in decafluorohydrazobenzene, instigated by the weaker base, hydrazine. This would add to the multiplicity of products observed.

Recent Work of Other Authors on Decafluoroazobenzene.

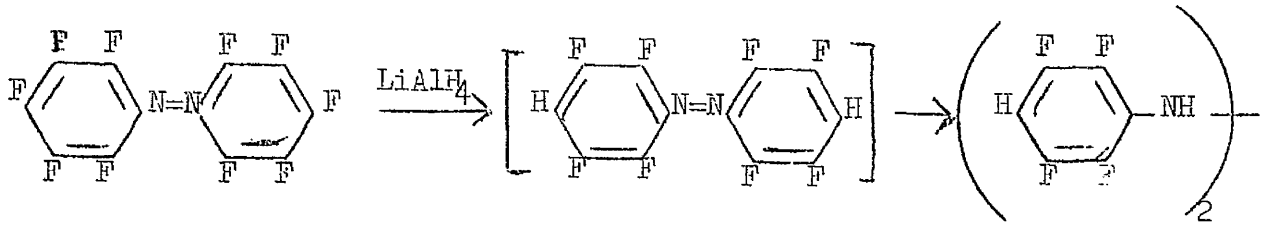
The paper by Burdon, Morton, and Thomas,[98] which has already been mentioned in connection with the azoxy-compounds (p.35),

also describes the preparation of decafluoroazobenzene and two other highly fluorinated azo-compounds by the oxidation of the anilines with aqueous sodium hypochlorite at room temperature. The yield of decafluoroazobenzene was only 25%, but the yields of the 4H,4'H- and 4Me,4'Me- octafluoroazobenzenes were slightly over 50%. Burden and his co-workers report that decafluoroazobenzene reacts with methoxide ion in ether at room temperature to give mono- and di-substituted products identical with those obtained by the present author, and that further reaction gives also the following compounds:



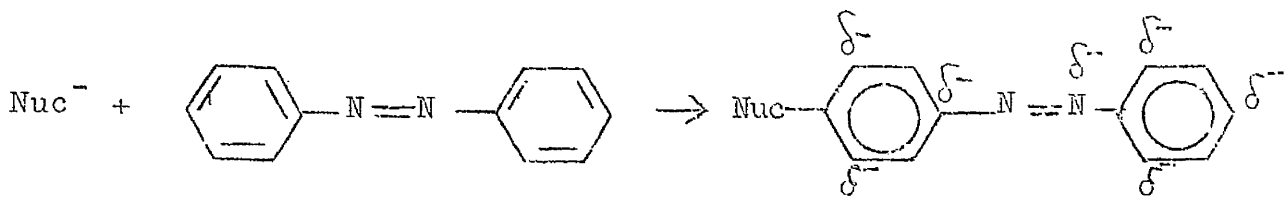


The reaction of decafluoroazobenzene with lithium aluminium hydride gave the octafluorohydrazo-compound in very low yield, and it was shown that in this reaction, the substitution preceded the reduction:



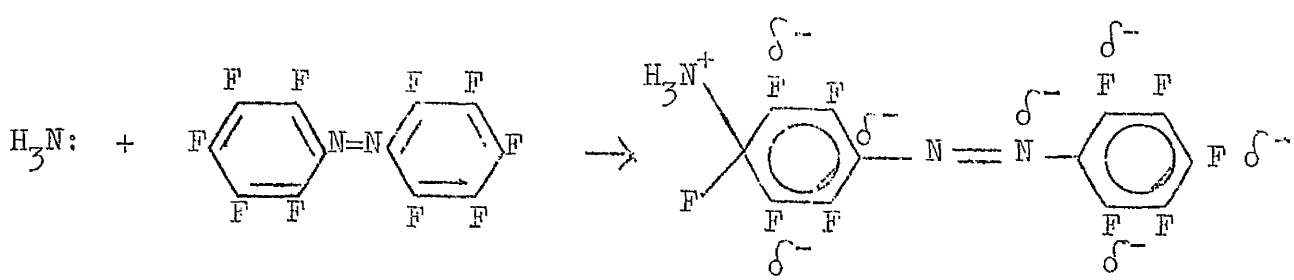
Tars were obtained from decafluoroazobenzene and methyl-lithium or hydrazine in ether, and also from the reactions with hydroxide ion and ammonia (both in ether), from which the present author obtained tractable products by using different solvents.

If tar-formation is taken to imply a high rate of reaction, then a comparison of Burdon's work with that of the author demonstrates a well known phenomenon: that reactions in which a dispersal of electric charge in the transition state occurs are impeded or slowed by an increase in the dielectric constant (or polarity) of the medium.[112]



Furthermore, Burdon's results imply that the fluorinated phenylazo-group is even more activating in nucleophilic substitution than could be inferred from the present author's work.

There is one anomaly, the reaction of ammonia with decafluoroazobenzene: here one would predict that the rate will be faster in ethanol than in ether, for the transition state will involve charge-separation, which is favoured by a polar medium:



The probable explanation is that if the ether were quite dry, and gaseous ammonia were dissolved in it (Burdon used these conditions for the reactions of $C_6F_5.NO_2$ with NH_3), the ammonia

would be a much stronger nucleophile in the absence of any hydrogen bonding (to water or ethanol), which would if present decrease the availability of the lone pair electrons on the nitrogen. Another matter which requires comment is the slowness of the reaction of decafluoroazobenzene with methoxide ion compared with that with ethoxide ion; the latter is a stronger nucleophile than methoxide, but the difference in reaction rates is actually fully explicable by solvent and temperature effects. The reactions were carried out under reflux, and methanol boils 14° lower than does ethanol, and is also the more polar of the two solvents. These solvent effects are of a similar magnitude to those observed on transferring from methanol to dioxan/methanol (a comparable system to ether/methanol) as the following table (calculated from data of Ho and Miller[13]) shows:

Table 4

Temperature and Solvent effects on the Rate of the C_6F_5Br/NaOMe Reaction.

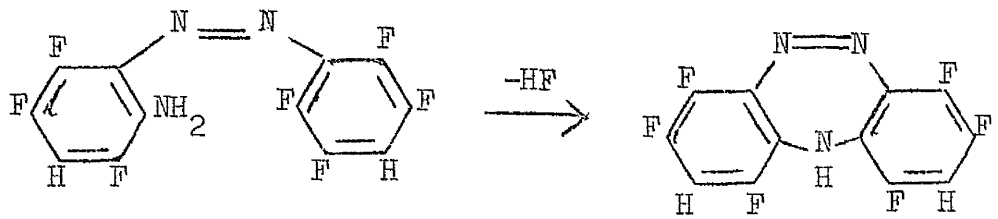
Temperature ($^{\circ}C$)	Room temp. (20°)	b.p.MeOH (64.7°)	b.p.EtOH (78.3°)
Rate constant (10^3k) in methanol	0.008	6.6	20.5
10^3k 5 pts. dioxan/ 1 pt. MeOH.	3.6	220	650

It is seen that - discounting effects due to polarity differences - reactions in refluxing methanol will occur at less than one third the rate observed in refluxing ethanol, and that on transferring to an ethereal solvent (dioxan or ether) the same reactions will occur at a comparable rate at room temperature. Tar formation from the reactions of decafluoroazobenzene with hydroxide ion and with ammonia is probably due to an additional factor - the increased nucleophilicity of the unsolvated reagents.

Burdon and his colleagues report a few of the compounds made by the present author, whose work is upheld by the published paper.

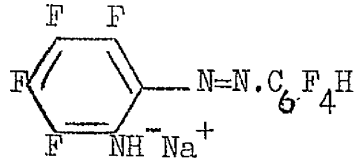
The Attempted Cyclization of 2-Amino-4H,4'H-heptafluoroazobenzene.

Two exploratory experiments were carried out in an attempt to achieve the following cyclization:



Firstly, the aminoazo-compound in the vapour state was passed over anhydrous potassium fluoride at 270° - the reagent has been used before to abstract hydrogen fluoride from partially fluorinated aliphatic compounds (with the formation of a C=C double bond). The reaction gave the starting material quantitatively, and was not investigated further.

In the second experiment, the aminoazo-compound was heated in an atmosphere of nitrogen under reflux with sodium hydride in toluene, in the expectation that the anion



would eliminate fluorine intramolecularly (polymerization would be expected not to occur, for this anion will be highly deactivated to nucleophilic attack). No reaction occurred.

Attempted Formation of Metal Complexes from 2-Amino-4H,4'H-heptafluoroazobenzene.

The formation of complexes from ortho amino- and ortho hydroxy-azo-compounds is well known, and attempts were made to make mercury, copper, and nickel complexes of the 2-amino-heptafluoro-compound. The azo-compound was heated with mercuric oxide in refluxing ethanol for 30 min., but no reaction occurred. With cupric or nickel salts in methanol solution containing a little aqueous ammonia,[113] darkening occurred as the azo-compound dissolved, but the presumed complex broke up on removal of the solvent. The instability of the complexes was probably due to inductive withdrawal of the amino-group electrons by the fluorinated aromatic ring. In addition, it is known that complexes derived from benzenoid azo-compounds are less stable than those obtained from polynuclear arenes.

Exploratory Reactions of Various Fluoroaromatic Compounds with Nucleophiles.

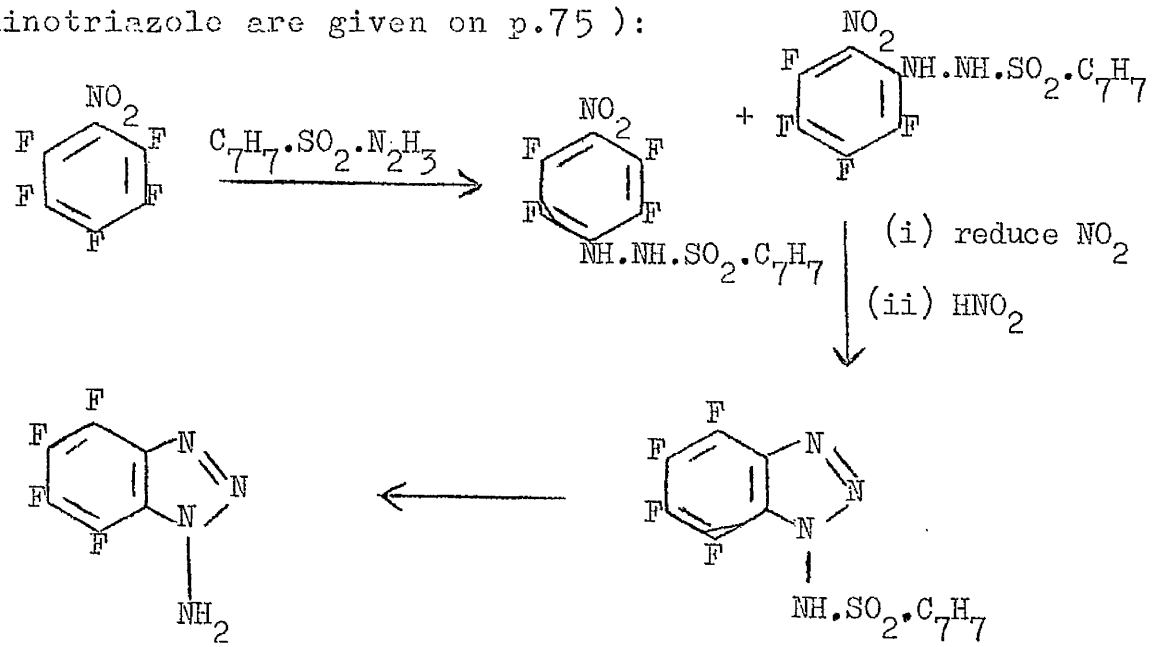
Pentafluoronitrosobenzene with Hydrazine Hydrate. The nitroso-compound,[86] stirred in ethanol at -15°, was treated with 1.5 mole of hydrazine in order to determine whether the reaction would aid the investigation of the reactions of the fluorinated azo- and nitro-compounds with the same nucleophile; an intractable tar was obtained.

Decafluorohydrazobenzene and Hydrazine Hydrate. Decafluorohydrazobenzene (91%) was recovered after treatment with hydrazine hydrate in refluxing ethanol. This reaction shows that in the reaction of decafluoroazobenzene with hydrazine (p. 62), substitution must have preceded reduction of the azo-group, and secondly, that the hydrazo-compound is greatly deactivated towards nucleophilic attack; in this it resembles both pentafluoroaniline and pentafluorophenylhydrazine (p. 6).

For this latter reason, together with the ready autoxidation and thermal instability of the hydrazo-compounds, the reactions of decafluorohydrazobenzene with nucleophiles were not investigated (they could provide a route to meta- - substituted azo-compounds, but these would be more conveniently obtained by oxidation of the anilines).

Pentafluoronitrobenzene with Toluene-p-sulphonylhydrazide. Equimolar quantities of the nitro-compound (p. 21) and the hydrazide were heated for 1 hr. in refluxing ethanol;

precipitation of the product with water gave unchanged pentafluoronitrobenzene. The reaction at room temperature (the hydrazide is somewhat unstable to heating) also gave starting material. The intention had been to achieve the following series of reactions (the reasons for requiring the aminotriazole are given on p.75):

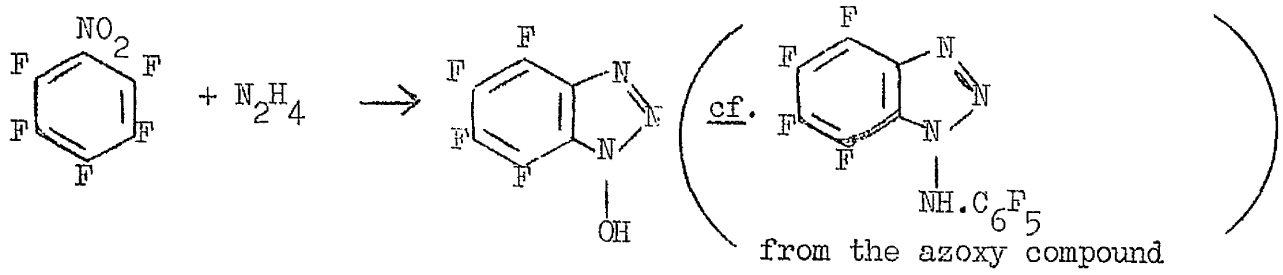


The failure of the first stage of this series is almost certainly due to the poor nucleophilicity of the acid hydrazide compared with that of hydrazine.

The Reaction of Pentafluoronitrobenzene with Hydrazine Hydrate.

The reaction of decafluoroazoxybenzene with hydrazine gave a 1-(phenylamino)benzotriazole, the identification of which presented certain difficulties (p.107). It was therefore decided to investigate the reaction of pentafluoronitrobenzene with hydrazine with the intention of obtaining a "model" compound for a proof of structure involving u.v. and n.m.r.

spectroscopy. The following is the anticipated reaction:

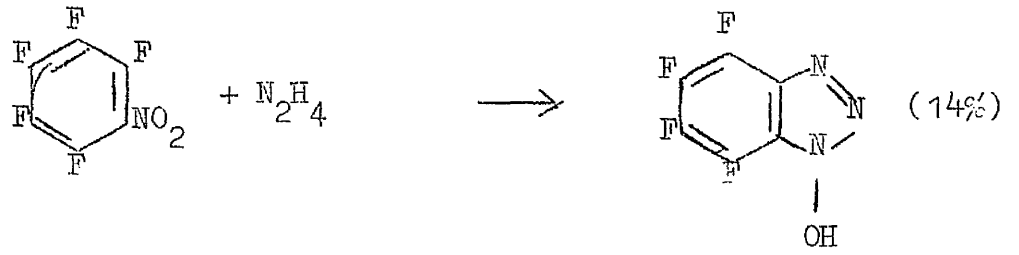


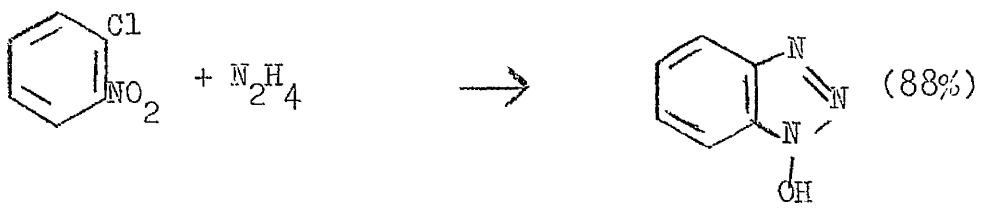
Preliminary experiments with hydrazine and pentafluoronitrobenzene are tabulated in the experimental section (p.179). Reactions were carried out using 1.5-2.5 mole of hydrazine/mole of nitro-compound, at room temperature or reflux in the following solvents: ethanol, ether, dioxan, propan-2-ol, aq. 90% methanol, and benzene. Failures and difficulties were due to two phenomena: (i) in the less polar solvents (e.g. ether), the product was intractable, probably due to polysubstitution; (ii) in solvents of high polarity, (e.g. ethanol) the reactions were (at first) irreproducible. A small yield of an explosive substance was sometimes obtained, and later work showed that this was, in fact, the desired triazolol.

It was eventually observed that the required product was generally isolated when the crude product was heated after removal of the solvent was complete. After this observation, a procedure was developed whereby the replacement of the extraction solvent by the recrystallization solvent was combined with this heating stage, enabling highly reproducible results to be obtained. An extensive purification led to

isolation of the product in 14% yield.

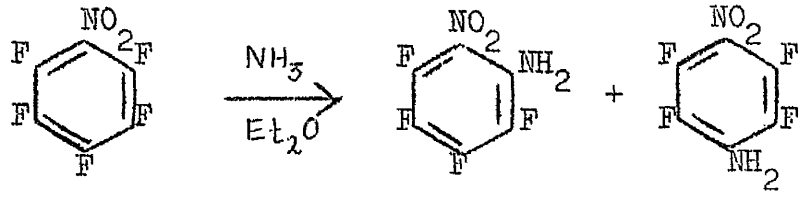
The reaction of pentafluoronitrobenzene with hydrazine to give tetrafluorobenzotriazol-1-ol can be represented thus, and is rather similar to the reaction of 2-chloronitrobenzene with hydrazine:[114]



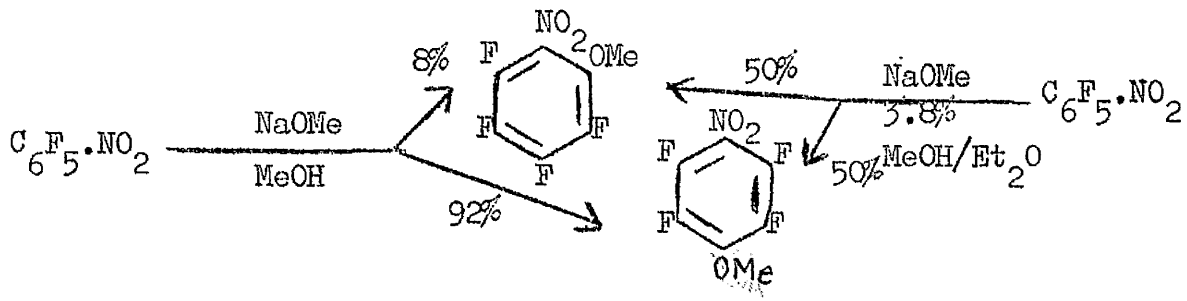


Similar reactions occur with dihalogenated nitro-compounds (with lower yields), and Müller and Hoffmann[115] have reported the preparation of a triazole from a nitro-compound containing o-, m-, and p-chlorine atoms; the yield was not stated:

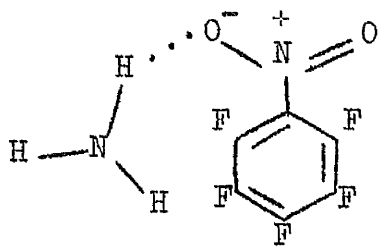
This last reaction is an example of the (more or less) specific activation in the ortho position that has been observed before in the reactions of nitro-compounds.[116] Two examples involving pentafluoronitrobenzene have already been reported,[42, 43, 16] and the second of these at least is solvent-dependent:[16]



Ratio 7 : 3



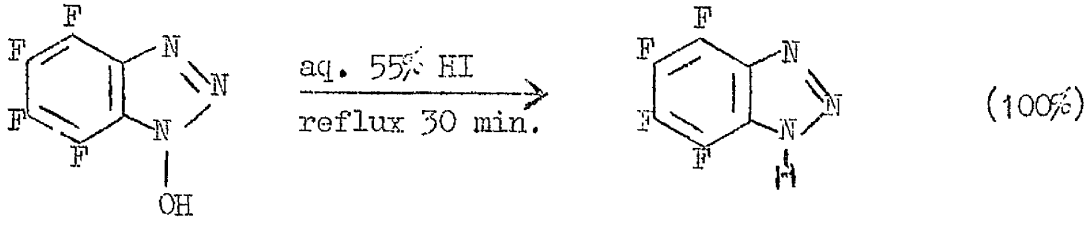
The reaction of pentafluoronitrobenzene with ammonia was originally explained in terms of hydrogen bonding between the incoming nucleophile and the nitro-group:



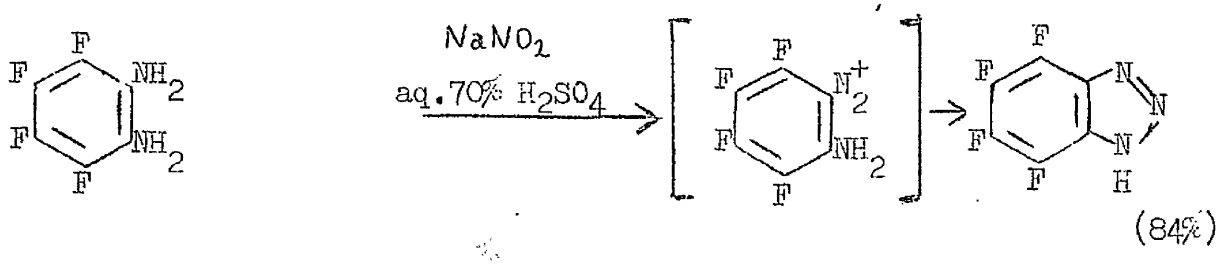
Whilst it would be unreasonable to dispute that such hydrogen bonding is a contributory factor to the course of the reaction, it clearly cannot explain ortho substitution with methoxide ion. The solvent effect provides a clue to the probable explanation, and this is discussed later (p.87) in connection with the pentafluorophenylazoxy-group.

Tetrafluorobenzotriazole

Tetrafluorobenzotriazol-1-ol was reduced quantitatively to tetrafluorobenzotriazole by refluxing aqueous hydriodic acid; the similar reduction of the unfluorinated compound has been known since 1900:[117]



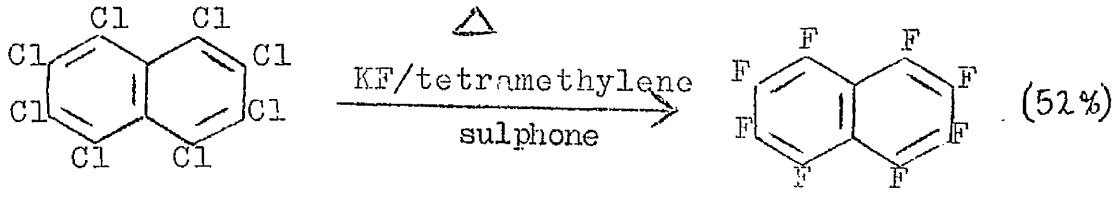
Tetrafluorobenzotriazole was also prepared by the diazotization of tetrafluoro-o-phenylenediamine (p. 87), and this reaction also is closely analogous to the preparation of benzotriazole from o-phenylenediamine:[118]



The scale of this experiment was small and the product was identified by infra-red spectroscopy. The reaction was not investigated further, for the diamine was not readily available in this Department. However, this route to tetrafluorobenzotriazole is at least as convenient as the preparation via pentafluoronitrobenzene and the triazolol, and the overall yield from pentafluoroaniline may be higher.

Tetrafluorobenzotriazole was characterized (p. 105) by elemental analysis, u.v., and n.m.r. spectroscopy.

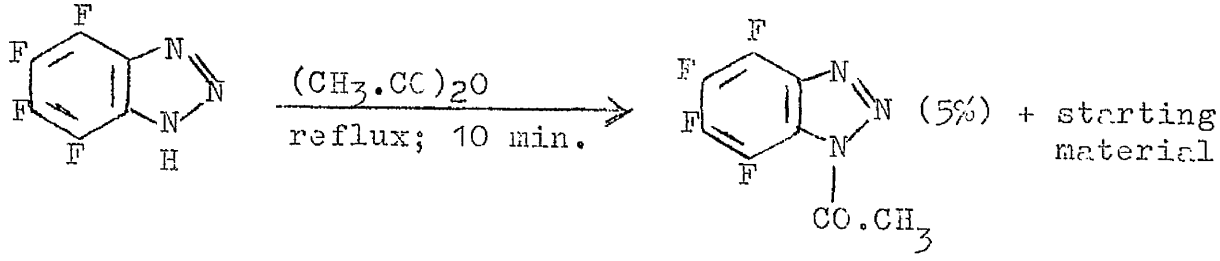
An attempt was made to fluorinate tetrachlorobenzotriazole by a procedure analogous to that used for the fluorination of octachloronaphthalene:[119]



Tetrachlorobenzotriazole[120] was prepared by the chlorination of benzotriazole[118] with refluxing aqua regia, and two attempts to fluorinate the chloro-compound were made; the reaction with anhydrous potassium fluoride in tetramethylene sulphone at 270° for 20 hr. gave a tar, and the same reagents, heated at 200° for 18 hr., gave starting material (14%) together with tar.

1-Acetyltetrafluorobenzotriazole.

Tetrafluorobenzotriazole was acetylated in the 1-position by refluxing acetic anhydride:

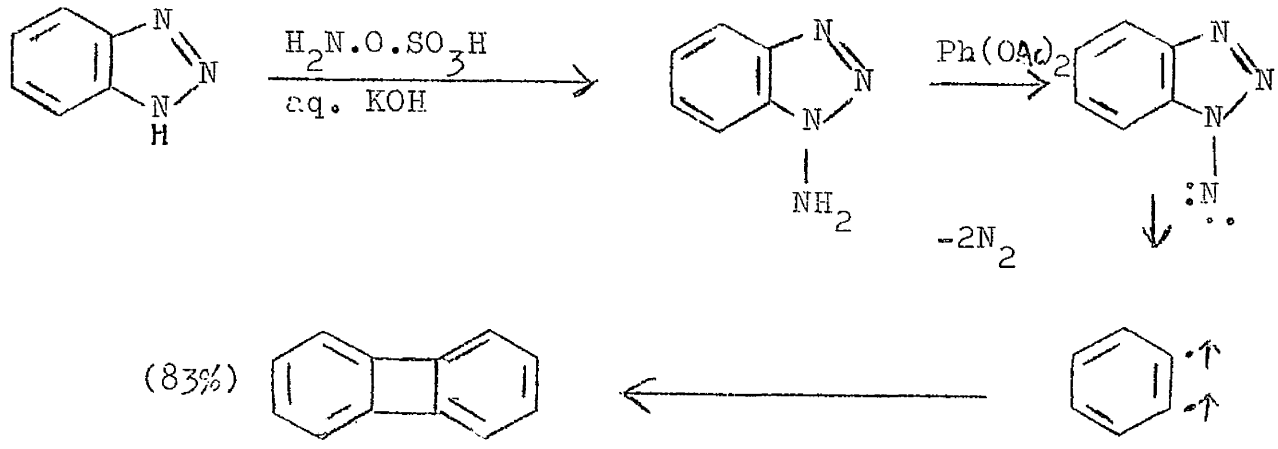


The product was rather difficult to isolate, since it was very readily hydrolysed; both in the position of acylation and in the ready hydrolysis of the product tetrafluorobenzotriazole

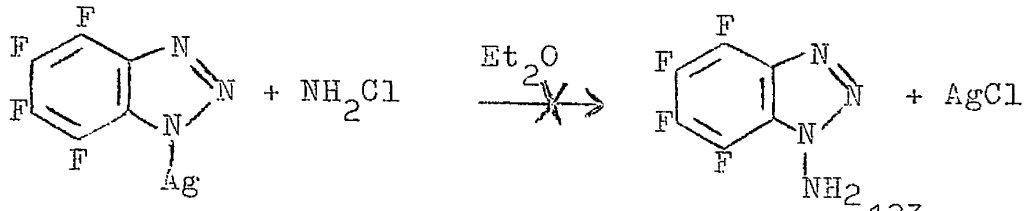
resembles its unfluorinated analogue.[121] The compound was characterized by elemental analysis, i.r. spectroscopy, and n.m.r. spectroscopy - this last established the position of the acetyl group (p.114).

The Attempted Synthesis of 1-Aminotetrafluorobenzotriazole.

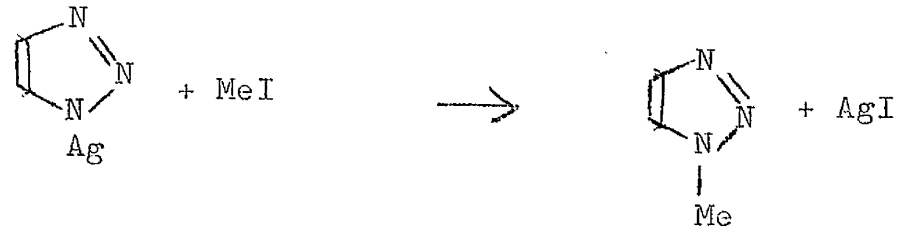
Shortly after tetrafluorobenzotriazole had been prepared, the following synthesis of biphenylene was reported by Campbell and Rees.[122]



Several unsuccessful attempts to prepare 1-aminotetrafluorobenzotriazole were made, with the intention of preparing octafluorobiphenylene by a comparable synthesis. Amination of tetrafluorobenzotriazole with hydroxylamine-O-sulphonic acid could not be achieved, so amination of the silver salt (precipitated by the addition of silver nitrate to an aqueous solution of the sodium salt) was attempted, but was unsuccessful.

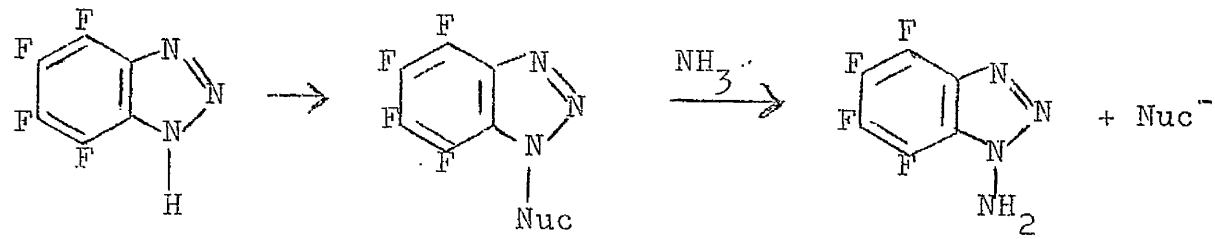


cf. the preparation of 1-methyl~~benzo~~triazole:[123]



Three attempts to nitrate* tetrafluorobenzotriazole, with the intention of reducing the nitro-triazole to the amino--triazole, gave only starting material. The lack of success of these electrophilic reactions is in accord with the difficulty of preparation of the 1-acetyl-triazole.

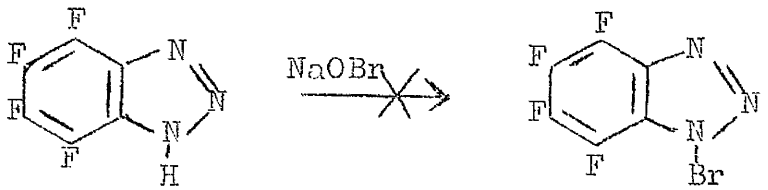
Attention was now turned to the preparation of compounds which could undergo nucleophilic amination:



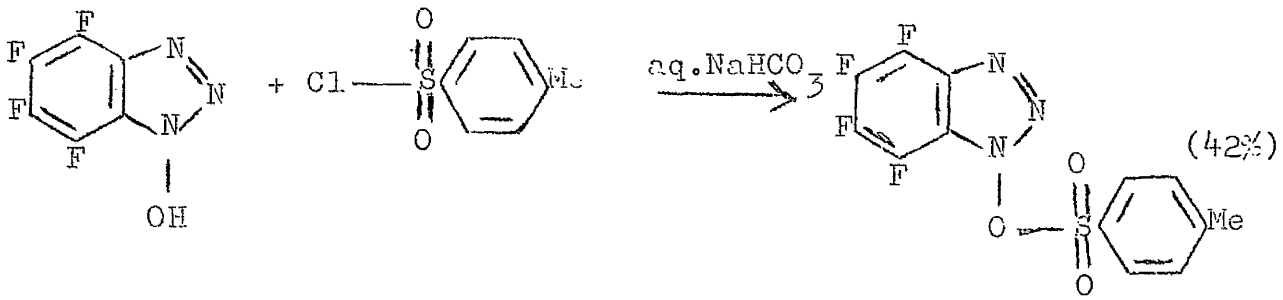
Chlorination of the triazole and bromination of the triazole were each unsuccessful:

---

* Reagents and conditions: (i) HNO_3/H_2SO_4; 0°; (ii) $HNO_3/(CF_3CO)_2O$; 20°; (iii) HNO_3/Ac_2O; reflux.

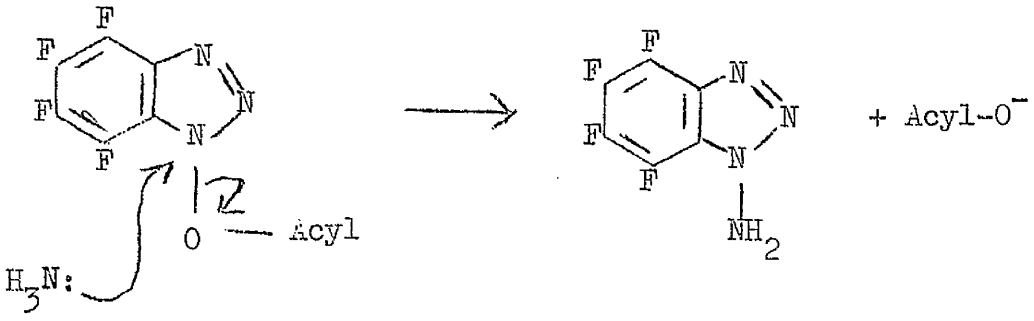


Tosylation and benzoylation of tetrafluorobenzotriazol-1-ol were achieved by Schotten-Baumann procedures with aqueous sodium bicarbonate and the acid chlorides, e.g:

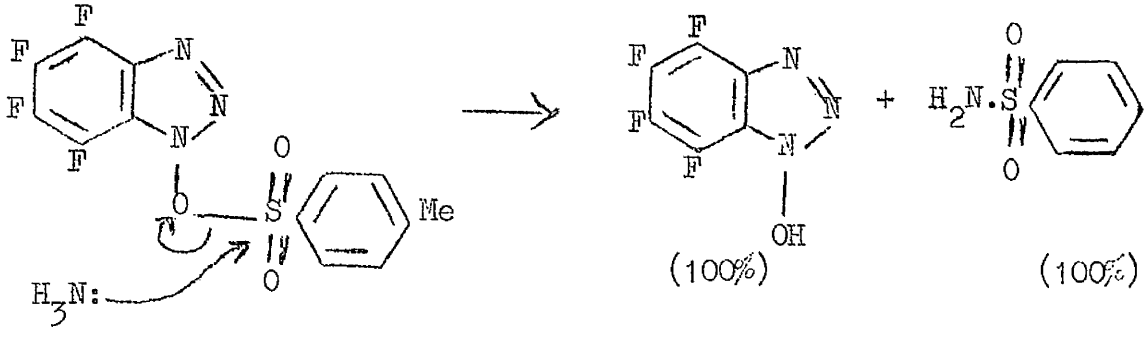


The products were characterized by the ammonolysis reactions described below. The tosyloxy-triazole was also analysed, but the benzoyloxy-triazole (prepared similarly in 80% yield) was not purified.

The following sequence might be expected to occur, in view of the probable increase in susceptibility of the triazole ring to nucleophilic attack owing to the presence of the fluorine atoms:

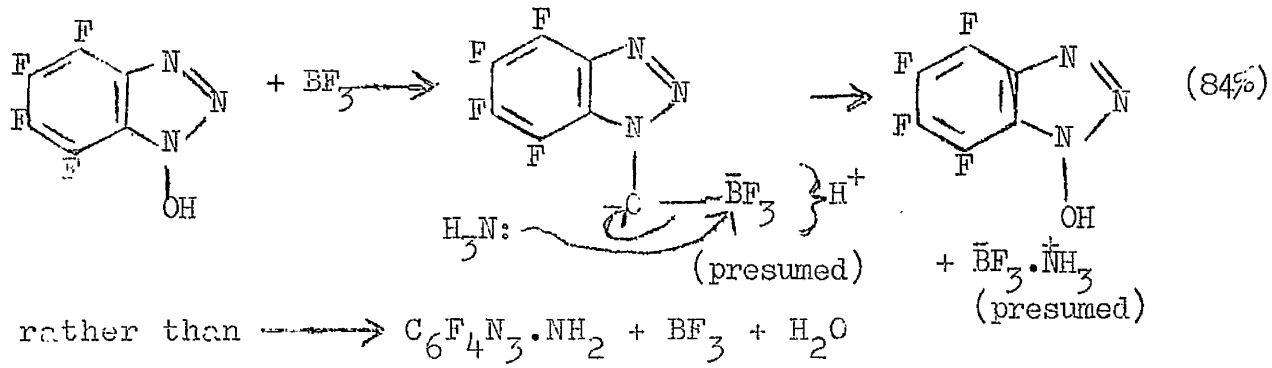


In fact, the reactions of the acyloxy-triazoles with refluxing aqueous ethanolic ammonia took the more usual course, viz.



The benzoyloxy-compound reacted similarly; all the ammonolysis products were identified by i.r. spectroscopy.

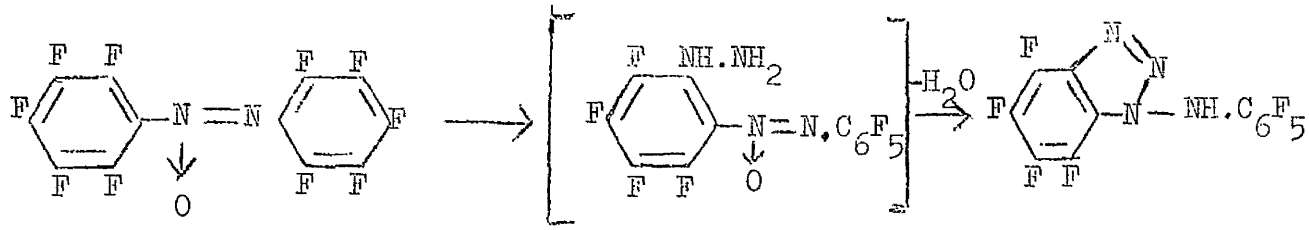
The preparation of 1-aminotetrafluorobenzotriazole was attempted by one more route. A large excess of boron trifluoride was added to the triazolol in dichloromethane, and the mixture was then saturated with anhydrous ammonia. Once more, the reaction took the usual course, i.e:



- rather than $\longrightarrow C_6F_4N_3.NH_2 + BF_3 + H_2O$

The Reaction of Decafluoroazoxybenzene with Hydrazine.

Decafluoroazoxybenzene and hydrazine hydrate (1.5 mole) were heated under reflux for 30 min. in ethanol; it was anticipated that either reduction or substitution (possibly both) would occur. However, a simple work-up gave 1-(pentafluorophenylamino)tetrafluorobenzotriazole in 28% yield:

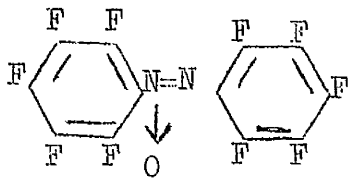
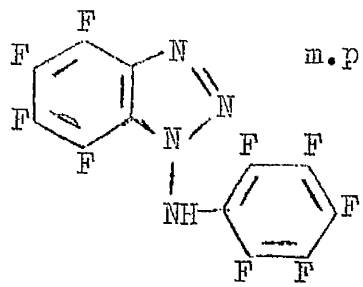
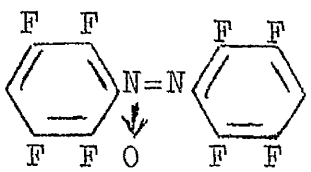
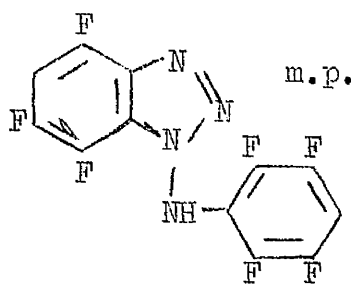
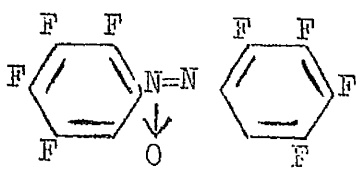
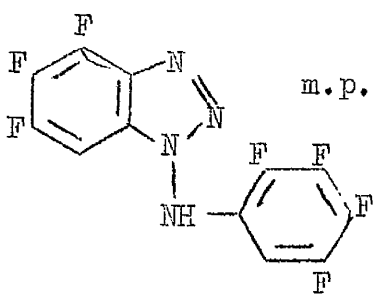
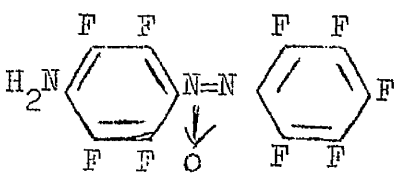
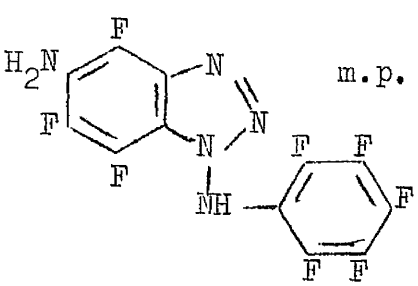
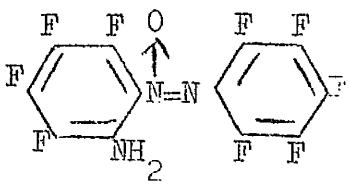
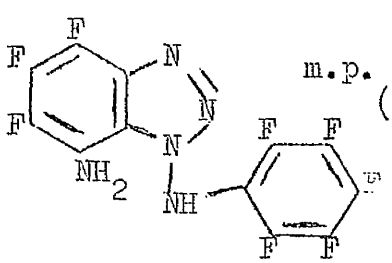


The identification of this compound presented some difficulty, and is discussed on p. 107 .

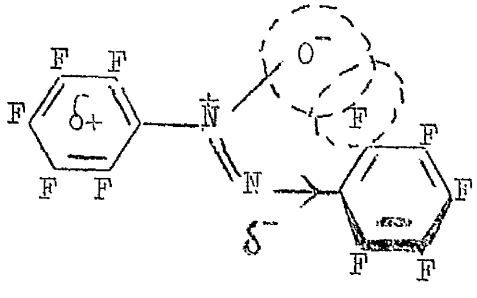
The reaction is closely analogous to those of 2-chloronitrobenzene and pentafluoronitrobenzene with hydrazine, but, as it happens, the preparation of 1-(phenylamino)benzotriazoles from halogenated azoxy-compounds appears never to have been reported or attempted before - it is probably quite general, and four more examples are reported in this thesis. These are included in the table below. Satisfactory analyses were obtained on all except the last compound (for which insufficient sample was available), and the spectroscopic characterizations of all five compounds are given on p.107 ff.

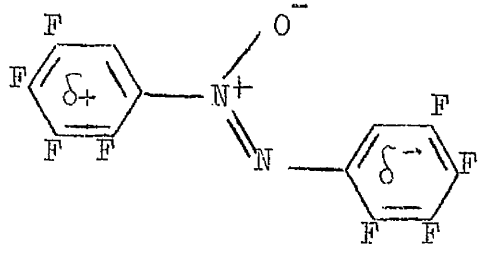
Table 5

The Preparation of 1-(Phenylamino)benzotriazoles from Azoxy-compounds

Starting Material	Product from reaction w. N_2H_4	Yield
	 m.p. 158-9°	28%
	 m.p. 162-4° (decomp.)	37%
	 m.p. 125-6°	34%
	 m.p. 152-3°	23%
	 m.p. 147° (decomp.)	9%

The experimental procedures for these reactions were comparable (the major variation was in the duration of reflux - 15 or 30 min., but since the reaction appeared to be fast, this factor may not be significant) and it is therefore possible to comment on the relative yields of the products. The highest yield was obtained from 4H,4'H-octafluoroazoxybenzene, in which the only positions activated to nucleophilic attack are those ortho to the azoxy-group, and the lowest yield was obtained from 2-(pentafluorophenylazoxy)tetrafluoroaniline, which is deactivated to nucleophilic attack by the amino-group, and which has only one ortho-position available in the ring next to the N⟶O bond. The high yield of triazole from the 2H,2'H-octafluoroazoxy-compound may be due to the planarity of this compound (p. 121), which should increase the difference in activation between the two rings, and favour substitution in the ring adjacent to the N⟶O groups:



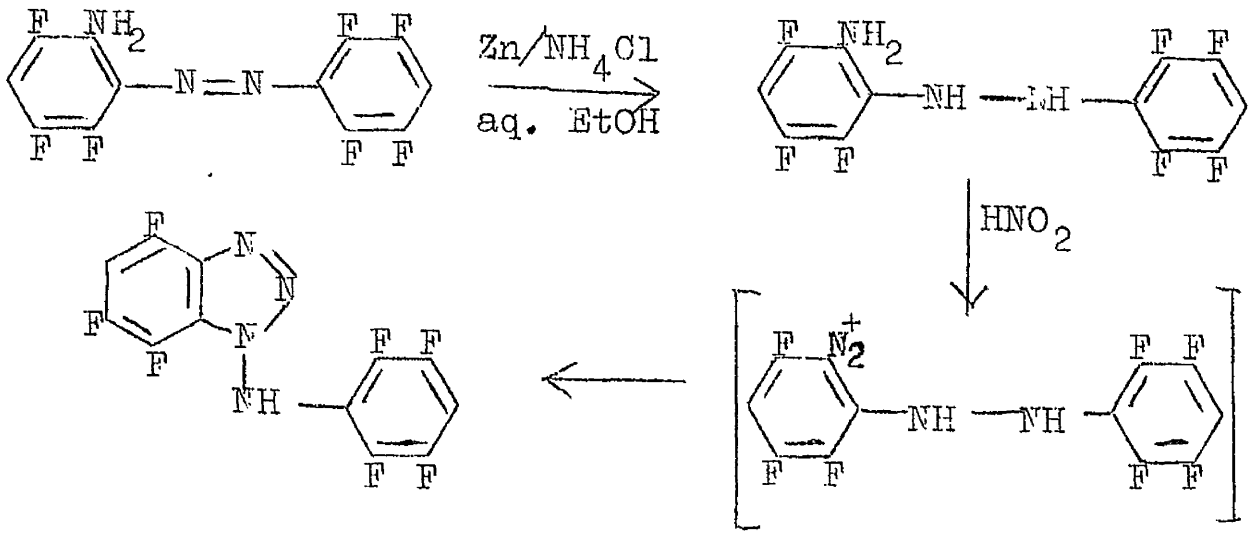


decafluoroazoxybenzene:
non-planarity limits deactivation of ring further from N⟶O group.

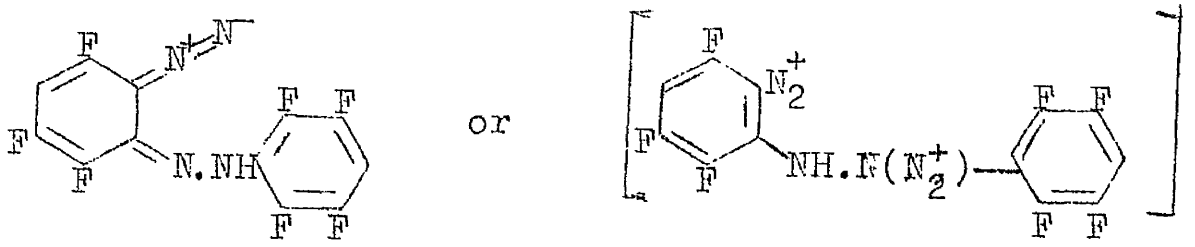
2H,2'H-octafluoroazoxybenzene:
ring further from N⟶O group deactivated by resonance.

The mother liquors from the crystallizations of each of the triazoles yielded tars, which were not further investigated; products due to polysubstitution, substitution in the 4-position, reduction, or defluorination (p.26) could have been present.

Since 2-amino-4H,4'H-heptafluoroazobenzene was available, it was decided to attempt an independent synthesis of one of the triazoles:



Thy hydrazo-compound was prepared similarly to decafluorohydrazobenzene, but it was found to be difficult to handle, since it is very readily autoxidized; accordingly, it was diazotized in situ. Sufficient sodium nitrite was used to destroy the ammonium ion present. The resulting product was intractable, but showed absorption at 4.7μ in the infra-red spectrum. This band was probably due to a diazonium cation, possibly either



The Oxidation of 1-(Pentafluorophenylamino)tetrafluorobenzotriazole with Lead Tetra-acetate.

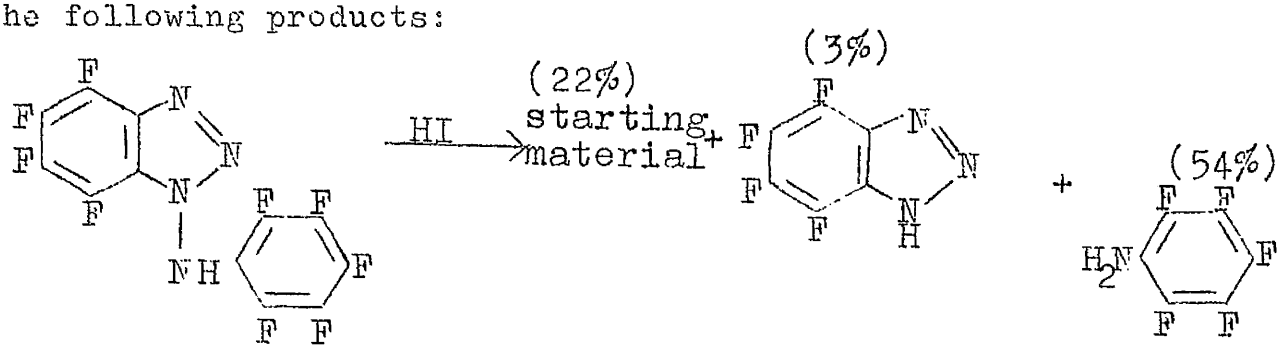
This reaction was carried out before the nature or identity of the triazole was known. Since the compound had been prepared from an azoxy-compound and a reducing agent (hydrazine) it seemed possible that to treat the (then unknown) product with an oxidant might aid its characterization.

Oxidation of the triazole with lead tetra-acetate in benzene, both at room temperature and under reflux, gave fair yields of an orange product melting over a wide range, and shown by n.m.r. spectroscopy to be a mixture of several compounds; its u.v. spectrum (λ_{max} 305-7 mμ, ε = 15800 and λ_{max} 457-9 mμ, ε = 708 in EtOH, cf. decafluoroazobenzene, p.130) suggested that the constituents were azo-compounds. This would involve the destruction of the triazole ring - this has been recently observed also in the oxidation of 1-aminobenzotriazole by the same oxidant (p.75).

Reductive Cleavage of 1-(Pentafluorophenylamino)tetrafluorobenzotriazole.

This reaction was carried out in order to provide a chemical proof of the structure of the triazole.

The triazole in an inert solvent (p-xylene) was heated under reflux for 3 days with aqueous hydriodic acid, and gave the following products:

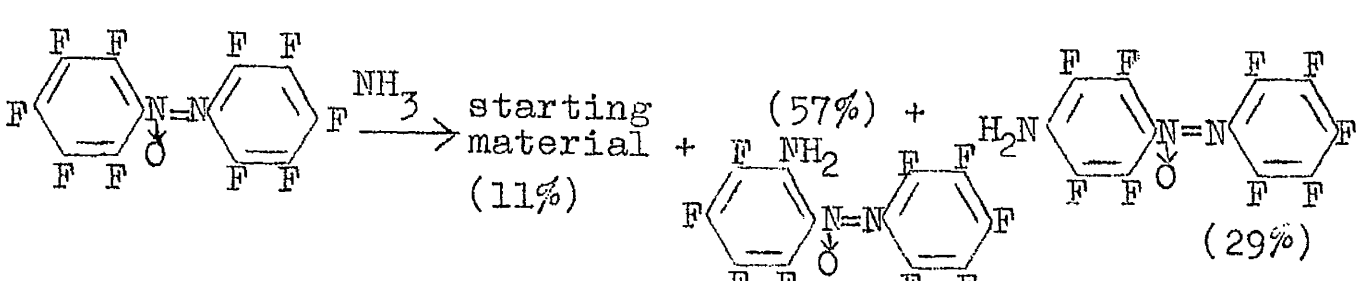


It is conceivable that the low-yield of tetrafluorobenzotriazole was due to further reduction to tetrafluoro-o-phenylenediamine during the prolonged reaction time necessary to cleave the phenylaminotriazole. If so, the diamine could have been distributed through the various aqueous phases during the work-up, and consequently escaped detection.

The cleavage has similarities to both the reduction of the triazol-1-ol (p.73) and the reduction of decafluorohydrazobenzene (p. 43), and the mechanism will not be discussed further.

The Reaction of Decafluoroazoxybenzene with Ammonia.

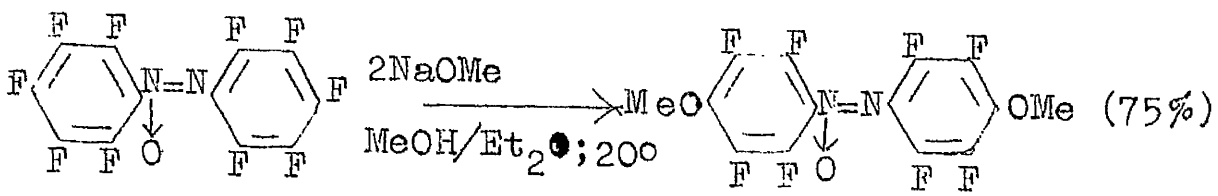
The reaction of decafluoroazoxybenzene with aqueous ethanolic ammonia at reflux temperature gave the following products, which were isolated by chromatography:



+ mixture of unidentified products (2%)

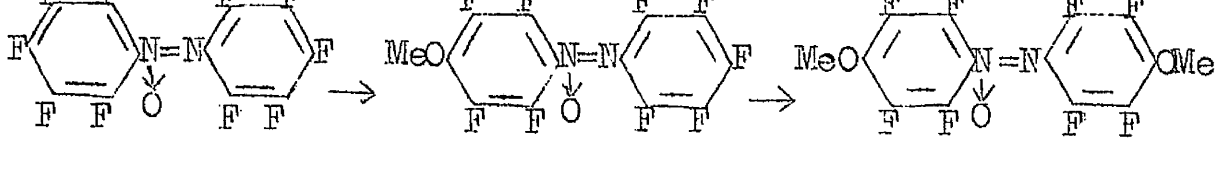
The products were characterized by elemental analysis, reductive cleavage, and by conversion into triazoles; these reactions, together with spectral data, are discussed on p. 116 .

The paper of Burdon, Morton, and Thomas,[98] which appeared before the above reaction was carried out, described the reaction of decafluoroazoxybenzene with methoxide; the authors avoided the problem of isomerism (which would have been difficult to investigate in ignorance of the reactions with hydrazine) by using two equivalents of the nucleophile:



The above reaction with ammonia was intended to complement Burdon's work, since by use of a deactivating nucleophile, the relative reactivities of the two rings [which will, of course, be different, for they have different substituents: -ArN=N(O)- and ArN(O)=N-] could be investigated. The ortho/para ratio of 2 in the reaction with ammonia (cf. the inferred ratio of $\leqslant 0.25$ in the reaction with methoxide) once again emphasizes the similarity of the arylazoxy-group to the nitro-group, and supports the early suggestion (p. 72) that hydrogen bonding is in part responsible for the high ortho/para ratio in the reaction of pentafluoronitrobenzene with ammonia.

Burdon's reaction presumably took the following course:

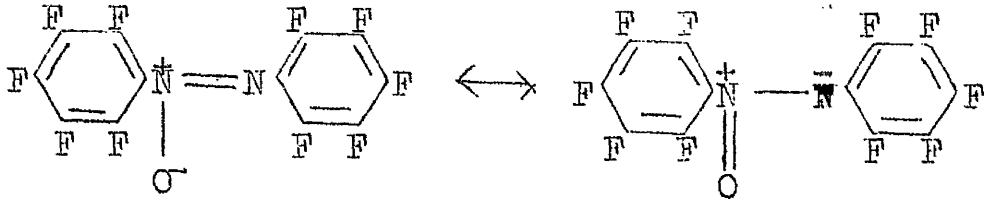


Since the methoxy-group is a weakly deactivating group[13] one would deduce that the $C_6F_5N{=}N(O)$- group is only slightly more activating than the $C_6F_5N(O){=}N$- group, in view of the fact that the second substituent goes into this other ring. It is therefore somewhat surprising that in the azoxy-compounds containing the strongly deactivating amino-group, a considerable proportion, at least, of hydrazine enters the already-substituted ring during the triazole-formation reactions (p.80); that this occurs is powerful circumstantial evidence that isomerization of the azoxy-compounds does not occur during these reactions, and this substantiates their use to prove the structure of the amino-compounds (p.116). For example, if the azoxy-compounds could equilibrate:

(a) $H_2N.C_6F_4.N(O){=}N.C_6F_5 \rightleftarrows$ (b) $H_2N.C_6F_4.N{=}N(O).C_6F_5$, one would expect the reactions with hydrazine to occur more readily with the forms (b), leading to products with the substituents in different rings.

Substitution on the ring next to the N$\longrightarrow$O group is precisely what one would expect in view of the similarity of this end of the molecule to the highly activating nitro-group,

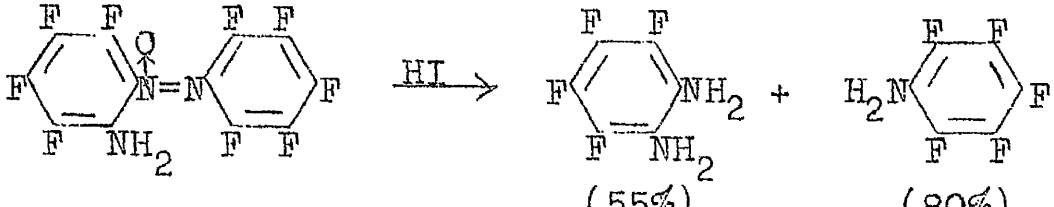
including the positive charge on the nitrogen atom. Furthermore, the other nitrogen atom has a partial negative charge, and would be deactivating in the ring to which it is attached:

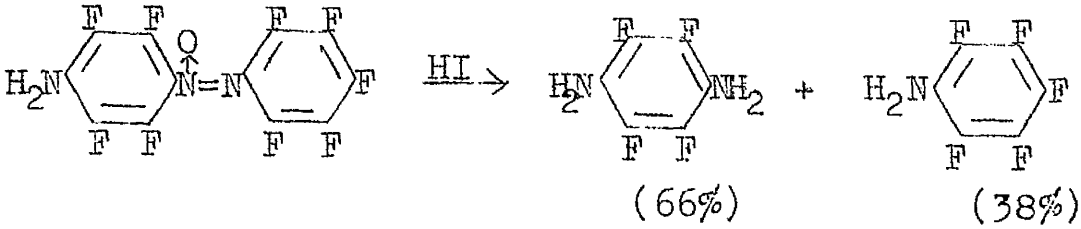


Thus, either the methoxide reaction can be considered as the typical one, and the course of the reactions with ammonia and hydrazine ascribed to hydrogen bonding, or the reactions with the amines can be considered as normal, in which case the course of the reaction with methoxide must be assumed to be due to the larger size of the solvated methoxide ion (see also p. 116).

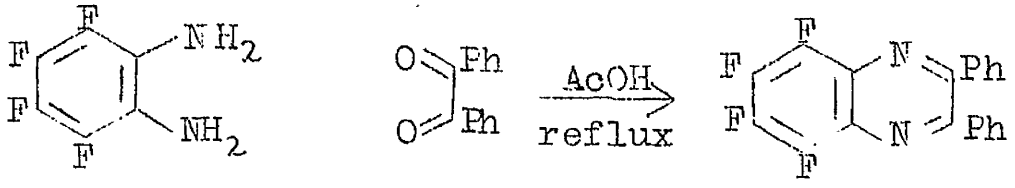
The Reductive Cleavage of the Amino-azoxy-Compounds.

These reactions were carried out to assist in the characterization of the azoxy-compounds:





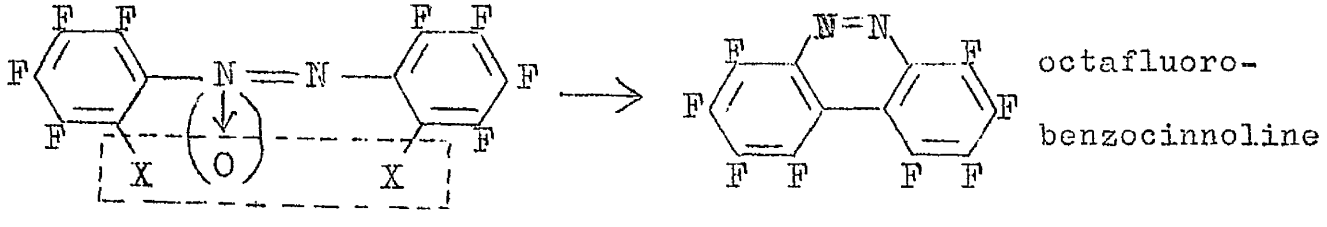
The ortho-diamine was converted into the benzil derivative (a new compound), which gave the correct analysis:



Further proof of the structure of this diamine was provided by its diazotization, which gave tetrafluorobenzotriazole (p.73). The other three products of these cleavage reactions were identified by infra-red spectroscopy.

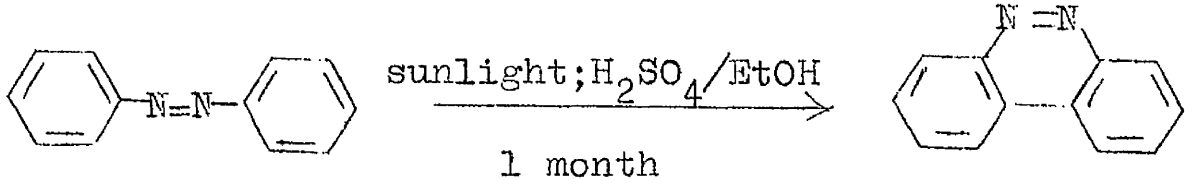
Attempted Preparations of Octafluorobenzocinnoline.

A number of attempts were made to prepare octafluorobenzocinnoline by the removal of ortho substituents from 2,2'-disubstituted octafluoro-azo- and azoxy-benzenes:

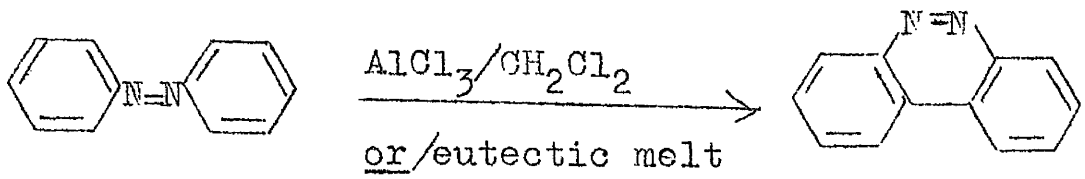


These experiments were based on five reactions known in the hydrocarbon series:

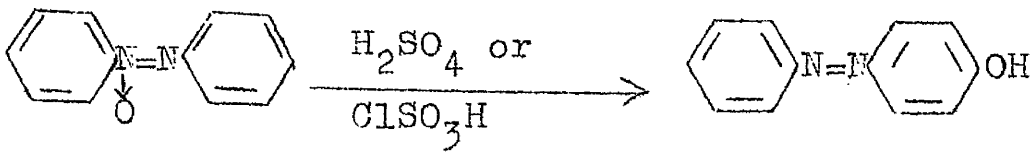
(a) The photolytic cyclization of azobenzene:[124]



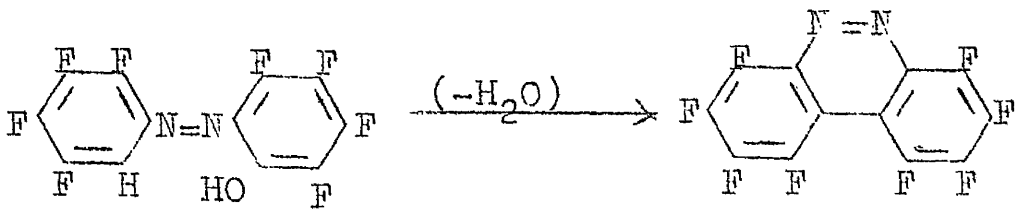
(b) The cyclization of azobenzene with aluminium chloride:[125]



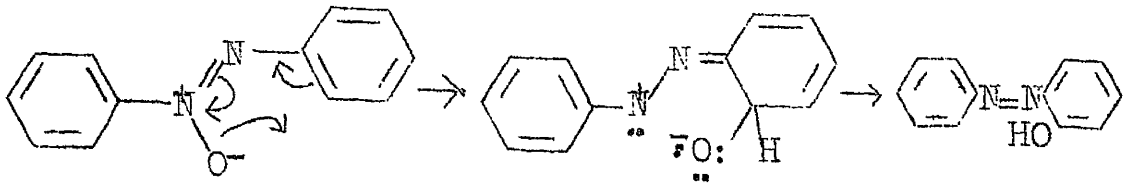
(c) The Wallach rearrangement, followed by dehydration:[126] This usually takes the following course (p.44):



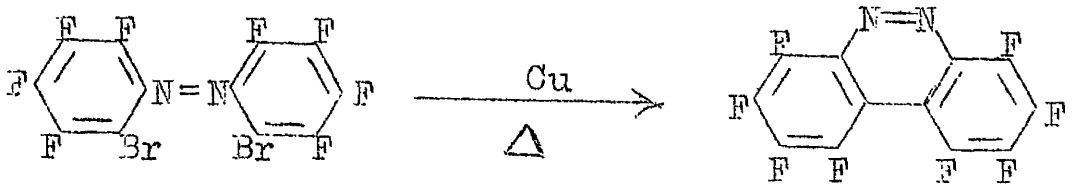
But 4,4'-disubstituted azoxy-compounds give the ortho-hydroxy-azo--compounds, and it was intended to dehydrate the rearrangement product of the octafluoro-compound:



(d) The photolytic rearrangement of azoxybenzene:[127]



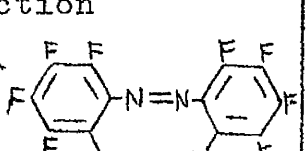
(e) The Ullmann reaction:[8] The abstraction of bromine from 2,2'-dibromo-octafluoroazobenzene was attempted:



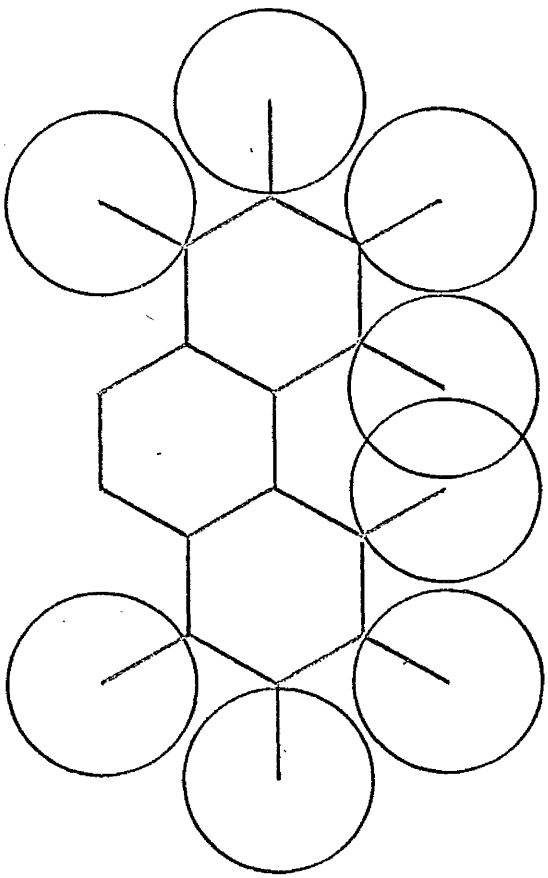
None of these experiments (tabulated below) was successful.

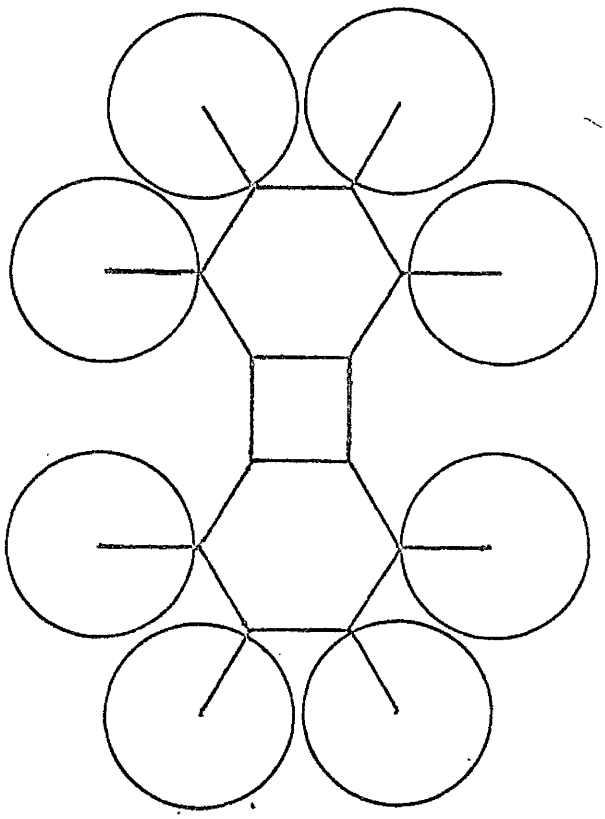
Table 6

Attempted Preparations of Octafluorobenzocinnoline

Reaction	Reagent	Solvent	Temp.	Time	Product
(a)	U.V. + H_2SO_4	aq.EtOH	20°	24 hr.	Starting material (82%)
"	" "	H_2SO_4	"	23 hr.	" " (80%)
(b)	$AlCl_3$	CH_2Cl_2	reflux	3 days	" " (96%)
"	$AlCl_3$/NaCl/NaF eutectic		90°	90 min.	" " (72%)
(c)	$ClSO_3H$	CCl_4	reflux	15 min.	intract. oil with band in I.R. at 4.63μ.
(d)	U.V.	EtOH	20°	18 hr.	starting material
(c) with (d)	U.V. + H_2SO_4	aq.EtOH	"	19 hr.	" "
(e)	Cu-bronze	$HCO.NMe_2$	reflux	1 hr.	reduction to 
"	"	none	200°	24 hr.	tar

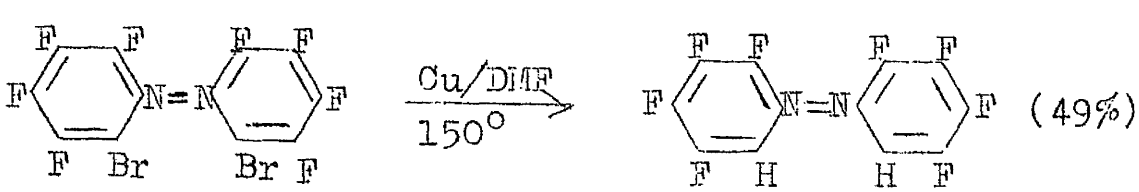
The failure of the cyclization reactions can be attributed to steric hindrance in the required product. Soon after this work was completed, octafluorobiphenylene was reported; it was prepared by an Ullmann reaction on 2,2'-di-iodo-octafluorobiphenyl,[128] but it can be seen that in this case, steric hindrance is non-existant:





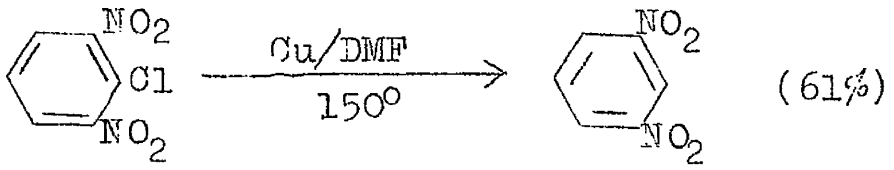
octafluorobenzocinnoline octafluorobiphenylene

This suggestion is supported by the reported difficulty[129] in obtaining pure perfluorophenanthrene, whose steric requirements are very similar to those of the cinnoline. The reduction of halogen-compounds in dimethylformamide has been observed before where there is steric hindrance to biaryl formation, as there is in this case:[130-1]



(identified by m.p. & i.r. spectrum)

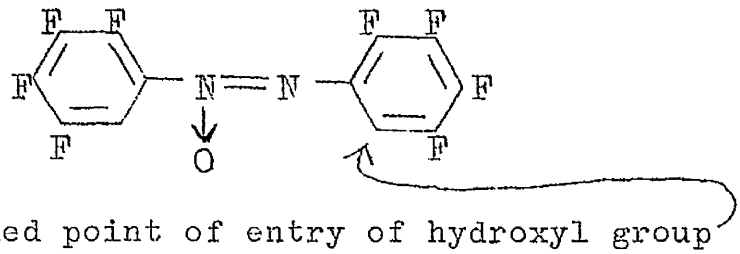
cf.[131]



(61%)

The reduction may also be assisted by electronic factors (cf. p. 55).

The Wallach rearrangement is known to be impeded by substituents ortho to the point of entry of the hydroxyl group,[132] and in the octafluoro-azoxy-compound, these are in effect two such substituents, F and $Ar(N_2O)$-



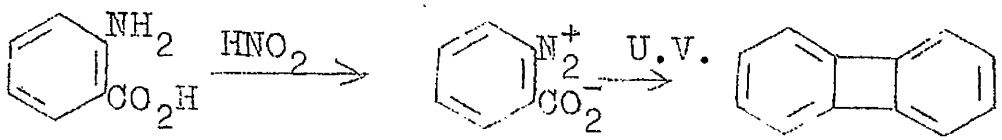
presumed point of entry of hydroxyl group

Its non-occurrence is therefore not surprising.

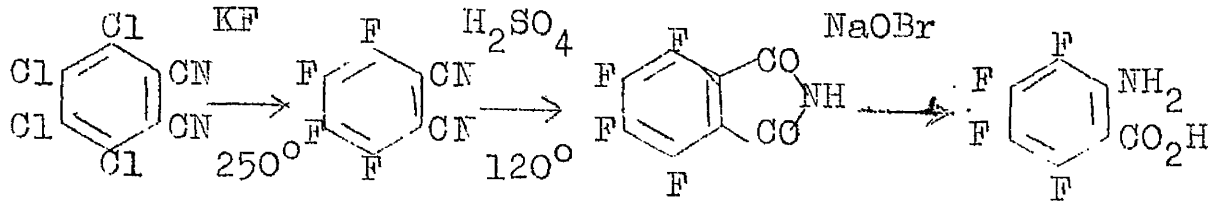
The photolytic rearrangement of azoxy-compounds is believed to be intramolecular, and should be impeded less, but it is in any case slow and the above experiments were not exhaustive.

The Diazotization of Tetrafluoroanthranilic Acid.

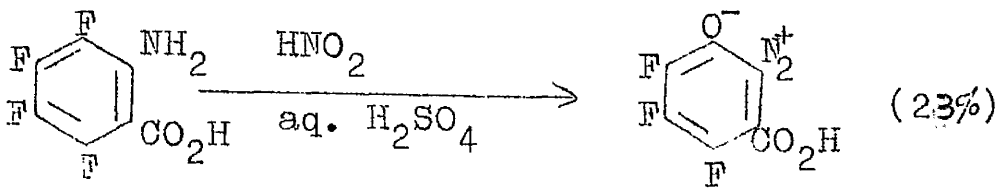
This reaction was carried out in an attempt to prepare octafluorobiphenylene by a sequence similar to a recently reported synthesis of the unfluorinated analogue:[133]



Tetrafluoroanthranilic acid was prepared by the following previously reported sequence:[3, 49]

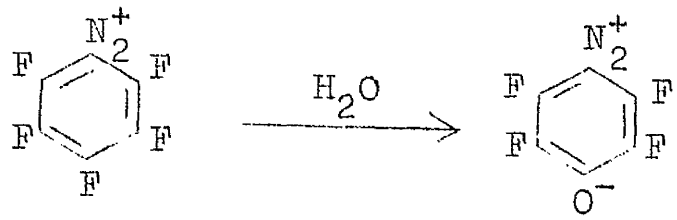


Tetrafluoroanthranilic acid was diazotized in aqueous sulphuric acid at 0°, and gave trifluorobenzenediazonium-2--oxide-6-carboxylic acid, nucleophilic replacement of the ortho fluorine atoms having occurred (the characterization of this product is given on p.123):

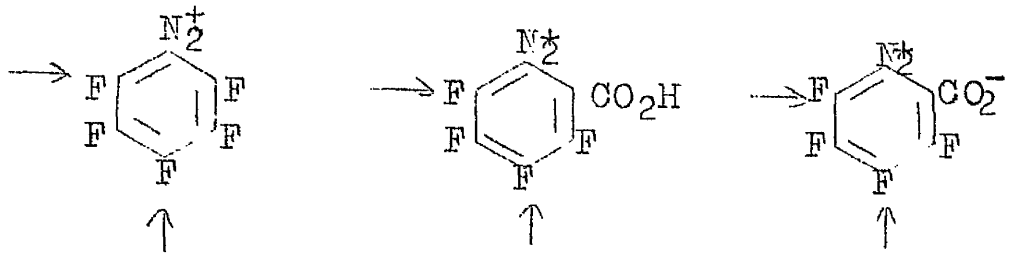


The relatively low yield was due to a low recovery on recrystallization; the i.r. spectrum of the crude product was very similar to that of the recrystallized sample, showing that the amount of substitution para to the diazonium group must have been small.

A simple but tentative explanation for the position of substitution can be given. In the pentafluorobenzenediazonium ion, substitution by water occurs in the para position:[1, 134]



It can be seen that in both the diazonium salt and in the diazonium-carboxylic acid (or the zwitterion) there are two possible positions of attack:



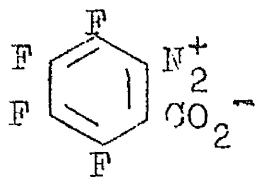
The different orientation found in the reaction of the two diazonium compounds is difficult to explain, but the following rationalization can be given.

In changing from the pentafluoro-compound to the carboxylic acid or the zwitterion, the activation of each of the potentially labile fluorine atoms has been changed, in each case by the replacement of a meta fluorine atom by a less activating meta CO_2H or CO_2^- group; the relative activation of the two sites is unchanged, but the absolute activation is lower. It is therefore quite possible that the diazonium-carboxylate is stable in aqueous solution, and reacts with water only in ether

solution (i.e. during the ether extraction); in the solvent of lower polarity, ortho substitution should be favoured, since it is probably due mainly to an inductive or direct-field effect.

The Photolysis of Trifluorobenzenediazonium-2-oxide-6--carboxylic Acid.

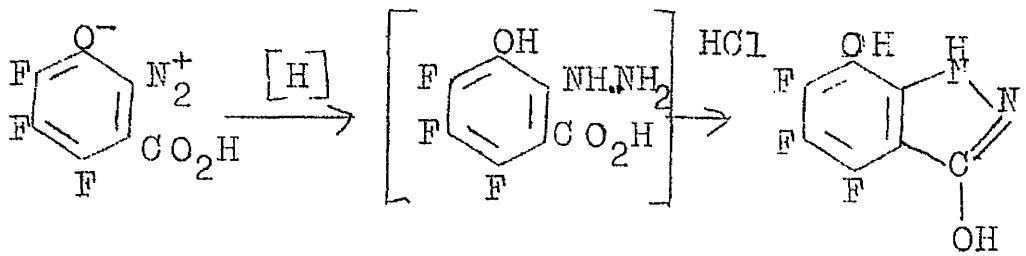
This reaction was carried out before it was discovered that the diazonium compound was not the tetrafluoro-carboxylate:



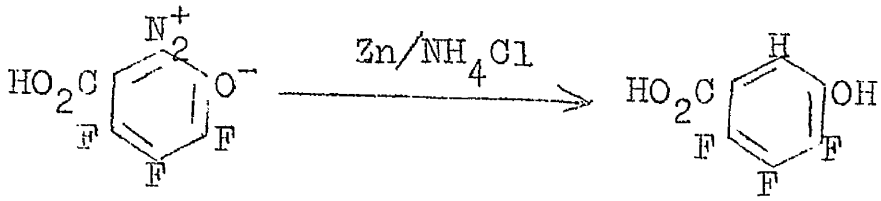
The diazo-oxide was found to be stable to u.v. irradiation for one week.

2,3,4-Trifluoro-5-hydroxybenzoic Acid.

The sequence described below was carried out in an attempt to synthesize an indazole derivate (cf. the synthesis of indazolone[135]):



Trifluorobenzenediazonium-2-oxide-6-carboxylic acid was reduced with zinc and ammonium chloride in aqueous methanol; some effervescence was observed. The liquid phase was heated with dilute hydrochloric acid and gave 2,3,4-trifluoro-5--hydroxybenzoic acid in 60% yield:



It was clear from the evolution of gas on the addition of ammonium chloride that the product was formed before the refluxing with hydrochloric acid was carried out, and this was confirmed by the isolation of the hydroxy-acid in 29% yield when the reaction was carried out without this last stage. The chief result of the treatment with hydrochloric acid appears to be the incidental facilitation of the purification of the product.

The de-amination process of the above sequence of reactions is closely similar to that reported by Hodgson and Marsden, who developed a general procedure for the process:[136]

$$ArNH_2 \xrightarrow[\text{(ii) naphthalene-1,5-disulphonic acid}]{\text{(i) } HNO_2} ArN_2^+ \left[C_{10}H_7S_2O_6\right]^-$$

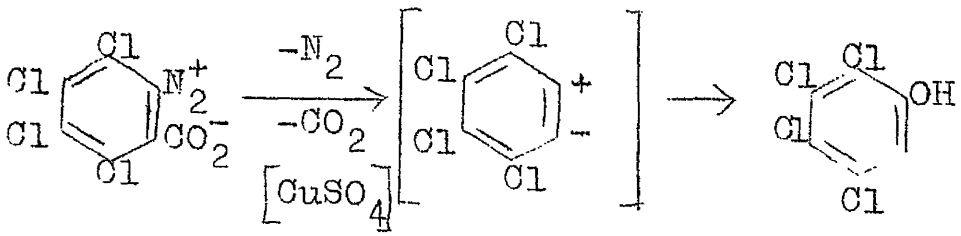
$$ArN_2^+ \left[C_{10}H_7S_2O_6\right]^- \xrightarrow[20^\circ]{Zn/EtOH} ArH\ (>90\%) + N_2$$

Hodgson and Marsden stated that the ethanol was not oxidized, and that the hydrogen necessary for the reduction apparently was derived from the sulphonic acid groups, which presumably were converted into the zinc salts. If this is the case, then the

above deamination procedure is almost identical in mechanism - the acid being the ammonium ion; the overall reaction would be:

$$ArN_2^+ + NH_4^+ + Zn \longrightarrow [ArN{=}NH] + NH_3 + Zn^{++}$$
$$[ArN{=}NH] \longrightarrow ArH + N_2$$

After the above reactions with tetrafluoroanthranilic acid dervatives were carried out, but before the products were fully characterized, a report appeared of the diazotization of tetrachloroanthranilic acid.[137] The chlorine atoms were not displaced on diazotization of the acid in concentrated sulphuric acid, nor by the subsequent dilution and steam distillation of the product, which gave a tetrachlorophenol:



A comparison of the above work[137] with that of the author illustrates the susceptibility of fluorine to nucleophilic replacement in fluoroaromatic systems.

SECTION 2

THE CHARACTERIZATION OF NEW COMPOUNDS

Introduction: The Interpretation of Spectra.

Infra-red, ultra-violet and nuclear magnetic resonance spectra were each recorded for nearly all of the new compounds. These spectraare discussed (i) as necessary to establish structures of new compounds, or (ii) where an obvious anomaly is present, or (iii) (briefly) in groups for each class of compound, but no attempt is made to mention every spectrum individually.

(a) Infra-red spectra. These were used (apart from routine identifications) entirely for the identification of those functional groups which absorb in the region 2.5-6μ , since no useful correlations (e.g. C-F stretching bands) could be made in the "fingerprint" region (6-15μ).

(b) Ultra-violet spectra. The electronic effects of fluorine in highly fluorinated compounds to some extent cancel each other, and the spectra of aromatic fluorocarbons are often very similar to those of their unfluorinated analogues; several examples of this similarity, and a few interesting exceptions, are presented in this section.

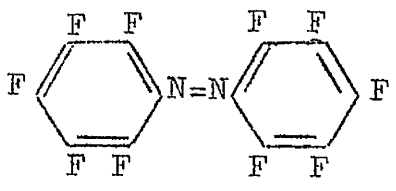
(c) Nuclear magnetic resonance spectra. ^{19}F spectra were obtained for many compounds, and a few proton resonance spectra were measured also. The assignments were made on the basis of chemical shifts and coupling constants; for the latter the following were regarded as typical values (in c./sec.) for

fluorinated benzenoid compounds:

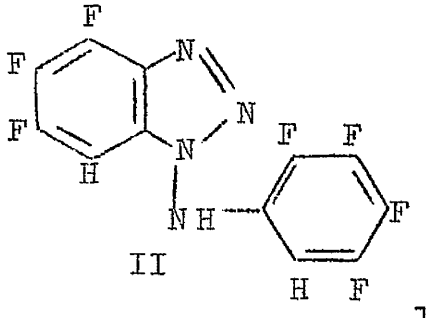
o-FF: 18-22; o-HF: 10; m-FF: 0-10; m-HF: 7; p-FF: 7-15;

p-HF: 2-3 c./sec.

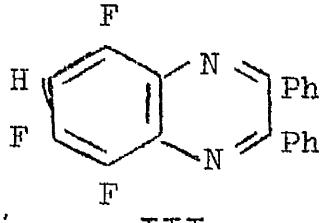
Chemical shifts were assumed to be determined by additive substituent contributions, superimposed upon the shift in hexafluorobenzene (83.25 ppm. to high field from trifluoroacetic acid). After a few preliminary assignments had been made, the reliability of this procedure was increased by using as reference compounds decafluoroazobenzene (I), the triazole (II), and the quinoxaline (III) (for comparison with the phenazines) the spectrum of each of these compounds was unambiguously analysed.



I



II



III

The following table, provided by Mowthorpe,[138] was used as a source of substituent contributions to chemical shifts:

Table 7

Fluorine Chemical Shifts relative to Hexafluorobenzene.

Compound	Substituent	ortho-F	meta-F	para-F
C_6F_5H	H	-23.55ppm	-0.55ppm	-9.05ppm
$C_6F_5.Br$	Br	-21.05	-1.45	-6.55
$C_6F_5.CO_2H$	CO_2H	-25	-1	-15
$C_6F_5.N{=}N.C_6F_5$	$N{=}N.C_6F_5$	-13.75	-0,55	-13.75
$C_6F_5NO_2$	NO_2	-15.55	-2.95	-13.95
$C_6F_5.NH_2$	NH_2	-3.05	+0.25	+5.15
$C_6F_5.OMe$	OMe	-4.25	+1.75	+1.75
$C_6F_5.OH$	OH	+1.15	+2.65	+7.95

The use of table 7 is best explained by reference to particular examples, and the reader is referred to p.114 , where the spectra of the benzotriazoles are discussed in detail.

Azo-compounds.

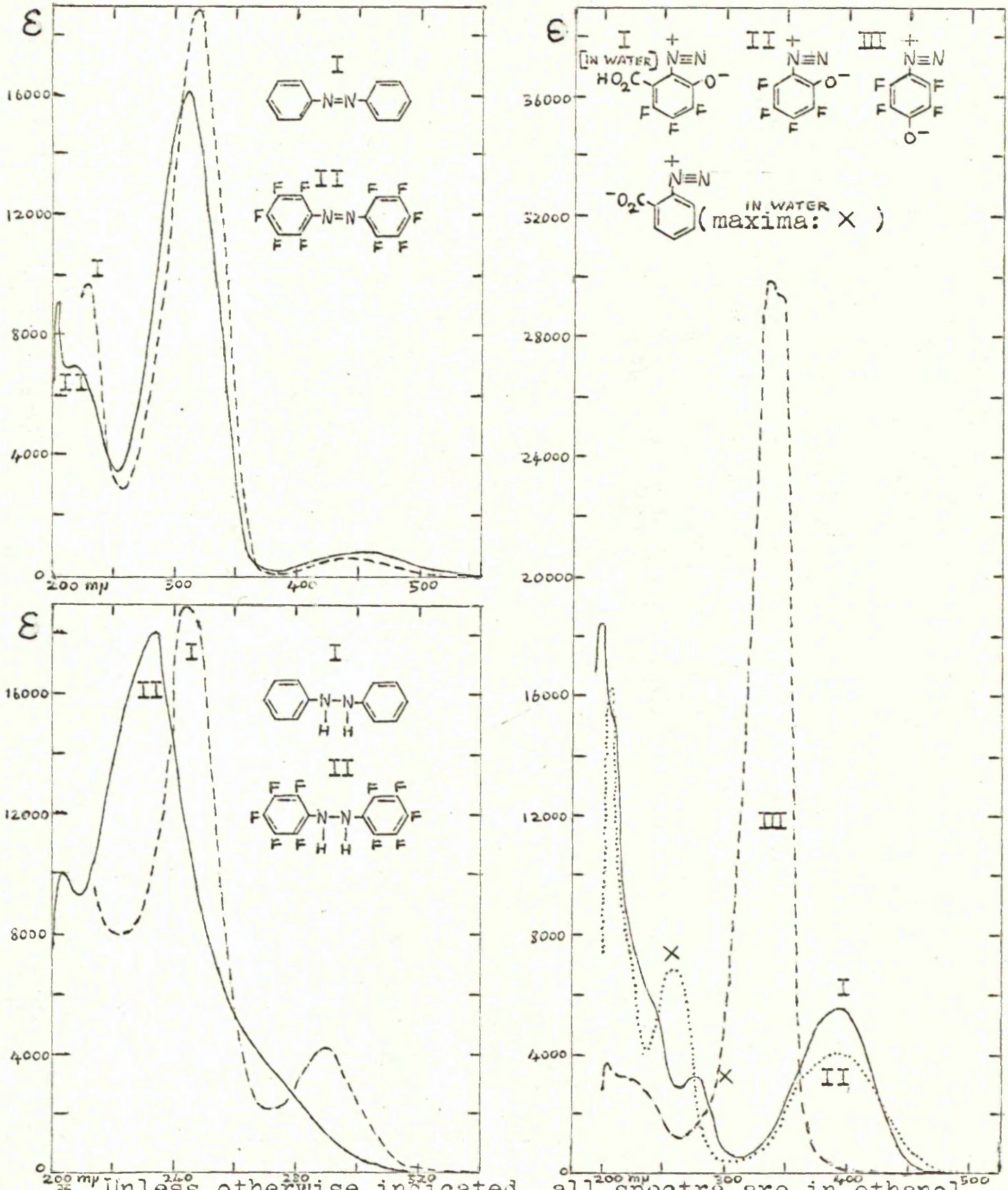
Decafluoroazobenzene was characterized not only by its elemental analysis and by its infra-red spectrum (which showed no N-H stretching absorptions), but also by its ultra-violet spectrum, which resembled that of azobenzene[139] very closely (p.100a). The nuclear magnetic resonance spectrum of decafluoroazobenzene shewed fluorine atoms in three environments, and was a typical AAPXX' system (p.139). The chemical shifts were close to those found for pentafluoronitrobenzene (p.99), with ortho and para fluorine atoms shifted considerably to low field relative to hexafluoro-benzene; this effect is found in other pentafluorophenyl compounds which are highly activated towards nucleophilic attack.

Other azo-compounds were also characterized by all the techniques used for the characterization of decafluoroazobenzene. Substituted azo-compounds prepared by nucleophilic reactions on other azo-compounds were characterized chemically by reductive cleavage to amines, and decafluoroazobenzene was also cleaved (to pentafluoroaniline). These reactions have been discussed earlier and are summarized in Table 8 (p.100b).

Satisfactory nuclear magnetic resonance spectra (p.139) were obtained for all but one of the azo-compounds (the dithiophenoxy--compound was insufficiently soluble); no anomalies were observed

Ultra-violet Spectra - I *

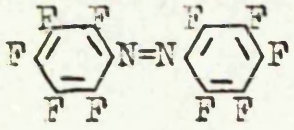
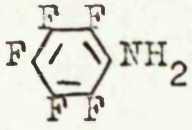
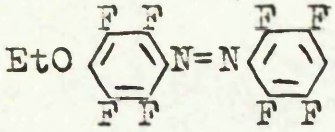
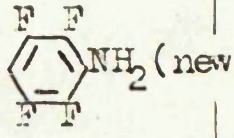
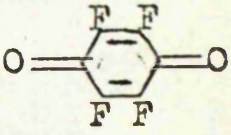
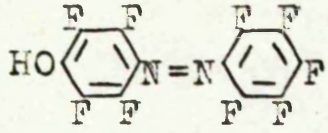
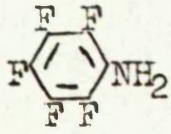
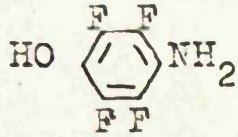
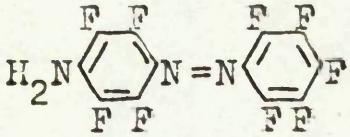
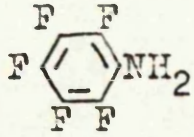
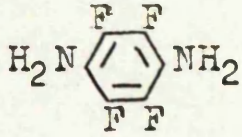
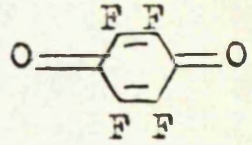
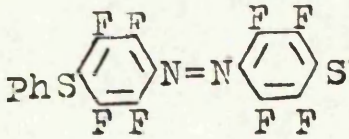
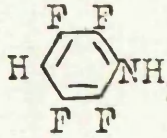
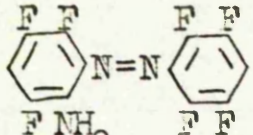
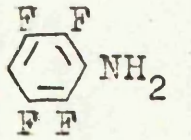
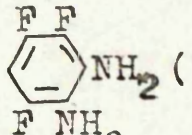
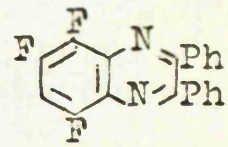
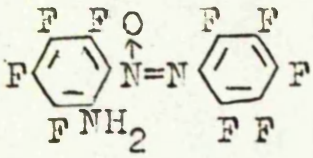
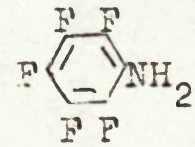
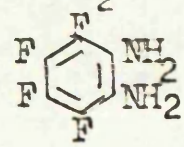
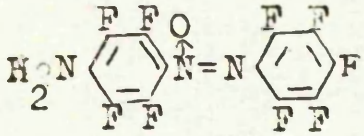
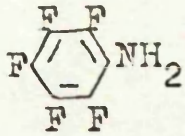
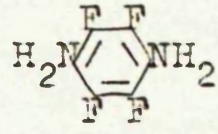
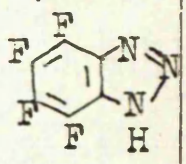
Azo- Hydrazo- and Diazo- Compounds



* Unless otherwise indicated, all spectra are in ethanol.

Table 8

The Characterization of Azo- and Azoxy-compounds.

Compound	Cleavage Product(s)	Reference Compound
	 (known)	(The azoxy- and the hydrazo-compounds are also cleaved to $C_6F_5NH_2$)
	EtI(known) +  (new)	
Dimethoxy-azo-compound: characterized similarly		
	 + 	
	 + 	
	PhS.SPh +  (known)	
	 +  (known)	
	 + 	 (new)
	 + 	

in either chemical shifts or coupling constants, and these spectra are not discussed.

Decafluorohydrazobenzene.

It was this compound which Wall and his co-workers (p. 33) identified incorrectly as decafluoroazobenzene. The hydrazo-compound was colourless when pure, and its ultra-violet spectrum (shown on p. 100a) was similar to that of hydrazobenzene.[139] The infra-red spectrum of decafluorohydrazobenzene (p. 125) shewed a strong sharp singlet at 2.93μ (N-H) which was absent (as expected) from the spectrum of the azo-compound. The erroneous characterization of this compound as decafluoroazobenzene was based entirely on its mass spectrum, which shewed a parent ion at m/c = 362($C_{12}F_{10}N_2^+$). The mass spectrum of authentic decafluorohydrazo-benzene (measured at 160°) gave the same parent ion, but also a strong peak due to pentafluoroaniline. Hydrazo-compounds[140] are known to disproportionate on heating, and the following reaction can be assumed to have occurred in the mass spectrometer:

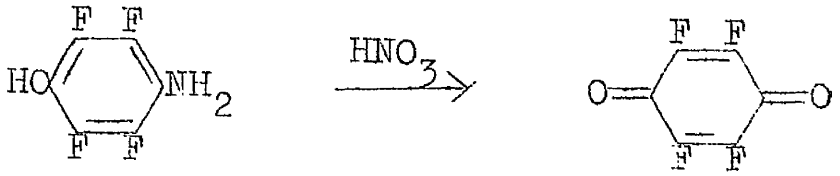
$$2C_6F_5.NH.NH.C_6F_5 \xrightarrow{\Delta} 2C_6F_5.NH_2 + C_6F_5.N{=}N.C_6F_5$$

Burdon and his co-workers[98] reported independently the dis-proportionation of decafluorohydrazobenzene at 130°, but did not comment on the mass spectrum of the compound.

4-Aminotetrafluorophenol.

This compound was characterized as a tetrafluoroaminophenol by its elemental analysis and its infra-red spectrum (p. 126), which shewed several absorptions in the O-H and N-H stretching region

(2.5-4μ). The <u>para</u> relationship of the substituents was established by the nuclear magnetic resonance spectrum (p.138), an A_2B_2 system; the <u>ortho</u> - or <u>meta</u>-aminophenols would give AGPX or ABXY spectra. The orientation of the substituents was confirmed chemically by oxidation to the known fluoranil:



4-Aminotetrafluorophenol was reported independently by Brooke, Forbes, Richardson and Tatlow;[134] their data on the compound agree with the present author's.

<u>The Phenazines</u>.

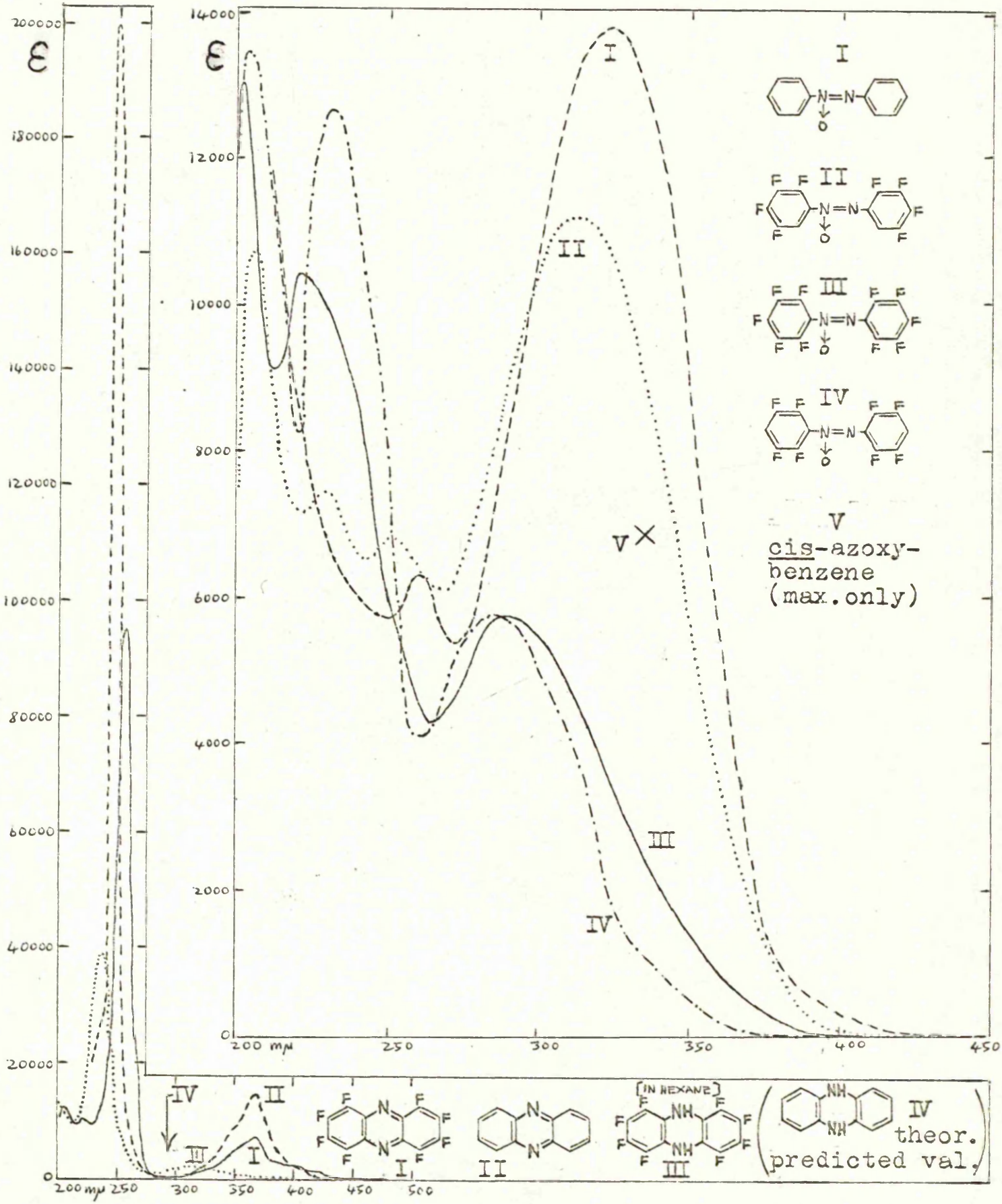
The molecular formulae of these compounds were established by elemental analysis, leaving a choice between the phenazine (IV) and benzocinnoline (V) structures:

IV V

The phenazine structures were indicated for all the compounds by their ultra-violet spectra (p.131), and the spectra of octafluorophenazine and phenazine[141] are compared graphically on p.102a. Further evidence (not in itself absolutely conclusive) was given by the nuclear magnetic resonance spectrum (p.141) of octafluorophenazine, which shewed only two regions of absorption, of equal intensity, suggesting an A_2X_2 system (probably with no inter-ring

Ultra-violet Spectra - II

Azoxy-compounds and Phenazines



coupling), but unfortunately the spectrum was not well enough resolved for coupling constants to be obtained. An ABXY system can not, therefore, be ruled out entirely on the basis of the n.m.r. spectrum alone.

By consideration of the phenazines and the structurally--related quinoxalines as a group, complete assignments of all these nuclear magnetic resonance spectra are possible (p.141), and the consistency obtained supports the assumption that the benzo-rings on the phenazines and the quinoxalines provide similar chemical environments for their H & F substituents.

2,3-Diphenyltetrafluoroquinoxaline.

This compound was characterized by elemental analysis, its ultra-violet spectrum (very similar to that of the trifluoro--compound) (p.135), and its nuclear magnetic resonance spectrum, whose chemical shifts were close to those predicted from the spectra of related compounds (p.141).

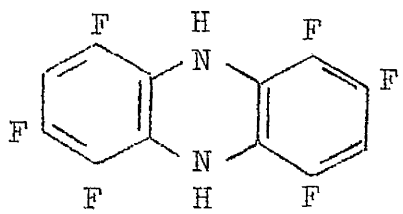
Dihydrophenazines.

None of the three dihydrophenazines was completely characterized. Octafluoro-5,10-dihydrophenazine was prepared in hexane solution, and an ultra-violet spectrum was obtained on this product. The spectrum shewed negligible absorption and no shoulders in the regions of the maxima in octafluorophenazine (the two spectra are compared graphically on p.102a), and this observation and the fact that the product obtained on evaporation of the hexane was colourless (but quickly darkened) shew that the product was pure.

This suggestion is supported also by the quantitative oxidation (p.46) of the presumed dihydrophenazine back to the starting compound.

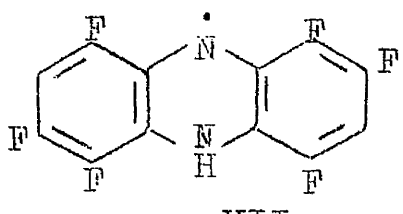
No spectrum of a simple dihydrophenazine has been published, but there has been one theoretical prediction[142] of the position of the longest wavelength absorption maximum; this predicted value is included on the graph on p. 102a.

The nuclear magnetic resonance spectrum of 2H,7H-hexafluoro--5,10-dihydrophenazine (VI) was obtained and analysed completely



VI

(p.141); the compound contained about 10% of the unreduced (probably re-oxidized) phenazine, and this impurity was identified by its chemical shifts. The nature of the spectrum shewed (i) that the green colour of the crude compound was due to a molecular complex and not a free-radical (VII) (which would have destroyed



VII

the resolution of the spectrum), and (ii) that in this complex, the phenazine and the dihydrophenazine exist as distinct entities, and do not exchange hydrogen rapidly (which would have given a weighted average of the chemical shifts).

Infra-red spectra were obtained for the three dihydrophenazines, but since they were each admixed with oxidized product, these spectra are not reported in full. The N-H absorptions can be given:

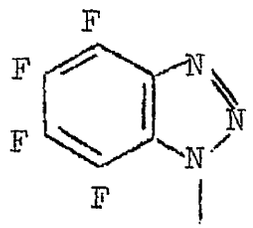
Octafluoro-5,10-dihydrophenazine: N-H absorption at 2.88μ

1H,6H-hexafluoro-5,10-dihydrophenazine: " " " 2.87μ

2H,7H-hexafluoro-5,10-dihydrophenazine: " " " 2.89μ

Tetrafluorobenzotriazol-1-ol.

Bearing in mind its mode of preparation, no structure can be assigned to the formula $C_6HF_4N_3O$ except the triazole structure (VIII). Further evidence is provided by its ultra-violet spectrum, which was compared with the spectra of some related compounds (p.105a).[143]



VIII

The nuclear magnetic resonance spectrum consisted of an AGPX system (p.142) which shows also an acidic proton at $\delta = -12.62$. This proton gives a strong very broad peak at 4μ in the infra-red spectrum. Chemical confirmation of the structure of this compound was achieved by its quantitative reduction to tetrafluorobenzotriazole.

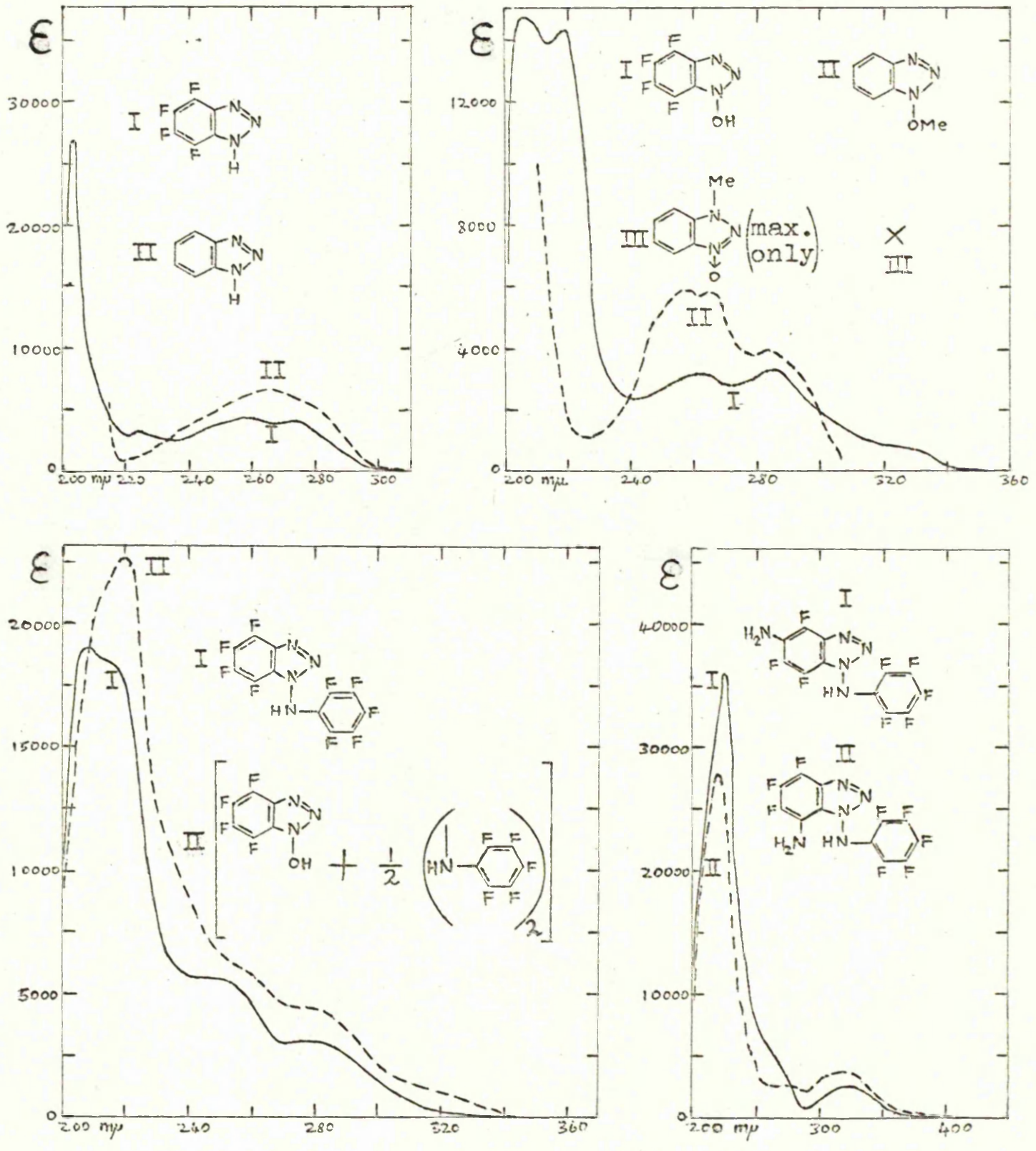
The tosyl and benzoyl derivatives of tetrafluorobenzotriazol-1-ol each gave the triazolol an ammonolysis (p.78), and gave satisfactory infra-red spectra.

Tetrafluorobenzotriazole.

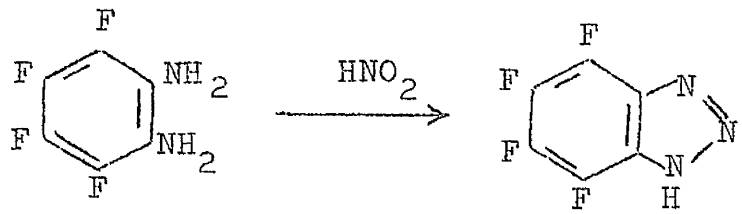
This compound was prepared by the reduction of tetrafluoro-

Ultra-violet Spectra - III

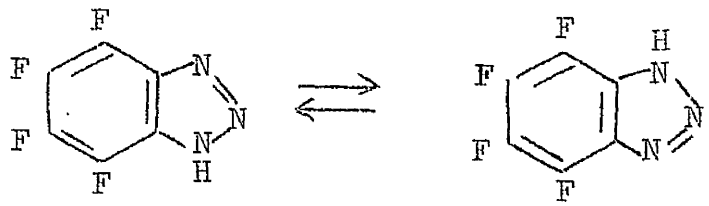
Benzotriazoles



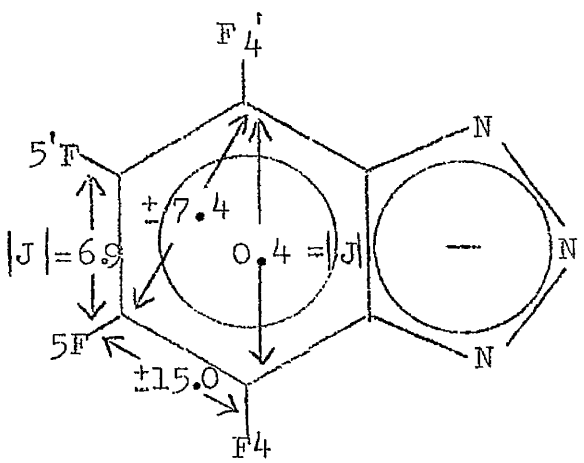
benzotriazol-1-ol, and characterized conclusively by its alternative preparation by the diazotization of tetrafluoro-o-phenylenediamine (p.73).



The nuclear magnetic resonance spectrum of this triazole shows a (poorly resolved) A_2X_2 system, indicating that the hydrogen atom is labile:



The low δ value of the proton (-13.25) supports this; the compound is acidic, and dissolves readily in dilute aqueous sodium hydroxide. The n.m.r. spectrum of the sodium salt is much better resolved, and shews the following coupling constants (c./sec.):



If the compound is regarded as an ortho-disubstituted tetrafluoro-

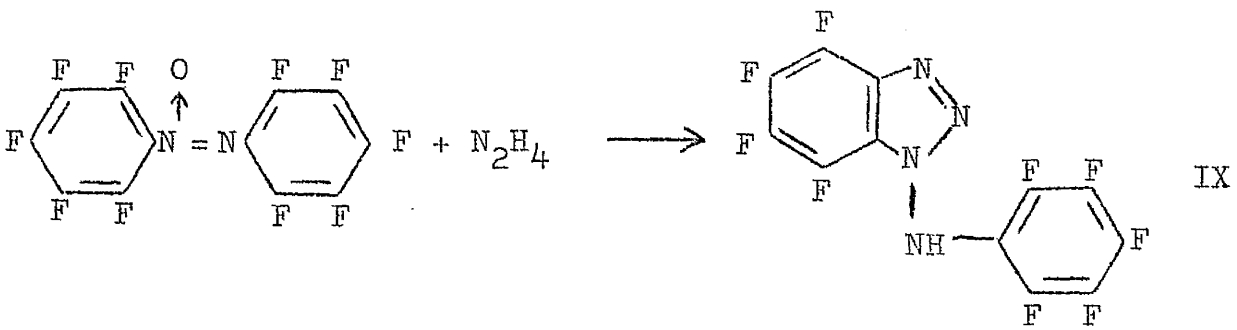
benzene, then these coupling constants are quite unprecedented. Firstly, the ortho-coupling of 6.9 c./sec. is half that of the previous lowest value ever observed (14.4 c./sec. in tetrafluorobenzene-1,4-diazo-oxide[4]). Secondly, J'_{44} and J_{45} are of the same sign. Assuming that J_{45} is still negative (cf. J_{FF}^{ortho} = -22.0 c./sec. in hexafluorobenzene[151]) this means a change of about 20 c./sec. from the usual value for J_{FF}^{para}. These coupling constants are sufficiently unusual as to raise doubts about the validity of assigning them in the usual way ($J_{FF}^{ortho} > J_{FF}^{para} > J_{FF}^{meta}$) in this compound; it is possible that the negative charge may have something to do with the anomaly, since the coupling constants in the unionized benzotriazoles are more or less normal (p.142). The negative charge in the anion can reside (by resonance) on the three nitrogen atoms and all six carbon atoms.

The ultra-violet spectrum of tetrafluorobenzotriazole is unexceptional, and is shown on p.105a, together with the spectrum of benzotriazole.[144]

The silver salt (p.75) and the 1-acetyl-derivative (p.75) of tetrafluorobenzotriazole have been discussed briefly already, and the n.m.r. spectrum of the latter is described on p.190.

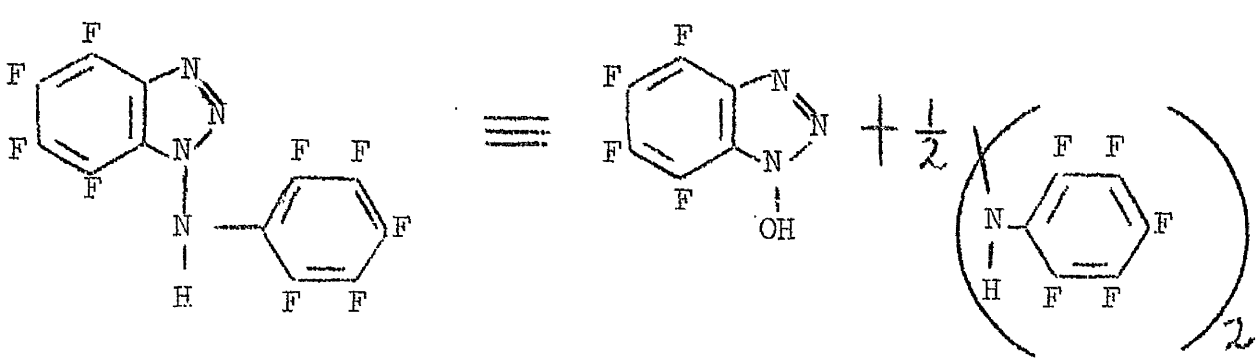
(Phenylamino)benzotriazoles.

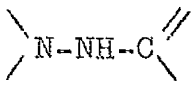
1-(Pentafluorophenylamino)tetrafluorobenzotriazole (IX) was obtained from the reaction of decafluoroazoxybenzene with hydrazine:

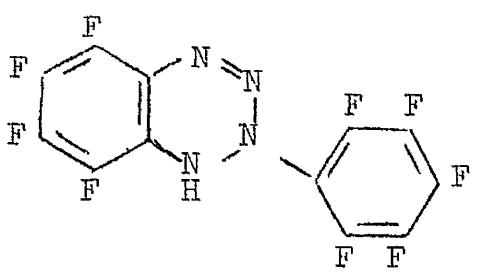


IX

Concordant analyses on the compound had to await improvements in the departmental analytical service, and the triazole was initially characterized spectroscopically. The nuclear magnetic resonance spectrum (p.142) shewed that the compound contained nine fluorine atoms, arranged on a pentafluorophenyl ring and on a 1,2,3,4--tetrafluoro-benzenoid ring. The simplicity of the N-H absorption in the infra-red spectrum (p.136) indicated that there was probably only one N-H bond in the molecule, and the benzotriazole structure was therefore suspected. With this in mind, tetrafluorobenzotriazol-1-ol was synthesized (p.69), and its ultra-violet spectrum (p.105a) was added arithmetically to half the spectrum of decafluorohydrazobenzene (p.100a), to give a predicted spectrum of the (phenylamino)benzotriazole:

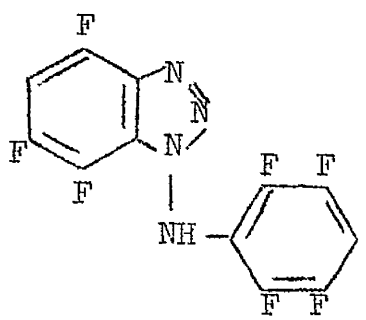


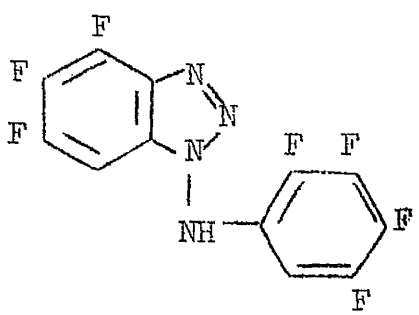
The result was eminently satisfactory, and is illustrated on p.105a. The success of the procedure can be ascribed to the fact that in both decafluorohydrazobenzene, and in the triazole, the ring systems are separated by at least two single bonds (); the chromophores are not in conjugation and therefore act separately. This spectroscopic work incidentally eliminates the alternative dihydrotetrazine structure (IXa), which contains different chromophores; this structure is also rendered highly improbable by the reductive cleavage of compound (IX) to tetrafluorobenzotriazole and pentafluoroaniline (p. 83):



IXa

Similar preparations of triazoles (X) and (II) from the two octafluoroazoxybenzenes were achieved.

X 



II

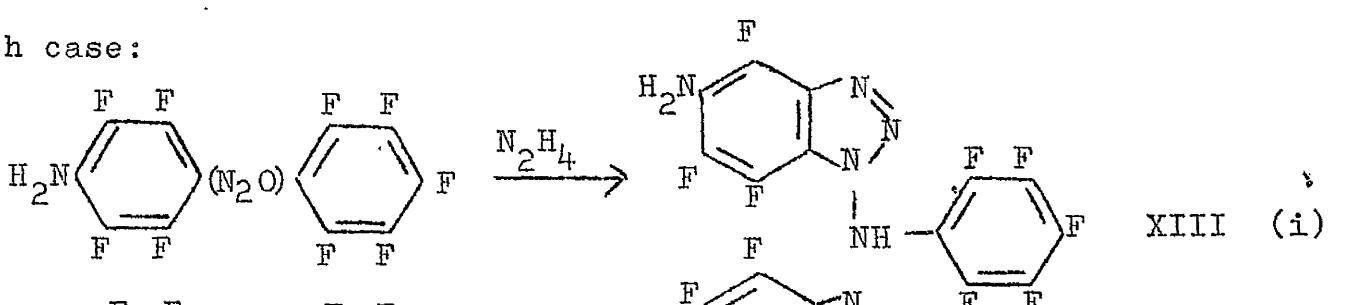
The presence of the benzotriazole structure (as opposed to the dihydrotetrazine system) in compounds (X) and (II), and also in the amino-compounds to be described later, was clearly shewn by their ultra-violet spectra, and additional support was provided by

the constancy of the secondary N-H vibrations in the i.r. spectra - in every case a singlet close to 3.1μ . The amino--compounds, of course, shewed extra N-H absorption in the infra--red; they also shewed an extra absorption at ca. 320mμ , of relatively low intensity, in the ultra-violet. This latter can be ascribed to the extension of the conjugated benzotriazole chromophore to include the π-electrons of the amino group.

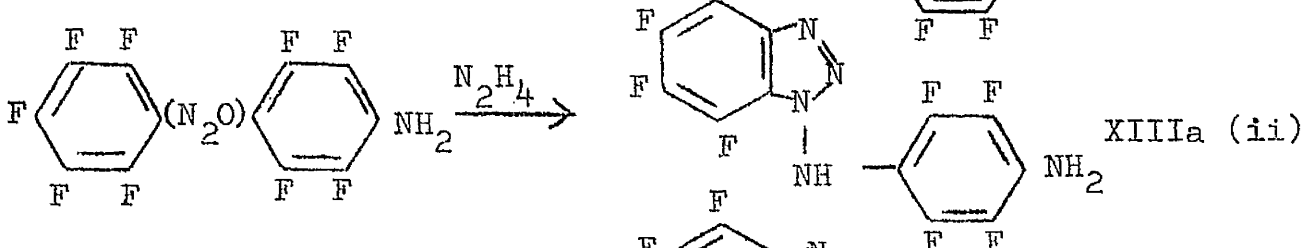
Decafluoroazoxybenzene reacted with ammonia to give two isomeric monosubstituted products, which were partially characterized (as ortho and para isomers) by reductive cleavage (p.100b):

$$C_6F_5(N_2O)C_6F_5 \xrightarrow[EtOH]{NH_3} \begin{cases} C_6F_5(N_2O)C_6F_4.NH_2\text{-}4 & \text{XI} \\ C_6F_5(N_2O)C_6F_4.NH_2\text{-}2 & \text{XII} \end{cases}$$

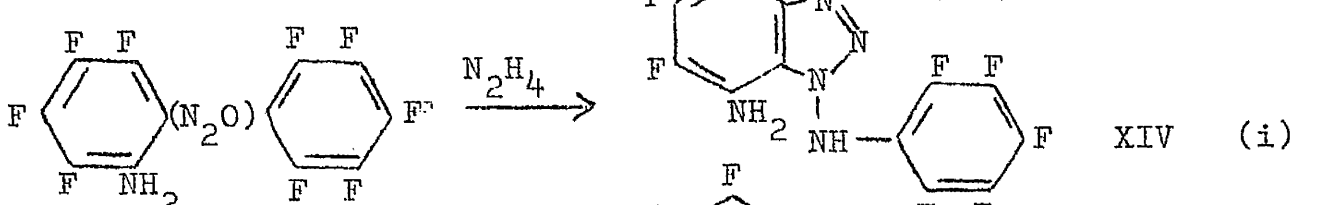
Each of these amino-azoxy compounds reacted with hydrazine to give a benzotriazole, and there are two possible structures in each case:

1) 

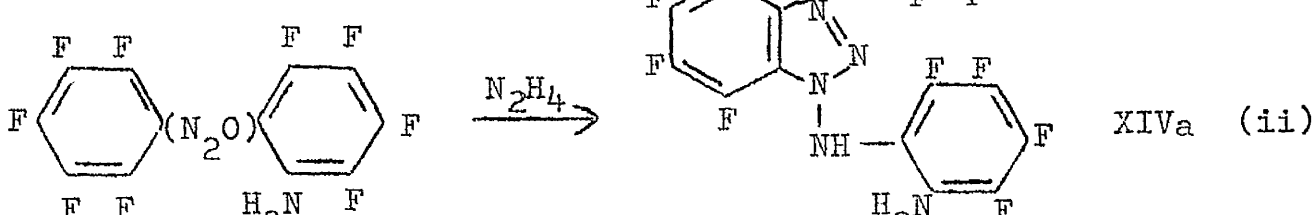
XIII (i)



XIIIa (ii)

2) 

XIV (i)



XIVa (ii)

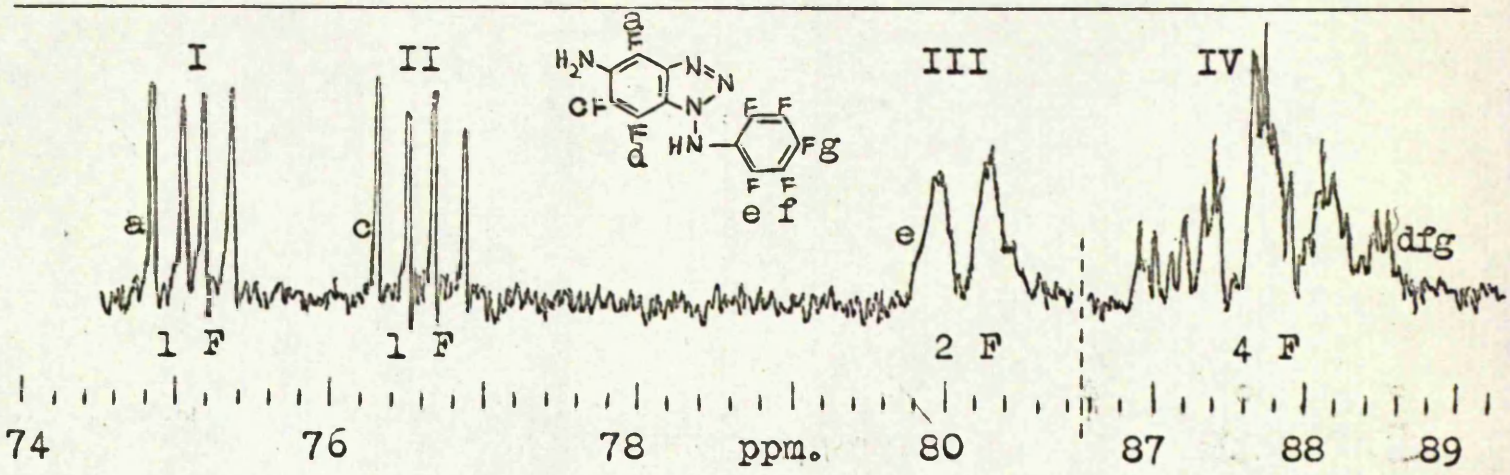
The amino-(phenylamino)benzotriazoles were characterized by their n.m.r. spectra. The first spectrum on p.111a is that of the product from reaction (1). Four bands are shewn, corresponding to one, one, two, and four fluorine atoms, respectively. Whichever structure (XIII or XIIIa) were correct, at least one of the bands due to only one fluorine atom must be due to one of the atoms on the benzotriazole ring. Both bands were doublets of doublets, suggesting that structure (XIII) was correct, and the rest of the spectrum was fully compatible with this structure.

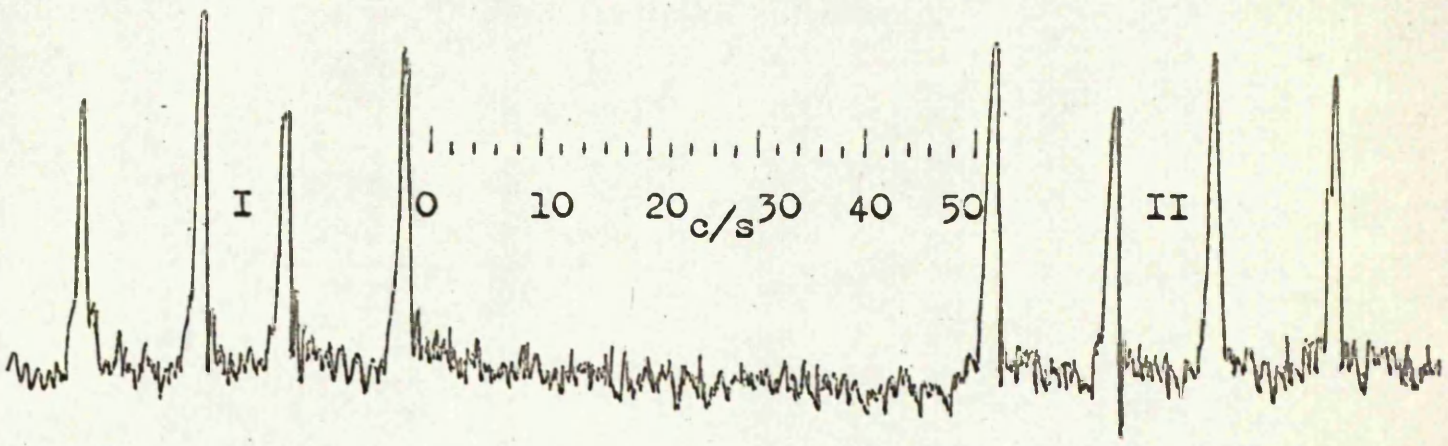
There is a possibility - admittedly remote - that the compound (XIIIa) could give rise to a similar spectrum; this would occur if the fluorine atoms producing bands I and II were meta to each other, with a mutual coupling constant of zero, or if, by coincidence, each were coupled to one of the two other fluorine atoms on the benzo-ring with a coupling constant of zero. This would require that the four-fluorine complex at 88 p.p.m. contained two of the bands due to the benzotriazole ring. The alternative, that band III is due to the other two fluorine atoms of the benzo-ring, is not possible, since it would imply that band IV must be due entirely to the phenyl ring in compound (XIIIa); this cannot be so, for the phenyl group must give an A_2X_2 or A_2B_2 system, and this is ruled out by the lack of symmetry in the band envelope IV. Thus, if the n.m.r. spectrum were due to compound (XIIIa), these absorptions due to the benzo-ring would have to be assigned as follows:

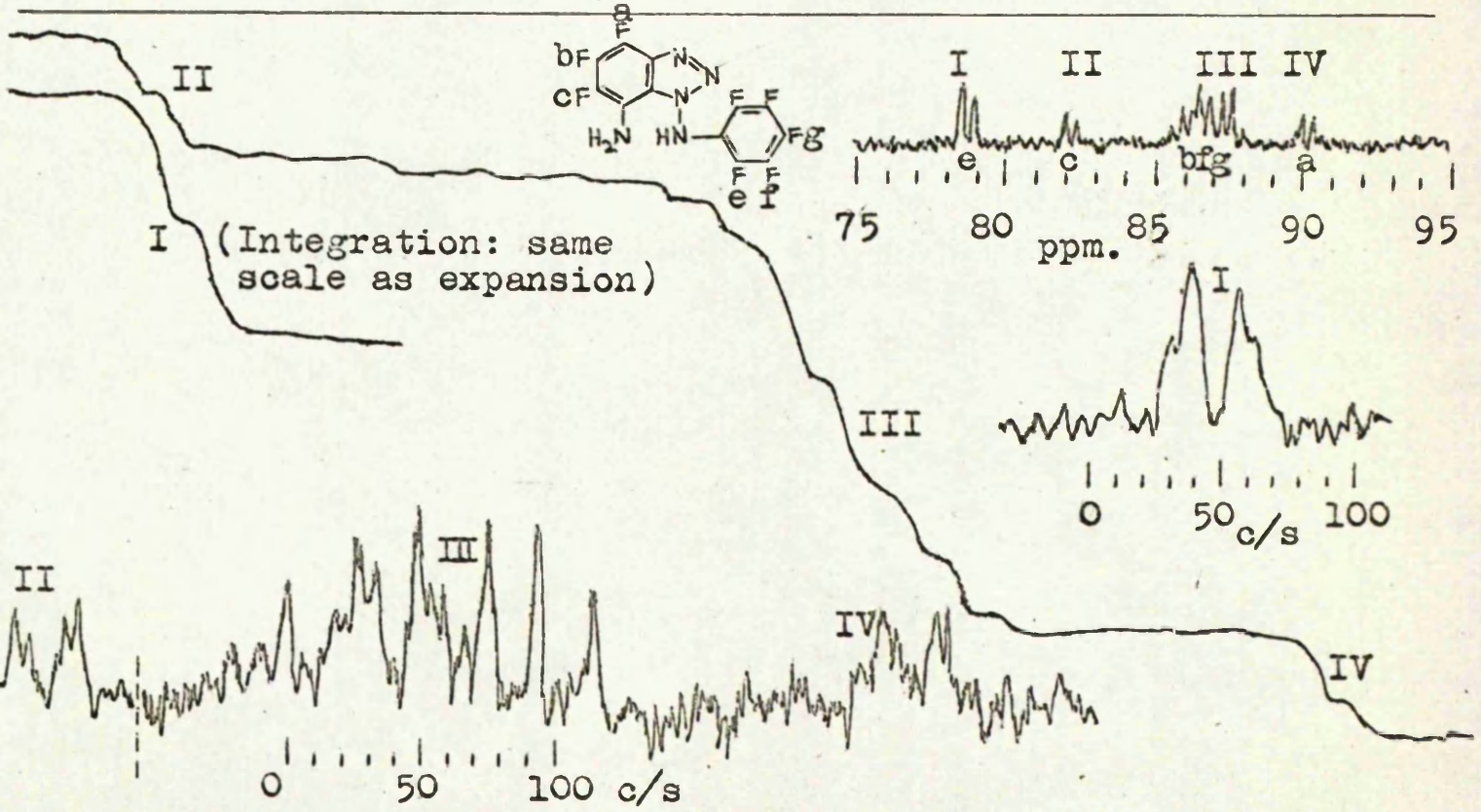
(to p.112)

Nuclear Magnetic Resonance Spectra - I

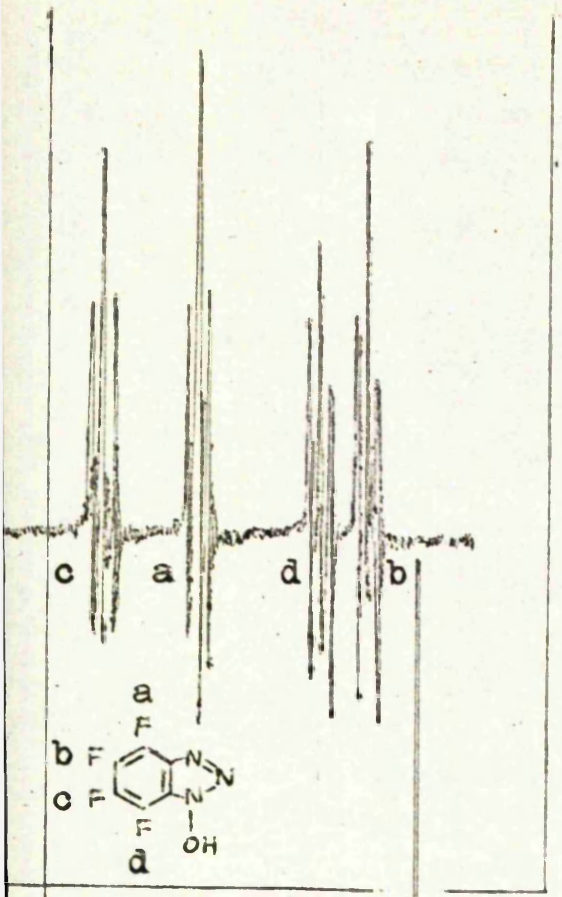
(^{19}F at 56.46 m/c. Solvent:  Reference: CF_3CO_2H ext.)

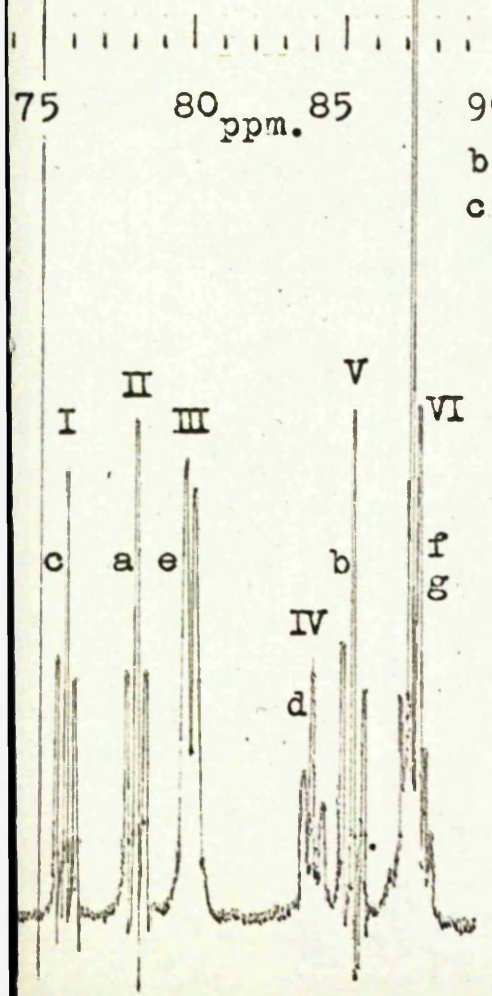


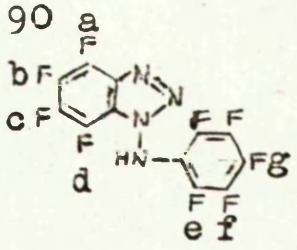


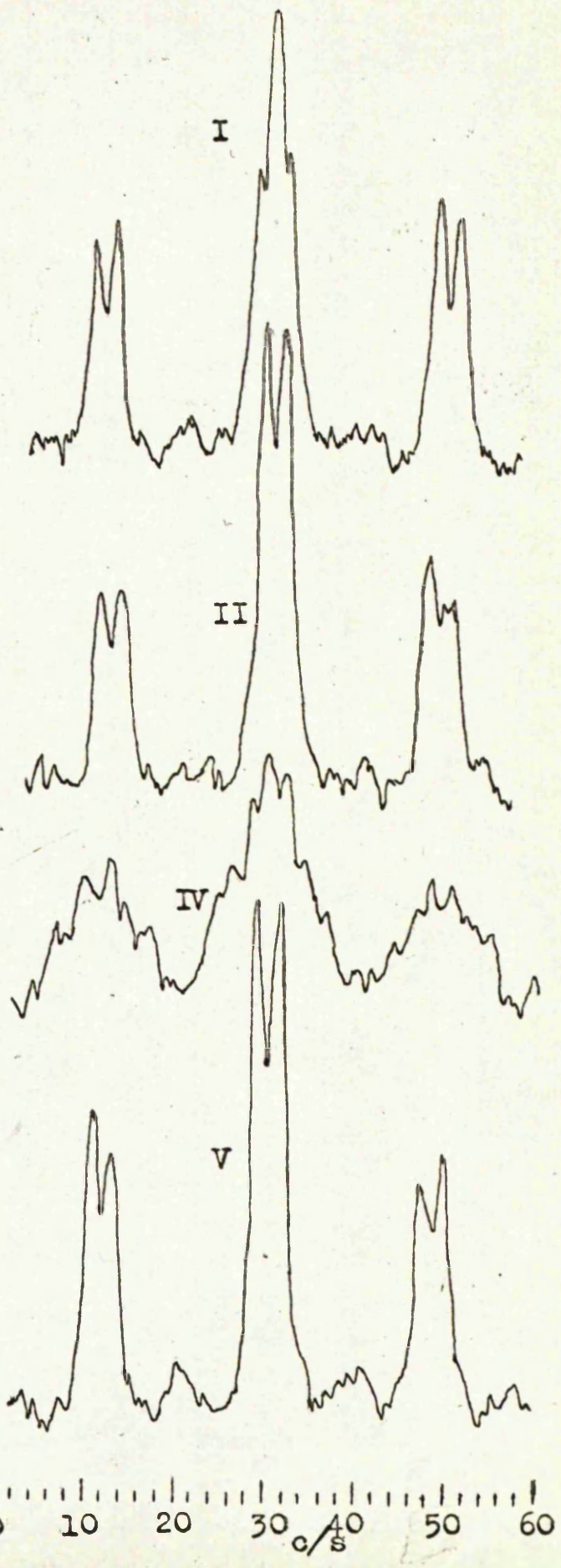


Nuclear Magnetic Resonance Spectra - II









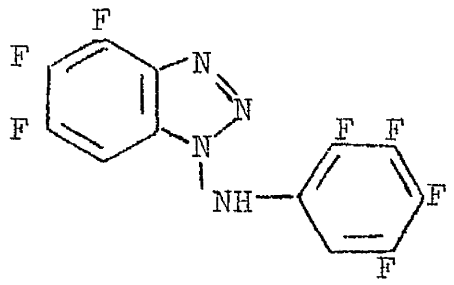
Compound	^{19}F absorption due to benzotriazole ring (increasing p.p.m.)			
(XIII) analysed as if it were (XIIIa)	75.1	76.6	~88	~88
(IX)	75.7	78.0	84.0	85.3
(VIII)	76.9	80.1	84.0	85.6

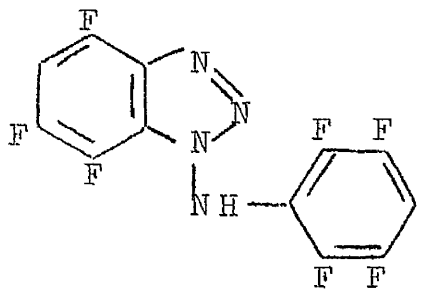
Comparison of the spectrum of (XIII) analysed as if it were (XIIIa) with the spectra of the two related compounds as shewn above indicates that the compound is not, in fact (XIIIa).

The rest of the argument will be given in less detail. It is seen from the spectra on pp. 111a, 111b, that the fine-structure of the benzotriazole portions of the spectra of compounds (VIII) and (IX) is also quite different from that in the spectrum of the triazole (XIII), and this also is a powerful argument against the assumptions necessary (e.g. coupling constants of zero) in order to analyse the spectrum of (XIII) as if it were that of (XIIIa). Finally, the values observed for the chemical shifts of the fluorine atoms on the benzotriazole ring in compound (XIII) agree well with those predicted from the consideration of the spectrum of compound (IX). The predicted chemical shifts are compared with those observed in Table 9.

The structure of compound (XIV) was established by a similar appraisal of its n.m.r. spectrum. The spectrum (p.111a) was poorly resolved, and though there can be no reasonable doubt about the assignments, an additional proof of the structure was available. This is conveniently considered later (p.119).

There is no ambiguity in the structure of the triazoles (II) and (X) prepared from the two octafluoroazoxybenzenes.

II 

X 

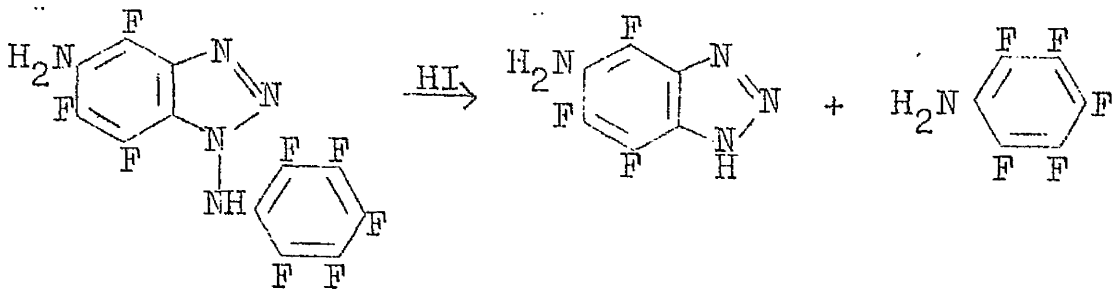
The triazole (II) was prepared specifically to aid the assignments in the n.m.r. spectra of the other triazoles, since, owing to the asymmetry of both ring systems, and the relative constancy of H-F coupling constants (cf.F-F), the spectrum could be completely assigned with high certainty. The rest of the spectra were assigned by the use of Mowthorpe's Table (p.99); the magnitudes of the coupling constants were, of course, taken into consideration as well as the chemical shifts in making the assignments. The consistency of the pattern obtained (Table 9 ; coupling constants are also tabulated, on p.142) increases the reliability of the individual analyses of these spectra. Table 9 serves also as an illustration of the procedure used in analysing many of the other n.m.r. spectra reported in this thesis.

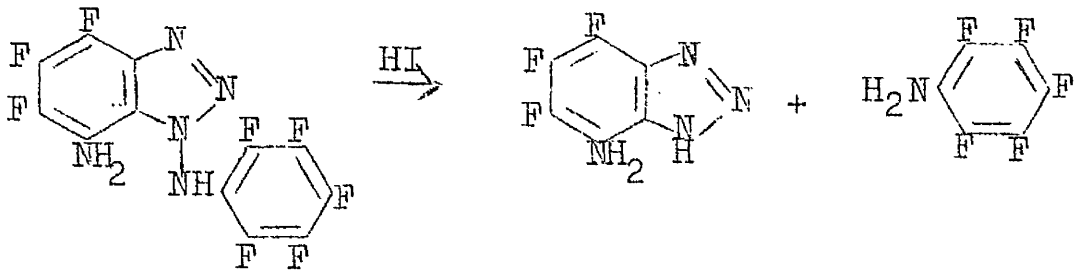
Table 9

Predicted and Observed Chemical Shifts in Benzotriazoles.

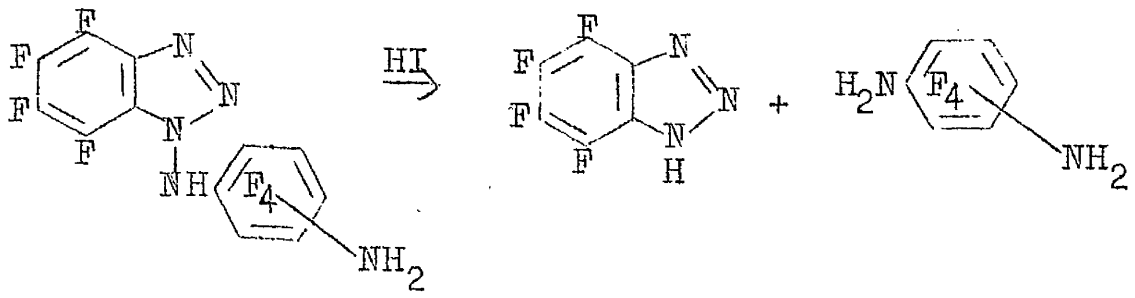
Standard notation (p. 142)			δ_4	δ_5	δ_6	δ_7	δ_2	δ_3	δ_4	δ_5	δ_6
Notation used on pp. 111a, 111b			a	b	c	d	e	f	g		
Substituents		Predicted or	BENZOTRIAZOLE-RING				PHENYLAMINO-RING				
Benzo	PhNH	Observed									
7H	2H	Observed	69.6	87.5	51.5	(H)	(H)	62.2	90.2	79.8	81.9
Change on repl. H by F:			+9.05	+0.55	+23.55			+23.55	+0.55	+9.05	+0.55
Perfluoro-comp.;		(Predicted:	78.65	88.05	75.05	-	-	85.75	90.75	88.85	82.45
"	"	(Observed	78.0	85.3	75.7	84.0	79.9	87.2	87.2	87.2	79.9
5H and 4H to replace F:			-23.55	(H)	-23.55	-0.55	-0.55	-23.55	(H)	-23.55	-0.55
5H	4H	(Predicted:	54.45	(H)	51.15	83.45	79.35	63.65	(H)	63.65	79.35
"	"	(Observed:	58.2	(H)	49.0	87.6	71.1	63.1	(H)	63.1	71.1
Perfluoro-comp.			78.0	85.3	75.7	84.0	79.9	87.2	87.2	87.2	79.9
$5NH_2$ to replace F:			-3.05	(NH_2)	-3.05	+0.25					
$5NH_2$	-	(Predicted:	74.95	(NH_2)	72.65	84.25	"	"	"	"	"
"	-	(Observed:	75.1	(NH_2)	76.6	87.8	80.1	87.8	88	87.8	80.1
Perfluoro-comp.			78.0	85.3	75.7	84.0	79.9	87.2	87.2	87.2	79.9
$7NH_2$ to replace F:			+5.15	+0.25	-3.05	(NH_2)					
$7NH_2$	-	(Predicted:	83.15	85.55	78.75	(NH_2)	"	"	"	"	"
"	-	(Observed:	90.2	87.7	82.1	(NH_2)	78.6	86.6	86.6	86.6	78.6
Perfluoro-comp.			78.0	85.3	75.7	84.0	$-NHC_6F_5$				
Tetrafluorobenzotriazol-1-ol			80.1	85.6	77.9	84.0	-OH replacing above				
1-Acetyl-			75.1	83.0	74.5	62.1	-CO.Me	"	"	-predictions	
tetrafluorobenzotriazole		or	74.5	or	75.1		less certain in this case.				

Completely conclusive characterizations of the triazoles could probably be achieved by reductive cleavage, but unfortunately, neither time nor quantities of materials available permitted this course of action during the present work:



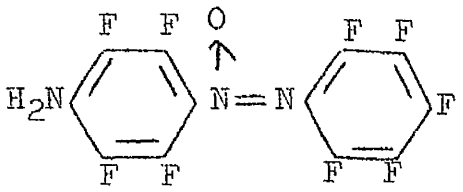


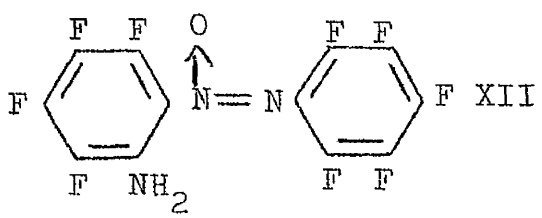
These reactions may occur more readily than the cleavage of the perfluoro-compound (cf. the ready cleavage of the two amino--azo-compounds, compared with the rather slow cleavage of decafluoroazobenzene). The isomeric triazoles would, of course, give tetrafluorobenzotriazole and the two tetrafluoroanilines:

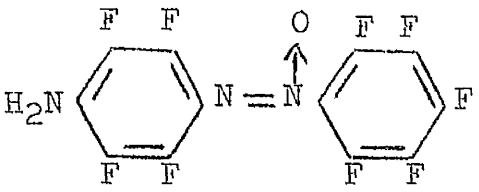


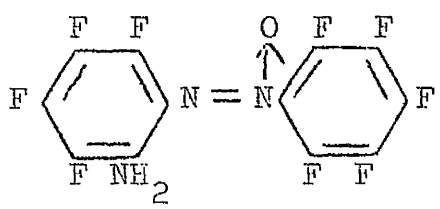
Azoxy - compounds.

The previously reported decafluoroazoxybenzene, and the symmetrically-substituted azoxy-compounds prepared by the oxidation of azo-compounds, presented no problem of constitution; they were characterized by elemental analyses and by their n.m.r. spectra (p.139). The n.m.r. spectra shewed two different types of ring, but it was not at first possible to assign these to the ArN(O)=N- and ArN=N(O)- groups, for the potentially useful compounds for comparison, $C_6F_5.N(O)=O$ and $C_6F_5.N=N.C_6F_5$, respectively, shew similar chemical shifts (p.99). Definite assignment became possible only when the structures of the amino-compounds (XI) and (XII) were fully elucidated.

XI 


XII

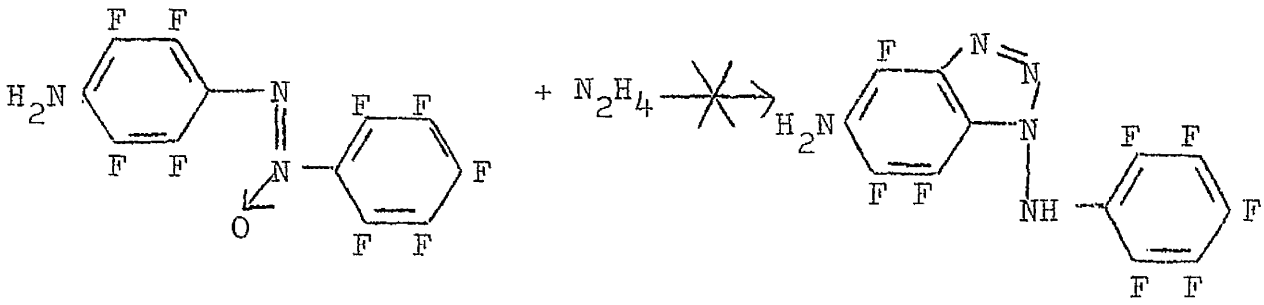
XIa 


XIIa

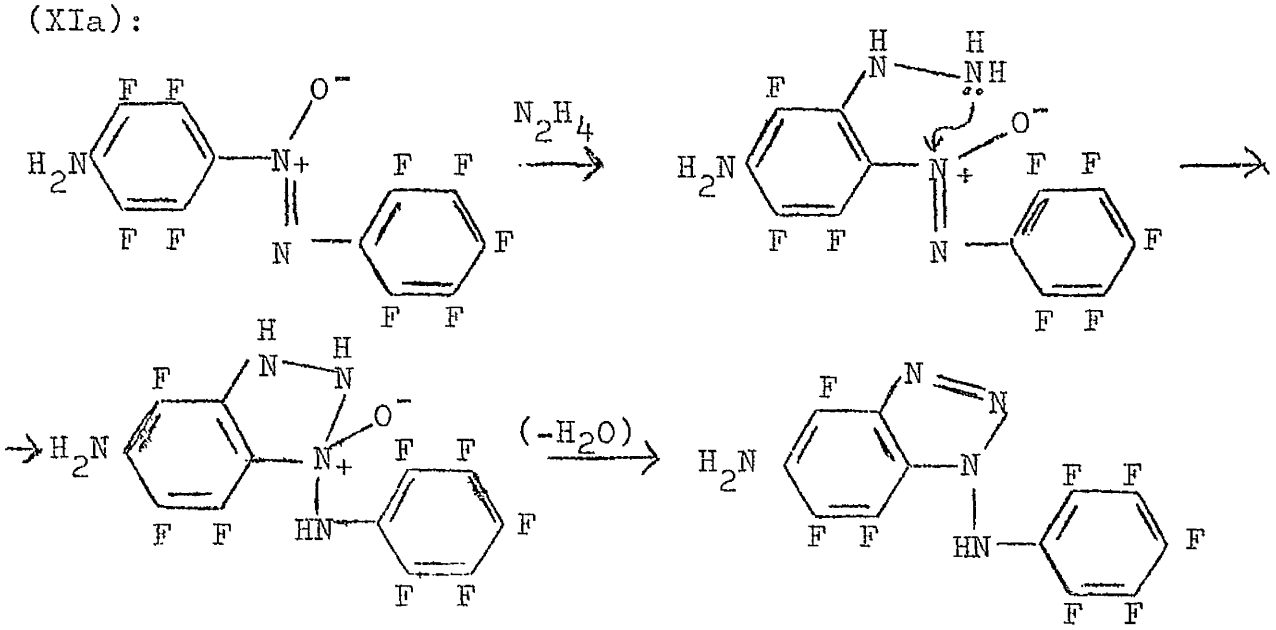
The orientation [i.e. ortho, meta or para relationship between the amino- and (N_2O)-groups] of these aminoazoxy-compounds was established by reductive cleavage; these experiments are tabulated on p.100b. The position of the amino-group relative to the N→O bond in these compounds is of interest and importance. Both aminoazoxy-compounds reacted with hydrazine to give triazoles of known structure, but this reaction, which completes their

characterization, requires discussion.

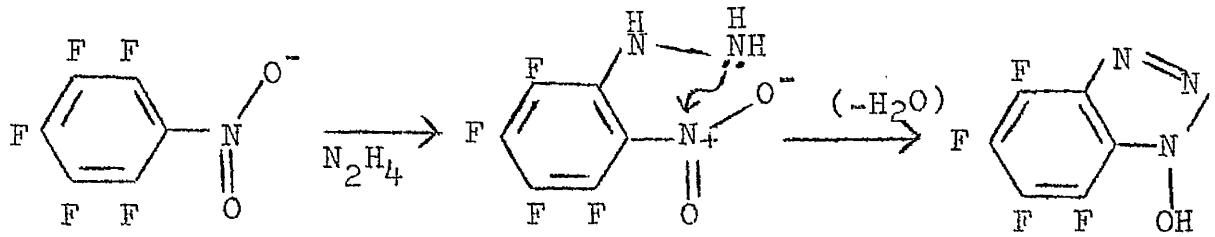
It has not been found possible to formulate an acceptable mechanism to explain the formation of the triazole (XIII) from the azoxy-compound (XIa) and the reaction must therefore be



assumed to take a path comparable to the reaction of pentafluoronitrobenzene with hydrazine, and to involve compound (XI) rather than (XIa):



cf:-



The most surprising observation to be made on the above reaction is that the hydrazine molecule - or species derived therefrom - reacts with the ring already bearing the strongly deactivating amino-group, whereas in the reaction of decafluoroazoxybenzene with methoxide, the 4,4'-disubstituted compound is formed, implying that the methoxy-group, which is normally less deactivating than an amino-group, is more so in this case:

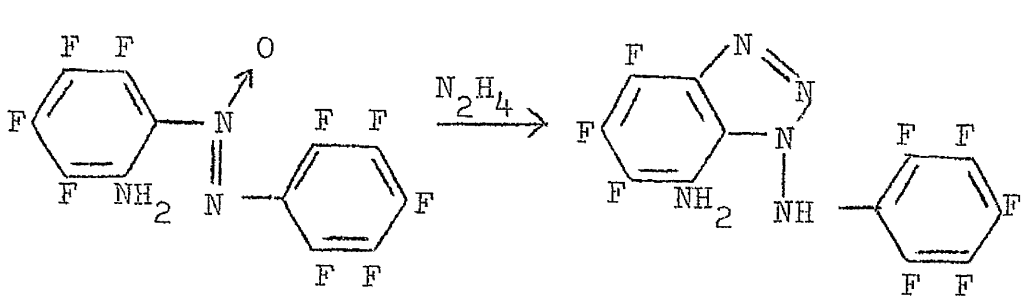
$$C_6F_5(N_2O)C_6F_5 \longrightarrow C_6F_5(N_2O)C_6F_4.OMe\text{-}4 \rightarrow MeO\text{-}C_6F_4\text{-}N{=}N(O)\text{-}C_6F_4\text{-}OMe$$

This last point can be explained in two ways, both of which require the formulation (XI) rather than (XIa) for the amino--compound. The simplest explanation would be that the ArN=N(O)- substituent is much more activating than the ArN(O)=N- group, and ammonia therefore reacts with decafluoroazoxybenzene in the ring next to the N→O group. The resulting amino-substituent is not sufficiently deactivating to overcome the powerful activating effect of the N→O group, and the second nucleophile (hydrazine) therefore reacts at the same ring. The 4,4'-disubstitution occurring in the reaction with methoxide ion can be ascribed to solvation effects. The first methoxy-group enters the 4-position (presumably in the ring bearing the N→O group) exclusively, since the solvated ion is too bulky to substitute in the 2-position on this ring. The second substituent enters the 4-position on the other ring, rather than the 2-position on the ring already bearing a 4-methoxy-group, for the same reason.

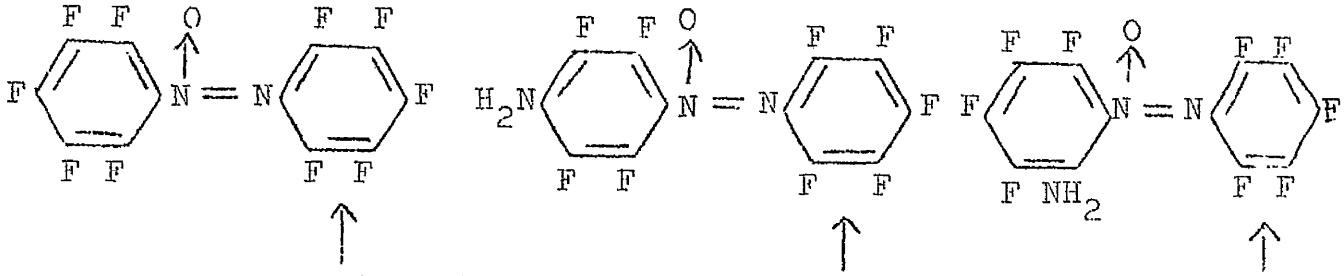
Alternatively, it is possible that ortho substitution with ammonia and with hydrazine are due to hydrogen bonding between the

incoming nucleophile and the N→O bond. It must be assumed also that in the reaction of the aminoazoxy-compounds with hydrazine, this hydrogen bonding is sufficiently powerful as to cause the nucleophile to enter the ring already deactivated by the amino--group. The different course of the reaction with methoxide ion (absence of ortho-substitution and the tendency of the second substituent to enter the other ring) is thus rationalised.

The azoxy-compound (XII) was also caused to react with hydrazine, but here the n.m.r. proof of structure of the triazole is open to some criticism owing to the poor resolution (due to the small sample size) of the spectrum. However, the pentafluorophenyl groups in the two aminoazoxy-compounds gave very similar well resolved n.m.r. spectra (p.139), and can therefore be presumed to be similarly situated in relation to the N→O group. In view of the above considerations on the mechanism of triazole formation, it is perhaps better in this case to regard the reaction as a proof of the structure of the triazole, rather than of the azoxy-compound, for which independent evidence is now available as explained above:

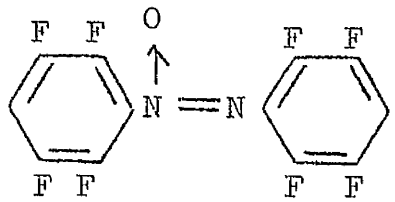
XII  XIV

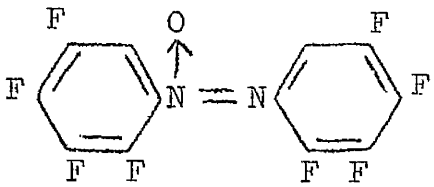
The n.m.r. spectrum of decafluoroazoxybenzene was assigned by comparison with the spectra of the two aminoazoxy--compounds:



rings in comparable chemical environments and shewing similar n.m.r. characteristics.

The spectrum of 4H,4'H-octafluoroazoxybenzene (XV) was assigned

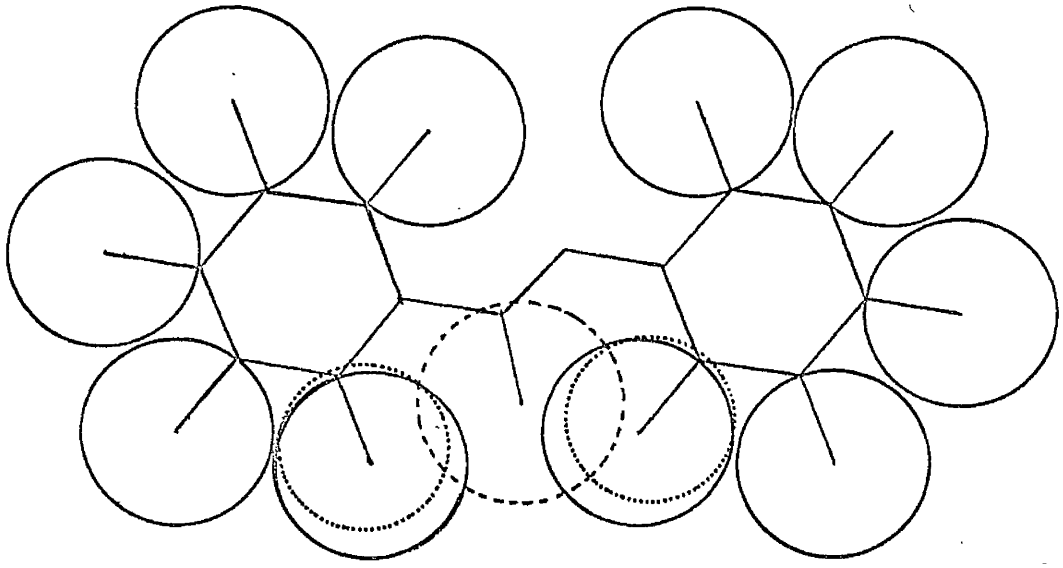
XV 

 XVI

by the use of Mowthorpe's table (cf. p.114), and the spectrum of the 2H,2'H-isomer (XVI) was tentatively assigned by a similar procedure. The chemical shifts were found to be somewhat anomalous in this latter spectrum, and there must therefore be some uncertainty about the assignments. However, the reason for the anomaly becomes clear on the examination of the ultra-violet spectra of these compounds.

The 2H,2'H-octafluoro-compound was the only one of the series which did not (taking the spectrum of the unfluorinated compound as the norm) have an anomalous ultra-violet spectrum (p.102a).

It can be seen from the diagram below that steric hindrance in



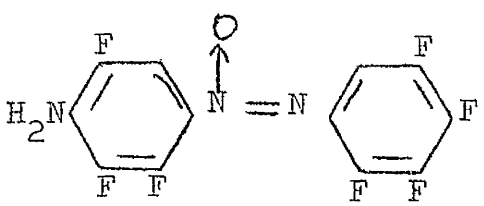
2H,2H-Octafluoroazoxybenzene and Decafluoroazoxybenzene

Continuous circles: fluorine; dotted circles: hydrogen; dashed circle: oxygen.

the 2H,2H-compound need be no greater than in azoxybenzene; hence this fluorinated compound will adopt the same configuration - more or less planar - as azoxybenzene. However, in the 4H,4H-isomer and in the decafluoro-compound, the increased steric interactions between fluorine and oxygen will force the molecule out of the planar conformation, with a resulting decrease in inter-ring conjugation. The resultant interference with the electronic structures of these two molecules will cause the effect observed in their spectra. Such shifts have been noted before in azoxy-compounds containing two bulky ortho-substituents (e.g. Me or Br),[139,145] but it apparently needs more than two ortho fluorine atoms to cause steric interaction.

This steric effect means that each phenyl ring in 2H,2H-octafluoroazoxybenzene contains an azoxy-substituent (represented as

planar-Ar.N(O)=N- and planar-Ar.N=N(O)-, respectively) which is not comparable to those found in the azoxy-compounds containing four ortho fluorine atoms (or three fluorines and one amino-group). These latter substituents can be represented as skew-Ar.N(O)=N- and skew-Ar.N=N(O)-, and would be expected to have different n.m.r. characteristics from the planar substituents. It is not possible to predict the precise effect of this difference on the n.m.r. spectra, and there must remain some uncertainty about the assignments in the spectrum of the 2H,2H-compound. A definite assignment could probably be made as a result of the synthesis of, for example, compound (XVII):



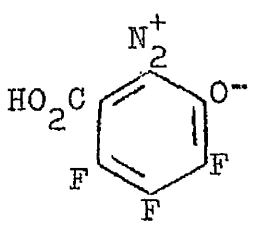
XVII

Anthranilic Acid Derivatives.

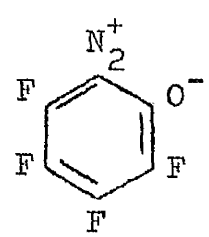
The diazo-oxide (XVIII) shewed -N̈≡N at 4.58μ in its infra-red spectrum, and was distinguished from its isomer (XVIIIa) by ultra-violet spectroscopy; the spectrum was compared with those of the diazo-oxides (XIV) and XIXa),[146] and with that of benzenediazonium-2-carboxylate.[147] These spectra are shown on p.100a.

The nuclear magnetic resonance spectrum of compound (XVIII) was equally compatible with that predicted for structure (XVIIIa)

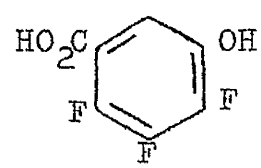
and did not assist the characterization. The diazo-oxide was reduced to the hydroxy-acid (XX) whose n.m.r. spectrum was compatible with the structure given, and quite incompatible with that expected for the isomeric compound (XXa) which would have been produced by reduction of the alternative diazo-oxide (XVIIa). The decisive feature of the spectrum of the hydroxy-acid was the H-F coupling of 2.8 c./sec., which can only reasonably be assigned to a <u>para</u> H-F group, since H-F coupling constants vary much less than do F-F couplings.



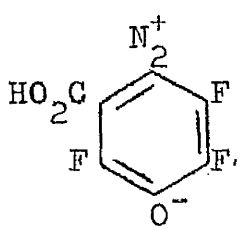
XVIII



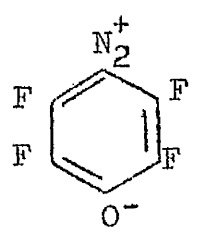
XIX



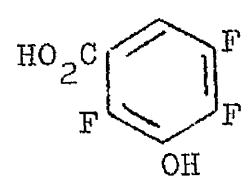
XX



XVIIIa



XIXa



XXa

INFRA-RED SPECTRA

Mulls in Nujol (paraffin) and HCB(hexachlorobutadiene); wavelengths are given in microns.

Decafluoroazobenzene: 6.11s, 6.66m, 6.99w, 7.19w, 7.25s, 7.62m, 7.89w, 8.35s, 8.73s, 9.83w, 10.03s, 10.27w, 10.94m, 12.13w, 12.53w, 13.86m.

4H,4'H-Octafluoroazobenzene: 3.40w, 5.85w, 6.22m, 6.62m, 7.24m, 7.82m, 7.84w, 8.48s, 9.67s, 10.50s, 11.67m, 11.79m, 13.43w, 13.96s, 14.30m.

2H,2'H-Octafluoroazobenzene: 3.23m, 5.74w, 6.13w, 6.24[illegible], 6.64m, 6.70m, 7.33m, 7.84m, 8.51m, 8.91m, 9.19w, 9.41s, 10.55s, 11.45s, 13.70m, 13.83m, 14.15w.

2,2'-Dibromo-octafluoroazobenzene: 6.16m, 6.64s, 6.77m, 7.33m, 8.55w, 8.72s, 9.33s, 10.29s, 11.24w, 11.82w, 12.03s, 12.98w, 13.37w, 18.85w.

4H-Nonafluoroazobenzene: 3.42w, 6.61w, 6.74w, 6.63s, 6.67m, 7.13m, 7.27m, 7.52w, 7.86m, 8.50s, 8.69w, 8.84w, 9.55w, 9.94m, 10.19s, 10.47m, 10.73s, 11.75-11.81s, 13.42w, 13.92m, 14.00m.

Octafluorophenazine: 5.95m, 6.35m, 6.61s, 6.75s, 7.36s, 7.49w, 8.72s, 8.90w, 9.15w, 9.31s, 9.47s, 11.87s, 13.90w.

2H,7H-Hexafluorophenazine: 3.26w, 5.82w, 6.03s, 6.62s, 7.06s, 7.35m, 7.53s, 7.97w, 8.28s, 8.37m, 8.65s, 8.74s, 8.88s, 9.92s, 11.55m, 11.64s, 11.86w, 13.12w, 13.41s.

1H,6H-Hexafluorophenazine: 3.27w, 5.72w, 5.99s, 6.02s, 6.27w, 6.41s, 6.64s, 6.69s, 6.81s, 7.25w, 7.35w, 7.60w, 8.16s, 8.24w, 8.52m, 8.71w, 8.92w, 9.17s, 9.59s, 9.81m, 9.88w, 10.00s, 10.05w, 11.41s, 11.85w, 12.09w, 13.32w, 13.80w, 15.00s.

Decafluoroazoxybenzene: 6.06m, 6.50w, 6.54m, 6.61m, 6.75w, 7.00m, 7.38m, 7.58m, 7.78w, 7.87w, 8.70s, 8.75s, 8.93w, 9.05w, 9.28w, 9.35w, 9.91s, 10.15s, 10.48m, 11.97s, 12.48w, 12.96w, 13.15w, 13.55s, 13.94m, 14.60w.

4H,4'H-Octafluoroazoxybenzene: 3.24m, 6.10w, 6.41m, 6.53s, 6.61s, 6.76w, 6.91w, 7.15s, 7.45s, 7.83s, 8.06w, 8.43s, 8.50s, 8.70w, 8.78w, 9.43m, 9.59s, 9.99s, 10.44s, 10.74s, 10.46m, 11.65m, 11.75m, 11.90m, 13.46m, 13.86m, 14.10s, 14.18s, 14.66w, 13.50m.

2H,2'H-Octafluoroazoxybenzene: 3.19w, 3.24w, 6.16s, 6.61s, 6.76s, 6.85m, 7.30s, 7.42m, 7.66w, 7.90-7.96m, 8.42m, 8.84w, 9.56s, 9.30m, 9.75s, 10.50s, 11.58s, 12.08s, 13.86s, 13.96w, 14.17m, 15.18w.

Decafluorohydrazobenzene: 2.93s, 6.52s, 6.60s, 6.94s, 7.38m, 7.59m, 7.78m, 8.54w, 8.73w, 8.87s, 9.03s, 9.86s, 9.96s, 10.28s, 10.45s, 12.10s, 12.78s, 13.86s, 14.40s, 14.88m.

4,4'-Diethoxyoctafluoroazobenzene: 3.35w, 6.13s, 6.28w, 6.71s, 6.78s, 6.92w, 7.11w, 7.25s, 7.35s, 7.64w, 8.66s, 9.08s, 10.00-10.11s, 11.73s, 13.38w.

4-Ethoxynonafluoroazobenzene: 3.34w, 6.08s, 6.63s, 6.70s, 6.79w, 6.91w, 7.12s, 7.21s, 7.31s, 7.58w, 8.55s, 8.74w, 9.02s, 9.52s, 9.97s, 10.12w, 10.41s, 11.45w, 12.33w, 12.61s, 13.48w, 14.34w.

4,4'-Dimethoxyoctafluoroazobenzene: 3.41w, 6.10s, 6.30w, 6.66s, 6.95m, 7.16s, 7.60m, 8.35m, 8.70s, 9.84s, 10.04s, 10.95w, 12.52w, 13.85s.

4-Methoxynonafluoroazobenzene: 3.41w, 6.12s, 6.35w, 6.67s, 7.00m, 7.14m, 7.25s, 7.65m, 7.89w, 8.39s, 8.69s, 8.75s, 10.03m, 10.41w, 12.15w, 12.59w, 13.90s.

4,4'-Dithiophenoxyoctafluoroazobenzene: 6.14m, 6.35w, 6.76s, 6.94m, 7.26s, 7.75m, 8.65w, 9.78w, 10.03w, 10.16s, 11.70m, 13.38m, 13.46s, 13.85m, 14.35w, 14.56m, 15.26w.

4-Thiophenoxynonafluoroazobenzene: 6.13m, 6.31w, 6.60s, 6.73s, 6.93m, 7.13s, 7.25m, 6.61m, 7.82w, 7.88w, 8.66w, 8.81w, 9.35w, 9.40w, 9.75w, 9.85m, 10.07s, 10.49m, 11.49s, 13.40w, 13.50s, 13.82s, 14.29m, 14.57s.

4-Aminotetrafluorophenol: 2.95s, 3.04s, 3.39m, 3.69w, 3.8m, 5.72w, 5.84w, 6.25s, 6.54m, 6.62s, 6.87w, 7.26s, 7.76s, 8.32s, 8.71s, 9.09m, 9.50w, 9.79m, 9.98s, 10.48s, 11.07s, 12.20m, 13.20w, 13.98s, 15.43m.

4-Aminononafluoroazobenzene: 2.83w, 2.93w, 6.03s, 6.12m, 6.25w, 6.39w, 6.62s, 6.94m, 7.13m, 7.27s, 7.63m, 7.73w, 8.57s, 9.01m, 9.19m, 10.25s, 10.78m, 13.7-13.9m.

4-Hydroxynonafluoroazobenzene: 2.92m, 3.13m, 6.07m, 6.40m, 6.63s, 7.09w, 7.23w, 7.40w, 7.58w, 7.93w, 8.47w, 8.66m, 9.81w, 10.03s, 10.16s, 10.55w, 12.55w, 13.88s.

2-Amino-4H,4'H-heptafluoroazobenzene: 2.85m, 2.99w, 3.23w, 6.29w, 6.41m, 6.67s, 7.10w, 7.19s, 7.24s, 7.77s, 7.97s, 8.51s, 8.96m, 9.03m, 9.84m, 10.68s, 11.55m, 11.73m, 13.38w, 13.87m, 14.02w, 14.46m.

5,6,8-Trifluoro-2,3-diphenylquinoxaline: 3.29w, 6.11m, 6.55w, 6.78m, 6.86m, 6.97m, 7.15w, 7.32m, 7.50m, 7.64w, 8.26w, 8.51m, 8.82w, 8.95m, 9.50m, 9.80w, 9.99w, 10.75w, 10.99w, 11.85w, 11.98w, 12.20w, 12.90m, 13.39w, 13.80s, 14.39s, 15.19w.

Tetrafluorobenzotriazol-1-ol: 3.8-4.4s, 6.41s, 6.70s, 7.08s, 7.34m, 7.73s, 8.03s, 8.12m, 8.32s, 8.48m, 8.96s, 9.04m, 9.42w, 9.57s, 9.72s, 10.02s, 10.16s, 10.25s, 10.68w, 11.82m, 12.00m, 12.05m, 12.67m, 13.7m, 13.85m.

Tetrafluorobenzotriazole: 3.6s, 6.39s, 6.73s, 7.26s, 7.50m, 8.15s, 8.40m, 9.12w, 9.50m, 9.73s, 10.32s, 10.41s, 12.28s, 13.40w.

Silver salt of tetrafluorobenzotriazole. 6.00w, 6.47s, 6.70w, 7.24w, 7.31w, 7.39w, 7.93w, 8.54s, 8.64s, 9.50w, 9.74s, 10.02s, 10.13m, 12.20s, 13.86s.

1-Acetyltetrafluorobenzotriazole: 5.30w, 5.60s, 6.01w, 6.44s, 6.71s, 6.99m, 7.24s, 7.39w, 7.46w, 7.65w, 7.75s, 7.86s, 8.45w, 8.52m, 8.68s, 9.07s, 9.37s, 9.61s, 9.85s, 10.11w, 10.28m, 10.51m, 10.65m, 12.26s, 13.36w, 14.16s.

1-(Pentafluorophenylamino)tetrafluorobenzotriazole: 3.11s, 3.40m, 6.03m, 6.13w, 6.38s, 6.58s, 8.73s, 8.86w, 7.13m, 7.23s, 5.57m, 7.85s, 7.92w, 8.01m, 8.70s, 8.83s, 8.45w, 9.08w, 9.37w,

9.71m, 9.83s, 10.13s, 10.27s, 10.94s, 12.19s, 12.99m, 13.23m, 13.32w, 13.60s, 13.84m, 14.02m, 14.54m, 14.77w.

1-(4H-Tetrafluorophenylamino)-5H-trifluorobenzotriazole: 3.11s, 3.23m, 3.31w, 5.94w, 6.04s, 6.08m, 6.15w, 6.41s, 6.53s, 6.71s, 6.80s, 7.04m, 7.15s, 7.24m, 7.89m, 7.96m, 8.03m, 8.26w, 8.42m, 8.51m, 8.70m, 8.81w, 9.02s, 9.38m, 9.60s, 10.33s, 11.50s, 11.86s, 11.94s, 13.19m, 13.39s, 13.94w, 14.15s, 14.59m.

1-(2H-Tetrafluorophenylamino)-7H-trifluorobenzotriazole: 3.08s, 6.05m, 6.18m, 6.47s, 6.53s, 6.61s, 6.77s, 6.98m, 7.12w, 7.26m, 7.77m, 7.83w, 7.95s, 8.17w, 8.33m, 8.46m, 8.73s, 8.87m, 9.25s, 9.39s, 10.41s, 10.68s, 11.40m, 11.91s, 12.04s, 12.52m, 13.74w, 13.90s, 14.25m, 14.55w, 14.82w, 15.27w.

1-(Pentafluorophenylamino)-5-aminotrifluorobenzotriazole: 2.90m, 3.01m, 3.13s, 5.98m, 6.11m, 6.40s, 6.59s, 6.77s, 7.13s, 7.37m, 7.59m, 7.83s, 7.97w, 8.06w, 8.34m, 8.62s, 8.71m, 8.82s, 9.72s, 9.98s, 10.16s, 10.42s, 10.89s, 12.58s, 12.97m, 13.58s, 14.65m.

1-(Pentafluorophenylamino)-7-aminotrifluorobenzotriazole: 2.95m, 3.17m, 6.10m, 6.44s, 6.55m, 6.80w, 7.06w, 7.60w, 7.75w, 7.90m, 7.97w, 9.29w, 8.65w, 8.76w, 8.91m, 9.17m, 9.79s, 10.15s, 10.60s, 11.12w, 12.3w, 12.75w, 13.18w, 13.85m, 14.87w.

4-(Pentafluorophenylazoxy)tetrafluoroaniline: 2.82m, 2.92m, 6.01s, 6.10m, 6.54s, 6.60s, 6.81m, 6.93w, 7.02w, 7.30w, 7.41s, 7.53m, 7.78w, 8.47m, 8.64m, 8.89m, 9.48w, 9.70w, 9.91m, 10.08m, 10.50s, 11.99s, 13.01w, 13.67m, 13.94m, 14.53m, 15.49m.

2-(Pentafluorophenylazoxy)tetrafluoroaniline: 2.83s, 2.91s, 5.99m, 6.20s, 6.53s, 6.59s, 6.83w, 7.01m, 7.40m, 7.59w, 7.69s, 7.80m, 8.54m, 8.81s, 9.54w, 9.75s, 9.91s, 10.05s, 10.25s, 10.56s, 12.08s, 12.94w, 13.57m, 13.94m, 14.65w.

2,3-Diphenyltetrafluoroquinoxaline: 6.05m, 6.50m, 6.68s, 6.94w, 7.62m, 7.40m, 7.51w, 7.61w, 8.01w, 8.28w, 8.50w, 8.62w, 9.19m, 9.32w, 9.58s, 9.78s, 10.21m, 10.59m, 12.21m, 12.65w, 12.91m, 12.99m, 13.64m, 13.8-13.9w, 14.13m, 14.32w, 14.42m, 15.29m.

Trifluorobenzenediazonium-2-oxide-6-carboxylic acid: 3.6s, 4.0s, 4.58s, 5.25s, 5.86m, 6.08m, 6.41s, 6.55s, 6.84s, 7.03w, 7.34w, 7.44w, 7.63m, 7.87w, 8.29s, 8.61s, 9.71s, 10.21s, 11.02s, 13.65s, 14.13s.

3-Hydroxy-4,5,6-trifluorobenzoic acid: 3.05s, 3.76w, 5.89s, 6.13s, 6.46m, 6.23s, 7.00m, 7.22m, 7.53m, 7.87s, 8.17s, 8.45s, 9.10m, 9.60s, 11.03m, 11.36m, 12.60s, 13.15-13.25w, 13.73s, 13.85m, 14.64s.

ULTRA-VIOLET SPECTRA

For most compounds, two spectra are given: the first, in ethanol, and the second, in hexane. Where only one solvent was used, this is shown by E (ethanol), H (hexane), or W (water). Extinction coefficients (ε) for absorption below 215mμ (ethanol) or 205mμ (hexane) are somewhat inaccurate (high) owing to solvent absorption.

Compound	Max.	ε	Min.	ε	Inflex.	ε
Decafluoro-azobenzene	203mμ	8800	211mμ	6800		
	218	6840	253	3410		
	312	16100	377	155		
	453	745				
	197	15000	212	6750		
	218-221	6900	253	3750		
	308	14800	370	90		
	451	715				
2H,2'H-Octa-fluoroazo-benzene	200	13900	221	7600		
	225-6	7750	251-2	1790		
	333-5	18100	391-3	278		
	440-3	548				
	198	16000	221-2	7750	322-330	17100-17700
	226	8050	255	1790		
	334	18200	388-390	243	344-8	16500-15800
	443	524				
					354-363	11900-8500
2,2'-Dibromo-octafluoro-azobenzene	207-8	26200	264-5	4300	224-233	8460-7980
	319	12300	391	170		
	464	515				
	208	26100	262-3	4440	226-233	8200-7960
	318	12300	386	118		
	465-9	458				

Compound	Max.	ε	Min.	ε	Inflex.	ε
4H-Nonafluoro-azobenzene (E)	202	12,300	247-9	5000	221-231	7400-6450
	302-4	17,400	381-4	196		
	450-4	714				
Octafluoro-phenazine	205	12500	215-6	9800	353-6	5580-5720
	223	10800	230	9400	387-394	2980-2660
	257	95000	293-4	640	404-413	2110-1820
	370	7740				
	200	14700	217-8	9400	351-4	4950-5140
	221	9650	232	6900	359-362	9110-9390
	258	122000	291-2	274	387-393	4400-4380
	369	12350	409	2870		
	413	3010				
5,10-Dihydro-octafluoro-phenazine (H)	199-200	13200	212-3	9900	256-8	7200-6320
	237-8	39500	279-281	1000		
	317-8	2030				
2H,7H-Hexa-fluoro-phenazine	206-7	12000	227-8	5050	216-220	8800-8100
	259	91500	293-4	390	345-350	3220-3420
	363	4460	388-393	2100	355-7	3960-4100
		2440			422-430	2090-1980
	195-6	13500	201-2	11800	215-9	7900-7200
	204	12200	227	3660	256-7	9550C
	259	113000	292-4	340		98500
	344	2620	347	2540	327-332	1400-1570
	360	3680	374-6	1960	353-6	3200-3280
	385-6	2120	395	2020	402-3	2380-2400
	407	2600	420	1750	411-4	2400-2380
	427	1930	429	1850	437-440	1540-1510
	432	2030				
1H,6H-Hexa-fluoro-phenazine	205-6	18800	225-6	10400	215-221	12050-11200
	248	89000	286-7	302		
	366	10200			350-4	8200-9000
					359-362	10100
					386-393	3280-2480

Compound	Max.	ε	Min.	ε	Inflex.	ε
	205	19700	226-7	9650	215-221	12100-11200
	249	116500	286-7	262		
	357	10200	361-2	10100	349-352	8300-8680
	364	10200			382-8	3510-2880
Decafluoro-azoxybenzene	201	13000	212	9100	228-237	10150-9240
	224	11100	265-6	4300		
	291-4	5760				
	198-9	14500	213	8850		
	226-7	10600	261	3590		
	291-3	5300				
4H,4'H-Octa-fluoroazoxy-benzene	203-4	13400	220-2	8200		
	233	8950	260-2	4050		
	284-290	5550				
	203-4	14700	220-1	9590		
	229-231	10000	258-9	4200		
	283-4	6200				
2H,2'H-Octa-fluoroazoxy-benzene	205	10750	220-2	7190		
	227-230	7400	241-3	6560		
	249-252	6800	266-9	6120		
	313-4	11200				
	203	12000	219-2	6940		
	229-231	7420	241-2	6540		
	253	7050	269-271	6110		
	319-321	12550				
Decafluoro-hydrazo-benzene	204	10000	208	9200		
	233	18100				
	201-2	7460	206	6700	243-5	6150-4120
	227-9	13900				

Compound	Max.	ε	Min.	ε	Inflex.	ε
4,4'-Diethoxy-octafluoro-azobenzene	204-5	9250	208-9	9200	231-8	7450-7050
	213	9250	265	2780		
	340-3	21600	399	970		
	441-7	1700				
	202-3	9750	259-260	2800	210-4	9100
	331-5	23300	390	460	229-234	7250-7050
	451-5	1500				
4-Ethoxy-nonafluoro-azobenzene	204-5	8300	210-1	8000	234-9	6580-5720
	214	8100	256-9	3300		
	329	19900	393	470		
	442	1110				
	202-3	9050	257-9	3760	210-7	8250
	323	19800	385	240	234-9	6600-5950
	448-451	1100				
4,4'Dimethoxy-octafluoro-azobenzene	213-5	9000	263	2640	205-8	8750=8850
	338-341	22400	399	805	231-5	7300-7050
	448	1350				
	203-6	9650	211	9250	229-236	7800-7200
	213-4	9450	261	3380		
	335-6	24500	389	460		
	448-452	1560				
4-Methoxy-nonafluoro-azobenzene	202	9050	210-1	7950	227-237	7250-6450
	214-5	8100	260-1	3360		
	328-331	19800	394	475		
	447-451	1170				
	200	10900	257-8	3600	210-6	8100-7950
	322-4	19600	381	220		
	452-5	1050				
4,4'-Dithio-phenoxyocta-fluoroazoben-zene (E)	205	-	233-5	-		
	245-8	-	312-6	-		
	367-8	-				

Compound	Max.	ε	Min.	ε	Inflex.	ε
4-Thiophenoxy-nonafluoro-azobenzene	206	21600	263-7	9000	230-241	11800-11700
	305-9	14200			332-346	13000-12800
					442-460	1650-1600
	204	21700	256-263	9050	213-9	17300-15000
	303-4	14400	330	13200		
	343-5	13400	430-3	1300	231-9	10800-10600
	459	1400				
4-Amino-tetrafluoro-phenol (E)	223-4	14150	247	725		
	278	1320				
4-Amino-nonafluoro-azobenzene	213-4	8800	295-7	2960	203-7	8350
	377-380	24400			226-240	7700-7550
					243-250	7400-7000
					429-457	8000-4950
	202	8900	206-7	8500	228-233	7650-7600
	213-5	9000	277-9	3250		
	352	23500	404-6	1940		
	435-442	2340				
4-Hydroxy-nonafluoro-azobenzene	202-3	7350	208-9	6700	232-241	6100-6000
	214-6	6950	267-9	3150		
	343-5	18000	393-7	6950		
	403	7050				
	202-3	8630	256	2840	209-212	8000-7950
	319-323	19500	381	330	217-222	7630-7000
	449-452	1100			345-359	11700-8750
2-Amino-4H,4H-heptafluoro-azobenzene	208-9	16300	266-7	2900	221-234	12700-9700
	318-9	12500	376	1410		
	463	6100				

Compound	Max.	ε	Min.	ε	Inflex.	ε
	206	26200	265	2560	197-201	22000-23200
	319-321	12650	371	1450		
	443-7	5180			222-234	12100-9550
5,6,8-Trifluoro-2,3-diphenylquinoxaline (E)	205-6	30400	230-1	16200	222-6	17300-16800
	246	30400	263	16800		
	274-5	17400	313-5	4620	268-272	17200-17300
	351	7800				
					280-6	17000
2,3-Diphenyltetrafluoroquinoxaline	205-6	36000	230-1	21600	219-227	23000-22300
	245	36000	260-2	19000		
	266-270	19700	313-4	4780	278-285	19000-17000
	353	9530				
	206	37600	217-9	24800	279-284	21700-21400
	225	25800	232	22800		
	245	36400	259	21400		
	267-274	22800	314			
	352	9400				
Tetrafluorobenzotriazol-1-ol	206-7	14700	213-4	13800	256-8	3030-3070
	218-9	14300	240-1	2180	319-327	390-290
	363	3170	270-1	2820		
	283	3300				
	205	-	221	-	252-5	-
	224	-	237	-		
	259	-	269	-		
	282	-				
Tetrafluorobenzotriazole (E)	203	26800	219-221	3020		
	223-4	3120	233-4	2620		
	257-9	4140	263-4	3980		
	270-2	4020				

Compound	Max.	ε	Min.	ε	Inflex.	ε
1-(Pentafluoro-phenylamino)-tetrafluoro-benzotriazole	207-8 280-2	19300 3310	272	3220	213-8 240-9	18500-17700 6110-6070
	208-210 249 286	22100 6300 3140	238-240 269	6090 2550	255-9	5380-4930
1-(4H-tetra-fluorophenyl-amino)-5H--trifluoro-benzo-triazole	211 254	28800 5810	252	5710	225-230 272-281	16100-15450 4220-3630
	212 253-4	27600 5550	224-5	5180	223-8 260-3	16500-13900 5060-4930
1-(2H-tetra-fluorophenyl-amino)-7H--trifluoro-benzo-triazole	203-4 249 274-6	24400 7800 5410	238-9 269-272	7090 5360		
	203-4 224-7 274-5	24600 7100 4120	233 266-7	5890 3970	320-330 350-6	248-234 127-106
1-(Pentafluoro-phenylamino)--5-aminotri-fluorobenzotriazole (E)	200 225 326-7	29400 43100 2590	205-6 290	24700 985	256-262	6820-5960
1-(Pentafluoro-phenylamino)--7-aminotrifluorobenzotriazole (E)	220-1 312-5	27650 3940	282	2340	262-273	2730-2580
4-(Pentafluoro-phenylazoxy)-tetrafluoro-aniline	203 227-8 283 353	26000 26400 77400 8950	211 265 287	18300 6180 7440	275-280 300-321	7170-7340 7860
	225 288-291	17100 9300	256	6000	203-8	12700-13500

Compound	Max.	ε	Min.	ε	Inflex.	ε
2-(Pentafluoro-	223	19100	266-8	5890	207-211	14350-
phenylazoxy)-	277-281	6150	344-6	3110		14900
tetrafluoro-	366-9	3300			238	8950
aniline						
	219-220	17850	286-9	5500	207-212	15400-
	293-9	5650				16000
					235-241	8300-8060
					263-273	5900
					336-355	4160
Trifluorobenz-	207-8	17800	311	473	226-231	7280-6200
enediazonium-	390-405	5450			224-252	4360-4100
-2-oxide-6-					267-276	3260-2940
carboxylic						
acid (E)	199	18400	265-6	2890	205-9	15800-
(W)	277-9	3230	313	569		15000
	394-7	5550			223-6	8900-8070
					241-6	5780-5150
2,3,4-Triflu-	205	17900	259	500	225-231	6600-6200
oro-5-hydroxy-	291	2400				
benzoic acid (E)						

NUCLEAR MAGNETIC RESONANCE SPECTRA

^{19}F at 56.46 Mc./sec. Solvent: THF; Reference : CF_3CO_2H - ext.

^{1}H at 60.00 Mc./sec. " " " Me_4Si - int.

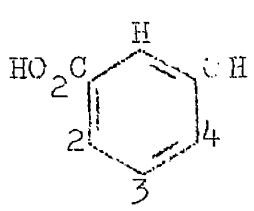
A Perkin-Elmer R.10 permanent magnet instrument operating at 14 kG and 35° was used. Fluorine chemical shifts (δ) are measured in parts per million to high field of trifluoroacetic acid (^{19}F), and proton shifts are relative to tetramethylsilane. Figures in parentheses ( ) refer to proton shifts and H-F coupling constants; all others to F - shifts and F-F coupling constants.

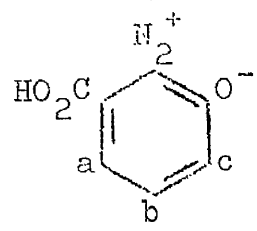
(a) Miscellaneous compounds

4-Aminotetrafluorophenol. In ethanol, a poorly-resolved A_2B_2 system: δ_{AB} = 87.6; J_{AB} ≈ 45-50 c./sec.

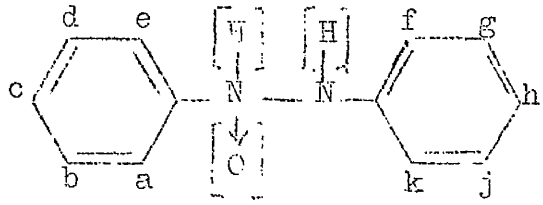
2,3,4-Trifluoro-5-hydroxybenzoic acid. In water; first order. δ_2 = 72.1; δ_3 = 86.6; δ_4 = 76.6 p.p.m. δ_H = 0.36 p.p.m. to low field of benzene interchange. $/J_{2H}/$ = 6.5; $/J_{3H}/$ = 2.8; $/J_{4H}/$ = 9.2; $/J_{23}/$ = 20.0; $/J_{24}/$ = 6.3; $/J_{34}/$ = 18.9 c./sec.

Trifluorobenzenediazonium-2-oxide-6-carboxylic acid. In N-methyl-pyrrolidone. δ_a = 72.2; δ_b = 68.9; δ_c = 62.8 p.p.m. $/J_{ab}/$ = 14.7; $/J_{ac}/$ = 3.4; $/J_{bc}/$ = 20.0 c./sec.; (see also p.122)





(b) Azo- / Hydrazo- / Azoxy- compounds

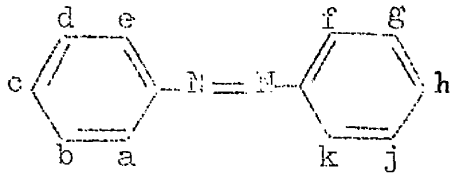


Substituents	Chemical shifts of ring nuclei δ_a	δ_b	δ_c	δ_d	δ_e	δ_f	δ_g	δ_h	δ_j	δ_k
Azo-compounds (parent compound: decafluoroazobenzene)										
None	72.5	86.4	73.6	86.4	72.5	72.5	86.4	73.6	86.4	72.5
4H,4'H	71.4	62.1	(-7.76)	62.1	71.4					
2H,2'H	(-7.66)	61.7	73.4	79.0	71.3					
2Br,2'Br	(Br)	53.5	74.1	78.9	73.1					
4H	72.7	62.5	(-7.74)	62.5	72.7	73.9	86.4	74.0	86.7	73.9
4EtO,4'EtO	75.7	83.4	(EtO)	83.4	75.7					
4EtO	73.4 or 73.6	82.1	(EtO)	82.1	73.4 or 73.6	73.6 or 73.4	87.9	75.4	87.9	73.6 or 73.4
4MeO,4'MeO	74.1	82.8	(MeO)	82.8	74.1					
4MeO	73.6	82.9	(MeO)	82.9	73.6	73.5	87.1	75.4	87.1	73.5
4PhS	72.8	56.8	(PhS)	56.8	72.8	72.3	86.4	73.5	86.4	72.3
$4NH_2$ (in EtOH)	73.0	88.6	(NH_2)	88.6	73.0	74.9	87.9	78.9	87.9	74.9
4OH	74.6	87.1	(OH)	87.1	74.6	74.4	87.2	76.6	87.2	74.4
$2NH_2$,4'H,4H	(-7.82)	61.5	(-7.25)	78.0	72.9	74.5	62.9	(-7.44)	62.9	74.5
Decafluorohydrazobenzene			93.1	88.7	82.0					
Azoxy-compounds										
None	71.7	83.7	74.0	83.7	71.7	65.2	86.5	78.5	86.5	65.2
4H,4'H	72.3	60.8	(-7.86)	60.8	72.3	66.1	62.5	(-7.26)	62.5	66.1
2H,2'H	(-7.99)	59.8	76.3	73.4	66.4*	(-8.33)	62.2	80.0	75.7	64.0
$4NH_2$	74.6	86.2	(NH_2)	86.2	74.6	65.4	86.6	79.8	86.6	65.4
$2NH_2$	(NH_2)	84.2	77.5	99.4	72.3	65.1	86.9	79.6	86.9	65.1

* δ_e is anomalous; alternatively the assignment of the rings could be interchanged, in which case δ_c and δ_k would be anomalous. This compound is discussed on p. 120.

Coupling Constants (moduli; c./sec.)

Azo-compounds



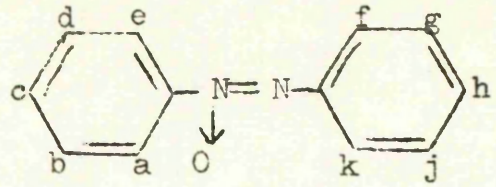
	Substituents	J_{ab} * ±	J_{ad} * ∓	J_{ac}	J_{bc}	J_{ae} *	J_{bd} *	J_{cd}	J_{ce}	J_{be} * ∓	J_{de} * ±
*	None	20.3	7.3	3.6	20.7	9.0	4.0	20.7	3.6	7.3	20.3
*	4H,4'H	20.8	13.1	(7.5)	(10.4)	5.7	0.7	(10.4)	(7.5)	13.1	20.8
	2H,2'H	(11.2)	(2.5)	(8.2)	20.6	(6.2)	2.2	19.7	6.0	11.5	18.2
	2Br,2'Br				21.8		2.4	19.2	5.2	9.6	19.2
*	4H	20.8	13.1	(7.5)	(10.5)	5.7	0.8	(10.5)	(7.5)	13.1	20.8
*	4EtO,4'EtO	~20.3	~7.1			~7.9	~0			~7.1	~20.3
*	4EtO	coupling constants not measurable									
*	4MeO,4'MeO	~20.8	~7.6			~6	~1			~7.6	~20.8
*	4MeO	coupling constants not measurable									
*	4PhS	21.7	11.3			5.7	3.0			11.3	21.7
*	$4NH_2$	~21	~7.5	~2	~20.8	~4	~1	~20.8	2	~7.5	~21
*	4OH	coupling constants not measurable									
	$2NH_2$,4H,4'H				(11.3)		4.3	(10.3)	(6.8)	13.7	20.6
*	Decafluorohydrazobenzene: coupling constants not measurable										

		J_{fg}	J_{fj}	J_{fh}	J_{gh}	J_{fk}	J_{gj}	J_{hj}	J_{hk}	J_{gk}	J_{jk}
*	4H	20.9	7.4	4.0	21.1	~12	<2	21.1	4.0	7.4	20.9
*	4EtO			~3.4	~20.8			~20.8	~3.4		
*	4MeO			~3.2	~20.6			~20.6	~3.2		
*	4PhS	20.6	7.2	4.1	20.6	7.1	2.2	20.6	4.1	7.2	20.6
*	$4NH_2$				20.6			20.6			
*	4OH				20.6			20.6			
*	$2NH_2$,4H,4'H	20.1	12.1	(7.3)	(10.2)	±4.0	±0.7	(10.2)	(7.3)	12.1	20.1

* AA'XX' and AA'PXX' systems: J_{ae}/J_{bd} not distinguished; J_{ab} and J_{de} of opposite sign to J_{ad} and J_{be} —— similarly, for J_{fk} etc.

Coupling Constants (moduli; c./sec.)

Azoxy-compounds

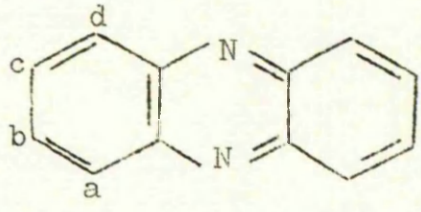


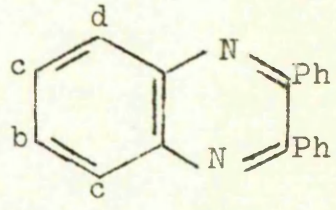
Substituents	J_{ab}	J_{ad}	J_{ac}	J_{bc}	J_{ae}	J_{bd}	J_{cd}	J_{ce}	J_{be}	J_{de}
	* ±	* ∓			*	*			* ∓	±
* None J_{NF} 1.1	21.5	6.3	3.6	20.3	6.7	2.1	20.3	3.6	6.3	21.5
* 4H,4H			(7.3)	(10.4)			(10.4)	(7.3)		
2H,2H	(10.5)	(2.0)	(7.7)	20.5	(7.1)	2.8	19.1	7.5	12.0	18.6
* $4NH_2$	25.9	10.6			10.7	<1			10.6	25.9
$2NH_2$				20.3		6.5	21.6	4.9	7.9	22.6

	J_{fg}	J_{fj}	J_{fh}	J_{gh}	J_{fk}	J_{gj}	J_{hj}	J_{hk}	J_{gk}	J_{jk}
* None J_{NF}=1.0	22.0	6.6	2.0	20.4	8.9	0.4	20.4	2.0	6.6	22.0
* 4H,4H			(7.3)	(10.4)			(10.4)	(7.3)		
2H,2H	(10.1)	(2.4)	(8.1)	20.7	(6.1)	1.4	19.1	4.8	10.9	19.2
* $4NH_2$	22.7	6.5	1.4	20.5	5.5	2.1	20.5	1.4	6.5	22.7
* $2NH_2$	21.6	6.0	1.3	20.3	5.6	2.1	20.3	1.3	6.0	21.6

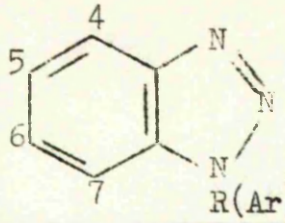
* AA'XX' and AA'PXX' systems: J_{ae}/J_{bd} not distinguished; J_{ab} and J_{de} of opposite sign to J_{ad} and J_{be} - similarly for J_{fk} etc.

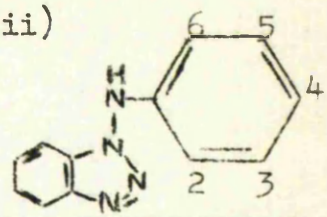
(c) Phenazines (P) and Quinoxalines (Q)





Substituents	δ_a	δ_b	δ_c	δ_d	J_{ab}	J_{ac}	J_{ad}	J_{bc}	J_{bd}	J_{cd}
None (P)	75.6	73.5	73.5	75.6	coupling constants not measurable					
" (Q)	76.5	78.9	78.9	76.5	"		"	"	"	
	or 78.9	76.5	76.5	78.9						
1H,6H(P)	(-8.05)	48.0	74.7	69.5	(9.9)	(7.5)	(3.0)			
2H,7H(P)	45.8	(-7.99)	52.8	77.2	(~9.9)			(~9.9)	(6.9)	
7H(Q)	48.5	(-7.64)	56.4	78.6	(10.2)	2.2	19.5	(11.3)	(6.8)	18.4
5,10-Dihydrophenazine:										
2H,7H	62.1	(-6.34)	69.4	88.4	(10.8)	2.3	10.7	(10.8)	(7.2)	21.8
	also shows: δ_{NH} -6.74; $J_{a(NH)} \sim J_{d(NH)} \sim$ 1.5 c/s.									

(d) Benzotriazoles (i) 

[Ar = C_6F_5.NH- or H.C_6F_4.NH-] (ii) 

(i) Substituents

Benzo-	R	δ_4	δ_5	δ_6	δ_7	δ_H [$\nu_{\frac{1}{2}}$]	J_{45}	J_{46}	J_{47}	J_{56}	J_{57}	J_{67}
None	H	76.1	83.8			(-13.25)[33]	(poorly-resolved AA'XX')					
"	Na	77.4	88.5	(in aq. 5% NaOH)			±15.0	±7.4	0.4	6.9	(see p.106)	
"	Ac	75.1	83.0	74.5	62.1		19.5	2.3	18.4	19.5	0.0	18.4
		or74.5		or75.1		[13]						
"	OH	80.1	85.6	76.9	84.0	(-12.62)	18.1	1.5	18.1	18.1	2.8	20.4
"	Ar	78.0	85.3	75.7	84.0		18.5	2.4	18.5	18.5	2.4	20.3
5H	Ar	58.2	(-7.32)	49.0	87.6		(10.7)	3.7	19.7	(9.6)	(4.6)	22.8
7H	Ar	69.6	87.5	51.5	(-7.57)		18.3	6.6	(2.1)	18.7	(6.0)	(8.7)
$5NH_2$	Ar	75.1	(NH_2)	76.6	87.8			11.1	18.8			20.5
$7NH_2$	Ar	90.2	87.7	82.1	(NH_2)		~21	~6		~18		

(ii) Substituents

Benzo-	Ar	δ_2	δ_3	δ_4	δ_5	δ_6	J_{23} * ±	J_{25} * ∓	J_{24}	J_{26} *	J_{35} *	J_{34}
*None	None	79.9	~87.2	~87.2	~87.2	79.9	not analysable					
*$5NH_2$	"	80.1	~87.8	~88	~87.8	80.1	"	"				
*$7NH_2$	"	78.6	~86.6	~86.6	~86.6	78.6	"	"				
*5H	4H	71.1	63.1	(-7.17)	63.1	71.1	21.5	10.7	(7.35)	1.46	0.52	(10.35)
7H	2H	(-6.16)	62.2	90.2	79.8	81.9	(11.5)	(2.6)	(7.2)	(7.8)	3.4	21.4

		J_{56}	J_{36}	J_{46}	J_{45}
7H	2H	19.0	10.4	3.2	20.6

*AA'PXX' systems: J_{26}/J_{35} not distinguished; J_{23} and J_{56} of opposite sign to J_{25} and J_{36}

EXPERIMENTAL SECTION

EXPERIMENTAL

General Techniques. - In many experiments, the crude product was chromatographed on alumina (Light's type "A", 100-200 mesh). Three columns were used (A, 60 x 30 cm.; B, 30 x 2.5 cm.; and C, 20 x 1.5 cm.). In all but one of the chromatographic separations, the products were sufficiently coloured for the separation to be monitored visually.

In photolytic experiments, the reaction vessel was placed ca. 30 cm. from a 500 w "Hanovia" mercury vapour lamp.

Fluorine and proton magnetic resonance spectra were recorded on a Perkin-Elmer R.10 60 m/c instrument, and ultra-violet and visible spectra were recorded on a Unicam S.P.700 spectrophotometer; for routine infra-red spectra, an Infracord 137 instrument was used, and the infra-red spectra of pure compounds were recorded on a Perkin-Elmer 21 spectrophotometer.

Yields are quoted on the crude product if its melting point was within 5° of that of the pure sample, and its infra-red spectrum was satisfactory.

Compounds new at the time of preparation are underlined at first mention; a few of these compounds have since been reported in the literature, and this is shown by quotation of the literature melting points in the usual way.

Decafluoroazobenzene and Octafluorophenazine. - (a) From pentafluoroaniline and lead tetra-acetate at room temperature. Lead tetra-acetate (3.25 g., 7.2 mmole) in benzene (100 ml.) was added to pentafluoroaniline (1.00 g., 5.5 mmole) in benzene (15 ml.).

After two days at room temperature the solids were filtered off, and the filtrate was washed with aqueous 2N sodium hydroxide (5 x 20 ml.), then with water (4 x 25 ml.), and dried ($MgSO_4$). The solution, which was deep red, was evaporated to dryness, and the residue was chromatographed on alumina (column B) with elution with light petroleum (b.p. 60-80°). An orange band followed the solvent front down the column, and was the only fraction collected. Evaporation of the eluent yielded an orange solid (0.50 g.; 51%), m.p. 135-8°, shown by infra-red spectroscopy to be decafluoroazobenzene.[88] Recrystallization from carbon tetrachloride gave a pure sample (Found: C, 40.0; H, 0.2; N, 7.5. $C_{12}F_{10}N_2$ requires C, 39.8; H, 0.0; N, 7.7%), m.p. 143° (lit.,[98] 142-143°).

(b) From pentafluoroaniline and lead tetra-acetate in refluxing benzene. Pentafluoroaniline (5.0 g., 27 mmole) was dissolved in benzene (150 ml.); lead tetra-acetate (25.0 g., 55 mmole) was added, and the mixture was heated under reflux for one hour. The resulting dark brown suspension was diluted with benzene (250 ml.), then washed successively with aqueous 50% acetic acid, saturated aqueous sodium bicarbonate, and water, then dried ($MgSO_4$). The solvent was evaporated and the residue was dissolved in a minimum of hot 30% benzene in light petroleum (b.p. 60-80°), and chromatographed on alumina (column A). Elution with the same solvent gave decafluoroazobenzene (2.3 g; 48%), m.p. 138°, identified by infra-red spectroscopy. Elution was continued with benzene; a yellow band developed on the column, and yielded yellow octafluorophenazine

(1.23 g.; 28%), m.p. 230-2°, on evaporation of the solvent. The infra-red spectrum was identical with that of a pure sample, m.p. 239°, which was obtained by recrystallization from benzene/light petroleum (b.p.80-100°) (Found: C, 44.5; H, 0.2; N, 8.9. $C_{12}F_8N_2$ requires: C, 44.5; H, 0.0; N, 8.6%). The compound was distinguished from the isomeric octafluorobenzocinnoline by its nuclear magnetic resonance spectrum, an AA'XX' system (p.141) and by its ultra-violet spectrum (p.102a), which was almost identical with that of phenazine.

In a second experiment, pentafluoroaniline (0.145 g., 0.80 mmole), lead tetra-acetate (0.60 g., 13.2 mmole), and benzene (3.0 ml.) yielded the azo-compound (0.061 g., 42%) and the phenazine (0.017 g.; 13%), both identified by infra-red spectroscopy.

(c) From pentafluoroaniline and bleaching powder. Pentafluoroaniline (10.0 g., 55 mmole) and bleaching powder (50.0 g.) were heated under reflux in carbon tetrachloride (120 ml.) for 3 hr.; the mixture became deep red. The solids were filtered off and washed until colourless with ether, and the combined filtrates were evaporated to low bulk (10-20 ml.) and allowed to cool slowly. The resulting solid was filtered off, washed once with carbon tetrachloride (10 ml.) then twice with light petroleum (b.p. 30-40°; 20 ml.), and identified as decafluoroazobenzene (5.0 g.; 51%), m.p. 138°, by infra-red spectroscopy.

Exploratory Oxidations of Pentafluoroaniline. - (a) Test-tube experiments. Qualitative experiments on the oxidation of pentafluoroaniline with bromine, potassium permanganate, ceric sulphate,

iodine monochloride, chloramine-T, and other oxidants were performed. Those in which promising colour changes occurred were repeated on a larger scale and worked up chromatographically. The reactions were done at reflux temperature, for one hour, except where otherwise shown.

Pentafluoroaniline	Oxidant	Solvent	$(C_6F_5)_2N_2$ ¤
0.50 g., 2.7 mmole	$Pb(OAc)_4$(2.0 g)	CCl_4(25 ml.)	44%
0.50 mmole	$C_2H_4(CO)_2NBr$(2 mmole)	$CHCl_3$(10 ml.)(5 min.)	trace
5.0 mmole	Bz_2O_2(10 mmole)	Me_2CO(50 ml.)	trace
20.0 mmole	O_2bubbled/CuCl(0.25 g.)	C_5H_5N(4.0 ml.)(25°C.)	5%
20.0 mmole	MnO_2(200 mmole)	petrol (100 ml.)(7 hr.) (b.p.100-120°)	none

¤ Decafluoroazobenzene was identified by infra-red spectroscopy, or presumed to be present (trace amounts) because of its chromatographic behaviour.

Oxidation of Pentafluorophenylhydrazine with bleaching powder. - The hydrazine (0.37 g., 1.92 mmole) and bleaching powder (0.92 g.) were kept in ether (7.4 ml.) for one day. Evolution of gas occurred for 30 min., by which time the mixture was orange. The mixture was evaporated to dryness and extracted with light petroleum (b.p. 60-80°). Chromatography of the extract on alumina (column C), eluting with light petroleum, gave an orange semi-solid product (0.08 g.), shown by infra-red spectroscopy to contain decafluoroazobenzene.

4H,4H-Octafluoroazobenzene and 2H,7H-Hexafluorophenazine. - (a) From 4H-tetrafluoroaniline and lead tetra-acetate. The aniline (6.53 g., 40 mmole) and lead tetra-acetate (30.0 g., 66 mmole) were heated under reflux for 1 hr. in benzene (150 ml.). Chromatographic work-up (column A) as for decafluoroazobenzene preparation (b), gave the orange-red octafluoroazo-compound (2.7 g.; 42%), m.p. 119-120° (lit.,[98] 118°), unchanged on recrystallization from light petroleum (b.p. 60-80°) (Found: C, 44.4; H, 0.8; N, 8.8 Calc. for $C_{12}H_2F_8N_2$: C, 44.2; H, 0.6; N, 8.6%) and 2H,7H-hexafluorophenazine (1.32 g., 23%), m.p. 205°, as bright yellow plates with a strong blue-green fluorescence in solution. The infra-red spectrum was identical with that of a pure sample, m.p. 208°, obtained by recrystallization (recovery 67%) from benzene/light petroleum (b.p. 60-80°) (Found: C, 50.1; H, 0.9; N, 9.4; F, 39.3. $C_{12}H_2F_6N_2$ requires: C, 50.0; H, 0.7; N, 9.7; F, 39.6%); the compound was further characterized by its ultra-violet spectrum (p.131).

(b) From 4H-tetrafluoroaniline and bleaching powder. The aniline (0.50 g., 3.0 mmole) and bleaching powder (2.5 g.) were heated under reflux for 3 hr. in carbon tetrachloride (5 ml.). The solids were filtered off and washed with ether until colourless. The filtrates were evaporated to dryness and chromatographed (column C) as above, to give the azo-compound (0.085 g.; 17%) m.p. 113-6°, identified by infra-red spectroscopy. No phenazine was isolated.

4H-Nonafluoroazobenzene. - 4H-Tetrafluoroaniline (5.0 g., 30 mmole), pentafluoroaniline (1.0 g., 5.5 mmole), and lead tetra-acetate (23.0 g., 5.5 mmole) in benzene (150 ml.) were heated under reflux for 30 min. The usual chromatographic work-up gave a fraction which was probably a mixture of azo-compounds (1.94 g.), and a phenazine fraction (0.68 g.) which was discarded. The azo-fraction was re-chromatographed (column A); elution with carbon tetrachloride (20%) in light petroleum (b.p. 60-80°) gave (i) crude nonafluoroazobenzene (0.243 g.), identified by infra-red spectroscopy, and (ii) crude octafluoroazobenzene (1.287 g.), identified similarly. The former product, m.p. 102-6°, was recrystallized three times from light petroleum (b.p. 60-80°), yielding the orange 4H-nonafluoroazobenzene (0.053 g.) (Found: C, 42.5; H, 0.8. $C_{12}HF_9N_2$ requires: C, 41.9; H, 0.3%), m.p. 118.5-119°. The analysis was done on only 7 mg. of sample, and the result is within the experimental error for a sample of this size. This compound was characterized by its nuclear magnetic resonance spectrum (p.139) and by its infra-red spectrum (p.124), which was quite distinct from that of a mixture of deca- and octa-fluoroazobenzenes. The mass spectrum showed peaks at 362, 344, and 326 mass units [corresponding to $(C_6F_5)_2N_2$, $C_6F_5.N_2.C_6F_4H$, and $(HC_6F_4)_2N_2$, respectively] in intensity ratio 0.45 : 98.5: 1.05%; if it is assumed that these figures correspond closely with the composition of the sample, the nonafluoro-compound was 98.5% pure.

2H,2'H-Octafluoroazobenzene and 1H,6H-Hexafluorophenazine. - (a) From 2H-tetrafluoroaniline and lead tetra-acetate. The aniline (0.653 g., 4.0 mmole) and lead tetra-acetate (3.0 g., 6.6 mmole) in benzene (15 ml.) were heated under reflux for 1 hr. The usual chromatographic work-up (alumina, column C) gave, on elution with 50% benzene in light petroleum (b.p. 60-80°), 2H,2'H-octafluoroazobenzene (0.28 g.; 43%), m.p. 108-110°, with an infra-red spectrum identical with that of a recrystallized sample (Found: C, 43.9; H, 0.8; N, 8.9. $C_{12}H_2F_8N_2$ requires: C, 44.2; H, 0.6; N, 8.6%), obtained as orange needles, m.p. 111-2° (from light petroleum, b.p.60-80°). Continued elution with ether gave 1H,6H-hexafluorophenazine (0.10 g., 18%) (Found: C, 50.1; H, 0.9; N, 9.9. $C_{12}H_2F_6N_2$ requires: C, 50.0; H, 0.7; N, 9.7%), m.p. 186°, as pale yellow plates with a blue-green fluorescence in solution. This compound was unchanged on recrystallization from benzene/light petroleum; it was characterized as a phenazine by its ultra-violet spectrum (p.131).

(b) From 2H-tetrafluoroaniline and bleaching powder. The aniline (5.0 g., 30 mmole) and bleaching powder (12.5 g.), in carbon tetrachloride (60 ml.), were heated under reflux for 2.5 hr. The solids were filtered off and washed with ether until colourless, the combined filtrates were evaporated to 5-7 ml. and deposited an orange solid. This was filtered off and washed first with carbon tetrachloride and then with light petroleum (b.p. 30-40°), to give the azo-compound (2.55 g., 52%), m.p. 110°, identified by infra-red spectroscopy.

Attempted synthesis of 2H-Nonafluoroazobenzene. - Pentafluoroaniline (4.35 g., 24 mmole), 2H-tetrafluoroaniline (4.35 g., 26 mmole), and bleaching powder (24 g.) were heated under reflux in carbon tetrachloride (100 ml.) for 3 hr. The solids were removed as above, and the filtrates were taken to dryness and chromatographed on alumina (column A), eluting with light petroleum (b.p. 60-80°), to give an orange solid (5.5 g.), presumably a mixture of azo-compounds; this could not be resolved by further chromatography.

2-Bromotetrafluoroaniline. - Bromine (4 ml., 75 mmole) acetic acid (70 ml.), and 2H-tetrafluoroaniline (10.0 g., 60 mmole) were kept for 2 hr. at room temperature, diluted with water (200 ml.), and chilled. The precipitate was filtered off, washed with water (20 ml.), and dried in vacuo, giving presumed 2-bromotetrafluoroaniline (9.6 g.; 66%) as a cream solid, m.p. 50-1°(lit.,[10] 52°). This product was used without further purification.

2,2'-Dibromo-octafluoroazobenzene. -2-Bromotetrafluoroaniline (9.0 g., 35 mmole) and bleaching powder (40 g.) were heated under reflux for 6 hr. in carbon tetrachloride (100 ml.). The mixture was filtered hot, and the solids were washed with ether until colourless. The filtrate was evaporated to about 5 ml., diluted with light petroleum (b.p. 60-80°; 20 ml.) and evaporated again to 5 ml. On cooling, the solution deposited an orange solid (1.8 g.), which was chromatographed on alumina (column B), eluting with 50% benzene in light petroleum (b.p. 60-80°). One band (orange) developed; this gave 2,2-dibromo-octafluoroazobenzene (1.6 g.; 18%)

as an orange solid, m.p. 112-4°, with a satisfactory infra-red spectrum. This product was recrystallized (63% recovery) from benzene/light petroleum (b.p.60-80°) to give a pure sample (Found: C, 30.1; H, 0.2; N, 6.0. $C_{12}Br_2F_8N_2$ requires: C, 29.8; H, 0.0; N, 5.8%), m.p. 114.5-115°, characterized further by its ultra-violet spectrum (p.130).

Attempted preparation of cis-decafluoroazobenzene. - Pure decafluoroazobenzene (1.0 g., 2.8 mmole) was dissolved in a mixture of 20% benzene and light petroleum (b.p. 60-80°) (60 ml.), and irradiated for 1 hr.; it was then chromatographed on alumina (column A, packed to a depth of 15 cm.), eluting with the same solvent, such that most of the azo-compound was recovered with little increase in the volume of the solution. The product was irradiated and recycled through the column three times in all. After the final irradiation the column was eluted until the eluent was almost colourless. The total eluent (about 1000 ml.) was evaporated to dryness, and gave decafluoroazobenzene (0.65 g.; 65%), m.p. 138-140°, identified by infra-red spectroscopy. The column was then eluted with ether, and yielded an orange-yellow solid (20 mg.), which followed the solvent front down the column. This product was shown by infra-red and ultraviolet spectroscopy to be impure decafluoroazobenzene, m.p. 94-8°; a band at 3.5μ indicated a hydrocarbon impurity, and the presence of the cis-isomer is made highly improbable by the absence of absorption in the 13-14μ region. This impure product was sublimed in a test-tube over a bunsen burner; it then melted at 135°, and its infra-red spectrum showed it to be considerably

more pure.

Decafluoroazoxybenzene. - (a) From pentafluoroaniline. The procedure was essentially that of Wall and his co-workers. Pentafluoroaniline (5.0 g., 27.5 mmole) in glacial acetic acid (50 ml.) and aqueous 80% hydrogen peroxide (5.0 ml.) were kept for four days at room temperature. The brown solution was diluted with water (150 ml.), and the organic layer (ca. 3 ml.) was separated. The aqueous layer was extracted with carbon tetrachloride (3 x 10 ml.) and the combined organic layers were evaporated to dryness. The semi-solid product was distilled twice in vacuo at 50°, and the distillate was collected as a sublimate, shown by infra-red spectroscopy to be decafluoroazoxybenzene (1.18 g.; 23%). The m.p., 47-9°, showed the product to be somewhat impure: a convenient preparation of the pure compound is given below.

(b) From decafluoroazobenzene. The azo-compound (5.0 g., 13.8 mmole), aqueous 85% hydrogen peroxide (2.5 ml.), trifluoroacetic anhydride (25 ml.), and dichloromethane (100 ml., dried by distillation from phosphorus pentoxide) were heated under reflux for 4 hr., during which time further trifluoroacetic anhydride (20 ml.) and hydrogen peroxide (8 ml.) were added in small portions. The mixture was protected from moisture by a calcium chloride tube during the reflux. The resulting yellow solution was diluted with water (100 ml.), and the organic layer was separated, washed with water, and dried ($MgSO_4$); on evaporation it yielded decafluoroazoxybenzene (4.9 g.; 94%) as a cream solid, m.p. 54°. The infra-red spectrum was

satisfactory. Recrystallization from light petroleum (b.p. 30-40°) gave a white solid (Found: C, 38.1; H, 0.1. Calc. for $C_{12}F_{10}N_2O$: C, 38.1; H, 0.0%), m.p. 54-5°, (Lit.,[19] 53-4°).

(c) Attempted condensation of pentafluoronitrobenzene with pentafluoroaniline. The nitro-compound (0.426 g., 2.0 mmole) and the aniline (0.366 g., 2.0 mmole) were kept in glacial acetic acid (10 ml.) for 4 days. The mixture was heated under reflux for 5 min., cooled, and poured into water (20 ml.), and a small quantity of pale brown oil was deposited. The mother liquor was decanted, and saturated aqueous sodium bicarbonate (10 ml.) was added to the residual oil, and the mixture was extracted with ether (10 ml.). The extract was dried ($MgSO_4$) and evaporated to give a pale brown oil which was shown to be pentafluoronitrobenzene (0.221 g.; 52%) by infra-red spectroscopy.

4H,4'H-Octafluoroazoxybenzene. - (a) With a high hydrogen peroxide/trifluoroacetic anhydride ratio. (cf. Burdon et al.[98]). 4H,4'H-Octafluoroazoxybenzene (3.16 g., 9.7 mmole), aqueous 85% hydrogen peroxide (15 ml.), trifluoroacetic anhydride (36 ml.), and dichloromethane (30 ml.) were heated under reflux. The mixture, initially red, was yellow after 2 hr. but red again after 24 hr., at which time more hydrogen peroxide solution (5 ml.) and trifluoroacetic anhydride (15 ml.) were added; and after a further 24 hr. more peroxide (3 ml.) and anhydride (10 ml.) were added, turning the mixture yellow once again. The product was added to water (100 ml.), separated, and extracted with dichloromethane

(3 x 30 ml.); the extracts were washed with water (2 x 5 ml.), dried ($MgSO_4$), filtered, and evaporated, to give a semi-solid yellow oil. This substance was chromatographed on alumina (column B) to give, on elution with light petroleum (b.p. 60-80°), a fairly pure sample of 4H,4'H-octafluoroazoxybenzene (1.46 g.; 44%), m.p. 48-50°, identified by infra-red spectroscopy. The pure compound m.p. 55-55.5° (lit.,[98] 52°), was obtained as white needles on recrystallization from methanol (Found: C, 42.2; H, 0.6; N, 8.2. Calc. for $C_{12}H_2F_8N_2O$: C, 42.1; H, 0.6; N, 8.2%. The ultraviolet spectrum of this compound (p.101a) resembled closely that of decafluoroazoxybenzene.

Continued elution of the column with ethanol gave a pale brown glassy substance (0.13 g.), which could not be recrystallized.

(b) Improved procedure using a low peroxide/anhydride ratio. 4H,4'H-Octafluoroazobenzene (0.158 g., 0.485 mmole), aqueous 85% hydrogen peroxide (0.52 ml.), trifluoroacetic anhydride (1.58 ml.), and dichloromethane (1.58 ml.) were heated under reflux for 1 hr. The mixture had become yellow after 40 min. The yellow solution was washed with water (5.2 ml.), the washings were extracted with dichloromethane (2 x 1 ml.), and the combined organic layer was washed with water (2 ml.) and dried ($MgSO_4$). Filtration and evaporation of the solvent yielded the azoxy-compound (0.162 g.; 98%) as a pale brown solid, m.p. 53-5°, identified by infra-red spectroscopy.

2H,2'H-Octafluoroazoxybenzene. - 2H,2'H-Octafluoroazobenzene (1.5 g., 4.4 mmole), dichloromethane (15 ml.), trifluoroacetic anhydride (15 ml.), and aqueous 85% hydrogen peroxide (5 ml.) were

heated under reflux for 1 hr.; the reaction mixture turned yellow. The mixture was washed with water (50 ml.) and the washings were extracted with dichloromethane (2 x 5 ml.). The organic layer was washed again with water (20 ml.), dried ($MgSO_4$), and evaporated, to give 2H,2'H-octafluoroazoxybenzene (1.59 g; 100%), m.p. 59-62°, identified by infra-red spectroscopy. Recrystallization from aqueous methanol gave the pure compound (Found: C, 42.2; H, 0.8; N, 8.4 $C_{12}H_2F_8N_2O$ requires: C, 42.1; H, 0.6; N, 8.2%) as pale orange-brown needles, m.p. 62-3°. Repeated treatment with charcoal and recrystallization would not decolourize this compound; however, a simple and satisfactory explanation for its colour is given in the discussion section (p.120).

Oxidation of Octafluorophenazine. - The phenazine (0.50 g., 1.54 mmole), trifluoroacetic anhydride (15 ml.) and aqueous 85% hydrogen peroxide (1.0 ml.) were heated under reflux for 10 min.; further peroxide (1.0 ml.) was added and heating was continued for 20 min. longer. The mixture was diluted with water (50 ml.), neutralized to pH 6 with solid sodium bicarbonate, and extracted with ether (50 + 2 x 25 ml.). The ethereal solution was dried ($MgSO_4$) and the solvent was removed; the resulting brown gum (0.30 g.) was stirred with a few ml. of light petroleum (b.p. 60-80°), which caused it to solidify. The solvent was evaporated, but the residual product could not be recrystallized.

The reaction was repeated with refluxing for only 1 min., and gave quantitative recovery of the starting compound. An identical

reaction mixture, on refluxing for 5 min., gave a yellow gum (0.40 g.), whose infra-red spectrum suggested that some starting material was present.

Oxidation of 2H,7H-hexafluorophenazine. - The phenazine (1.0 g., 3.6 mmole), dichloromethane (50 ml.), trifluoroacetic anhydride (15 ml.), and aqueous 85% hydrogen peroxide (3 ml.) were heated under reflux for 18 hr. Dichloromethane and water (50 ml. each) were added, and the layers were separated. The aqueous layer was extracted with ether (3 x 50 ml.), and the combined organic layer was washed with water (3 x 10 ml.), dried ($MgSO_4$) and evaporated to dryness, yielding a pale brown gum (1.27 g.). This product was chromatographed on alumina (column B); a yellow band appeared on elution with ether. This band gave starting material (0.13 g.; 13%) identified by its infra-red spectrum. Elution with ethanol gave no more substances, and the column was eluted with glacial acetic acid; a brown band followed the solvent front down the column, and gave a brown solid (4 g.) presumably containing aluminium salts. This product yielded no tractable fractions on subsequent chromatography on silica.

Decafluorohydrazobenzene. - (a) From decafluoroazoxybenzene. This procedure is that of Wall et al.,[19] who wrongly characterized the product as the azo-compound. Decafluoroazoxybenzene (1.18 g., 3.13 mmole), ammonium chloride (1.18 g.), zinc dust (3.7 g.), water (2.35 ml.), and ethanol (18 ml.) were heated under reflux for 30 min. The mixture was filtered hot, and the residue was

washed with a little hot ethanol. The combined filtrates were diluted with water (50 ml.) and cooled. The resulting precipitate was filtered off, dried in vacuo over phosphorus pentoxide, and sublimed in vacuo at 50-55° to give colourless crystals of decafluorohydrazobenzene (Found: C, 39.45; H, 0.6. $C_{12}H_2F_{10}N_2$ requires: C, 39.6; H, 0.55%), m.p. 62-3 (lit.,[98] 57°). This compound showed a sharp singlet (N-H) at 2.93μ in its infra-red spectrum, and was further characterized by its ultra-violet spectrum (p.100a).

(b) From decafluoroazobenzene with zinc and ammonium chloride. The azo-compound (2.0 g., 5.5 mmole), ammonium chloride (2.0 g.), zinc dust (6.0 g.), water (5 ml.), and ethanol (50 ml.) were shaken in a stoppered flask. The red compound dissolved, but the resulting solution was colourless. The mixture was filtered and the filtrate was poured into water (ca. 100 ml.) and cooled; it gave decafluorohydrazobenzene (1.6 g.; 80%) as a white solid, m.p. 61-3°, with an infra-red spectrum identical with that of the above sample.

(c) From decafluoroazobenzene with sodium hydrosulphite. The azo-compound (2.0 g., 5.5 mmole), in methanol (50 ml.), was heated under reflux, and sodium hydrosulphite (4.6 g., purity 85%) in water (25 ml.) was added during 5 min. The mixture became colourless after 10 ml. of solution had been added. The product was diluted with water (50 ml.) and distilled; 100 ml. of distillate were collected, and dilution of this distillate with water (150 ml.)

caused a white precipitate to appear, which was identified as decafluorohydrazobenzene (1.66 g.), m.p. 58-60°, by infra-red spectroscopy. Ether-extraction of the filtrate gave more product (0.04 g.), the total yield (1.7 g.) being 85%. The odour of pentafluoroaniline was completely absent.

(d) From decafluoroazobenzene with tin and hydrochloric acid. The azo-compound (1.0 g., 2.75 mmole), granulated tin (5.0 g.), concentrated hydrochloric acid (10 ml.) and dimethylformamide (20 ml.) were heated under reflux for 30 min. The mixture was made alkaline and extracted with ether (2 x 50 ml.), and the extracts were washed with water to remove dimethylformamide, dried (CaO), and on evaporation yielded a pale orange solid (0.60 g.), m.p. 40-50°, shown by infra-red spectroscopy to be impure decafluorohydrazobenzene.

Unsuccessful reductions of decafluoroazobenzene. - (a) With triethanolamine. Decafluoroazobenzene (1.0 g., 2.75 mmole) and triethanolamine (6.0 g.) were heated for 2 hr. at 95°, then poured into water (150 ml.) and extracted with chloroform (50 ml.). The extract was evaporated to give an intractable tar with a strong odour of pentafluoroaniline.

(b) With zinc and alkali. The azo-compound (2.0 g., 5.5 mmole), zinc dust (0.38 g.), sodium hydroxide (0.45 g.), and methanol (60 ml.) were heated under reflux for 2.5 hr. Pure azo-compound was recovered quantitatively.

Reductive cleavage of decafluoroazobenzene with hydriodic acid. - The azo-compound (2.0 g., 5.5 mmole) and aqueous 55% hydriodic acid (15 ml.) were heated under reflux for 3 hr. Solid sodium metabisulphite was added to remove iodine and the solution was diluted with water (100 ml.) and distilled. Pentafluoroaniline (1.15 g.; 57%), m.p. 29-31° (lit.,[18] 33.5-35°), was filtered from the distillate and identified by infra-red spectroscopy.

Reductive cleavage of decafluoroazoxybenzene. - The azoxy-compound (1.0 g., 2.65 mmole) and aqueous 55% hydriodic acid (10 ml.) were heated under reflux for 6.5 hr., then diluted with water (30 ml.), decolourized with solid sodium metabisulphite, and neutralized with solid sodium carbonate. The solution was steam-distilled to give pentafluoroaniline (0.32 g.; 33%), m.p. and mixed m.p. 32-3°, which was filtered off from the first 10 ml. of distillate and dried over phosphorus pentoxide.

In an earlier experiment, the starting material was recovered in 74% yield after 2.5 hr. in half the above quantity of refluxing hydriodic acid.

Reductive cleavage of decafluorohydrazobenzene. - Deca-fluorohydrazobenzene (2.0 g., 5.5 mmole) and aqueous 55% hydriodic acid (10 ml.) were heated under reflux for 3 hr., and worked up as for the above reaction to give pentafluoroaniline (1.28 g.; 63%), m.p. 33°, identified by infra-red spectroscopy.

Octafluoro-5,10-dihydrophenazine. - Octafluorophenazine (10.0 mg., 0.031 mmole) in spectroscopically pure hexane (25.0 ml.)

was shaken with aqueous 55% hydriodic acid (5 ml.) for 30 min. The mixture was then decolourized with solid sodium metabisulphite, and the organic layer was separated and dried ($MgSO_4$). An ultra-violet spectrum (p.102a) was run on this solution; unfortunately neither the spectrum of 5,10-dihydrophenazine nor that of any closely related compound has been reported in the literature, but the observed spectrum was in reasonable agreement with a theoretically predicted spectrum. Evaporation of the solvent left a white solid (10 m.g.; 99%), m.p. 189°, the presumed dihydrophenazine. The infra-red spectrum of this product showed a sharp N-H singlet at 2.88μ. The substance was too sensitive towards autoxidation for further work to be convenient; in air it quickly became green, then violet (presumably phenazhydrin-type molecular complexes).

The crude dihydrophenazine (0.50 g.) was dissolved in ether (50 ml.) and air was bubbled through the solution for 10 min.; ether was added as necessary to maintain the volume of the solution. A greenish colour appeared in the solution and gradually gave way to yellow. The product was dried ($MgSO_4$) and filtered, and the filtrate was evaporated, yielding octafluorophenazine (0.47 g., 97%), m.p. 232°, identified by infra-red spectroscopy.

<u>2H,7H-Hexafluoro-5,10-dihydrophenazine</u>. - 2H,7H-Hexafluorophenazine (0.50 g., 1.74 mmole) was shaken in toluene (10 ml.) for 30 min. with aqueous 55% hydriodic acid (10 ml.). Potassium iodide was added to break up the resulting emulsion, and the mixture was decolourized with solid sodium metabisulphite and extracted with

ether (ca. 50 ml.). The extract was dried ($MgSO_4$) and yielded on evaporation a green solid (0.515 g.). Recrystallization of this product from ethanol, and again from light petroleum (b.p. 80-100°), gave green needles (0.170 g.), m.p. 224-6°, shown by nuclear magnetic resonance spectroscopy (p.104) to consist of presumed 2H,7H-hexafluoro-5,10-dihydrophenazine (90%) and starting material (10%) (Found: C, 49.8; H, 1.2; N, 9.5. $C_{12}H_4F_6N_2$ requires: C, 49.6; H, 1.4; N, 9.7%), showing an N-H singlet at 2.89μ in the infra-red spectrum.

Attempted preparation of a complex between Decafluoroazobenzene and Boron Trifluoride. - The azo-compound (1.00 g., 2.7 mmole) was dissolved in a solution of an excess of boron trifluoride in dichloromethane (20 ml. of 0.92M solution; 18.4 mmole BF_3). The solution was stirred at room temperature for 1 min. (no colour change occurred) and evaporated to dryness in vacuo. Starting material (1.00 g.), m.p. 138°, was obtained and was identified by infra-red spectroscopy.

4,4'-Diethoxyoctafluoroazobenzene. - A solution of sodium ethoxide (15.2 mmole) prepared from sodium (0.35 g.) and ethanol (70 ml.) was added dropwise during 30 min. to decafluoroazobenzene (2.5 g., 6.9 mmole) in refluxing ethanol (100 ml.). The reaction was stopped after a further $2\frac{1}{2}$ hr. reflux by the addition of water (250 ml.). Ether extraction (100 + 50 ml.) yielded 2.8 g. of crude product, m.p. ca.107°, which on recrystallization from cyclohexane gave orange 4,4'-diethoxyoctafluoroazobenzene (1.68 g.; 59%), m.p. 110-112°, identified by infra-red spectroscopy. The melting point was raised

to 113.5-114.5° by further recrystallization (Found: C, 46.5; H, 1.3. $C_{16}H_{10}F_8N_2O_2$ requires: C, 46.5; H, 1.1%), m.p. 113.5-114.5°.

4-Ethoxynonafluoroazobenzene. - Decafluoroazobenzene (2.0 g., 5.5 mmole) was heated under reflux for 2 hr. in ethanol (40 ml.). During the first hour a solution of potassium ethoxide (5.5 mmole) [from potassium (0.22 g.) and ethanol (22 ml.)] was added dropwise. The mixture was poured into water (400 ml.) and extracted with ether (3 x 50 ml.). The extracts were dried ($MgSO_4$) and yielded an orange solid (2.2 g.), m.p. 70-80°, which was chromatographed on alumina (column B), eluting with 25% benzene in light petroleum (b.p. 60-80°). Three bands developed, yielding respectively (i) decafluoroazobenzene (0.26 g.), identified by infra-red spectroscopy, (ii) an orange solid (1.20 g.), m.p. 74-6°, shown by infra-red spectroscopy to be 4-ethoxynonafluoroazobenzene containing some decafluoroazobenzene and diethoxyoctafluoroazobenzene, and (iii) (elution with ether) crude diethoxyoctafluoroazobenzene (0.51 g.), m.p. 101-3°, identified by infra-red spectroscopy. The product from band (ii) was twice recrystallized from cyclohexane to give orange 4-ethoxynonafluoroazobenzene (Found: C, 43.1; H, 1.6; N, 7.6. $C_{14}H_5F_9N_2O$ requires: C, 43.3; H, 1.3; N, 7.2%), m.p. 82-82.5°.

Reaction of 4-ethoxynonafluoroazobenzene with ethoxide ion. - The monoethoxy-compound (0.50 g., 1.25 mmole) was heated under reflux in ethanol (20 ml.). Potassium ethoxide (1.37 mmole; an excess of 10%) in ethanol (11 ml.) was added dropwise during 30 min., and heating was continued for another 30 min. The mixture

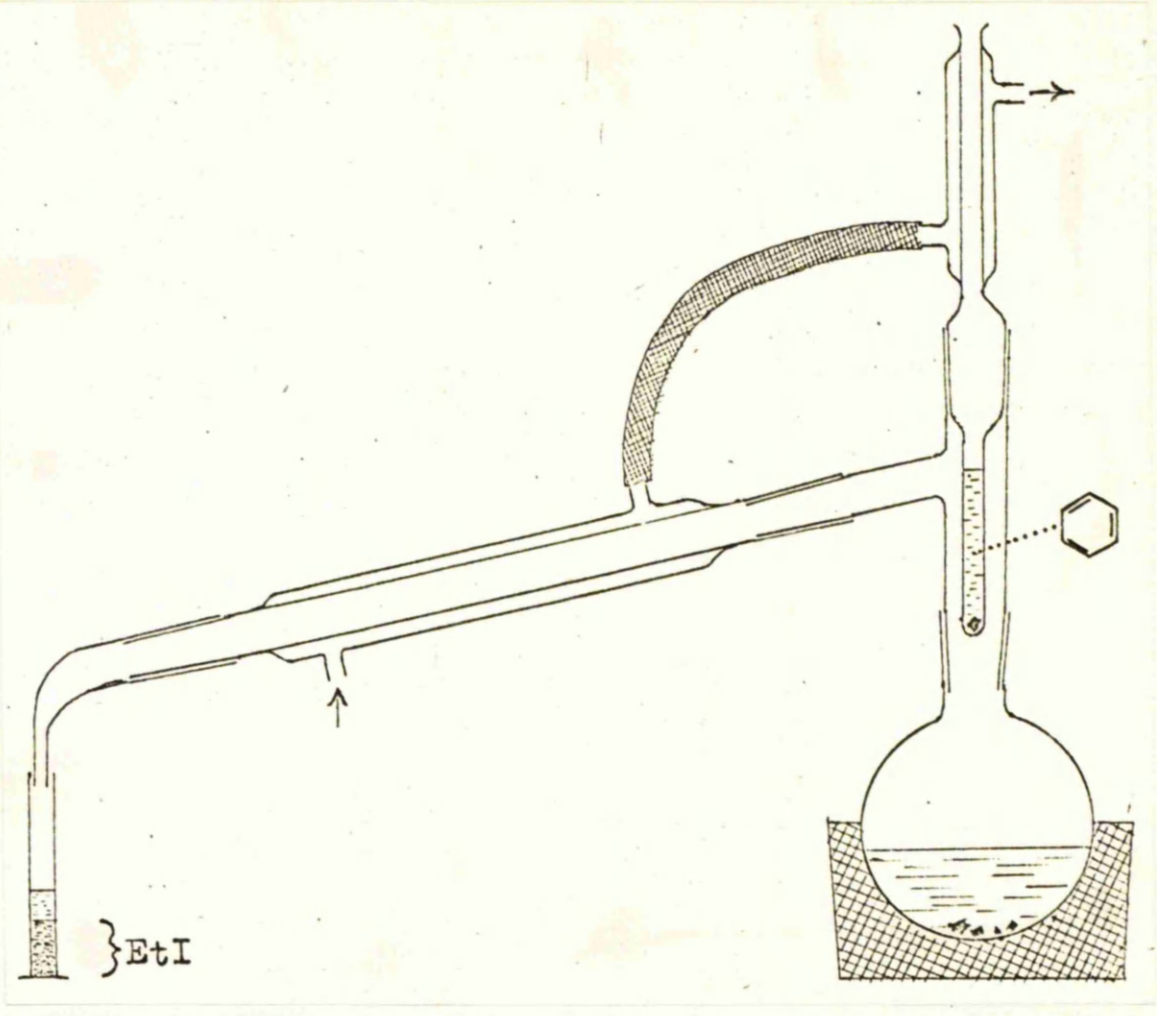
was poured into water (100 ml.) and extracted with ether. The extracts were dried ($MgSO_4$) and evaporated to give 4,4'-diethoxy-octafluoroazobenzene (0.55 g.; quantitative), m.p. 98-100°, mixed m.p. with a pure sample, 98-104°, identified also by its infra-red spectrum.

This reaction, the nuclear magnetic resonance spectra (p.139), and the reductive cleavage (below) to 4-aminotetrafluorophenol, prove the structures of these two ethoxy-compounds.

Reductive Cleavage of 4,4'-diethoxyoctafluoroazobenzene. - The azo-compound (2.0 g., 4.8 mmole) and aqueous 55% hydriodic acid (10 ml.) were heated under reflux for 1 hr. in a distillation apparatus fitted with a partial condenser containing refluxing benzene (see diagram overleaf).

A few ml. of distillate was collected; this separated into two layers. The upper layer (aqueous) was discarded, and the lower layer (0.74 ml.), which contained some iodine, was decolourized with a little solid sodium metabisulphite, dried ($MgSO_4$) and identified as iodoethane (1.43 g., calc. from volume of crude product, 9.2 mmole; 95%) by infra-red spectroscopy.

The residue in the reaction flask was diluted with water to 100 ml., decolourized with solid sodium metabisulphite, and neutralized carefully with solid sodium carbonate. Ether extraction (5 x 20 ml. + 10 z 10 ml.) yielded 4-aminotetrafluorophenol, (1.72 g., 9.5 mmole); 98%) as a white solid, m.p. 177-8° (decomp.), identified by infra-red spectroscopy. Two recrystallizations



The vertical socket in the still head contained a cold finger, the top of which was fitted with a reflux condenser. The side arm of the still head was connected to another condenser which led to a small graduated receiver. The cold finger contained benzene which was maintained under reflux at 80° by the boiling reaction mixture. This device enabled a small quantity of volatile distillate to be removed from the reaction mixture during the course of the reflux.

from 1,2-dichloroethane were carried out rapidly (discolouration occurred if the product was kept in contact with the hot solution) and yielded a pure sample (Found: C, 40.0; H, 2.0; N, 7.9. $C_6H_3F_4NO$ requires: C, 39.8; H, 1.7; N, 7.7%), m.p. 180-1° (decomp.) (lit., [134] 177.5-178°).

Oxidation of 4-aminotetrafluorophenol to fluoranil. - The amino-phenol (1.2 g., 6.6 mmole) was heated on a steam bath with nitric acid (10 ml.; 4.7M) in a flask fitted with a reflux condenser. The solution (initially purple) turned yellow suddenly after a few minutes, and the quinone sublimed into the condenser. After a total of 10 min. heating, the reaction mixture was cooled and extracted with ether (20 + 6 x 5 ml.), and the combined extracts were washed with water (5 x 5 ml.). The washings plus residual solution were partially neutralized (to pH 3) with solid sodium carbonate and further extracted with ether (10 + 5 x 5 ml.). The combined ethereal layer (ca. 80 ml.) was dried ($MgSO_4$) and evaporated in vacuo at room temperature to give fluoranil (1.0 g., 5.8 mmole; 87%), m.p. (sealed tube) 163-6° (lit.[80] 179°), identified by infra-red spectroscopy, its colour, and its characteristic odour.

Attempted de-ethylation of diethoxyoctafluoroazobenzene.- 4,4'-Diethoxyoctafluoroazobenzene (1.5 g., 3.6 mmole) was heated under reflux for 3 hr. with bromine-free aqueous 30% hydrobromic acid (15 ml.). Starting material identified by infra-red spectroscopy was recovered quantitatively.

Reaction of Decafluoroazobenzene with Methoxide. - Sodium methoxide (17.4 mmole) prepared from sodium (0.40 g.) and methanol (80 ml.) was added dropwise during 1 hr. to decafluoroazobenzene (4.0 g., 11 mmole) in refluxing methanol (100 ml.). Heating was continued a further 18 hr., and the mixture was poured into water (180 ml.) and extracted with ether (200 + 100 + 2 x 25 ml.).

The ethereal extract was dried ($MgSO_4$) and evaporated to give an orange solid (4.07 g.), m.p. 118-135°, which was chromatographed on alumina (column A) and eluted with hot light petroleum (b.p. 60-80°) to give two orange solids, m.p. 89.5-92° (1.3 g.) and m.p. 160-2° (2.5 g.). The former, on two recrystallizations from light petroleum (b.p.60-80°), gave the red 4-methoxynonafluoroazobenzene (Found: C, 42.0; H, 0.9; N, 7.6. $C_{13}H_3F_9N_2O$ requires C, 41.7; H, 0.8; N, 7.5%), m.p. 98° (lit.,[98] 94-6°). The other fraction was recrystallized twice from light petroleum (b.p. 100-120°), and gave 4,4'-dimethoxyoctafluoroazobenzene (Found: C, 43.7; H, 1.7; N, 7.2 $C_{14}H_6F_8N_2O_2$ requires C, 43.5; H, 1.6; N, 7.3%), as brick red needles, m.p. 164° (lit.,[98] 164-5°).

Reaction of 4-methoxynonafluoroazobenzene with methoxide ion. The azo-compound (0.20 g., 0.53 mmole) was heated under reflux for 20 hr. in methanol (12.5 ml.). During the first hour, sodium methoxide (0.54 mmole) prepared from sodium (12.5 mg.) in methanol (12.5 ml.) was added dropwise. The reaction mixture was poured into water (150 ml.) and extracted with ether (25 + 10 ml.). The extracts were washed with water (100 ml.), dried ($MgSO_4$), and evaporated to give an orange product (0.21 g.), m.p. 140-150°, shown by infra-red spectroscopy to be 4,4'-dimethoxyoctafluoroazobenzene together with some starting material. One recrystallization from light petroleum (b.p. 100-120°) raised the m.p. to 154-60°, and this product, though probably still containing some starting material, gave a satisfactory infra-red spectrum.

Reductive cleavage of 4,4'-dimethoxyoctafluoroazobenzene. - The azo-compound (0.30 g., 0.78 mmole) was heated under reflux for 1 hr. with aqueous 55% hydriodic acid (10 ml.). Oily droplets (almost certainly iodomethane) were observed refluxing; but no attempt was made to isolate this product. The mixture was decolourized with saturated aqueous sodium metabisulphite, then neutralized with saturated aqueous sodium carbonate. The solution (now ca. 70 ml.) was extracted with ether (15 + 4 x 10 ml.), and the extracts were dried ($MgSO_4$) and evaporated to give 4-aminotetrafluorophenol (0.29 g.; quantitative), m.p. 175-7° (decomp.), shown by infra-red spectroscopy to be identical with the sample prepared earlier (p.164).

4-Aminononafluoroazobenzene (perfluoro-aniline yellow). - Decafluoroazobenzene (2.0 g., 5.5 mmole), ethanol (75 ml.), and aqueous ammonia (m.g. 0.88; 10 ml.) were heated under reflux for 3 hr. The mixture was poured into saturated aqueous ammonium chloride (250 ml.) and extracted with ether (50 + 2 x 25 ml.). The extracts were washed with water, dried ($MgSO_4$), and evaporated, to leave an orange product (2.0 g.); this was chromatographed on alumina (column B) with elution by ether to give crude decafluoroazobenzene (0.66 g.; 33% recovery), m.p. 139-40°, identified by infra-red spectroscopy, and crude 4-aminononafluoroazobenzene (1.34 g.; 67%; 99% based on unrecovered starting material), m.p. ca. 133° , identified by infra-red spectroscopy. Three recrystallizations of the latter from cyclohexane gave a pure product (0.91 g.; 68% based on starting material consumed) (Found C, 40.5; H, 0.8; N, 11.7. $C_{12}H_2F_9N_2$ requires:

C, 40.2; H, 0.6; N, 11.7%), m.p. 139.5°. An N-H doublet was observed in the infra-red spectrum at 2.84μ and 2.94μ, and the product was further characterized by reductive cleavage (p.100b) and nuclear magnetic resonance spectroscopy (p.139).

In a second experiment, the crude product was shown by nuclear magnetic resonance spectroscopy to contain 4-aminononafluoroazobenzene (68%), decafluoroazobenzene (24%), and other fluorine-containing substances (8%). Chromatography of this product on a longer column gave a crimson product (7%), m.p. ca. 100-110°, just preceding the decafluoroazobenzene fraction, but this substance could not be satisfactorily recrystallized. From its colour (very similar to that of 2-amino-4H,4'H-heptafluoroazobenzene, p.60), chromatographic behaviour, and position of N-H absorptions in the infra-red spectrum, again very similar to those of the 2-aminoheptafluoro-compound, this product may be tentatively identified as 2-aminononafluoroazobenzene, probably containing some decafluoroazobenzene. There was insufficient sample for nuclear magnetic resonance spectroscopy.

Traces of two more polar products were also obtained.

Reductive cleavage of 4-aminononafluoroazobenzene. - The amino-azo-compound (1.0 g., 2.8 mmole) was heated under reflux with aqueous 55% hydriodic acid (10 ml.) for 2 hr. Iodine was removed with solid sodium metabisulphite, and the acidity was adjusted to pH5 with sodium carbonate. The mixture was diluted to 40 ml. and extracted with ether (10 + 5 x 5 ml.). The ethereal solution was dried ($MgSO_4$) and the solvent was removed by distillation through a

15 cm. column packed with glass helices, leaving an almost colourless gummy residue (1.14 g.), shown by infra-red spectroscopy to be a mixture of pentafluoroaniline and tetrafluoro-p-phenylenediamine. This mixture was recrystallized from cyclohexane (25 ml.), to give tetrafluoro-p-phenylenediamine (0.32 g.; 63%) as colourless needles, m.p. and mixed [x] m.p. 137° (lit.,[23] 143.5-144°) identified also by infra-red spectroscopy. The mother liquor was distilled through a fractionating column (as used above) to give a residue of pentafluoroaniline (0.36 g.; 71%), m.p. 34-6° (lit.[18] 33.5-35°) shown by infra-red spectroscopy to contain a little of the above diamine.

Oxidation of tetrafluoro-p-phenylenediamine to fluoranil. - The diamine (50 mg., 0.28 mmole) and 4.7M nitric acid (1.0 ml.) were boiled for one minute, cooled, and diluted with water to 20 ml. The solution was extracted with ether (10 + 5 ml.); the extracts were dried ($MgSO_4$) and evaporated to give fluoranil (29.5 mg.; 59%), m.p. 172-5°, shown by infra-red spectroscopy to be identical with the sample prepared from 4-aminotetrafluorophenol (p. 51).

2-Amino-4H,4H-heptafluoroazobenzene. - 4H,4H-Octafluoroazobenzene (4.0 g., 12.3 mmole), ethanol (80 ml.), and aqueous ammonia (s.g. 0.88; 25 ml.) were heated under reflux for 21 hr., and the resulting mixture was poured into water and extracted with ether; the extracts yielded a deep red solid, which was chromatographed on alumina (column A).

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[x] With an authentic sample kindly supplied by E.S.Wilks.

Elution with 50% benzene in light petroleum caused two bands to develop, yielding respectively starting material (0.10 g.; 3%) and 2-amino-4H,4'H-heptafluoroazobenzene (3.1 g.; 78%), m.p. 163-5°. Both products were identified by infra-red spectroscopy; the latter was purified by recrystallization from 200 ml. of light petroleum (b.p. 80-100°) to give pure 2-amino-4H,4'H-heptafluoroazobenzene (2.4 g; 78% recovery) (Found: C, 44.8; H, 1.4; N, 13.1. $C_{12}H_4F_2N_3$ requires: C, 44.6; H, 1.2; N, 13.0%), as scarlet crystals, m.p.168-9°. This compound was characterized by reductive cleavage (below) and by its nuclear magnetic resonance spectrum (p.139).

Reductive cleavage of 2-Amino-4H,4'H-heptafluoroazobenzene. - The azo-compound (0.40 g., 1.24 mmole) and aqueous 55% hydriodic acid (5.0 ml.) were heated under reflux for 30 min. The mixture was decolourized with solid sodium metabisulphite and neutralized with solid sodium carbonate, and the resulting solution was extracted with ether (25 + 2 x 10 ml.). The extracts were dried ($MgSO_4$) and on evaporation yielded a nearly colourless solid (0.36 g.) with an odour of 4H-tetrafluoroaniline. This product was dissolved in hot light petroleum (b.p. 30-40°; 10 ml.), and on cooling to room temperature the solution deposited 3,4,6-trifluoro-o-phenylenediamine (0.099 g.; 48%), m.p. 70-2° (lit.[148], 75°), which was characterized by the preparation of the benzil derivative, 2,3-diphenyl-5,6,8-trifluoroquinoxaline, by the method of Bost and Towell;[149] this compound (Found: C, 71.4; H, 3.4. Calc. for $C_{20}H_{11}F_3N_4$: C, 71.4; H, 3.3%) was obtained as colourless needles m.p. 167-8° (from ethanol)

(lit.,[148] m.p. 169.5-170°).

4-Hydroxynonafluoroazobenzene. - Potassium hydroxide (0.41 g., 7.3 mmole) was dissolved in hot t-butanol (35 ml.) and added to a hot solution of decafluoroazobenzene (2.0 g., 5.5 mmole) in the same solvent (25 ml.) The mixture was heated under reflux for 30 min. and then poured into water (200 ml.), and the alcohol was distilled off. The residue was acidified to pH 3 with conc. hydrochloric acid, then extracted with ether (2 x 50 + 25 ml.). The extracts were washed with water (2 x 20 ml.), dried ($MgSO_4$), and evaporated. The resulting purple solid was chromatographed (column A) on silica (B.D.H. reagent grade precipitated silica; neither alumina nor chromatographic silica gave a good separation). Elution with benzene gave (i) decafluoroazobenzene (1.0 g.; 50% recovery), m.p. 131-8°, identified by infra-red spectroscopy, (ii) a brown-purple solid (0.08 g.; 40%, or 80% based on decafluoroazobenzene consumed), m.p. 156-9°, shown by infra-red spectroscopy to be 4-hydroxynonafluoroazobenzene, and (iii) a dark-brown solid (0.08 g.), m.p. 208-210°, which could not be purified and was discarded. Product (ii) was crystallized from a large volume of water to give pure 4-hydroxynonafluoroazobenzene (Found: C, 40.2; H, 0.4; F, 48.0. $C_{12}HF_9N_2O$ requires: C, 40.0; H, 0.3; F, 47.5%) as a pale yellow powder, m.p. 164°. The infra-red spectrum (p.126) confirmed the presence of an O-H group, which absorbed at 2.92μ. The colour of this compound was due to its state of fine subdivision; solutions were red, and its ultra-violet

and visible spectrum is given on p.134. The position of the hydroxyl group was confirmed by nuclear magnetic resonance spectroscopy (p.139) and by reductive cleavage (below).

Reductive cleavage of 4-hydroxynonafluoroazobenzene. The hydroxy-azo-compound (0.60 g., 1.67 mmole) was heated under reflux with aqueous 55% hydriodic acid (6.0 ml.) for 1 hr. The mixture was diluted with water (50 ml.), decolourized with solid sodium metabisulphite, and neutralized with solid sodium carbonate. The solution was extracted with ether (5 x 10 ml.) and the extracts were dried ($MgSO_4$). Removal of the ether *in vacuo* yielded a cream solid (0.54 g.) with a strong odour of pentafluoroaniline. The infra-red spectrum showed that this product was a mixture of 4-aminotetrafluorophenol and pentafluoroaniline; it was recrystallized from trichloroethylene (20 ml.), to give the aminophenol (0.24 g.; 80%), m.p. 177-8° (decomp.) (lit.,[134] 177.5-178°) shown by infra-red spectroscopy to be identical with the sample prepared earlier (p.164). The filtrate was extracted with concentrated hydrochloric acid (3 x 3 ml.), and the extract was made alkaline with aqueous potassium hydroxide; the volume of the solution was now *ca.* 30 ml. This aqueous phase was extracted with ether (5 + 3 x 3 ml.), and the extracts were washed with saturated aqueous potassium chloride (3 x 3 ml.), dried ($MgSO_4$), and evaporated *in vacuo*, to give pentafluoroaniline (0.14 g.; 47%), m.p. 30-31.5°, mixed m.p. with an authentic sample[*] 32° (lit.[18] 33.5-35°), identified also by infra-red

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* Imperial Smelting Corporation.

spectroscopy.

Reaction of decafluoroazobenzene with thiophenoxide ion. - (a) With two equivalents of thiophenoxide. Thiophenoxide ion (17 mmole) was obtained by the addition of sodium (0.40 g.) to a solution of thiophenol (1.97 g.) in methanol (40 ml.). The resulting solution was added dropwise during 30 min. to decafluoroazobenzene (3.07 g., 8.7 mmole) in refluxing methanol (100 ml.). Heating was continued for a further 2.5 min. and the mixture was poured into water (150 ml.) and filtered. The precipitate was washed with water and dried in vacuo, to give 4,4'-dithiophenoxyoctafluoroazobenzene (4.73 g.; quantitative), m.p. 202-6°, identified by infra-red spectroscopy. One crystallization from a large volume of light petroleum (b.p. 100-120°) gave the pure compound (3.75 g.; 81%) as orange-brown needles (Found: C, 53.1; H, 1.8; N, 5.4. $C_{24}H_{10}F_8N_2S_2$ requires: C, 53.1; H, 1.8; N, 5.2%), m.p. 208.5-210°.

(b) With 0.7 equivalents of thiophenoxide ion. Thiophenol (0.75 g.) and sodium (0.18 g.) were dissolved in methanol (250 ml.), and the resulting solution (containing 6.8 mmole thiophenoxide ion) was added dropwise during 18 hr. to decafluoroazobenzene (3.5 g., 9.7 mmole) in refluxing methanol (100 ml.). On cooling, the reaction mixture deposition 1.0 g. of the above di-thiophenoxy-compound (m.p. 190-5°), which was filtered off and identified by infra-red spectroscopy - it contained also decafluoroazobenzene and some of the mono-substituted compound described below. The filtrate was diluted with water (350 ml.) and extracted with ether

(2 x 200 ml.). The extracts were washed with water (3 x 50 ml.) and dried ($MgSO_4$). The product from these extracts (41 g.) was chromatographed on alumina (column B), eluting with hot 33% benzene in light petroleum (b.p. 60-80°), to give decafluoroazobenzene (0.87 g.; 25% recovery) m.p. 135-8°, identified by infra-red spectroscopy, and an orange solid, m.p. 83-92° (0.86 g.). Elution with ether gave a trace of the dithiophenoxy-compound (0.003 g.), most of which presumably remained on the column. The orange product, m.p. 83-92°, was recrystallized three times from light petroleum (b.p. 100-120°) to give 4-thiophenoxynonafluoroazobenzene (0.20 g.; 6% based on decafluoroazobenzene consumed) (Found: C, 47.8; H, 1.3; N, 6.5. $C_{18}H_5F_9N_2S$ requires: C, 47.8; H, 1.1; N, 6.2%) as brick-red needles, m.p. 111-2°. The compound gave a well-resolved nuclear magnetic resonance spectrum (p.139) and was further characterized by the reactions described below.

Reaction of 4-thiophenoxynonafluoroazobenzene with thiophenoxide ion. - A solution of thiophenoxide (2.0 mmole) in methanol (50 ml.) was added dropwise during 20 min. to the azo-compound (0.0914 g., 2.0 mmole) in refluxing methanol (20 ml.). The mixture was heated for a further 5 minutes, then diluted with water (50 ml.). An orange precipitate (0.144 g.) m.p. 180-5°, was obtained, and identified as a mixture of 4,4'-dithiophenoxy-octafluoroazobenzene containing a little starting material. One crystallization from light petroleum (b.p. 100-120°) gave a product (0.059 g.; 54%), m.p. 204-8°, with a satisfactory infra-red spectrum.

Reductive cleavage of 4,4'-dithiophenoxyoctafluoroazobenzene.- The azo-compound (0.50 g., 0.92 mmole) was heated under reflux for 30 min. with aqueous 55% hydriodic acid (5.0 ml.). The mixture was diluted with water (10 ml.), decolourized with solid sodium metabisulphite, and extracted with dichloromethane (10 + 2 ml.); the aqueous layer was neutralized with solid sodium carbonate and re-extracted with dichloromethane (5 + 2 ml.). The extracts were combined and dried ($MgSO_4$) and yielded a yellow oil (0.45 g.), which was chromatographed on alumina (column C), eluting with light petroleum b.p.30-40°. A white solid appeared at the bottom of the column where the eluent was evaporating, and elution was continued until this solid had completely dissolved in the eluent. This first product proved to be diphenyl disulphide (0.20 g., 98%)

m.p. 51°, (lit.,* [150] m.p. 61°), and was identified by infra-red spectroscopy. The column was then eluted with ether; evaporation of the first few ml. of ethereal eluent gave 4H-tetrafluoroaniline (0.18 g., 58%), m.p. just above room temperature (lit.[18] 23.5-26.5°), identified by infra-red spectroscopy.

Reactions of decafluoroazobenzene with other nucleophiles. - (a) Reaction with sodium hydrosulphide. A solution of sodium hydroxide (2.0 g., 50 mmole) in ethylene glycol (10 ml.) was saturated with hydrogen sulphide. This solution was added dropwise during 25 min. to decafluoroazobenzene (2.0 g., 5.5 mmole) in refluxing methanol (100 ml.), and the mixture was heated for a further 2.5 hr., by which time it had become deep red. The solution was neutralized with concentrated hydrochloric acid and extracted with ether (200 + 4 x 50 ml.) and the extracts were dried ($MgSO_4$). Evaporation of the extracts yielded a grey gummy solid (1.78 g.), showing multiple N-H absorption in the infra-red spectrum, but no S-H. Dissolution in ether (10 ml.) left a residue of sulphur (0.22 g.), m.p. 117-124°, identified by combustion to sulphur dioxide; the ethereal extract yielded a gummy solid (1.62 g.), which resisted attempts at recrystallization and which could not be chromatographed.

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* J.E. Waller (this Department) gives m.p. 54°, raised to the quoted figure only on prolonged storage in a desiccator.

(b) Reaction with methyl-lithium. Methyl-lithium (6.5 mmole), in ether (40 ml.), was added dropwise during 25 min. to decafluoroazobenzene (30 g., 8.3 mmole) in dry ether (700 ml.), stirred at 0-5° under nitrogen. After 2 hr. the mixture was allowed to warm to 20° overnight. The solution was evaporated in vacuo to 150 ml., water was then added and the layers were separated. The ethereal layer was washed with dilute hydrochloric acid and then with water, and dried ($MgSO_4$). The ether was removed, leaving a brown gum (2.4 g.), which gave many poorly separated products when it was chromatographed on alumina.

(c) Reaction with phenyl-lithium. Phenyl-lithium (13 mmole) in ether (30 ml.), was added dropwise with stirring during 15 min. to decafluoroazobenzene (3.0 g., 8.3 mmole) in dry ether (200 ml.) under nitrogen. The mixture was kept overnight and then poured into water, and the ethereal layer was washed with dilute hydrochloric acid and then with water and dried ($MgSO_4$). Evaporation yielded a brown tar (4.0 g.), which on chromatography on silica gave a poorly-resolved mixture of gummy products.

A second reaction in THF at −20° gave an equally intractable product.

(d) Reaction with hydrazine. The experiments tabulated below all gave intractable tars showing multiple N-H absorption in the infra-red; a little decafluoroazobenzene (DFAB) was

sometimes recovered. The products were often pale brown, suggesting that reduction of the azo-group had occurred. Work-up was by chromatography.

DFAB (mmole)	Hydrazine (mmole)	Solvent; ml.	Temp. (°C)	Time	DFAB recov.	No. of products	Major product
1.4	1.4	MeOH; 40	reflux	½ hr.	35%	6+	20% intract. solid m.p. 53-8°
4.1	4.5	MeOH; 275	20°	3 days	27%	?	47% intract. gum
2.7	5.5	EtOH; 32	reflux	10 min.	20% (impure)	6+	30% intract. gum
5.5*	20.6	dioxan; 25	reflux	4 hr.	none	?	tar
2.7	5.5	Et_2O; 50	reflux	15 min.	none	large	100% gum
2.7	20.6	pyridine; 50	20°	6 hr.	none	?	trace solid m.p. ca 170°

* This procedure was repeated with azobenzene itself: no reaction occurred.

Attempted bromination of 2H,2'H-octafluoroazobenzene. - (a) With bromine in oleum. The azo-compound (1.65 g., 5.1 mmole), bromine (6.0 g., 37.5 mmole), and 20% sulphur trioxide in sulphuric acid (15 ml.) were stirred for 4 hr. at 60°, cooled, and poured onto ice. The product was filtered, washed, and

dried *in vacuo* over phosphorus pentoxide; it was shown by infra-red spectroscopy to be starting material (1.60g.; 97% recovery).

(b) *With bromine in acetic acid.* The azo-compound (1.60 g., 4.9 mmole), bromine (4.8 g., 30 mmole), and glacial acetic acid (32 ml.) were heated under reflux for 1 hr., poured into water, and filtered. The solid was washed and dried and shown by infra-red spectroscopy to be starting material (1.30 g.; 81% recovery).

Attempted cyclization of 2-amino-4H,4'H-heptafluoroazobenzene.- (a) *With potassium fluoride.* A Pyrex tube (40 x 1.5 cm.) was packed with powdered dried potassium fluoride and placed in a horizontal furnace. The azo-compound (0.50 g., 1.55 mmole) was placed in a small flask wound with heating tape, and the flask was connected to the Pyrex tube, the other end of which led to a trap cooled in liquid nitrogen. The furnace was heated to 270°, the cold trap was connected to a "Hivac" pump, and the heating tape was adjusted so that all the azo-compound had been vapourized through the potassium fluoride tube during 30 min. The azo-compound (0.50 g., 100%) was recovered in the tube leading to the cold trap, and identified by infra-red spectroscopy. Nothing had condensed in the cold trap.

(b) *With sodium hydride.* The azo-compound (0.50 g., 1.55 mmole) and sodium hydride (0.045 g., 1.96 mmole, in 0.2 g. of paraffin) in toluene (20 ml.), under nitrogen, were

heated under reflux for 30 min. The solution was washed with water, evaporated to dryness, and chromatographed on alumina; elution with 50% benzene in light petroleum (b.p. 60-80°) gave the starting material (0.50 g.; 100%), identified by infra-red spectroscopy. An earlier reaction at room temperature also gave starting material.

Attempted complex formation from 2-amino-4H,4'H-heptafluoroazobenzene. - (a) Reaction with mercuric oxide. The azo-compound (0.50 g., 1.55 mmole) was heated under reflux for 30 min. with mercuric oxide (5.0 g.) in ethanol (25 ml.). The suspension was filtered hot; the residue was washed with hot ethanol, and the azo-compound (0.50 g., 100%; identified by infra-red spectroscopy) was precipitated from the combined filtrates by the addition of water.

(b) Reaction with cupric ion. The azo-compound (0.250 g., 0.78 mmole) was shaken with cupric chloride (0.78 mmole in 0.5 ml. of aq. ammonia s.g. 0.88) in methanol (25 ml.). Darkening occurred at once, but the complex decomposed on removal of the solvent in vacuo, and the azo-compound was recovered quantitatively from the residue by chromatography and identified by infra-red spectroscopy.

(c) Reaction with nickel ion. The above procedure was repeated, the copper salt being replaced by an equimolar quantity of nickel chloride. Darkening was again observed, and again the azo-compound was recovered quantitatively.

Reactions of hydrazines with fluoroaromatic compounds. - (a) Hydrazine and pentafluoronitrosobenzene. The nitroso-compound (1.0 g., 5.1 mmole) was stirred in ethanol (100 ml.) at -15°. Hydrazine hydrate (0.38 g., 7.6 mmole) in ethanol (20 ml.) was added dropwise during 30 min. The addition of water precipitated a tar (extracted with ether) which had a complicated infra-red spectrum showing many peaks in the N-H region. The spectrum did not resemble that of tetrafluoro-benzotriazole.

(b) Hydrazine and decafluorohydrazobenzene. The hydrazo-compound (1.0g., 2.7 mmole), hydrazine hydrate (0.28 g., 5.5 mmole), and ethanol (10 ml.), were heated under reflux for 30 min. and then poured into water (30 ml.), and the resulting solution was extracted with ether (4 x 10 ml.). The extracts were washed with water (10 ml.), dried ($MgSO_4$), and evaporated, giving decafluorohydrazobenzene (0.91 g.; 91% recovery), identified by infra-red spectroscopy.

(c) Tosylhydrazide and pentafluoronitrobenzene. Penta-fluoronitrobenzene[43] (see also p.183) (1.0 g., 4.7 mmole), tosylhydrazide (0.88 g., 4.7 mmole) and ethanol (50 ml.), were heated under reflux for 1 hr. The mixture was poured into water and extracted with ether. The extracts were dried ($MgSO_4$) and on evaporation yielded a pale brown oil (1.0 g.), identified by infra-red spectroscopy as pentafluoronitrobenzene containing a little ethanol. The reaction was repeated at

room temperature, but no reaction occurred when the mixture was kept overnight.

Tetrafluorobenzotriazol-1-ol. - (a) Preliminary experiments (tabulated). Pentafluoronitrobenzene[43] was prepared in 86% yield by the oxidation of pentafluoroaniline with peroxytrifluoroacetic acid (from trifluoroacetic anhydride and aq. 85% hydrogen peroxide) in refluxing dichloromethane.

Solvent	$C_6F_5NO_2$ / Ml. solvent	$N_2H_4 \cdot H_2O$ / Ml. solvent	Mole ratio $N_2H_4/C_6F_5NO_2$	Duration of addition of hydrazine	Total duration of experiment	Initial → maximum reaction temp.	Product
EtOH	0.38 g. 7.5 ml.	0.18 g. 7.5ml.	2	30 min.	65 min. reflux		tar (i)
"	0.22 5	0.13	2.5	mixed	10	20 30°	intract. solid, m.p. ca.43-5°; 0.14 g.
"	1.93 40	0.155 then more →pH7	-	ca.3	30	20 30°	tar
Et_2O	1.00 25	0.59	2.5	mixed	15	20 30°	brown solid, m.p. ca.80; 0.71 g.
EtOH	1.00 25	0.59	2.5	mixed	15	20 30°	ditto; 0.65 g.
"	2.13 20	6M/EtOH, added (2.8 ml.) pH7	1.74	ca.5	ca.5	20 35°	crude, 1.6g. fairly pure, 0.2g.

continued...

Solvent	$C_6F_5NO_2$	Ml. solvent	$N_2H_4.H_2O$	Ml. solvent	Mole ratio $N_2H_4/C_6F_5NO_2$	Duration of addition of hydrazine	Total duration of experiment	Initial → maximum reaction temp.	Product
" (ii)	5.18	30	1.84	20	1.5	20	25	20-40°	oil, 4.5g. pure, 0.50g.
" (iii)	0.50	5	0.23		1.9	mixed	30	20 30°	intract. gums 0.4 0.5g.

Notes: (i) Reactions done at room temperature showed a spontaneous temperature rise. (ii) This procedure proved not to be reproducible (hence subsequent experiments). In one experiment, when the crude product was left on the steam bath for 15 min. after evaporation of solvent, sudden frothing followed by solidification of the product occurred; a reasonable yield was obtained from this experiment. However, if the crude product was heated for too long, it was liable to explode. These observations led to the development of the definitive procedure. (iii) In turn, experiments were done using ether, dioxan, isopropanol, aq. 90% methanol, and benzene as solvents.

(b) Definitive procedure. Pentafluoronitrobenzene[43] (6.0 g., 28.2 mmole) was stirred in ethanol (50 ml.) on a water bath at 60°. Hydrazine hydrate (2.2 g., 4.4 mmole) in ethanol (50 ml.) was added dropwise during 10 min.; the temperature

rose to 65° and the reaction mixture turned brown, and a precipitate of hydrazinium fluoride appeared. Stirring was continued at 60° for a further 30 min., then the mixture was poured into water (100 ml.) and extracted with ether (5 x 40 ml.). The extracts were washed with saturated aqueous calcium chloride (10 ml.) to remove ethanol, and evaporated to dryness. 1,2-Dichloroethane (50 ml.) was added, and the mixture was carefully boiled down to about 10 ml. (An experiment on five times this scale exploded rather feebly at this stage, but no explosions were encountered on this scale of preparation). Light petroleum (b.p. 60-80°; 5 ml.) was added, and the mixture was allowed to cool. A brown powder (2.2 g.), shown by infra-red spectroscopy to consist largely of tetrafluorobenzotriazol-1-ol, was obtained.

The product from five such experiments (10.5 g.) was recrystallized from a mixture of 1,2-dichloroethane (200 ml.) and light petroleum (b.p. 60-80°; 100 ml.), to give a somewhat purer product (7.1 g.); this was boiled with water (100 ml.) and largely dissolved, leaving a black tarry residue. The aqueous layer was decanted, charcoaled, filtered, and extracted with ether (5 x 40 ml.). The extracts were dried ($MgSO_4$) and the solvent was removed. The residue was crystallized from 50% 1,2-dichloroethane in light petroleum (b.p. 60-80°), to give pure tetrafluorobenzotriazol-1-ol (4.0 g.; 14%), as a bulky white power (Found: C, 34.7; H, 0.5; N, 20.5. $C_6HF_4N_3O$

requires: C, 34.8; H, 0.5; N, 20.3%), exploding at 144°. The triazolol showed O-H stretching vibrations at 4.0μ (strong, very broad) in its infra-red spectrum (p.127), and was further characterized by its ultra-violet spectrum (p.105a) and its nuclear magnetic resonance spectrum (p.111b). Reduction of this compound gave tetrafluorobenzotriazole (p.73), which was also completely characterized.

Tosyl and Benzoyl derivatives of Tetrafluorobenzotriazol-1-ol. - (a) Preparation. The triazolol (0.20 g., 0.97 mmole), sodium bicarbonate (1.0 g.), and toluene-p-sulphonyl chloride (1.0 g.), were shaken in water (20 ml.) for 30 min. The mixture was then boiled for 5 min., cooled, and filtered. The solid product was charcoaled in and recrystallized twice from light petroleum (b.p. 60-80°) and gave tetrafluorobenzotriazol-1-yl toluene-p-sulphonate (0.146 g; 42%)(Found: C, 43.4; H, 1.95; N, 11.9. $C_{13}H_7F_4N_3O_3S$ requires: C, 43.2; H, 1.9; N, 11.6%), as colourless granular crystals, m.p. 95-6°. The infra-red spectrum was rather similar to that of tetrafluorobenzotriazol-1-ol, but contained extra peaks due to the tosyl group.

A similar reaction, using benzoyl chloride (0.80 g.) instead of tosyl chloride, gave (presumed) tetrafluorobenzotriazol-1-yl benzoate (crude product: 0.24 g.; 80%), m.p. 48-50°, again with a satisfactory infra-red spectrum. The product was not characterized further, except by the ammonolysis reaction

described below.

(b) Ammonolysis of the acyl derivatives. The tosyl derivative (0.20 g., 0.55 mmole) was heated under reflux for 5 min. with aqueous ammonia (s.g. 0.88; 2.0 ml.) and ethanol (8.0 ml.); the mixture was then diluted with water (20 ml.) and extracted with ether (4 x 10 ml.). The extracts were washed with water and dried ($MgSO_4$), and evaporation of the solvent gave toluene-p-sulphonamide (0.103 g.; 100%); acidification of the aqueous phase, followed by ether extraction (4 x 10 ml.) gave tetrafluorobenzotriazol-1-ol (0.127 g.; 100%) - both products were identified by infra-red spectroscopy.

1-Benzoyloxytetrafluorobenzotriazole, when treated similarly to the tosyloxy-compound, gave benzamide and the same triazolol.

Attempted Preparation of 1-Chlorotetrafluorobenzotriazole. - The triazolol (0.25 g., 1.2 mmole) and phosphorus pentachloride (0.30 g., 1.4 mmole) were heated under reflux for 1 hr. in dry toluene (10 ml.) then evaporated to dryness. The resulting oil (0.40 g.) was shown by infra-red spectroscopy to consist largely of the triazolol.

Tetrafluorobenzotriazole. - (a) From the triazolol. Tetrafluorobenzotriazole (0.250 g., 1.2 mmole) and aqueous 55% hydriodic acid (2.5 ml.) were heated under reflux for 30 min. The solution was decolourized with solid sodium metabisulphite and partly neutralized (pH6) with saturated aqueous sodium carbonate. The solution was extracted with ether (5 x 10 ml.)

and the extracts were dried ($MgSO_4$) and evaporated to give almost pure tetrafluorobenzotriazole (0.241 g.; 100%), as a white solid, m.p. 160-2°, identified by infra-red spectroscopy. Recrystallization of this product from benzene yielded the pure compound (Found: C, 37.8; H, 0.6; N, 21.9. $C_6HF_4N_3$ requires: C, 37.7; H, 0.5; N, 22.0%), as colourless glistening plates with a pleasant odour (0.100 g.; 42% recovery), m.p. 162.5°. The compound was further characterized by its ultra-violet spectrum (p.105a), the nuclear magnetic resonance spectrum (an A_2X_2 system, p.106) of its anion, and by the independent synthesis described below.

(b) From tetrafluoro-o-phenylenediamine. The diamine (p.87), (21.0 mg., 0.117 mmole), sodium nitrite (10.5 mg., 0.15 mmole), and aq. 70% sulphuric acid (1.0 g.) were heated to 75° in a water bath; the colour changed from green to brown. The mixture was diluted to 50 ml., partly neutralized (pH 6.5) with sodium carbonate, and extracted with ether (3 x 10 ml.). The extracts were dried ($MgSO_4$) and evaporated to give tetrafluorobenzotriazole (18.7 mg.; 84%) as a somewhat gummy solid, identified by infra-red spectroscopy.

(c) Attempted preparation from tetrachlorobenzotriazole. The chlorinated triazole (m.p. 254-9°, lit.,[120] 256-260°) was prepared by refluxing benzotriazole with aqua regia. A mixture of anhydrous potassium fluoride (12.5 g., 180 mmole) in tetramethylene sulphone (30 g.) was dried by azeotropic

distillation with benzene (15 ml.), then stirred at 235°. Tetrachlorobenzotriazole (8.0 g., 31 mmole) was added to the mixture, which was then stirred a further 20 hr. with heating; the temperature rose to 270° overnight. The product was poured into water (100 ml.) and boiled, and yielded a black tar.

In a second reaction the triazole (5.0 g., 19 mmole), potassium fluoride (10 g., 145 mmole), and tetramethylene sulphone (30 g.) were stirred at 200° for 18 hr. The product was diluted with benzene (50 ml.), poured into water, extracted with ether, washed with water, and dried ($MgSO_4$). The ether was removed, and the residue was dissolved in benzene, charcoaled, and crystallized, to give tetrachlorobenzotriazole (0.71 g.; 14% recovery), m.p. 255-9°, identified by its infra-red spectrum. The mother liquor was evaporated and gave a tar (1.06 g.).

1-Acetyltetrafluorobenzotriazole. - Tetrafluorobenzotriazole (0.50 g., 2.6 mmole) and acetic anhydride (5 ml.) were heated under reflux for 10 min. The mixture was cooled to 0° and diluted with ice-water (50 ml.). A white precipitate (0.54 g.), shown by infra-red spectroscopy to be starting material and the 1-acetyl-derivative, was filtered off, and dried *in vacuo* over phosphorus pentoxide. This product (m.p. 98-100°) was recrystallized from light petroleum (b.p 60-80°), to give 1-acetyltetrafluorobenzotriazole (30 mg.; 5%) (Found: C, 41.4; H, 1.5; N, 18.2. $C_8H_3F_4N_3O$ requires: C, 41.2; H, 1.3;

N, 18.0%) as white needles, m.p. 112-3°. The position of the acetyl group was established by the nuclear magnetic resonance spectrum (p.142), which showed four fluorine atoms in different environments - an AGPX system - whereas the 2-acetyl isomer would be expected to give an A_2X_2 system.

This compound was very readily hydrolysed, even in neutral solution, to give acetic acid and the parent triazole.

Silver Salt of Tetrafluorobenzotriazole. Tetrafluorobenzotriazole (0.50 g., 2.6 mmole) was dissolved in aqueous 0.065N sodium hydroxide (40 ml., 2.6 mmole) with slight warming. Silver nitrate (0.445 g., 2.6 mmole) in water (10 ml.) was added, and a black precipitate (0.68 g.; 87%) of the presumed silver salt was obtained. The infra-red spectrum (p.127), though somewhat similar to that of the parent triazole, had no H-stretching absorption, and several bands were shifted considerably. In a second experiment the product was pale violet, but had an identical infra-red spectrum; the pure compound is expected to be colourless.

Attempted Nitration of Tetrafluorobenzotriazole.

Tetrafluoro-benzotriazole	Reagents	Duration	Temperature	Product *
0.164 g.	Conc. HNO_3 (2.5 ml.) + H_2SO_4 (2.5 ml.)	2 hr.	0°	SM, 0.114g.
0.200 g.	96% HNO_3 (0.10 g.) + 20% SO_3/H_2SO_4 (4 ml.)	30 min.	40°	SM, 0.193g.

continued...

Tetrafluoro-benzotriazole	Reagents	Duration	Temperature	Product*
0.250 g.	Conc.HNO_3(0.34 g.) + $(CF_3CO)_2O$(4.0 ml.)	3 days	20°	SM
0.191 g.	Conc.HNO_3(0.4 ml.) + Ac_2O(3.6 ml.)	10 min.	reflux	SM + 1--acetyl--derivative

* SM = starting material

Attempted Bromination of Tetrafluorobenzotriazole. - The triazole (0.10 g., 0.52 mmole) was dissolved in aqueous 4% sodium hydroxide (5.0 ml.) and cooled to 0°. Bromine (0.10 g., 0.63 mmole) was added, and a bulky precipitate appeared but dissolved almost instantaneously. The liquid gave no product on ether extraction, so it was acidified with hydrochloric acid and re-extracted with ether (2 x 20 ml.). Tetrafluorobenzotriazole was recovered quantitatively and identified by its infra-red spectrum.

Attempted Preparation of 1-Aminotetrafluorobenzotriazole - (a) From the parent triazole. Tetrafluorobenzotriazole (0.20 g., 1.05 mmole) and aqueous 10% potassium hydroxide (30 ml) were stirred at 60°. Hydroxylamine-O-sulphonic acid (2.0 g., 18 mmole) in water (20 ml.) was added during 5 min. The mixture was stirred at 60° for 1 hr., acidified with concentrated hydrochloric acid, and extracted with ether, to give starting

material (0.192 g.; 86%), m.p. ca. 160°, identified by infra-red spectroscopy.

(b) From the triazole silver salt. The silver salt (0.30 g., 1.0 mmole) was shaken for 5 min. with ether (10 ml.) containing chloramine (0.065 g., 1.3 mmole). The suspension was filtered, and the filtrate yielded an intractable gum (0.02 g.).

(c) From the triazolol. Tetrafluorobenzotriazol-1-ol (0.250 g., 1.2 mmole) in dry dichloromethane (25 ml.) was mixed with boron trifluoride in the same solvent (15 ml.; 0.9M solution; i.e. 13 mmole of BF_3). The mixture was saturated with gaseous ammonia and gave a white precipitate (presumably of $\bar{B}F_3.\dot{N}H_3$). Water (30 ml.) was added, and the layers were separated. The aqueous layer was acidified with concentrated hydrochloric acid and extracted with ether (2x 25 ml.), and yielded starting material (0.21 g.; 84%), exploding at 144°, identified by infra-red spectroscopy. The dichloromethane layer yielded traces of a yellow partly-solid oil, which was not examined further.

1-(Pentafluorophenylamino)-tetrafluorobenzotriazole. - Decafluoroazoxybenzene (5.0 g., 13.2 mmole), hydrazine hydrate (1.0 g., 20 mmole), and ethanol (50 ml.) were heated under reflux for 30 min. and the mixture was then poured into water (100 ml.) and extracted with ether (3 x 50 ml.) to give a solid product (4.5 g.). This was charcoaled and recrystallized from

1,2-dichloroethane and light petroleum (b.p. 80-100°), and the product was washed with a little light petroleum (b.p. 30-40°). 1-(Pentafluorophenylamino)-tetrafluorobenzotriazole (1.4 g.; 28%) (Found: C, 38.9; H, 0.6; N, 15.3. $C_{12}HF_9N_4$ requires: C, 38.7; H, 0.3; N, 15.0%), m.p. 158-9° (unchanged on recrystallization from the same solvent) was obtained; it formed extremely voluminous white needles, which appeared to be charged with static electricity. The compound was distinguished from the much less likely isomer (a dihydrotetrazine) by comparison of its ultraviolet spectrum with a predicted spectrum (p.105a).

Reductive Cleavage of 1-(Pentafluorophenylamino)-tetrafluorobenzotriazole. - The triazole (0.50 g., 1.34 mmole), aqueous 55% hydriodic acid (5.0 ml.), and p-xylene (5.0 ml.; inert solvent) were heated under reflux for 72 hr. The mixture was diluted with water to 100 ml., decolourized with solid sodium metabisulphite, and partly neutralized (to pH 6) with solid sodium carbonate. The solution was extracted with ether (100 + 5 x 20 ml.) and the extracts were washed with water (25 ml.). Benzene (25 ml.) was added and the mixture was distilled through a 15 cm. column packed with glass helices until the volume had been reduced to 25 ml. This residual product was extracted with concentrated hydrochloric acid (5 + 2 x 2.5 ml.), and these extracts were neutralized with solid sodium carbonate and extracted with ether (5 x 5 ml.).

The ethereal extracts were dried ($MgSO_4$) and evaporated *in vacuo* to give pentafluoroaniline (0.132 g.; 54%; 84% based on unrecovered starting material), as an oil which solidified on standing. It was identified by infra-red spectroscopy.

The residual benzene solution was extracted with aqueous 1.0N sodium hydroxide (3 x 10 ml.); these extracts were neutralized with concentrated hydrochloric acid and extracted with ether (5 x 5 ml.). The extracts were dried ($MgSO_4$) and yielded crude tetrafluorobenzotriazole (7 mg.; 3%; 4% based on starting material consumed) as an almost colourless gummy solid, identified by infra-red spectroscopy.

The remaining benzene layer was dried ($MgSO_4$) and evaporated to dryness *in vacuo* to give unreacted 1-(pentafluorophenylamino)-tetrafluorobenzotriazole (0.109 g.; 22% recovery), identified by infra-red spectroscopy.

Reaction of 1-(Pentafluorophenylamino)-tetrafluorobenzotriazole with lead tetra-acetate. - (a) *In refluxing benzene.* The triazole (1.7 g., 4.6 mmole) and lead tetra-acetate (3.4 g., 7.7 mmole) were heated under reflux in benzene (50 ml.) for 30 min. The solids were filtered off and the mixture was washed with aqueous 2N sodium hydroxide (5 x 20 ml.). The aqueous washings were extracted with ether (*ca.* 50 ml.), and the combined organic layers were dried ($MgSO_4$) and evaporated to dryness, to give a red oil (1.77 g.), which was chromatographed (column B) on alumina. Elution with 33%

benzene in light petroleum (b.p. 60-80°) gave red gummy crystals (0.95 g.), which were shown by ultra-violet and nuclear magnetic resonance spectroscopy to be a complex mixture of highly fluorinated azobenzenes.

(b) At room temperature. The triazole (0.211 g., 0.57 mmole), lead tetra-acetate (0.42 g., 0.95 mmole), and benzene (15 ml.) were shaken at 20° for 1 hr. The mixture turned red, and a chromatographic work-up as above gave a similar mixture of azo-compounds (0.148 g.), m.p. 36-60°.

1-(4H-Tetrafluorophenylamino)-5H-trifluorobenzotriazole. - (a) From 4H,4'H-octafluoroazoxybenzene. The azoxy-compound (0.40 g., 1.17 mmole), hydrazine hydrate (0.10 g., 2.0 mmole), and ethanol (4.0 ml.) were heated under reflux for 15 min., poured into water (25 ml.), and extracted with ether (4 x 25 ml.). The extracts were washed with water (2 x 10 ml.), dried ($MgSO_4$), and evaporated to yield a partly--crystalline red oil (0.40 g.), which was charcoaled and recrystallized from light petroleum (b.p. 60-80°; 20 ml.), to give bulky white needles of 1-(4H-tetrafluorophenylamino)-5H-trifluorobenzotriazole (0.15 g.; 37%) (Found: C, 42.8; H, 0.8; N, 17.0. $C_{12}H_3F_7N_4$ requires: C, 42.8; H, 0.9; N, 17.0%), m.p. 162-4° (decomp.). The ultraviolet spectrum (p.136) was similar to that of the nonafluoro-compound (p.105a).

(b) Attempted synthesis from 2-amino-4H,4'H-heptafluoro-azobenzene. The azo-compound (0.50 g., 1.54 mmole), zinc

dust (4.0 g.), ammonium chloride (0.50 g.), water (1.0 ml.), and ethanol (10 ml.) were shaken at 20° for 5 min. The liquid, now colourless, was filtered and collected in a flask containing aqueous 50% acetic acid (40 ml.) at 0°. Sodium nitrite (0.80 g.; diazotization and destruction of ammonium ion require 0.752 g.) in water (2.0 ml.) was added in one portion. The mixture was heated to 80°, then cooled, diluted with water (50 ml.), and extracted with ether (50 + 5 x 20 ml.). The extracts were washed with saturated aqueous sodium bicarbonate (3 x 50 ml.), dried ($MgSO_4$), and evaporated, yielding a red oil (0.28 g.). The infra-red spectrum showed a strong peak at 4.7μ, presumably diazonium cation. The product was recrystallized from benzene and light petroleum, but only tars could be obtained.

The reaction was repeated with 5% sulphuric acid instead of acetic acid, but a similar intractable product was obtained.

1-(2H-Tetrafluorophenylamino)-7H-trifluorobenzotriazole. - 2H,2'H-Octafluoroazoxybenzene (0.60 g., 1.75 mmole), hydrazine hydrate (0.15 g., 3 mmole) and ethanol (6.0 ml.) were heated under reflux for 15 min. and the product was worked up similarly to its isomer (above section). The first recrystallization of the crude product gave fairly pure 1-(2H-tetrafluorophenylamino)-7H-trifluorobenzotriazole (0.203 g.; 34%), m.p. 120°, identified by infra-red spectroscopy; a further crystallization gave the pure compound (0.121 g.) (Found: C, 43.1; H, 1.2; N, 17.0.

$C_{12}H_3F_7N_4$ requires: C, 42.8; H, 0.9; N, 16.7%), m.p. 125-6°, as white needles. The ultraviolet spectrum (p.136) resembled that of the nonafluoro-compound.

The Reaction of Decafluoroazoxybenzene with Ammonia. - Decafluoroazoxybenzene (4.25 g., 11.2 mmole) was heated under reflux in ethanol (30 ml.). Aqueous ammonia (s.g.0.88; 8.0 ml.) was added in 1 ml. portions every 30 min., and the mixture was refluxed for a total of 4 hr. The solution was poured into water (100 ml.) and extracted with ether (4 x 30 ml.). The extracts were dried ($MgSO_4$) and evaporated to give a semi-solid yellow product (4.35 g.), which was chromatographed on alumina (column A), eluting with 33% benzene in light petroleum (b.p. 60-80°); three bands developed, very pale brown, yellow, and cream coloured, respectively. Band (i) gave decafluoroazoxybenzene (0.46 g.; 11% recovery), m.p. 54°, identified by infra-red spectroscopy and band (ii) gave crude 2-(pentafluoroazoxy)-tetrafluoroaniline (2.42 g.; 57%), m.p. 70-4°, containing a little of the 4-isomer, identified by infra-red spectroscopy. The pure 2-isomer (0.38 g.) was obtained by two recrystallizations from light petroleum (b.p. 40-60°) (Found: C, 38.6; H, 0.7; N, 11.2. $C_{12}H_2F_9N_2O$ requires: C, 38.4; H, 0.5; N, 11.2%), as yellow plates, m.p. 69.5°. Band (iii) gave 4-(pentafluorophenylazoxy)-tetrafluoroaniline (1.21 g.; 29%) m.p. 93°, identified by infra-red spectroscopy. Recrystallization from light petroleum (b.p. 60-80°) gave the pure compound (0.87 g.)

(Found: C, 38.8; H, 0.7; N, 11.4. $C_{12}H_2F_9N_2O$ requires: C, 38.4; H, 0.5; N, 11.2%) as cream needles, m.p. 93°. The ortho-para orientation in these compounds was established by reductive cleavage (below), and the alternative possibilities due to the asymmetry of the azoxy-group were eliminated by benzotriazole-formation in conjunction with nuclear magnetic resonance data (p.116).

A minor fourth band on the column yielded a yellow substance (73 mg.) m.p. ca. 130° which was shown by nuclear magnetic resonance spectroscopy to be a mixture, and which was not investigated further.

Reductive Cleavage of 2-(Pentafluorophenylazoxy)-tetrafluoroaniline. - The azoxy-compound (0.50 g., 1.34 mmole) and aqueous 55% hydriodic acid (5.0 ml.) were heated under reflux for 1 hr., and the mixture was then diluted with water to 10 ml., decolourized with solid sodium metabisulphite, neutralized with solid sodium carbonate, and extracted with ether (5 x 10 ml.). The ethereal extracts were washed with water (5 ml.), dried ($MgSO_4$) and evaporated *in vacuo*, to give a pink solid (0.427 g.), m.p. 60-90°, identified by infra-red spectroscopy as a mixture of tetrafluoro-o-phenylenediamine and pentafluoroaniline. The crude product was crystallized from light petroleum (b.p. 80-100°; 10 ml.), and gave tetrafluoro-o-phenylenediamine (0.133 g.; 55%), m.p. 117-20° (lit.[43] 131°), identified by infra-red spectroscopy, by

diazotization (p.73), and by conversion to the benzil derivative, which was analysed (p.88).

The petroleum filtrate from the above crystallization of the diamine was extracted with concentrated hydrochloric acid (7 + 3 ml.), and these extracts were neutralized with solid sodium carbonate and extracted with ether (10 + 5 ml.). The ethereal extracts were dried ($MgSO_4$) and evaporated to give crude pentafluoroaniline (0.185 g.; 80%), as a semi-solid product containing a little of the above diamine, identified by infra-red spectroscopy.

2,3-Diphenyl-5,6,7,8-tetrafluoroquinoxaline. Tetrafluoro-o-phenylenediamine (90 mg., 0.50 mmole), benzil (105 mg., 0.50 mmole), and glacial acetic acid (2.0 ml.) were heated under reflux for 1 hr., and the mixture was then cooled and diluted with water (5.0 ml.). The crude product (135 mg.), which was fairly pure, m.p. 176-8°, was filtered off, washed thoroughly with water, and dried in vacuo over phosphorus pentoxide. Recrystallization from ethanol (30 ml.) gave pure 2,3-diphenyl--5,6,7,8-tetrafluoroquinoxaline, (116 mg.; 66%) (Found: C, 67.9; H, 2.95; N, 8.1. $C_{20}H_{10}F_4N_2$ requires: C, 67.9; H, 2.8; N, 7.9%) as fine white needles, m.p. 182°. This quinoxaline was characterized by its ultra-violet spectrum (p.135) which was closely similar to that of the related trifluoro-compound.

Reductive Cleavage of 4-(Pentafluorophenylazoxy)-tetrafluoroaniline. - The azoxy-compound (0.407 g., 1.1 mmole) and

aqueous 55% hydriodic acid (4.0 ml.) were heated under reflux for 90 min. The mixture was diluted to 10 ml., decolourized with solid sodium metabisulphite, neutralized with solid sodium carbonate, and extracted with ether (5 x 10 ml.). The extracts were washed with water (5 ml.), dried ($MgSO_4$), and evaporated *in vacuo* to give a nearly-white solid, (0.342 g.), m.p. 30-110°, which was identified by infra-red spectroscopy as a mixture of pentafluoroaniline and tetrafluoro-*p*-phenylenediamine. This product was recrystallized from light petroleum (b.p. 80-100°; *ca.* 10 ml.) and yielded the diamine (0.129 g.; 66%), m.p. 137-8°, identical with the sample obtained previously (p.170). The filtrate was extracted with concentrated hydrochloric acid (7 + 3 ml.), and the extracts were made alkaline with solid sodium carbonate and extracted with ether (10 + 5 ml.). These extracts were dried ($MgSO_4$) and evaporated *in vacuo*, yielding an almost white gummy solid (0.075 g.; 38%), identified by infra-red spectroscopy as pentafluoroaniline, containing a little of the above diamine.

1-Pentafluorophenylamino-5-aminotrifluorobenzotriazole. - 4-(Pentafluorophenylazoxy)-tetrafluoroaniline (0.40 g., 1.07 mmole), hydrazine hydrate (0.10 g., 2.0 mmole), and ethanol (4.0 ml.) were heated under reflux for 30 min., and the mixture was then poured into water (25 ml.) and extracted with ether (4 x 25 ml.). The extracts were washed with water (2 x 10 ml.), dried ($MgSO_4$), and evaporated to give a

solid product (0.314 g.), which was recrystallized from benzene/light petroleum (b.p. 60-80°; ca. 20 ml.). 1-Pentafluorophenylamino-5-aminotrifluorobenzotriazole (0.092 g.; 23%) (Found: C, 39.2; H, 1.1; N, 19.2. $C_{12}H_3F_8N_5$ requires: C, 39.0; H, 0.8; N, 18.9%) was obtained as white needles, m.p. 152-3° (decomp.). The compound was identified as a phenylaminobenzotriazole by ultra-violet spectroscopy (p.105a), and distinguished conclusively from the only possible isomer 1-(4-aminotetrafluorophenylamino) tetrafluorobenzotriazole by its nuclear magnetic resonance spectrum (p.111).

1-Pentafluorophenylamino-7-aminotrifluorobenzotriazole. - 2-(Pentafluorophenylazoxy)-tetrafluoroaniline (0.232 g., 0.62 mmole), and hydrazine hydrate (2.5% solution in ethanol; 2.5 ml., 0.63 mmole) were heated under reflux for 15 min., and the mixture was then poured into water (20 ml.) and extracted with ether (5 x 10 ml.). The extracts were washed with water (5 ml.), dried ($MgSO_4$), and evaporated to give a red oil (0.235 g.), which was charcoaled and recrystallized from benzene/light petroleum (b.p. 60-80°) to give 1-pentafluorophenylamino-7-aminotrifluorobenzotriazole (0.021 g.; 9%), as white needles, m.p. 147° (decomp.). The compound was characterized similarly to its isomer (previous section), and spectra and elemental analysis (Found: C, 37.7; H, 1.2. $C_{12}H_3F_8N_5$ requires: C, 39.0; H, 0.8%) were carried out on 13 mg. of the compound recovered from the nuclear magnetic

resonance tube. The analysis was inevitably rather unsatisfactory, but the nuclear magnetic resonance spectrum (p.111a) showed no fluorine-containing impurity.

Attempted Cyclization of 2H,2'H-Octafluoroazobenzene to Octafluorobenzocinnoline. - (a) With aluminium chloride in dichloromethane. 2H,2'H-Octafluoroazobenzene (0.250 g., 0.77 mmole) and anhydrous aluminium chloride (2.0 g.) were heated under reflux for 3 days in dichloromethane; the reaction mixture was protected from moisture with a calcium chloride tube. The solution was washed with water, dried ($MgSO_4$), and evaporated to give the unchanged azo-compound (0.240 g.; 96%), m.p. 110-2°, identified by infra-red spectroscopy.

(b) With fused aluminium chloride. The azo-compound (0.250 g., 0.77 mmole), aluminium chloride (8.0 g.), sodium chloride (1.0 g.), and sodium fluoride (0.125 g.) were heated on a steam bath at 80-90° for 90 min. The melt was poured into water and extracted with ether; the extract yielded a tar, which was chromatographed on alumina (column C) to give starting material (0.18 g.; 72%), eluted with benzene and identified by infra-red spectroscopy, as the only tractable product.

(c) By irradiation. The azo-compound (0.50 g., 1.53 mmole), concentrated sulphuric acid (96 ml.) ethanol (50 ml.), and water (to 200 ml.), were irradiated by ultra-violet light for 24 hr. - a considerable quantity of the starting material had precipitated out of the reaction mixture. The

mixture was diluted with water and extracted with ether to give the unchanged azo-compound (0.411 g.; 82%), identified by infra-red spectroscopy.

A second experiment was done in concentrated sulphuric acid only (50 ml.) in which the azo-compound was soluble; chromatographic work-up gave only the starting material (0.40 g., 80%), identified by infra-red spectroscopy.

Attempted Wallach Rearrangement of 2H,2'H-Octafluoroazoxybenzene. - The azoxy-compound (0.100 g., 0.29 mmole), chlorosulphonic acid (1.0 ml.), and carbon tetrachloride (4.0 ml.) were heated under reflux for 15 min., and the mixture was then diluted with water (60 ml.) and extracted with dichloromethane (20 + 5 ml.). The extracts were washed with water (50 ml.) and dried ($MgSO_4$). Evaporation of the solvent gave an orange oil (0.059 g.), with an infra-red spectrum somewhat different from that of the starting material; in particular, there was a strong band at 4.63μ., suggesting that cleavage to a diazonium salt had occurred. The oil could not be recrystallized.

Attempted Photochemical Rearrangement of 2H,2'H-Octafluoroazoxybenzene. - (a) In neutral solution. The azoxy-compound (0.250 g., 0.71 mmole) in ethanol (65 ml.) was irradiated for 18 hr. The solution was evaporated to 5 ml., and water (30 ml.) was added. Extraction with ether (4 x 7 ml.) yielded the starting material (0.20 g.; 80%), m.p. 61-3°, mixed

m.p. 63-5°, identified by infra-red spectroscopy. This product was a very pale orange, suggesting that a minute proportion of an azo-compound was present.

(b) In acidic solution. The azoxy-compound (0.20 g., 0.58 mmole), concentrated sulphuric acid (9.6 ml.), ethanol (5.0 ml.), and water (44 ml.) were irradiated for 19 hr. Water was added and the mixture was extracted with ether; the unchanged azoxy-compound (ca. 0.15 g.), m.p. 60-2°, was obtained, and was identified by infra-red spectroscopy.

Attempted Ullmann Reaction on 2, 2'-Dibromo-octafluoroazobenzene. - (a) In dimethylformamide. The azo-compound (0.40 g., 0.83 mmole), copper bronze (4.0 g.), and dimethylformamide (40 ml.) were heated under reflux for 1 hr. and filtered hot. The solids were washed with hot dimethylformamide (10 ml.) and the combined filtrates were added to water (100 ml.) to give a precipitate, which was chromatographed on alumina (column B). One tractable product was obtained (eluted with 50% benzene/light petroleum b.p. 60-80°), namely, 2H,2'H-octafluoroazobenzene (0.132 g.; 49%), m.p. 110-2°, identified by infra-red spectroscopy.

(b) Without a solvent. The azo-compound (0.60 g.) and copper bronze (1.20 g.) were sealed in vacuo in a small Pyrex tube, and placed in a bath of refluxing ethylene glycol at 200° for 24 hr. The tube was opened and the contents were extracted with ether; evaporation of the solvent and chromatography

on alumina, with successive elution with light petroleum (b.p. 60-80°), benzene, and ether gave no product; elution with acetone caused a yellow band to move down the column. This band yielded only a trace of brownish-yellow oil.

Tetrafluoroanthranilic Acid. - Tetrafluorophthalonitrile was prepared in 68% yield by the procedure of Evans,[3] which consisted of heating tetrachlorophthalonitrile with a fourfold excess of dried potassium fluoride at 250° for 24 hr. The nitrile was hydrolysed to give tetrafluorophthalimide (72%) by heating in 10 parts of concentrated suphuric acid at 120° for 3.5 hr. - the procedure was again that of Evans.[3] The phthalimide was subjected to a Hofmann degradation, to give tetrafluoroanthranilic acid, m.p. 138-140° (lit.,[49] 141-2°), with a satisfactory infra-red spectrum, by the procedure of Tatlow and his co-workers.[49] Work on a 20 g. scale easily raised the yield to 75%.

Diazotization of Tetrafluoroanthranilic Acid. - The acid (2.0 g., 9.5 mmole) was dissolved in 20% sulphuric acid (200 ml.) and cooled to 0°. Sodium nitrite (20 g., 290 mmole) in water (100 ml.) was added in one portion. The mixture was warmed to 60° for 5 min., the blue colour of the nitrous acid giving way to yellow. The mixture was cooled and extracted with ether (5 x 100 ml.); the extracts were washed with water (2 x 40 ml.), dried ($MgSO_4$), and evaporated to dryness, yielding a yellow solid (1.7 g.), which was washed with a few ml. of ice-cold

water and dried in vacuo. Two recystallizations from 50 parts of water gave trifluorobenzenediazonium-2-oxide-6-carboxylic acid (0.47 g.; 23%)(Found: C, 38.0; H, 0.2; F, 25.2; N, 12.8. $C_7HF_3N_2O_3$ requires: C, 38.6; H, 0.5; F, 26.1; N, 12.8%), as yellow crystals, exploding at 191°. The compound showed a strong $-\overset{+}{N}\equiv N$ absorption at 4.58μ in the infra-red spectrum, and was distinguished from its isomer (the 4-oxide) by ultra-violet spectroscopy (p.100a) and by reductive replacement of the diazonium group (p.123) to give a hydroxy-acid, whose structure was confirmed by nuclear magnetic resonance spectroscopy.

Photolysis of Trifluorobenzenediazonium-2-oxide-6-carboxylic acid. - The diazo-oxide (0.65 g., 3.0 mmole) was deposited from ether solution as a thin film over about 150 cm^2. - half the inside surface of a silica tube. The tube was evacuated and sealed, irradiated for 7 days, and then opened. The contents were extracted with dichloromethane and yielded the starting material (0.58 g.; 90%), identified by infra-red spectroscopy.

Reduction of Trifluorobenzenediazonium-2-oxide-6-carboxylic acid. - The diazo-oxide (0.50 g., 2.3 mmole) was shaken for 1 min. with ether (50 ml.), aqueous 5% ammonium chloride (10 ml.), and zinc dust (1.0 g.) in an open flask. Both liquid phases were colourless. The ether layer was separated, and the aqueous layer was extracted with more ether (5 x 25 ml.). The combined ethereal extracts were dried ($MgSO_4$) and evaporated to

dryness, to give a glassy solid (0.10 g.; 29%), identified by infra-red spectroscopy as crude 2,3,4-trifluoro-5-hydroxybenzoic acid, which was prepared better by the procedure below.

2,3,4-Trifluoro-5-hydroxybenzoic acid. - Trifluorobenzene-diazonium-2-oxide-6-carboxylic acid (0.50 g., 2.3 mmole), zinc dust (1.0 g.), and methanol (25 ml.) were mixed. Aqueous 10% ammonium chloride (2.5 ml.) was added and effervescence occurred; the solution became colourless. The liquid was filtered, and 0.2N hydrochloric acid (50 ml.) was added. The resulting solution was heated under reflux for 30 min. and extracted with ether (50 + 4 x 25 ml.). The extracts were dried ($MgSO_4$) and yielded a buff solid (0.45 g.), which on two recrystallizations from toluene gave 2,3,4-trifluoro-5-hydroxybenzoic acid (0.21 g.; 60%) (Found: C, 43.9; H, 1.6; N, <1; F, 30.0. $C_7H_2F_3O_2$ requires: C, 43.8; H, 1.5; N, 0.0; F, 29.7%) as a pink powder, m.p. 164.5-165°. If the recrystallization was done instead from 1,2-dichloroethane, a colourless sample, m.p. 162-3°, was obtained (in much lower recovery) with an identical infra-red spectrum. The structure of this compound was established by the ^{19}F and ^{1}H nuclear magnetic resonance spectra, (p.138) which show fluorine atoms in the 1,2,3-relationship, with a hydrogen para to the middle fluorine atom.

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