

**472. Aromatic Polyfluoro-compounds. Part XXIII.<sup>1</sup> Polyfluoro-azo-, -azoxy-, and -hydrazo-benzenes**

By J. BURDON, C. J. MORTON, and D. F. THOMAS

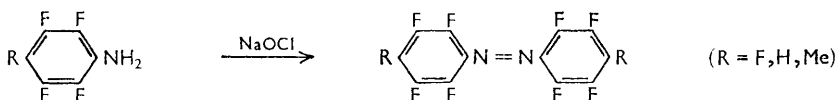
Polyfluoroazo-compounds ( $\text{RC}_6\text{F}_4\cdot\text{N} = \text{N}\cdot\text{C}_6\text{F}_4\text{R}$ ;  $\text{R} = p\text{-H, } p\text{-F, } p\text{-Me}$ ) have been prepared by oxidation of the corresponding anilines ( $\text{RC}_6\text{F}_4\cdot\text{NH}_2$ ) with aqueous sodium hypochlorite. Pyrolysis of penta- and 2,3,5,6-tetra-fluoronitrosobenzene gave deca- and 4*H*,4'*H*-octa-fluoroazoxybenzene. Reduction of the azo-compounds with hydrogen and palladium gave hydrazo-compounds. Decafluoroazobenzene reacted with methoxide with replacement, successively, of the 4,4',2-, and 2'-fluorines; and with lithium aluminium hydride to give decafluorohydrazobenzene and 4*H*,4'*H*-octafluoro-hydrazo- and azo-benzene. Methoxide replaced the 4- and 4'-fluorines of decafluoro-azoxybenzene.

In a recent Paper,<sup>2</sup> Wall and his co-workers described the oxidation of pentafluoroaniline to decafluoroazoxybenzene by means of peracetic acid; they also claimed to have reduced the azoxy-compound to decafluoroazobenzene. We have repeated this work and confirmed the azoxy preparation, but it is clear from the melting points of the compounds concerned that Wall's decafluoroazobenzene is, in fact, decafluorohydrazobenzene.

<sup>1</sup> Part XXII, J. Burdon, P. L. Coe, and M. Fulton, *J.*, 1965, 2094.

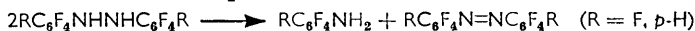
<sup>2</sup> L. A. Wall, W. J. Pummer, J. E. Fearn, and J. M. Antonucci, *J. Res. Nat. Bur. Stand.*, 1963, **67A**, 481.

We have now prepared decafluoroazobenzene (25% yield) and two other polyfluoroazo-compounds by what promises to be a general method for symmetric polyfluoroazo-compounds: this is the oxidation of the corresponding anilines with aqueous sodium hypochlorite; the reagent has been used before<sup>3</sup> in the non-fluorine field. Oxidation of pentafluoroaniline with sodium hypobromite gave a similar yield, but potassium permanganate gave only 3%.



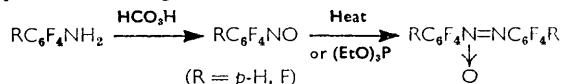
Attempts to prepare decafluoroazobenzene by the condensation of pentafluoroaniline and pentafluoronitrosobenzene led to a mixture of at least eleven products; nucleophilic replacement as well as condensation must have occurred.

Reduction of polyfluoroazo-compounds with tin and hydrochloric acid cleaved them to the corresponding anilines. With hydrogen and palladium, hydrazo-compounds were formed. Decafluorohydrazobenzene is more stable to oxidation than hydrazobenzene, but it still decomposed in air, presumably to the azo-compound. Both decafluoro- and 4*H*,4'*H*-octafluorohydrazobenzene decomposed to the corresponding azo-compounds (and probably to the anilines as well) on being heated to 170°. This reaction also occurs<sup>4</sup> with hydrazobenzene, but at lower temperatures.



4*H*,4'*H*- and 4,4'-dimethoxy-octafluoroazobenzene (II) gave the corresponding azoxy-compounds on treatment with peroxytrifluoroacetic acid, the latter more readily than the former. Decafluoroazobenzene, however, was unaffected by this reagent and by peracetic, performic, and fuming nitric acids. This order of oxidation, and the much greater resistance to oxidation of decafluoroazobenzene than that of azobenzene (which is oxidised<sup>5</sup> even by peracetic acid, the weakest of the reagents) is readily understandable; the electronegative fluorine substituents will render the electron-abstraction necessary for the oxidation more difficult. The greater stability of the polyfluorohydrazo-compounds mentioned earlier can be attributed to the same factor. As decafluoroazobenzene is unaffected by peracetic acid, Wall's conversion<sup>2</sup> of pentafluoroaniline into decafluoroazoxybenzene cannot have proceeded *via* the azo-compound. Condensations of the classical type, perhaps between pentafluoronitrosobenzene and pentafluorophenylhydroxylamine, may have occurred, although in view of the complexity of the pentafluoroaniline-pentafluoronitrosobenzene reaction, other mechanisms ought to be considered.

We have established other routes to decafluoroazoxybenzene from pentafluoronitrosobenzene. The residue remaining after the preparation<sup>6</sup> of pentafluoronitrosobenzene has now been found to be the azoxy-compound (17% yield). It might not have been produced during the actual oxidation of pentafluoroaniline with performic acid, but during working-up, since we have also shown that pyrolysis of the nitroso-compound gives the azoxy-compound. This type of pyrolytic conversion was discovered<sup>7</sup> many years ago in another field and the mechanism is unknown. Pentafluoronitrosobenzene has also been converted into the azoxy-compound (80% yield) with triethyl phosphite, a reagent introduced for this purpose by Bunyan and Cadogan.<sup>8</sup>



Hydrogenation of decafluoroazoxybenzene gave decafluorohydrazobenzene.

<sup>3</sup> E. Bamberger and F. Tschirner, *Ber.*, 1898, **31**, 1523.

<sup>4</sup> J. Biehringer and A. Busch, *Ber.*, 1903, **36**, 339.

<sup>5</sup> A. Angeli, *Atti R. Accad. Lincei*, 1910, **19**, 793 (*Brit. Abs.*, 1910, **98**, i, 645).

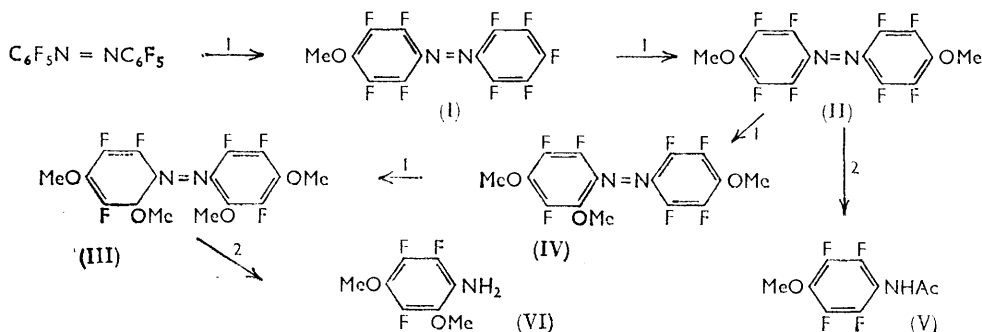
<sup>6</sup> G. M. Brooke, J. Burdon, and J. C. Tatlow, *Chem. and Ind.*, 1961, 832.

<sup>7</sup> E. Bamberger, *Ber.*, 1902, **35**, 1606.

<sup>8</sup> P. J. Bunyan and J. I. G. Cadogan, *Proc. Chem. Soc.*, 1962, 78.

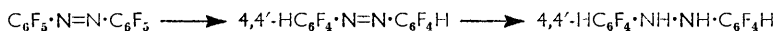
4*H*,4'*H*-Octafluoroazoxybenzene has also been prepared by the first route; it was a by-product in the oxidation of 2,3,5,6-tetrafluoroaniline to 2,3,5,6-tetrafluoronitrosobenzene. It is of interest that this nitroso-compound is colourless in the solid state and therefore dimeric, whereas pentafluoronitrosobenzene is green and monomeric.<sup>6</sup>

The only sequence of nucleophilic replacement reactions which has been carried out satisfactorily on decafluoroazobenzene is that with methoxide.



Treatment of the azo-compound with one and two equivalents of sodium methoxide in methanol gave the mono- and di-methoxy-compounds (I) and (II), respectively. Further treatment of the dimethoxy-compound (II) gave a mixture of the tri- and tetramethoxy-compounds (III) and (IV). As the dimethoxy-compound could be made from the mono-compound, all the methoxy-compounds are related. Reductive cleavage of the dimethoxy-compound gave *N*-acetyl 2,3,5,6-tetrafluoro-*p*-anisidine (V) which has also been synthesised from 4-amino-2,3,5,6-tetrafluorophenol, whose structure was established<sup>9</sup> by oxidation to tetrafluoro-*p*-benzoquinone. This demonstrates that the initial positions of nucleophilic attack in decafluoroazobenzene were 4,4'. The proton magnetic resonance spectrum of the tetramethoxy-compound (III) showed<sup>10</sup> that one type of methoxy-group was adjacent to two *ortho*-fluorines and the other to one, thus establishing that the structures of the tri- and tetra-methoxy-compounds (III) and (IV) are as shown. Also, reduction of the tetra-methoxy-compound (III) gave the dimethoxy-aniline (VI), a substance we have obtained by another route,<sup>11</sup> and from which we have independent proton magnetic resonance evidence for the same structure.

The only other example of nucleophilic replacement that we have found with decafluoroazobenzene occurs in its reaction with lithium aluminium hydride. The major reaction was reduction to decafluorohydrazobenzene (a reaction that proceeds much more slowly in the non-fluorine field<sup>12</sup>) but some evidence for the presence of 4*H*,4'*H*-octafluorohydrizo- and -azo-benzene was also obtained. Since decafluorohydrazobenzene itself did not react with lithium aluminium hydride under the conditions employed, the following reaction sequence must have occurred to some extent:



No definite results were obtained with any other nucleophile and decafluoroazobenzene. Two equivalents of dimethylamine gave at least 15 products, as indicated by column chromatography, and two of methyl-lithium at least four. Only tars were obtained from reactions with hydrazine, hydroxide ion, and ammonia. Since the reaction with ammonia

<sup>9</sup> G. M. Brooke, E. J. Forbes, R. D. Richardson, and J. C. Tatlow, Part XXI, *J.*, 1965, 2088.

<sup>10</sup> J. Burdon, *Tetrahedron*, 1965, in the press.

<sup>11</sup> J. G. Allen, J. Burdon, and J. C. Tatlow, *J.*, 1965, 1045.

<sup>12</sup> R. F. Nystrom and W. G. Brown, *J. Amer. Chem. Soc.*, 1948, **70**, 3738; F. Bohlmann, *Chem. Ber.*, 1952, **85**, 390.

proceeded at room temperature, this indicates that decafluoroazobenzene is much more reactive towards nucleophiles than hexafluorobenzene, which requires temperatures of over 150° to react.<sup>13</sup> This is hardly surprising in view of the known<sup>14</sup> activation caused by the phenylazo-group.

Decafluoroazoxybenzene reacted with sodium methoxide to give octafluoro-4,4'-dimethoxyazoxybenzene, as was shown by oxidation of the corresponding azo-compound to the same material.

4*H*,4'*H*-Octafluoroazobenzene also gave a dimethoxy-compound with methoxide. The proton magnetic resonance spectrum of this compound suggested that the aromatic proton was adjacent to two *ortho*-fluorines and the methoxy-group to one; this is only consistent with 4*H*,4'*H*-hexafluoro-2,2'-dimethoxyazobenzene.

In their reactions with methoxide, therefore, decafluoroazo- and -azoxy-benzenes are behaving as do most other C<sub>6</sub>F<sub>5</sub>X compounds in that the fluorine *para* to X (here, X is C<sub>6</sub>F<sub>5</sub>N=N- or C<sub>6</sub>F<sub>5</sub>N=N-) is the one most easily replaced.<sup>15</sup> It is reasonable that the



third fluorine to be replaced in decafluoroazobenzene should be the one *ortho* to the powerful electron-attracting pentafluorophenylazo-group. In view of our recent finding<sup>11</sup> that pentafluoronitrobenzene reacts with amines mainly at the position *ortho* to the nitro-group and with methoxide mainly at the position *para*, the position of attack of methoxide on the azo- and azoxy-compounds might not be the only possible one. With pentafluoronitrobenzene, we attributed the predominant *ortho* attack to hydrogen-bonding between the nitro-group and the incoming amine nucleophile; such bonding is clearly possible with the azoxy-compound.

#### EXPERIMENTAL

*Preparation of Polyfluoroazo-compounds.*—(a) *Decafluoroazobenzene.* A mixture of pentafluoroaniline<sup>13</sup> (10.0 g.) and aqueous sodium hypochlorite (360 ml., 10–14% w/v available chlorine) was stirred vigorously for 4 hr. at room temperature. The crude product (4 g.) was isolated by ether-extraction (1 × 200 ml.), washed with water to remove traces of sodium chloride, and crystallised from ethanol to give the orange *decafluoroazobenzene* (2.5 g.), m. p. 142–143° (Found: C, 39.4; H, 0.2; N, 7.4. C<sub>12</sub>F<sub>10</sub>N<sub>2</sub> requires C, 39.8; H, 0.0; N, 7.7%), λ<sub>max.</sub> (EtOH) 262 mμ (log ε 4.4), 308 mμ (log ε 4.3), and 420 mμ (log ε 4.2), λ<sub>infl.</sub> 220 mμ (log ε 4.2).

(b) 4*H*,4'*H*-Octafluoroazobenzene. 2,3,5,6-Tetrafluoroaniline<sup>13</sup> (2.4 g.) was oxidised, as in (a), with aqueous sodium hypochlorite (150 ml.) for 2 hr. to give 4*H*,4'*H*-octafluoroazobenzene (1.2 g.), m. p. 118° (from ethanol) (Found: C, 44.7; H, 0.6. C<sub>12</sub>H<sub>2</sub>F<sub>8</sub>N<sub>2</sub> requires C, 44.2; H, 0.6%), λ<sub>max.</sub> (EtOH) 262 mμ (log ε 4.3), 304 mμ (log ε 4.0), and 420 mμ (log ε 3.4), λ<sub>infl.</sub> 236 mμ (log ε 4.0).

(c) Octafluoro-4,4'-dimethylazobenzene.—2,3,5,6-Tetrafluoro-*p*-toluidine<sup>16</sup> (0.7 g.) was oxidised with aqueous sodium hypochlorite (35 ml.) to give orange needles of octafluoro-4,4'-dimethylazobenzene (0.4 g.), m. p. 150° (Found: C, 47.3; H, 1.9. C<sub>14</sub>H<sub>6</sub>F<sub>8</sub>N<sub>2</sub> requires C, 47.5; H, 1.7%).

*Oxidation of Polyfluoroazo-compounds.*—(a) Octafluoro-4,4'-dimethoxyazobenzene (II). A mixture of hydrogen peroxide (89%; 8 ml.) and trifluoroacetic anhydride (5 ml.) was added to a solution of the azo-compound (II) (0.75 g.) in methylene chloride (30 ml.). The red solution was refluxed for 15 min., when it had become yellow, and then poured into water. Evaporation of the dried (MgSO<sub>4</sub>) organic layer left octafluoro-4,4'-dimethoxyazoxybenzene (0.64 g.), m. p. 130° (yellow needles from methanol) (Found: C, 41.5; H, 1.9. C<sub>14</sub>H<sub>6</sub>F<sub>8</sub>N<sub>2</sub>O<sub>3</sub> requires C, 41.8; H, 1.5%).

(b) 4*H*,4'*H*-Octafluoroazobenzene. The azo-compound (1.16 g.) in methylene chloride (10 ml.) was refluxed with hydrogen peroxide (89%; 5 ml.) in trifluoroacetic anhydride (12 ml.). Even after 50 hr. the reaction mixture was still red. Isolation as in (a) gave an oil (1.02 g.), which deposited orange crystals (0.37 g.), m. p. 116° (from ethanol), alone and on admixture with the

<sup>13</sup> G. M. Brooke, J. Burdon, M. Stacey, and J. C. Tatlow, *J.*, 1960, 1768.

<sup>14</sup> G. M. Badger, J. W. Cook, and W. P. Vidal, *J.*, 1947, 1109.

<sup>15</sup> J. C. Tatlow, *Endeavour*, 1963, 22, 89.

<sup>16</sup> J. Burdon, W. B. Hollyhead, C. R. Patrick, and J. C. Tatlow, unpublished work.

starting material. The liquid filtrate was purified by passage through a column of alumina with light petroleum (b. p. 60—80°) as eluent to give 4H,4'H-octafluoroazoxybenzene (0.47 g.), m. p. 52° (from methanol) (Found: C, 42.2; H, 0.7.  $C_{12}H_2F_8N_2O$  requires C, 42.1; H, 0.6%),  $\lambda_{\max}$  (EtOH) 232  $m\mu$  ( $\log \epsilon$  3.9) and 288  $m\mu$  ( $\log \epsilon$  3.7).

(c) *Decafluoroazobenzene*.—Oxidation as in (a) led to a 90% recovery of the azo-compound even after 72 hr. refluxing. The azo-compound was recovered in 95% yield either after being refluxed for 4 days with performic acid in methylene chloride, or after being stirred for 5 days at room temperature with peracetic acid. The recovery was 80% after treatment for 5 days at room temperature with fuming nitric acid.

*Decafluorohydrazobenzene*.—Decafluoroazobenzene (0.52 g.) in light petroleum (b. p. 60—80°) ether (1 : 1 v/v) (35 ml.) was hydrogenated over 5% palladium on asbestos at atmospheric pressure and room temperature. The red solution became colourless after 30 min. and no more hydrogen was absorbed, even after a further 16 hr. Filtration and evaporation left a yellow solid (0.45 g.), m. p. 47°, which was crystallised with some difficulty from light petroleum (b. p. 60—80°) to give the pale yellow *decafluorohydrazobenzene*, m. p. 57° (Found: C, 40.2; H, 0.7;  $C_{12}H_2F_{10}N_2$  requires C, 39.6; H, 0.6%)

This compound decomposed quite quickly in solution to a red material, but in the solid state it decomposed much more slowly. It had  $\nu_{\max}$  at 3400  $cm^{-1}$  (NH).

Decafluoroazoxybenzene (0.4 g.), hydrogenated in the same way, gave decafluorohydrazobenzene (0.3 g.), m. p. and mixed m. p. with the previous compound, 55° (cf. Wall<sup>2</sup>).

4H,4'H-*Octafluorohydrazobenzene*.—4H,4'H-Octafluoroazobenzene (1.1 g.) was hydrogenated as in the previous experiment. The red solution became colourless after 3 hr. The crude yellow product (1.0 g.), m. p. 108°, was crystallised from light petroleum (b. p. 60—80°) to give colourless needles of 4H,4'H-*octafluorohydrazobenzene* (0.6 g.), m. p. 120° (Found: C, 44.0; H, 1.2.  $C_{12}H_2F_8N_2$  requires C, 43.9; H, 1.2%)

*Action of Heat on Polyfluorohydrazo-compounds*.—(a) *Decafluorohydrazobenzene*. A few milligrams of this compound were heated in a capillary tube. The melt began to turn red at 130° and was deep red at 150°, when a red solid had begun to sublime up the tube. The tube was finally heated for 1 hr. at 170° when two bands appeared; the lower red one, m. p. 134°, had an infrared spectrum identical with that of decafluoroazobenzene; the upper white one, m. p. 30° (cited<sup>13</sup> for pentafluoroaniline 33.5—35°) was insufficient for infrared spectroscopy.

(b) *Octafluorohydrazobenzene*. Treated as in (a), this compound became red at 155° and was kept at 170° for 1 hr. Some charring occurred and a red solid, m. p. 116°, sublimed up the tube; it had an infrared spectrum identical with that of 4H,4'H-octafluoroazobenzene.

*Oxidation of Polyfluorohydrazo-compounds*.—Both deca- and octa-fluorohydrazobenzene were treated with aqueous sodium hypochlorite for 2 hr. at room temperature as described in the first experiment. The corresponding azo-compounds were isolated in 90 and 98% yields, respectively, and were identified by mixed m. p. determinations.

*Decafluoroazoxybenzene*. (a) *From pentafluoroaniline*. The aniline<sup>13</sup> (5.0 g.) was oxidised with performic acid as described previously<sup>5</sup> to give pentafluoronitrosobenzene (2.1 g.), m. p. 44° (lit.,<sup>6</sup> 44.5—45°). The brown solid remaining after distillation of the nitroso-compound was crystallised from methanol to give the yellow decafluoroazoxybenzene (0.85 g.), m. p. and mixed m. p. with a specimen prepared by Wall's method,<sup>2</sup> 49—51° (lit.,<sup>2</sup> 53—54°) (Found: C, 38.2; H, 0.2. Calc. for  $C_{12}F_{10}N_2O$ : C, 38.1; H, 0.0%),  $\lambda_{\max}$  (EtOH) 228  $m\mu$  ( $\log \epsilon$  3.9) and 293  $m\mu$  ( $\log \epsilon$  3.7).

(b) *By the action of heat on pentafluoronitrosobenzene*. The nitroso-compound (1.7 g.) was heated in a sealed tube at 60° for 5 hr., by which time the green liquid had become brown. The product was passed down a column (1 ft.  $\times$  1 in. diam.) of alumina in light petroleum (b. p. 60—80°) as eluent. Two bands developed. The first was washed off with the above eluent and the second with methanol. Evaporation of the solvents gave:

*Band 1* (brown). Crystallisation from methanol gave decafluoroazoxybenzene (0.47 g.), m. p. and mixed m. p. 50°.

*Band 2* (green). A green solid (0.86 g.), m. p. 44°, with an infrared spectrum identical with that of pentafluoronitrosobenzene.

(c) *From pentafluoronitrosobenzene and triethyl phosphite*. The nitroso-compound (0.55 g.) and triethyl phosphite (1 ml.) were heated at 60° in benzene for 30 min. The mixture was washed with water and evaporated, and the brown residue was crystallised from methanol to give the azoxy-compound (0.42 g.), m. p. 48°, identified by infrared spectroscopy.

*Oxidation of 2,3,5,6-Tetrafluoroaniline.*—The aniline<sup>13</sup> (1.5 g.) in methylene chloride (20 ml.) was stirred and refluxed with performic acid [from formic acid (90%, 10 ml.), hydrogen peroxide (89%, 10 ml.), and methylene chloride (50 ml.)] for 5 hr. The mixture was washed with water, dried (MgSO<sub>4</sub>) and the solvent removed by distillation through a 6 in. column packed with glass helices. The residue was distilled at 28°/0.01 mm. to give a green liquid (0.5 g.), which crystallised from ethanol at 0° to white needles of 2,3,5,6-tetrafluoronitrosobenzene, m. p. 66° (Found: C, 40.2; H, 1.0. C<sub>6</sub>HF<sub>4</sub>NO requires C, 40.2; H, 0.6%). The brown oil remaining after the vacuum distillation crystallised from methanol to give 4*H*,4'*H*-octafluoroazoxybenzene (0.35 g.), m. p. and mixed m. p. with the compound obtained previously, 52°.

4*H*,4'*H*-Hexafluoro-2,2'-dimethoxyazobenzene.—Sodium methoxide in methanol (47 ml.; 0.52*N*) was added, over 25 min. with stirring and at room temperature, to a solution of 4*H*,4'*H*-octafluoroazobenzene (0.32 g.) in ether (20 ml.). Filtration, and evaporation of the reaction mixture *in vacuo* at room temperature left a residue, which was crystallised from ethanol to give red needles of 4*H*,4'*H*-hexafluoro-2,2'-dimethoxyazoxybenzene (0.31 g.), m. p. 118° (Found: C, 48.2; H, 2.5. C<sub>14</sub>H<sub>8</sub>F<sub>6</sub>N<sub>2</sub>O<sub>2</sub> requires C, 48.0; H, 2.3%). The proton magnetic resonance spectrum, in acetone, showed a doublet ( $J = 1.0$  c./sec.) at 3.93 p.p.m. and a doublet ( $J = 7.6$  c./sec.) of triplets ( $J = 11.1$  c./sec.) at 7.43 p.p.m.

Nonafluoro-4-methoxyazobenzene (I).—Decafluoroazobenzene (1.0 g.) in dry ether (100 ml.) was treated with sodium methoxide in methanol (27.6 ml.; 0.1*N*) as in the previous experiment. The product (1.1 g.) was chromatographed on alumina (54 cm. × 3 cm. diam. column) with benzene as eluent. Four bands developed and were washed from the column with the eluent. The last three were in very small amount and were not investigated. Evaporation of the solvent from the first left a red residue (0.94 g.), which was crystallised from light petroleum (b. p. 80—100°). Two crystal forms appeared and were separated by hand. Recrystallisation of each from the same solvent gave red plates of nonafluoro-4-methoxyazobenzene (I) (0.31 g.), m. p. 94—96° (Found: C, 41.9; H, 0.8. C<sub>13</sub>H<sub>3</sub>F<sub>9</sub>N<sub>2</sub>O requires C, 41.7; H, 0.8%) and orange needles of octafluoro-4,4'-dimethoxyazobenzene (II) (0.19 g.), m. p. and mixed m. p. with the specimen obtained later, 159—162°.

Octafluoro-4,4'-dimethoxyazobenzene (II).—The previous reaction was repeated with 0.5 g. of decafluoroazobenzene, and the crude product after evaporation was crystallised from light petroleum (b. p. 60—80°) to give the orange octafluoro-4,4'-dimethoxyazobenzene (II) (0.25 g.), m. p. 164—165° (Found: C, 43.7; H, 1.4. C<sub>14</sub>H<sub>6</sub>F<sub>8</sub>N<sub>2</sub>O<sub>2</sub> requires C, 43.5; H, 1.6%).

*Reaction of Methoxide with Nonafluoro-4-methoxyazobenzene (I).*—The azo-compound (0.28 g.) in ether (40 ml.) was treated with sodium methoxide in methanol (7.6 ml. of 0.1*N*) as in the previous experiment to give octafluoro-4,4'-dimethoxyazobenzene (II) (0.11 g.), m. p. and mixed m. p. with specimen obtained above, 159—163°.

*Reaction of Methoxide with Octafluoro-4,4'-dimethoxyazobenzene (II).*—Treatment of the azo-compound (0.20 g.) with two equivalents of sodium methoxide in methanol gave a product, which was chromatographed on alumina (70 cm. × 2.4 cm. diam. column) with light petroleum (b. p. 80—100°) as eluent. Two bands developed and were washed from the column with the eluent.

*Band 1.* Crystallisation from aqueous ethanol gave orange needles of heptafluoro-2,2',4-trimethoxyazobenzene (IV) (0.13 g.), m. p. 105.5—106.5° (Found: C, 45.3; H, 2.2. C<sub>15</sub>H<sub>9</sub>F<sub>7</sub>N<sub>2</sub>O<sub>3</sub> requires C, 45.2; H, 2.3%).

*Band 2.* Crystallisation from ethanol gave orange needles of hexafluoro-2,2',4,4'-tetramethoxyazobenzene (III) (0.04 g.), m. p. 150—152° (Found: C, 46.9; H, 3.0. C<sub>16</sub>H<sub>12</sub>F<sub>6</sub>N<sub>2</sub>O<sub>4</sub> requires C, 46.8; H, 3.0%). The proton magnetic resonance spectrum, in acetone, showed a doublet ( $\delta = 3.93$  p.p.m.,  $J = 0.7$  c./sec.) and a triplet ( $\delta = 4.11$  p.p.m.,  $J = 1.6$  c./sec.) of equal intensity.

*Reductive Cleavage of Polyfluoroazo-compounds.*—(a) *Decafluoroazobenzene.* The azo-compound (0.50 g.), tin (8 g.), hydrochloric acid (20 ml., 1*N*) and glacial acetic acid (2 ml.) were refluxed for 5 hr. Aqueous sodium hydroxide (40 g. in 100 ml.) was added and the product was isolated by ether-extraction. It was pentafluoroaniline (0.25 g.), m. p. 30° (lit.,<sup>13</sup> 33.5—35°), identified by its infrared spectrum.

(b) *Octafluoro-4,4'-dimethoxyazobenzene (II).* The azo-compound (0.13 g.) was treated with tin (2 g.), hydrochloric acid (5 ml., 1*N*), and glacial acetic acid (10 ml.) as in (a) to give *N*-acetyl 2,3,5,6-tetrafluoro-*p*-anisidine (V) (0.03 g.), m. p. 116—117° [from light petroleum (b. p. 60—80°)] (Found: C, 45.4; H, 2.8. C<sub>9</sub>H<sub>7</sub>F<sub>4</sub>NO<sub>2</sub> requires C, 45.6; H, 3.0%).

(c) *Octafluoro-2,2',4,4'-tetramethoxyazobenzene* (III). Treatment of the azo-compound (0.80 g.) with tin (13 g.), hydrochloric acid (32 ml., 11*N*), and glacial acetic acid (8 ml.) as in (a) gave *2,3,5-trifluoro-4,6-dimethoxyaniline* (VI) (0.35 g.), m. p. 43—45° [from light petroleum (b. p. 60—80°)] (Found: C, 46.5; H, 3.7.  $C_8H_5F_3NO_2$  requires C, 46.4; H, 3.9%).

*2,3,5,6-Tetrafluoro-p-anisidine*.—*2,3,5,6-Tetrafluoro-4-aminophenol*<sup>9</sup> (0.18 g.) in ether (3 ml.) was treated with diazomethane in ether (2 ml.; ca. 0.6*N*) at -35°. Evaporation of the ether left a residue which was crystallised from aqueous ethanol to give the anisidine (0.03 g.), m. p. 74—75.5° (lit.,<sup>2</sup> 75—76.5°) (Found: C, 43.4; H, 2.5. Calc. for  $C_7H_5F_4NO$ : C, 43.1; H, 2.6%).

The compound gave an *N*-acetyl derivative (with sulphuric acid and acetic anhydride), m. p. and mixed m. p. with the compound obtained earlier, 116—117°.

*Decafluoroazobenzene and Lithium Aluminium Hydride*.—The azo-compound (0.76 g.) was refluxed for 30 min. with lithium aluminium hydride (0.05 g.) in dry ether (50 ml.). Water and then dilute hydrochloric acid were added to dissolve the inorganic products. The red ether layer was dried ( $MgSO_4$ ) and evaporated to leave an orange paste (0.72 g.), which was chromatographed on alumina (1 ft. × 1 in. diam. column) with light petroleum as eluent. Two fractions were collected. The first yielded a red solid (0.36 g.), m. p. 66—75°, whose infrared spectrum was consistent with it being a mixture of *4H,4'H*-octafluoro- and decafluoro-azobenzene. The second gave decafluorohydrazobenzene (0.28 g.), m. p. 54°, identified by its infrared spectrum.

The experiment was repeated with azo-compound (0.83 g.) and lithium aluminium hydride (0.40 g.), and the crude product, (0.68 g.) was treated with light petroleum (b. p. 60—80°) at 0°. Crystals separated and were recrystallised from the same solvent to give white needles of *4H,4'H*-octafluorohydrazobenzene (0.08 g.), m. p. 118°, identified by its infrared spectrum. No other pure compounds were isolated from the reaction mixture.

No reaction occurred when decafluorohydrazobenzene was treated with lithium aluminium hydride under the same conditions.

*Reaction of Decafluoroazoxybenzene with Sodium Methoxide*.—The azoxy-compound (0.58 g.) in ether (15 ml.) was treated with sodium methoxide in methanol (14.4 ml.; 0.25*N*) as described for the azo-compounds. The product was crystallised from methanol to give yellow needles of octafluoro-4,4'-dimethoxyazoxybenzene (0.46 g.), m. p. and mixed m. p. with the specimen obtained previously, 130°.

*Proton Magnetic Resonance Spectra*.—Proton magnetic resonance spectra were measured on a Varian A60 instrument at 60 Mc./sec. The chemical shifts are in p.p.m. downfield from tetramethylsilane as internal reference.

We thank Professor J. C. Tatlow for his interest and advice and the D.S.I.R. for a maintenance grant (to C. J. M.).

THE CHEMISTRY DEPARTMENT, THE UNIVERSITY,  
EDGBASTON, BIRMINGHAM 15.

[Received, September 23rd, 1964.]