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Polyfluoroarenes. Part X.¹ Polyfluoroaromatic Azo-compounds

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Polyfluoroaromatic azo-compounds (XC₆F₄·N:N·C₆F₄X; X = F, p-H, o-H, or o-Br) are obtained by the oxidation of polyfluoro-anilines with bleaching powder or with lead tetra-acetate; the latter reagent yields fluoro-phenazines as by-products. Reduction of decafluoroazobenzene with zinc and ammonium chloride or with sodium dithionite gives decafluorohydrazobenzene, and hydriodic acid cleaves both the azo- and the hydrazo-compound to pentafluoroaniline. Reactions of decafluoroazobenzene with ammonia and with ethoxide, hydroxide, or benzenethiolate ions are described.

DECAFLUOROAZOBENZENE (I) and 4H,4'H-octafluoroazobenzene have been prepared by Burdon, Morton, and Thomas² by oxidation of the corresponding anilines with aqueous sodium hypochlorite, and Hudson, Pedler, and Tatlow have recently described the formation of decafluoroazobenzene (18%) and octafluorophenazine (6%) during the electrochemical oxidation (II)of pentafluoroaniline.³ Catalytic hydrogenation of decafluoroazobenzene yielded the hydrazo-compound, whilst reductive cleavage to pentafluoroaniline was achieved with tin and hydrochloric acid. Treatment of the azo-compound with methoxide ion gave successive replacement of the 4-, 4'-, 2-, and 2'-fluorine atoms.² The present paper describes alternative routes to most of these compounds (often in better yields), and extends considerably the reactions of decafluoroazobenzene with nucleophiles.

Preparation of the Azo-compounds and Phenazines.— In this Department, decafluoroazobenzene was first prepared in 50% yield by Wilkinson by the oxidation of pentafluoroaniline with lead tetra-acetate in benzene at room temperature.⁴ We have now found that at reflux temperature (80°) the azo-compound (I) is formed in 48% yield together with the yellow octafluorophenazine (II) (28%). Similar oxidation of 4H-tetrafluoroaniline gives comparable yields of 4H,4'H-octafluoro-

$$C_{6}F_{5}\cdot NH_{2} \xrightarrow{Pb(OAc)_{4}} C_{6}F_{5}\cdot N:N\cdot C_{6}F_{5} + F_{F} \xrightarrow{F}_{F} N \xrightarrow{F}_{F} F_{F}$$
(1)

azobenzene and 2H,7H-hexafluorophenazine (III), and 2H-tetrafluoroaniline yields 2H, 2'H-octafluoroazobenzene and 1H,6H-hexafluorophenazine (IV).



The phenazines are characterised by their u.v. spectra, which are closely similar to that of phenazine itself and do not contain the strong 290-310 nm. band exhibited

Part IX, J. M. Birchall, F. L. Bowden, R. N. Haszeldine, and A. B. P. Lever, *J. Chem. Soc.* (A), 1967, 747.
 J. Burdon, C. J. Morton, and D. F. Thomas, *J. Chem. Soc.*,

1965, 2621.

by the isomeric benzocinnoline. Further support for their structures is provided by their ¹⁹F n.m.r. spectra (Table 1); octafluorophenazine gives an AA'XX' system, whereas octafluorobenzo[c]cinnoline (V) would show an AGPX pattern. The cinnoline (V) could conceivably be formed by a number of routes from the pentafluorophenylimino-radicals generated during the oxidation.

The crude phenazine (IV) is of high purity, and its n.m.r. spectrum reveals no hepta- or octa-fluorophenazine, showing that in its formation fluorine (rather than hydrogen) is replaced with high specificity at the ortho-position. This observation is in accord with the earlier report that phenazines are formed by the electrochemical oxidation of 2-aminopolyfluorodiphenylamines



only if a 2'-fluorine atom is present,3 and the electrochemical and lead tetra-acetate oxidations of polyfluoroanilines seem likely to proceed by similar mechanisms

Decafluoroazobenzene is also obtained by the oxidation of pentafluoroaniline with bleaching powder in refluxing carbon tetrachloride. The yield (51%) is comparable with that obtained by the lead tetra-acetate procedure, the method is much more convenient, and the phenazine by-product is not formed. Azo-compounds are obtained similarly from 4H-tetrafluoroaniline (17%), from 2H-tetrafluoroaniline (52%), and from 2-bromotetrafluoroaniline (17%).

4H-Nonafluoroazobenzene is formed in low yield together with the symmetrical azo-compounds by oxidation with lead tetra-acetate of a mixture of pentafluoroaniline and 4H-tetrafluoroaniline, but oxidation of a mixture of pentafluoro- and 2H-tetrafluoro-aniline with bleaching powder gave an inseparable mixture.

Reactions with Reducing Agents.—Reduction of decafluoroazobenzene with zinc and ammonium chloride in aqueous ethanol proceeds rapidly at room temperature to give an 80% yield of decafluorohydrazobenzene,

³ A. G. Hudson, A. E. Pedler, and J. C. Tatlow, Tetrahedron Letters, 1968, no. 17, 2143.

⁴ M. Wilkinson, Ph.D. Thesis, Manchester, 1966.

identical with a sample produced from decafluoroazoxybenzene and the same reductant.² The hydrazocompound is also obtained, in slightly higher yield, from the azo-compound and sodium dithionite. Decafluorohydrazobenzene and decafluoroazobenzene are each cleaved to pentafluoroaniline in moderate yields (63 and 57%, respectively) by aqueous hydriodic acid under reflux. This unorthodox reagent has been used before in the fluorocarbon field, to reduce pentafluorophenylhydrazine to the same aniline,⁵ and preliminary experiments indicated that it was more effective for cleavage of the fluoroaromatic azo-compounds than tin and hydrochloric acid.

A solution of octafluorophenazine in hexane is quickly reduced by aqueous hydriodic acid at room temperature to colourless octafluoro-5,10-dihydrophenazine (VI). This compound, prepared previously by catalytic



hydrogenation of the phenazine,³ shows an N–H stretching vibration at 2.88 μ m. and its u.v. spectrum demonstrates the lack of phenazine resonance. The dihydrophenazine becomes green and then violet on exposure to air, presumably owing to the formation of molecular complexes (' phenazhydrins ') ⁶ with octafluorophenazine, regenerated by spontaneous oxidation; indeed, octafluorophenazine is readily obtained (97%) by deliberate oxidation with air of an ethereal solution of the dihydrophenazine.

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octafluoroazobenzene (VII); this last compound is cleaved by hydriodic acid to give very good yields of

$$\begin{array}{c} p\text{-EtO} \cdot \mathrm{C_6F_4} \cdot \mathrm{N} \cdot \mathrm{N} \cdot \mathrm{C_6F_4} \cdot \mathrm{OEt} \text{-} p \xrightarrow[\mathrm{refiux}]{\mathrm{refiux}} p\text{-}\mathrm{HO} \cdot \mathrm{C_6F_4} \cdot \mathrm{NH_2} + \mathrm{EtI} \\ \mathrm{(VII)} \qquad 98\% \qquad 95\% \end{array}$$

iodoethane and 4-aminotetrafluorophenol, and similar preparation and cleavage of the previously reported 2 4,4'-dimethoxyoctafluoroazobenzene has been achieved.

The previously unobtainable ² 4-aminononafluoroazobenzene and nonafluoro-4-hydroxyazobenzene have been prepared by the use of alcoholic rather than ethereal solvents. Decafluoroazobenzene reacts with refluxing aqueous ethanolic ammonia to give the 4-aminocompound (VIII) (68%), starting material (24%), and other fluorine-containing compounds (8%), identified by analysis of the crude product by n.m.r. spectroscopy. Chromatography on alumina readily separates



the starting material and the major product (VIII) (characterised by reductive cleavage to tetrafluoro*p*-phenylenediamine and pentafluoroaniline), and also gives a more highly coloured by-product. This minor product shows N-H absorptions in its i.r. spectrum (at 2.85 and 2.99 μ m.) identical in position with those of 2-amino-4H,4'H-heptafluoroazobenzene (X), which it also resembles in colour; it is therefore probably

				Таві	LE 1								
		N.m.	r. spec	ctra of	the phe	nazines *	k						
Substituents	Chemical shifts (p.p.m.)					Coupling constants (moduli; in Hz)							
Octafluoro- (II)	δ <u>1</u> 75·6	δ <u>2</u> 73·5	δ_3 73.5	δ ₄ 75·6	δ_{5}	J _{1.2}	J _{1.3}	J1.4	J1.5	J 2.3	J 2, 4	J 3. 4	J 4.5
2H,7H-Hexafluoro- (III) 1H,6H-Hexafluoro- (IV)	52.8 (-8.05)	(-7.99) 48.0	45·8 74·7	$77.2 \\ 69.5$		(ca. 9.9) (9.9)	(7.5)	(3.0)	(ca. 9·9)	(6.9)		
2H,7H-Hexafluoro-5,10-dihydro-	`62·1 ´	(-6.34)	69.4	88.4	(6.74	l) (Ì0·8́)	` 2∙3́	Ì0∙7́	(1.5)	(10.8)	(7.2)	21.8	(1.5)
	*	For explat	natory	notes	see Expe	rimental	section						

Colourless products are also obtained from the other phenazines [(III) and (IV)] by reduction either with hydriodic acid or with zinc and ammonium chloride, but purification of the dihydro-compounds is difficult. A well resolved n.m.r. spectrum of 2H,7H-hexafluoro-5,10-dihydrophenazine has been obtained (Table 1), but the material was contaminated with the parent phenazine.

Reactions with Nucleophiles.—Decafluoroazobenzene reacts readily with ethoxide ion in refluxing ethanol to give 4-ethoxynonafluoroazobenzene, which reacts with a second mole of ethoxide to give 4,4'-diethoxy-

⁵ J. M. Birchall, R. N. Haszeldine, and A. R. Parkinson, J. Chem. Soc., 1962, 4966. 2-aminononafluoroazobenzene (IX). The 4H,4'H-compound itself (X) is obtained in high yield from aqueous alcoholic ammonia and 4H,4'H-octafluoroazobenzene, and characterised by hydriodic acid reduction to the (known) anilines.

Nonafluoro-4-hydroxyazobenzene is obtained [80% yield based on decafluoroazobenzene consumed (50%)] from the reaction of decafluoroazobenzene with potassium hydroxide in t-butyl alcohol.⁷ Cleavage of the

⁶ G. P. Ramage and J. K. Landquist, in 'The Chemistry of Carbon Compounds,' ed. E. H. Rodd, Elsevier, Amsterdam, 1959, vol. IV, 1386.

vol. IV, 1386. ⁷ Cf. J. M. Birchall and R. N. Haszeldine, J. Chem. Soc., 1959, 13.

	Ch	emical s	hifts of the	azobenz	enes (p.p.	m.)				
Substituents	δ_2	δ_3	δ_4	δ_5	δ_6	$\delta_{2'}$	δ3,	$\delta_{4'}$	$\delta_{5'}$	$\delta_{6'}$
Decafluoro- (I)	72.5	86.4	73.6	86.4	72.5					
4H,4'H-Octafluoro-	71.4	$62 \cdot 1$	(-7.76)	$62 \cdot 1$	71.4					
2H.2'H-Octafluoro-	(-7.66)	61.7	73.4	79 ·0	71.3					
2.2'-Dibromo-octafluoro-) (Br)	53.5	74.1	78.9	$73 \cdot 1$					
4H-Nonafluoro-	72.7	62.5	(-7.74)	62.5	72.7	73.9	86.4	74.0	86.7	73.9
4-Ethoxynonafluoro-	$73 \cdot 4$	$82 \cdot 1$	(EtO)	82.1	73.4	$73 \cdot 6$	87.9	$75 \cdot 4$	87.9	7 3·6
	or		• •		or	or				or
	73.6				73.6	73.4				$73 \cdot 4$
4.4'-Diethoxyoctafluoro- (VII)	75.7	83.4	(EtO)	83.4	75.7					
4-Aminononafluoro- (VIII) *	73.0	88.6	(NH,)	88.6	73.0	74.9	87.9	78.9	87.9	74.9
2-Amino-4H-4'H-heptafluoro-	(-7.82)	61.5	(-7.25)	78.0	72.9	74.5	$62 \cdot 9$	(-7.44)	$62 \cdot 9$	74.5
(A) Nonafluoro-4-hydroxy-	74.6	87.1	(OH)	87.1	74.6	74.4	87.2	76.6	87.2	74.4
Nonafluoro-4-phenylthio-	72.8	56.8	(PhS)	56.8	72.8	72.3	86.4	73.5	86.4	72.3
			* In	ethanol.						

TABLE 2

TABLE	3
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Coupling constants for the azobenzenes (moduli; Hz)

	oouj				(,			
Substituents	$J_{\frac{2.3}{+}}$	J _{2,5}	$J_{2,4}$	$J_{3,4}$	J 2, 6	J _{3,5}	J 4.5	J 4, 6	$J_{3.6}$	J 5.6
* Decafluoro- (I)	20.3	7.3	3.6	20.7	9.0	4.0	20.7	$3 \cdot 6$	7.3	20.3
* 4H.4'H-Octafluoro-	20.8	13.1	(7.5)	(10.4)	5.7	0.7	(10.4)	(7.5)	13.1	20.8
2H.2'H-Octafluoro-	(11.2)	(2.5)	$(8\cdot 2)$	20.6	(6.2)	$2 \cdot 2$	19.7	6.0	11.5	18.2
2.2'-Dibromo-octafluoro-	· · ·	· · ·	• •	$21 \cdot 8$		$2 \cdot 4$	19.2	$5 \cdot 2$	$9 \cdot 6$	19.2
* 4H-Nonafluoro-	20.8	13.1	(7.5)	(10.5)	5.7	0.8	(10.5)	(7.5)	$13 \cdot 1$	20.8
* 4-Ethoxynonafluoro-					Not measu	ırable	• •	. ,		
* 4.4'-Diethoxyoctafluoro- (VII)	a. 20.3	$ca. 7 \cdot 1$			ca. 7·9	ca.0			$ca. 7 \cdot 1$	ca. 20·3
* 4-Aminononafluoro- (VIII)	21.5	ca. 8			ca. 12	$<\!2$			ca. 8	21.5
2-Amino-4H.4'H-heptafluoro- (X)			(11.3)		4.3	(10.3)	(6.8)	13.7	20.6
* Nonafluoro-4-hydroxy-	/			· ·	Not mea	asurable		. ,		
* Nonafluoro-4-phenylthio-	21.7	11.3			5.7	$3 \cdot 0$			11.3	21.7
	1 or 3'	12'5	12'.4'	J 3'.4'	J 2'. 6'	J 3'. 5'	JA'.5'	I 4' 6'	I3' 6'	Ι _{5' 6'}
* 4H-Nonafluoro-	20.9	7.4	4.0	21.1	7.7	2.4	21.1	4.0	7.4	20.9
* 4-Ethoxynonafluoro-	200	• -	ca. 3.4	ca. 20.8			ca. 20.8	ca. 3.4	• •	200
* 4-Aminononafluoro- (VIII)	ca 21	ca 7.5	ca. 2	ca. 20.8	ca. 4	ca. 1	ca. 20.8	ca. 2	ca. 7.5	ca 21
2-Amino-4H 4'H-bentafluoro- (X)	20.1	12.1	(7.3)	(10.2)	4.0	0.7	(10.2)	(7.3)	12.1	20.1
* Nonafluoro-4-hydroxy-		~ *	()	20.6		•••	20.6	()		201
* Nonafluoro-4-phenylthio-	20.6	7.2	4.1	20.6	7.1	$2 \cdot 2$	20.6	4.1	7.2	20.6
ronandoro r phonyrano	-00	• -							• -	400

* AA'XX' and AA'PXX' systems: $J_{2,6}$ and $J_{3,5}$ are indistinguishable; $J_{2,3}$ and $J_{5,6}$ are of opposite sign to $J_{2,5}$ and $J_{3,6}$; similarly for $J_{2',6'}$ etc.

hydroxy-azo-compound with hydriodic acid gives 4-aminotetrafluorophenol and pentafluoroaniline.

Decafluoroazobenzene reacts with sodium benzenethiolate (2 equiv.) in refluxing methanol to give octafluoro-4,4'-bisphenylthioazobenzene (XI) in high yield (81% after purification). This compound and recovered starting material are also the main products when the azo-compound is treated with a deficiency of benzenethiolate ion, and only a low yield of the monophenylthio-compound is obtained. Treatment of the last compound with more benzenethiolate ion gives the same bisphenylthio-compound (XI), which yields 4Htetrafluoroaniline and diphenyl disulphide on treatment with hydriodic acid.

This cleavage of the sulphur compound contrasts with the cleavage of the dialkoxy-azo-compounds to the alkyl iodide and a phenol. Diaryl thioethers are usually inert to hydriodic acid,⁸ and the ready cleavage of a C-S bond in this case can be ascribed to stabilisation of the departing carbanion (XII), in the suggested Scheme shown, by the inductive effects of the fluorine atoms and of the protonated nitrogen atom. Protonation

8 R. C. Burwell, jun., Chem. Rev., 1954, 54, 615.

would cause the hydrazo- and amino-groups to be activating as well as the azo-group, but it is here arbitrarily assumed that cleavage of the thioether occurs before the reduction stage. The ability of the sulphur atom to accommodate more electrons in its valency shell



would be expected to facilitate a nucleophilic attack of the type shown.

Chemical proofs have thus been obtained for the structures of all the compounds derived from nucleophilic attack on the azo-compounds, and the n.m.r. spectra (Tables 2 and 3) of the products are completely consistent with the formulations given. All the u.v. spectra, except that of the very sparingly soluble octafluoro-4,4'-bisphenylthioazobenzene (XI), show typical azobenzene absorption at ca. 450 nm.

EXPERIMENTAL

Alumina for chromatography was Light's type A, 100-200 mesh. Known compounds were identified by i.r. spectroscopy and (where applicable) m.p. and mixed m.p. determination.

Oxidations with Lead Tetra-acetate .--- (a) Pentafluoroaniline. Lead tetra-acetate (25.0 g., 55 mmoles) was added to pentafluoroaniline (5.0 g., 27 mmoles) in benzene (150 ml.), and the mixture was heated under reflux for 1 hr. The resulting brown suspension was diluted with benzene (250 ml.), washed successively with aqueous 50% acetic acid, saturated aqueous sodium hydrogen carbonate, and water, and dried (MgSO₄). The solvent was evaporated off and the residue was dissolved in the minimum of hot benzene (30%) in light petroleum (b.p. 60-80°), and chromatographed on alumina. Elution with the same solvent gave orange decafluoroazobenzene (2.30 g., 48%), m.p. 138°; recrystallisation from carbon tetrachloride gave a pure sample (Found: C, 40.0; N, 7.5. Calc. for $C_{12}F_{10}N_2: \ C, \ 39.8; \ N, \ 7.7\%), \ m.p. \ 143^\circ \ (lit.,^2 \ 142-143^\circ).$ Elution was continued with benzene and yielded yellow octafluorophenazine (1.23 g., 28%), m.p. $230-232^{\circ}$, the i.r. spectrum of which was identical with that of a pure sample, m.p. 239° (lit., 3234°), obtained by recrystallisation from benzene-light petroleum (b.p. 80-100°) (Found: C, 44.5; N, 8.9. Calc. for $C_{12}F_8N_2$: C, 44.5; N, 8.6% $[\lambda_{\rm max},\,221$ (log ϵ 3.98), 258 (5.09), 369 (4.09), and 413 nm. (3.48); $\lambda_{infl.} 352 (3.70)$, 360 (3.96), and 390 nm. (3.64)].

(b) 4H-Tetrafluoroaniline. An identical procedure with lead tetra-acetate (30.0 g., 66 mmoles) and this amine (6.53 g., 40 mmoles) in benzene (150 ml.), followed by chromatographic separation, gave orange-red 4H,4'Hoctafluoroazobenzene (2.70 g., 42%), m.p. 119-120° (lit.,2 118°), unchanged on recrystallisation from light petroleum (b.p. 60-80°) (Found: C, 44·4; H, 0·8; N, 8·8. Calc. for C₁₂H₂F₈N₂: C, 44·2; H, 0·6; N, 8·6%), and 2H,7Hhexafluorophenazine (1.32 g., 23%), m.p. 205°, as bright yellow plates with a strong blue-green fluorescence in solution. The i.r. spectrum of the crude phenazine was identical with that of a pure specimen, m.p. 208°, obtained by recrystallisation from benzene-light petroleum (b.p. 60–80°) (Found: C, 50·1; H, 0·9; F, 39·3; N, 9·4. $C_{12}H_2F_6N_2$ requires C, 50·0; H, 0·7; F, 39·6; N, 9·7%) $\begin{bmatrix} \lambda_{max} & 259 \ (\log \ \varepsilon \ 5\cdot05), \ 344 \ (3\cdot42), \ 360 \ (3\cdot57), \ 385 \ (3\cdot33), \ 407 \ (3\cdot42), \ 427 \ (3\cdot29), \ and \ 432 \ nm. \ (3\cdot31); \ \lambda_{infl.} \ 216 \ (3\cdot89), \ \end{bmatrix}$ 256 (4.98), 329 (3.17), 354 (3.51), 402 (3.38), 412 (3.38), and 438 nm. (3.18)].

(c) 2H-*Tetrafluoroaniline*. The amine (0.653 g., 4.0 mmoles) and lead tetra-acetate (3.00 g., 6.6 mmoles) were heated under reflux in benzene (15 ml.) for 1 hr. The resulting mixture was treated as in (a), and elution of the chromatography column with benzene (50%) in light

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petroleum (b.p. 60—80°) gave an orange solid (0·28 g., 43%), m.p. 108—110°, which was recrystallised from light petroleum (b.p. 60—80°) to give needles of 2H,2'H-octa-fluoroazobenzene (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%) [λ_{max} . 226 (log ε 3·91), 334 (4·26), and 443 nm. (2·72); λ_{infd} . 326 (4·24), 346 (4·21), and 358 nm. (4·01)], m.p. 111—112°. Continued elution with ether gave pale yellow plates of 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%) [λ_{max} . 249 (log ε 5·07), 357 (4·01), and 364 nm. (4·01); λ_{infd} . 218 (4·07), 350 (3·93), and 385 nm. (3·51)], m.p. 186°, unchanged on recrystallisation from benzene-light petroleum.

(d) Pentafluoroaniline and 4H-tetrafluoroaniline. Pentafluoroaniline (1.00 g., 5.5 mmoles), 4H-tetrafluoroaniline (5.00 g., 30 mmoles), and lead tetra-acetate (23.0 g., 51 mmoles) were heated under reflux in benzene (150 ml.) for 30 min. The usual chromatographic work-up gave a mixture of azo-compounds (1.94 g.) and a phenazine fraction (0.68 g.), which was discarded. The azo-fraction was re-chromatographed, elution with carbon tetrachloride (20%) in light petroleum (b.p. 60-80°) giving crude nonafluoroazobenzene (0.24 g.) and crude octafluoroazobenzene (1.29 g.), identified by i.r. spectroscopy. The former product, m.p. 102-106°, was recrystallised three times from light petroleum (b.p. 60-80°) and yielded orange 4H-nonafluoroazobenzene (0.053 g.) (Found: C, 42.5; H, 0.8. C₁₂HF₉N₂ requires C, 41.9; H, 0.3%) $[\lambda_{max}]$ (ethanol) 302 (log $\varepsilon 4.24$) and 452 nm. (2.85); λ_{infl} 226 nm. (3.84)], m.p. 118.5-119°; the apparent inaccuracy of the analysis reflects the very small sample employed. The compound was characterised by its n.m.r. spectrum and by its i.r. spectrum, which was quite distinct from that of a mixture of deca- and octa-fluoroazobenzenes. The mass spectrum showed peaks at m/e 362, 344, and 326 [corresponding to $(C_6F_5)_2N_2, \quad C_6F_5 \cdot N_2 \cdot C_6F_4H,$ and $(HC_6F_4)_2N_2$, respectively] in intensities which indicated that the nonafluoro-compound contained not more than 2% of the symmetrical azo-compounds.

Oxidations with Bleaching Powder.—(a) Pentafluoroaniline. The amine (10.0 g., 55 mmoles) and bleaching powder (50.0 g.) were heated under reflux in carbon tetrachloride (120 ml.) for 3 hr. The solids were filtered off and washed with ether until colourless, and the combined filtrates were evaporated to low bulk (10—20 ml.) and allowed to cool. The resulting solid was washed with carbon tetrachloride and then with light petroleum (b.p. 30— 40°) to give decafluoroazobenzene (5.0 g., 51°).

(b) 2H-*Tetrafluoroaniline*. In a similar experiment, 2H-tetrafluoroaniline (5.00 g., 30 mmoles) and bleaching powder (12.5 g.) in carbon tetrachloride (60 ml.) yielded 2H, 2'H-octafluoroazobenzene (2.55 g., 52%).

(c) 4H-*Tetrafluoroaniline*. The aniline (0.50 g., 3.0 mmoles) and bleaching powder (2.5 g.) were heated under reflux in carbon tetrachloride (5 ml.) for 3 hr. The solids were filtered off and washed with ether until colourless, and the combined filtrates were evaporated to dryness. The coloured material so obtained was dissolved in benzene (30%) in light petroleum (b.p. 60-80°) and chromatographed on alumina, to give 4H,4'H-octafluoroazobenzene (0.085 g., 17%). No phenazine was obtained.

(d) 2-Bromotetrafluoroaniline. The aniline (9.0 g., 35 mmoles) (obtained by treatment of 2H-tetrafluoroaniline

with bromine in acetic acid ⁹) and bleaching powder (40 g.) were heated under reflux in carbon tetrachloride (100 ml.) for 6 hr. The mixture was filtered hot, and the solids were washed with ether until colourless. The combined filtrates were 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 dissolved in benzene (50%) in light petroleum (b.p. 60—80°) and chromatographed, to give 2,2'-dibromo-octafluoroazobenzene (1·6 g., 18%) (Found: C, 30·1; N, 6·0. C₁₂Br₂F₈N₂ requires C, 29·8; N, 5·8%) [λ_{max} 318 (log ε 4·09) and 467 nm. (2·66); λ_{infl} . 229 nm. (3·91)], m.p. 114·5—115° [from benzene-light petroleum (b.p. 60—80°)].

Decafluorohydrazobenzene.—Decafluoroazobenzene (2.00 g., 5.5 mmoles), zinc dust (6.0 g.), ammonium chloride (2.0 g.), water (5 ml.), and ethanol (50 ml.) were shaken in a stoppered flask until the red compound dissolved and the solution became colourless. The mixture was filtered and the filtrate was poured into water (ca. 100 ml.) and cooled, to give white crystals of decafluorohydrazobenzene (1.60 g., 80%), m.p. 61—63°; its i.r. spectrum, which contained a strong N-H singlet at 2.93 µm., was identical with that of an analytically pure specimen, m.p. 62—63° (lit.,² 57°), obtained by sublimation at 50—55° (bath) in vacuo (Found: C, 39.5; H, 0.6. Calc. for $C_{12}H_2F_{10}N_2$: C, 39.6; H, 0.6%).

In a second experiment, the azo-compound (2.00 g.) was heated under reflux in methanol (50 ml.), and sodium dithionite (4.6 g.; purity 85%) in water (25 ml.) was added during 5 min. The mixture became colourless after 10 ml. of the solution had been added. The product was isolated by steam-distillation and identified as decafluorohydrazobenzene (1.70 g., 85%).

Reduction of the Phenazines.—(a) Octafluorophenazine. The phenazine (10 mg., 0.031 mmole) in hexane (25 ml.) was shaken with aqueous 55% hydriodic acid (5 ml.) for 30 min. The mixture was then decolourised with solid sodium disulphite, the organic layer was dried (MgSO₄), and the solvent was evaporated to leave a white solid (10 mg., 99%), m.p. 189° (lit.,³ 186°), the presumed octafluoro-5,10-dihydrophenazine [λ_{max} 237 (log ε 4.60) and 317 nm. (3.31); λ_{infl} 257 nm. (3.83)]. The i.r. spectrum of this product showed a sharp N-H singlet at 2.88 µm. The substance was too sensitive towards oxidation for further work to be convenient; in air it quickly became green, then violet (presumably phenazhydrin-type molecular complexes).

Air was bubbled through the crude dihydrophenazine (0.50 g.) in ether (50 ml.) for 10 min.; the solution turned green and then yellow. The product was dried (MgSO₄), and evaporation of the solvent left octafluorophenazine (0.47 g., 97%).

(b) 2H,7H-Hexafluorophenazine. The phenazine (0.50 g., 1.74 mmole) was shaken in toluene (10 ml.) with aqueous 55% hydriodic acid (10 ml.) for 30 min. Potassium iodide was added to break up the resulting emulsion, and the mixture was decolourised with solid sodium disulphite and extracted with ether (50 ml.). The extract was dried (MgSO₄) and evaporated to yield a green solid (0.515 g.). Recrystallisation of this from ethanol and then from light petroleum (b.p. 80—100°) gave green needles (0.170 g.),

⁹ Cf. J. A. Castellano, J. Green, and J. M. Kauffman, J. Org. Chem., 1966, **31**, 821.

m.p. 224—226°, shown by n.m.r. spectroscopy to be 2H,7H-hexafluoro-5,10-dihydrophenazine (90%) contaminated with 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%); the product showed an N-H singlet at 2.89 μ m.

Treatment of the phenazine (0.20 g.) with zinc dust (1.5 g.) and ammonium chloride (0.50 g.) in ethanol (12.5 ml.) and water (1.25 ml.) at 20° for 15 min. yielded a sample of the crude dihydro-phenazine (0.16 g., 79%), m.p. 225—230°, with an i.r. spectrum identical with that of the sample already described.

(c) 1H,6H-Hexafluorophenazine. The phenazine (0.095 g., 0.33 mmole), zinc dust (1.0 g.), ammonium chloride (0.50 g.), ethanol (10 ml.), and water (1 ml.) were shaken at 20° for 15 min. and then extracted with ether (2 \times 20 ml.). The extracts yielded presumed 1H,6H-hexafluoro-5,10-dihydrophenazine (0.085 g., 89%) as pale blue needles, m.p. 174—178°, showing N–H absorption at 2.87 μ m.

4-Ethoxynonafluoroazobenzene.-Potassium ethoxide (5.5 mmoles) in ethanol (22 ml.) was added during 1 hr. to refluxing ethanol (40 ml.) containing decafluoroazobenzene (2.00 g., 5.5 mmoles), and the mixture was heated under reflux for a further 1 hr. The mixture was poured into water (400 ml.) and extracted with ether $(3 \times 50$ ml.). The extracts were dried (MgSO₄) and evaporated, and the resulting orange solid (2.20 g.), m.p. 70-80°, was dissolved in benzene (25%) in light petroleum (b.p. 60-80°) and chromatographed on alumina. Three bands developed, yielding respectively (i) decafluoroazobenzene (0.26 g.), (ii) crude 4-ethoxynonafluoroazobenzene (1.20 g.), m.p. 74-76°, containing decafluoroazobenzene and 4,4'-diethoxyoctafluoroazobenzene, and (iii) (elution with ether) crude 4,4'-diethoxyoctafluoroazobenzene (0.51 g.), m.p. 101-103°; all fractions were identified by i.r. spectroscopy. The product from band (ii) was recrystallised twice from cyclohexane to give orange 4-ethoxynonafluoroazobenzene (Found: C, 43.1; H, 1.6; N, 7.6. C14H5F9N2O requires C, 43·3; H, 1·3; N, 7·2%) $[\lambda_{max}$ 323 (log ε 4·30) and 449 nm. (3·04); λ_{infl} 213 (3·92) and 236 nm. (3·79)], m.p. 82-82.5°.

4,4'-Diethoxyoctafluoroazobenzene.—(a) From decafluoroazobenzene. Sodium ethoxide (15·2 mmoles) in ethanol (70 ml.) was added during 30 min. to decafluoroazobenzene (2·5 g., 6·9 mmoles) in refluxing ethanol (100 ml.). The mixture was heated under reflux for a further $2\frac{1}{2}$ hr., water (250 ml.) was added, and the mixture was extracted with ether (100 + 50 ml.), yielding 2·8 g. of crude product, m.p. ca. 107°. Recrystallisation from cyclohexane gave 4,4'-diethoxyoctafluoroazobenzene (1·68 g., 59%) (Found: C, 46·5; H, 1·3. C₁₆H₁₀F₈N₂O₂ requires C, 46·5; H, 1·1%) [λ_{max} . 333 (log ε 4·37) and 453 nm. (3·18); λ_{infl} . 212 (3·96) and 231 nm. (3·85)], m.p. 113·5—114·5°.

(b) From 4-ethoxynonafluoroazobenzene. Potassium ethoxide (1.37 mmole) in ethanol (11 ml.) was added during 30 min. to the monoethoxy-compound (0.50 g., 1.25 mmole) in refluxing ethanol (20 ml.). Heating was continued for a further 30 min., and the mixture was then poured into water and extracted with ether to give 4,4'-diethoxyoctafluoroazobenzene (0.55 g., 100%).

4-Aminononafluoroazobenzene.—Decafluoroazobenzene (2.00 g., 5.5 mmoles), ethanol (75 ml.), and aqueous ammonia ($d \ 0.88$; 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 × 25 ml.). The extracts were washed with water, dried (MgSO₄), and evaporated, to leave an orange product (2·0 g.); this was chromatographed on alumina; elution with ether gave decafluoroazobenzene (0·66 g., 33% recovery) and the crude product (1·34 g.), m.p. ca. 133°. Three recrystallisations of the latter from cyclohexane gave 4-aminononafluoro-azobenzene (0·91 g., 68% based on decafluoroazobenzene consumed) (Found: C, 40·5; H, 0·8; N, 11·7. C₁₂H₂F₉N₂ requires C, 40·2; H, 0·6; H, 11·7%) [λ_{max} . 214 (log ε 3·95), 352 (4·37), and 438 nm. (3·37); λ_{infl} . 230 nm. (3·88)], m.p. 139·5°, showing an N-H doublet at 2·84 and 2·94 µm.

In a second experiment, the crude product was shown by n.m.r. spectroscopy to contain 4-aminononafluoroazobenzene (ca. 68%), decafluoroazobenzene (24%), and other fluorine-containing compounds (7%). Repeated chromatography of this material yielded a crimson product, probably 2-aminononafluoroazobenzene, m.p. ca. 100—110°, eluted just before the decafluoroazobenzene, but satisfactory purification and characterisation was not achieved.

2-Amino-4H,4'H-heptafluoroazobenzene.—4H,4'H-Octafluoroazobenzene (4·0 g., 12·3 mmoles), ethanol (80 ml.), and aqueous ammonia (d 0·88; 25 ml.) were heated under reflux for 21 hr., and the resulting mixture was poured into water and extracted with ether to yield a deep red solid. This was chromatographed in benzene (50%) in light petroleum (b.p. 60—80°) and gave starting material (0·10 g., 3%) and a solid (3·1 g.), m.p. 163—165°, which was recrystallised from light petroleum (b.p. 80—100°; 200 ml.) to give scarlet crystals of 2-amino-4H,4'H-heptafluoroazobenzene (2·4 g., 61%) (Found: C, 44·8; H, 1·4; N, 13·1. C₁₂H₄F₂N₃ requires C, 44·6; H, 1·2; N, 13·0%) [λ_{max.} 320 (log ε 4·10) and 445 nm. (3·71); λ_{infl.} 228 nm. (4·03)], m.p. 168—169°.

Nonafluoro-4-hydroxyazobenzene.-Potassium hydroxide (0.41 g., 7.3 mmoles), t-butyl alcohol (60 ml.), and decafluoroazobenzene (2.00 g., 5.5 mmoles) were heated under reflux for 30 min. The mixture was poured into water (200 ml.), the alcohol was distilled out, and the residue was acidified to pH 3 with concentrated hydrochloric acid and extracted with ether (3 imes 50 ml.). The extracts were washed with water $(2 \times 20 \text{ ml.})$, dried (MgSO₄), and evaporated, and the resulting purple solid was chromatographed on silica (B.D.H. reagent grade, precipitated silica; neither alumina nor chromatographic silica gave a good separation). Elution with benzene gave decafluoroazobenzene (1.00 g., 50% recovery), a brown solid (0.80 g., 80% based on decafluoroazobenzene consumed), m.p. 156-159°, and a dark brown solid (0.08 g.), m.p. 208-210°. The last material could not be purified, but the solid of m.p. 156-159° was recrystallised from a large volume of water to give nonafluoro-4-hydroxyazobenzene (Found: C, 40.2; H, 0.4; F, 48.0. C12HF9N2O requires C, 40.0; H, 0.3; F, 47.5%) [λ_{max} , 321 (log ε 4.29) and 450 nm. (3.04); λ_{infl} , 211 (3.90), 219 (3.87), and 352 nm. (4.03)] as a pale yellow powder, m.p. 164°. The colour of this compound was due to its state of fine subdivision; it was red in solution. Its i.r. spectrum shows O-H absorption at 2.92 µm.

Nonafluoro-4-phenylthioazobenzene.—Sodium benzenethiolate (6.8 mmoles) in methanol (250 ml.) was added during 18 hr. to decafluoroazobenzene (3.50 g., 9.7 mmoles)

¹⁰ G. M. Brooke, J. Burdon, M. Stacey, and J. C. Tatlow, *J. Chem. Soc.*, 1960, 1768.

J. Chem. Soc. (C), 1970

in refluxing methanol (100 ml.). The orange solid (1.00 g.), m.p. 190-195°, which was deposited on cooling, was filtered off and identified by comparison of its i.r. spectrum with that of the sample described later as impure octafluoro-4,4'-bisphenylthioazobenzene. The filtrate was diluted with water (350 ml.) and extracted with ether $(2 \times 200$ ml.), and the extracts were washed with water (3 \times 50 ml.) and dried (MgSO₄). The product from the extraction (4.10 g.) was chromatographed on alumina, and elution with hot benzene (33%) in light petroleum (b.p. 60-80°) gave decafluoroazobenzene (0.87 g., 25% recovery), m.p. 135—138°, and an orange solid (0.86 g.). The latter was recrystallised three times from light petroleum (b.p. $100-120^{\circ}$) to give nonafluoro-4-phenylthioazobenzene (0.20 g., 6% based on decafluoroazobenzene consumed) (Found: C, 47.8; H, 1.3; N, 6.5. C₁₈H₅F₉N₂S requires C, 47.8; H, 1·1; N, 6·2%) $[\lambda_{max}$ 303 (log ε 4·16), 344 (4·13), and 459 nm. (3·15); $\lambda_{infl.}$ 216 (4·21) and 235 nm. (4·03)] as brickred needles, m.p. 111-112°.

Octafluoro-4,4'-bisphenylthioazobenzene.—(a) From decafluoroazobenzene. Sodium benzenethiolate (17 mmoles) in methanol (40 ml.) was added during 30 min. to decafluoroazobenzene (3.07 g., 8.7 mmoles) in refluxing methanol (100 ml.). Heating was continued for a further 2.5 min., and the mixture was then poured into water (150 ml.). The resulting precipitate (4.73 g.), m.p. 202—206°, was recrystallised from a large volume of light petroleum (b.p. 100—120°) to give orange needles of octafluoro-4,4'bisphenylthioazobenzene (Found: C, 53.1; H, 1.8; N, 5.4. C₂₄H₁₀F₈N₂S₂ requires C, 53.1; H, 1.8; N, 5.2%) [λ_{max} . (ethanol) 246 and 367 nm. (very sparingly soluble)], m.p. 208.5—210°.

(b) From nonafluoro-4-phenylthioazobenzene. Sodium benzenethiolate (2.0 mmoles) in methanol (50 ml.) was added during 20 min. to the azo-compound (0.0914 g., 2.0 mmoles) in refluxing methanol (20 ml.), and heating was continued for 5 min. more. The mixture was poured into water (50 ml.), and the resulting precipitate (0.144 g.) was recrystallised from light petroleum (b.p. $100-120^{\circ}$) to give the 4,4'-bisphenylthio-compound (0.059 g., 54°_{0}).

Reductive Cleavage of the Azo-compounds.—(a) Decafluoroazobenzene. The azo-compound (2.00 g., 5.5 mmoles) and aqueous 55% hydriodic acid (15 ml.) were heated under reflux for 3 hr. and then diluted with water (100 ml.), decolourised with solid sodium disulphite, and neutralised with solid sodium carbonate. Steam-distillation gave pentafluoroaniline (1.15 g., 57%), m.p. 29—31° (lit.,¹⁰ 33.5—35°), identified by i.r. spectroscopy.

(b) Decafluorohydrazobenzene. A similar experiment with the hydrazo-compound (2.00 g., 5.5 mmoles) and aqueous 55% hydriodic acid (10 ml.) gave pentafluoro-aniline (1.28 g., 63%).

(c) 4,4'-Diethoxyoctafluoroazobenzene. The azo-compound (2.00 g., 4.8 mmoles) and aqueous 55% hydriodic acid (10 ml.) were boiled for 1 hr. under a partial reflux condenser containing boiling benzene. The material passing through the condenser was collected, dried (MgSO₄), and identified as iodoethane (1.43 g., 95%) by i.r. spectroscopy. The residue in the vessel was diluted with water (to 100 ml.), decolourised with sodium disulphite, and neutralised with sodium carbonate. Ether extraction (5 × 20 ml. + 10 × 10 ml.) yielded 4-aminotetrafluorophenol (1.72 g., 98%), m.p. 177–178° (decomp.), identified by i.r. spectroscopy.

were carried out rapidly (discolouration occurred if the product was kept in contact with the hot solution) and vielded a pure sample (Found: C, 40.0; H, 2.0; N, 7.9. Calc. for C₆H₃F₄NO: C, 39.8; H, 1.7; N, 7.7%), m.p. 180—181° (decomp.) (lit.,¹¹ 177.5—178°). This compound was further identified by conversion into fluoranil (87% vield) on treatment with nitric acid.¹¹

(d) 4-Aminononafluoroazobenzene. The amino-azo-compound (1.00 g., 2.8 mmoles) was heated under reflux with aqueous 55% hydriodic acid (10 ml.) for 2 hr. Iodine was removed with solid sodium disulphite, and the pH was adjusted to 5 with sodium carbonate. The mixture was diluted with water (to 40 ml.) and extracted with ether $(10 + 5 \times 5 \text{ ml.})$ and the extracts were dried (MgSO₄). Removal of the ether by careful distillation left a gummy residue (1.14 g.), shown by i.r. spectroscopy to consist of pentafluoroaniline and tetrafluoro-p-phenylenediamine. The mixture was recrystallised from cyclohexane (25 ml.) to give tetrafluoro-p-phenylenediamine (0.32 g., 63%) as colourless needles, m.p. 137° (lit.,¹² 143.5-144°), identified by i.r. spectroscopy and by conversion into fluoranil (59%)yield) on treatment with nitric acid. The mother liquor was concentrated by careful distillation and yielded pentafluoroaniline (0.36 g., 71%), shown by i.r. spectroscopy to contain a little of the diamine.

(e) 2-Amino-4H,4'H-heptafluoroazobenzene. The azocompound (0.40 g., 1.24 mmole) and aqueous 55% hydriodic acid (5.0 ml.) were heated under reflux for 30 min. Decolourisation and neutralisation of the solution, followed by extraction with ether, yielded a colourless solid (0.36 g.), which was recrystallised from light petroleum (b.p. 30-40°) and yielded 3,4,6-trifluoro-o-phenylenediamine (0.099 g., 48%), m.p. 70-72° (lit., 13 75°). This compound was characterised by the preparation of its benzil derivative, 5,6,8-trifluoro-2,3-diphenylquinoxaline (Found: C, 71.4; H, 3·4. Calc. for $C_{20}H_{11}F_3N_4$: C, 71·4; H, 3·3%), m.p. 167-168° (from ethanol) (lit.,¹³ 169.5-170°).

(f) Nonafluoro-4-hydroxyazobenzene. The hydroxy-azocompound (0.60 g., 1.67 mmole) was heated under reflux with aqueous 55% hydriodic acid (6.0 ml.) for 1 hr. Decolourisation, neutralisation, and extraction with ether yielded a cream-coloured solid (0.54 g.) shown to consist of 4-aminotetrafluorophenol and pentafluoroaniline by i.r. spectroscopy. Recrystallisation from trichloroethylene (20 ml.) gave the aminophenol (0.24 g., 80%), and the mother liquor was extracted with concentrated hydrochloric acid (3 imes 3 ml.). The extract was basified with

aqueous potassium hydroxide, and extraction with ether $(5 + 3 \times 3 \text{ ml.})$ then gave pentafluoroaniline (0.14 g., 47%).

(g) Octafluoro-4,4'-bisphenylthioazobenzene. The azocompound (0.50 g., 0.92 mmole) was heated under reflux with aqueous 55% hydriodic acid (5.0 ml.) for 30 min. The mixture was diluted with water (10 ml.), decolourised with sodium disulphite, and extracted with dichloromethane (10 + 2 ml.); the aqueous layer was neutralised with sodium carbonate and extracted again with dichloromethane (5 + 2 ml.). The combined extracts were dried $(MgSO_4)$ and yielded a yellow oil (0.45 g.), which was chromatographed on alumina to give diphenyl disulphide (0.20 g., 98%), m.p. 51° (lit., 14 61°), eluted with light petroleum, and 4H-tetrafluoroaniline (0.18 g., 58%), m.p. ca. 21° (lit.,¹⁰ 23.5-26.5°), eluted with ether; both products were identified by i.r. spectroscopy.

Spectroscopic Data.—N.m.r. spectra (Tables 1, 2, and 3) were measured for solutions in tetrahydrofuran with a Perkin-Elmer R10 instrument; ¹⁹F spectra were measured at 54.46 MHz and chemical shifts are relative to external trifluoroacetic acid; ¹H spectra were measured at 60.00 MHz and are relative to internal tetramethylsilane. Values shown in parentheses are those involving 'H nuclei; the remainder involve only ¹⁹F nuclei. Coupling constants not shown could not be determined from the spectra obtained. Analyses are based on accepted procedures, and assignments of chemical shifts and coupling constants are in accord with previously reported values for these parameters in polyfluoroarenes.¹⁵ Assignments given in Table 1 are based partly on analogy with the well resolved spectrum obtained from 5,6,8-trifluoro-2,3-diphenylquinoxaline, which showed δ_5 78.6, δ_6 48.5, δ_7 (-7.64), and δ_8 56.4 p.p.m., with $|J_{5.6}|$ 19.5, $|J_{6.7}|$ (10.2), $|J_{7.8}|$ (11.3), $|J_{5,7}|$ (6.8), $|J_{5,8}|$ 18.4, and $|J_{6,8}|$ 2.2 Hz.

U.v. spectra were measured (in hexane, except where otherwise stated) over the range 210-800 nm. with a Unicam SP 700 instrument. I.r. spectra (mulls in Nujol and hexachlorobutadiene) were recorded with a Perkin-Elmer No. 21 instrument.

We thank Pennwalt Corporation for a grant, and I. I. O. Allinson and M. G. Barlow for assistance with the interpretation of n.m.r. spectra.

[9/1134 Received, July 4th, 1969]

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