

966. *Polyfluoroarenes. Part V.*<sup>1</sup> *Pentafluorophenylhydrazine and the Pentafluorophenyl Radical.*

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Pentafluorophenylhydrazine decomposes at 180°, probably by initial N-N fission, to give pentafluoroaniline and pentafluorobenzene. The hydrazine reacts with bromine in ethanol, to give bromopentafluorobenzene and pentafluorophenyl azide, and with hydriodic acid to give pentafluoroaniline. Pure pentafluorophenyl azide is obtained by reaction of the hydrazine with nitrous acid or nitrosyl chloride. Oxidation of pentafluorophenylhydrazine in aqueous media gives pentafluorobenzene and 1,2,4,5-tetrafluorobenzene, and oxidation in non-aqueous media provides an excellent route to the pentafluorophenyl radical. Reaction of this radical with benzene gives 2,3,4,5,6-pentafluorobiphenyl in good yield, and with dibromodifluoromethane gives bromopentafluorobenzene, with methyl iodide gives pentafluoroiodobenzene, and with mercury gives bispentafluorophenylmercury. Oxidation of pentafluorophenylhydrazine in hexafluorobenzene gives mostly pentafluorobenzene, but a small amount of decafluorobiphenyl is also formed.

NUCLEOPHILIC substitution of hexafluorobenzene by the action of sodamide in liquid ammonia has been shown to give pentafluoroaniline,<sup>2</sup> but until recently this reaction provided the only known example of a reaction of a polyfluoroarene with a nitrogen base. The reactions of hexafluorobenzene and of pentafluorobenzene with aqueous ammonia and with hydrazine hydrate, and the reaction of hexafluorobenzene with dimethylamine, were reported<sup>3</sup> after the work described in the present communication was begun.

*Pentafluorophenylhydrazine.*—Hydrazine hydrate and hexafluorobenzene in refluxing ethanol give pentafluorophenylhydrazine in 71% yield. More recent work in this Department has shown that an excellent yield (>95%) is obtained if the reaction is carried out in dioxan.<sup>4</sup> The crystalline hydrazine may be characterised conveniently through its hydrochloride, formed in 97% yield by reaction with dry hydrogen chloride in ether, and the reducing action of the free base is demonstrated by its reactions with Fehling's solution and with ammoniacal silver nitrate.

TABLE I.  
Ionisation constants.

	$K_b$		$K_a$
$C_6F_5 \cdot NH \cdot NH_2$ .....	$1.4 \times 10^{-10}$	$C_6F_5 \cdot OH$ <sup>6</sup> .....	$1.6 \times 10^{-6}$
$C_6H_5 \cdot NH \cdot NH_2$ <sup>5a</sup> .....	$1.6 \times 10^{-9}$	$C_6H_5 \cdot OH$ <sup>7</sup> .....	$1.3 \times 10^{-10}$
$C_6F_5 \cdot CH_2 \cdot NH_2$ <sup>1</sup> .....	$5.0 \times 10^{-7}$		
$C_6H_5 \cdot CH_2 \cdot NH_2$ <sup>5b</sup> .....	$2 \times 10^{-5}$		

Table I shows that pentafluorophenylhydrazine is a weaker base than phenylhydrazine, the decrease in ionisation constant being similar in magnitude to that observed for the benzylamines, but very much less than for the phenols; this is attributed to the secondary -NH- group, which insulates the basic terminal nitrogen atom from the electronic effects of substituents in the ring.

<sup>1</sup> Part IV, Birchall and Haszeldine, *J.*, 1961, 3719.

<sup>2</sup> Forbes, Richardson, and Tatlow, *Chem. and Ind.*, 1958, 630.

<sup>3</sup> Brooke, Burdon, Stacey, and Tatlow, *J.*, 1960, 1768.

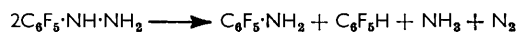
<sup>4</sup> Birchall, Haszeldine, and Woodfine, unpublished results.

<sup>5</sup> Lange (ed.), "Handbook of Chemistry," McGraw-Hill Book Co., New York, 10th edn., 1961, (a) p. 1204; (b) p. 1202.

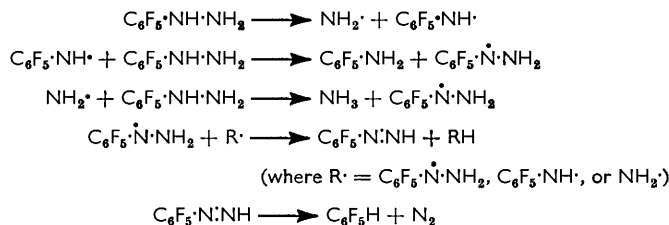
<sup>6</sup> Birchall and Haszeldine, *J.*, 1959, 3653.

<sup>7</sup> Walker and Cormack, *J.*, 1900, 77, 18.

*Thermal decomposition of pentafluorophenylhydrazine.* Pentafluorophenylhydrazine is stable at moderate temperatures, but slow thermal decomposition begins at about 180° and proceeds, in a similar manner to that for phenylhydrazine itself,<sup>8</sup> according to the equation:



The products and stoichiometry of this reaction ( $\text{C}_6\text{F}_5\cdot\text{NH}_2$ , 44%;  $\text{C}_6\text{F}_5\text{H}$ , 39%;  $\text{NH}_3$ , 42%;  $\text{N}_2$ , 49%) are best explained by primary fission of the N-N bond to give amino- ( $\text{NH}_2\cdot$ ) and pentafluorophenylamino- ( $\text{C}_6\text{F}_5\cdot\text{NH}\cdot$ ) radicals, benzylic resonance in the latter facilitating this mode of decomposition:



*Reactions of pentafluorophenylhydrazine with bromine and with hydriodic acid.* Diazotisation of pentafluoroaniline has been shown to be an unsatisfactory route to pentafluorobenzenediazonium salts:<sup>2</sup> the diazonium group activates the aromatic ring towards nucleophilic substitution, and extensive loss of fluoride occurs under the normal conditions for diazotisation. Similar results have frequently been observed with less highly fluorinated aromatic compounds; thus, when dry 2,4-difluorobenzenediazonium fluoroborate is gently heated with lithium chloride, 2-chloro-4-fluorobenzenediazonium fluoroborate is obtained in good yield.<sup>9</sup>

Oxidation of primary aromatic hydrazines by halogens provides an alternative to direct diazotisation of amino-compounds for the preparation of diazonium salts and their reaction products. Thus, pure benzenediazonium chloride or bromide may be isolated after the action of chlorine or bromine on an ethanolic solution of phenylhydrazine at -80°.<sup>10</sup> Similarly, the reaction of phenylhydrazine with bromine in aqueous hydrochloric acid gives a good yield of bromobenzene through the intermediate diazonium compound.<sup>11</sup> The reaction of phenylhydrazine with two molecular proportions of iodine in aqueous solution gives iodobenzene,<sup>12</sup> but with one molecular proportion of iodine, aniline and phenyl azide are formed in equivalent amounts.<sup>13</sup> The last two reactions probably both proceed through benzenediazonium iodide, since an aqueous solution of phenylhydrazine and iodine couples with alkaline  $\beta$ -naphthol to give the corresponding azo-compound.<sup>14</sup>

The pure diazonium salt cannot be isolated when pentafluorophenylhydrazine and bromine, in a molar ratio of 1 : 2, are allowed to react in ethanolic solution at -60°, and the solution does not give the azo-compound with neutral, acidic, or alkaline solutions of  $\beta$ -naphthol. A yellow oil, which becomes red when kept, is obtained by distillation of the solution, and infrared spectroscopy shows this to contain only bromopentafluorobenzene and pentafluorophenyl azide, obtained in 24% and 38% yield, respectively. Pentafluoroaniline (5%) is obtained from the tarry residue. Bromopentafluorobenzene

<sup>8</sup> Chattaway and Aldridge, *J.*, 1911, **99**, 404.

<sup>9</sup> Finger, Reed, and Oesterling, *J. Amer. Chem. Soc.*, 1951, **73**, 152; Finger and Oesterling, *ibid.*, 1956, **78**, 2593.

<sup>10</sup> Chattaway, *J.*, 1908, **93**, 852.

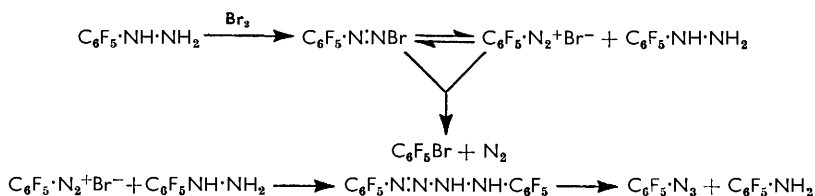
<sup>11</sup> Chattaway, *J.*, 1909, **95**, 1065.

<sup>12</sup> von Meyer, *J. prakt. Chem.*, 1887, **36**, 115.

<sup>13</sup> Fischer, *Ber.*, 1877, **10**, 1335.

<sup>14</sup> Miller and Furman, *J. Amer. Chem. Soc.*, 1937, **59**, 161.

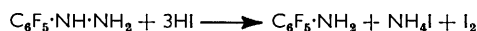
probably results from decomposition of the intermediate diazonium salt, and the formation of the azide and the aniline could proceed by the route outlined:



Diazonium salts are known to react with primary aromatic hydrazines to form tetrazens, which are readily cleaved to give amino-compounds and aryl azides.<sup>15</sup>

Attempts to improve the yield of bromopentafluorobenzene by treatment of pentafluorophenylhydrazine with bromine in aqueous hydrochloric acid or in aqueous hydrobromic acid gave high yields of nitrogen, but resulted in complex mixtures of organic products. The large numbers of products from these reactions presumably arose through displacement of fluoride from the intermediate diazonium compound by chloride and bromide ions present in solution.

Pentafluorophenylhydrazine with a solution of two molar proportions of iodine in aqueous hydriodic acid gives only pentafluoroaniline (65%); neither pentafluoroiodobenzene nor pentafluorophenyl azide is produced, and the colour of the iodine is not discharged during the reaction. This reaction clearly does not proceed by either of the expected routes,<sup>12,13</sup> and reduction by the hydriodic acid must occur instead of oxidation of the hydrazino-group by iodine:



This conclusion is confirmed by the isolation of pentafluoroaniline in 75% yield on reaction of pentafluorophenylhydrazine with aqueous hydriodic acid alone.

*Pentafluorophenyl Azide.*—2,4-Dinitrophenyl azide may be prepared in good yield by the reaction of chloro-2,4-dinitrobenzene with azide ion in aqueous acetone,<sup>16</sup> and, in view of the established susceptibility of polyfluoroarenes to nucleophilic substitution, a similar reaction with hexafluorobenzene might be expected to give pentafluorophenyl azide. Synthesis of this compound was desirable in order to establish its formation in the reaction of pentafluorophenylhydrazine with bromine. However, hexafluorobenzene does not react to an appreciable extent with azide ion in aqueous acetone, being recovered in 90% yield after prolonged heating.

Diazotisation of pentafluorophenylhydrazine with sodium nitrite in hydrochloric acid, however, does give pentafluorophenyl azide. The product is contaminated with pentafluoroaniline, but this impurity may be removed as its hydrochloride, and the pure azide is thus obtained, as a yellow oil, in 30% yield. A 52% yield of the azide is obtained by diazotisation of pentafluorophenylhydrazine with nitrosyl chloride in glacial acetic acid. Related reactions with phenylhydrazine give phenyl azide.<sup>17</sup>

Pentafluorophenyl azide may be distilled under reduced pressure without decomposition, but thermal decomposition begins at 80° and proceeds smoothly at 120°, with evolution of one mole of nitrogen per mole of azide.

*Oxidation of Pentafluorophenylhydrazine in Aqueous Media.*—Primary arylhydrazines are readily oxidised to the related hydrocarbons in excellent yield by a number of oxidising agents: Fehling's solution, aqueous copper sulphate, ferric chloride, permanganates,

<sup>15</sup> Sidgwick, "The Organic Chemistry of Nitrogen," Clarendon Press, Oxford, 1949, p. 382.

<sup>16</sup> Müller and Weisbrod, *J. prakt. Chem.*, 1926, **113**, 30.

<sup>17</sup> Lindsay and Allen, *Org. Synth.*, Coll. Vol. III, p. 710; Tilden and Millar, *J.*, 1893, **63**, 257.



would be expected to be dependent on the concentration and potential of any reducing inorganic ions present in the system. That this is the case is demonstrated by the reactions of pentafluorophenylhydrazine with a number of other oxidising agents, the results of which are summarised in Table 2.

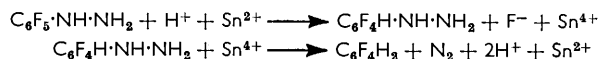
TABLE 2.

Reactions of pentafluorophenylhydrazine with oxidising agents at 80°.

Reagent	Products (mole %)			Proportion of C <sub>6</sub> F <sub>4</sub> H <sub>2</sub> (%)
	C <sub>6</sub> F <sub>5</sub> H	C <sub>6</sub> F <sub>4</sub> H <sub>2</sub>	Total	
NaOBr, aq. ....	43	0	43	0
CuSO <sub>4</sub> , aq. ....	77	4	81	5
Fehling's soln. ....	26	53	79	67
SnCl <sub>2</sub> -conc.HCl .....	0	66	66	100

Thus, with sodium hypobromite, where no redox system is present and only oxidation can occur, only pentafluorobenzene is produced, whilst in the presence of large amounts of the powerfully reducing stannous chloride, only 1,2,4,5-tetrafluorobenzene is formed. The results with aqueous copper sulphate and Fehling's solution are also accommodated on this basis.

A possible explanation of the function of the stannous chloride system as an *oxidising* agent for the removal of the hydrazino-group may be that reduction of the hydrazine occurs first, generating stannic ion which then effects the oxidation:



It is unlikely that the reduction occurring with any of the reagents employed is a direct reduction of pentafluorobenzene, since this compound is unaffected by stannous chloride in refluxing hydrochloric acid.<sup>4</sup>

*The Pentafluorophenyl Radical.*—Oxidation of arylhydrazines by a number of reagents under non-aqueous conditions has recently been shown to give aryl radicals.<sup>21</sup> In aromatic solvents, such oxidations give rise to the formation of biaryls by the well-established process of homolytic aromatic arylation.<sup>22</sup> In general, the yields of biaryls resulting from the use of arylhydrazines as radical sources are low, with side reactions leading to the formation of anilines, phenols, azobenzene derivatives, and tars accounting for much of the loss. The best results are usually obtained when silver oxide is used as the oxidising agent and 2,4-dinitrophenylhydrazine is the source of radicals: yields of 2,4-dinitro-biphenyl of up to 40% result from this reaction in benzene solution.<sup>21</sup>

The susceptibility of pentafluorophenylhydrazine to oxidation in aqueous media has been discussed above, and the oxidation in organic solvents was next examined as a route to the hitherto unknown pentafluorophenyl radical.

When pentafluorophenylhydrazine is treated with silver oxide in a large excess of benzene at 0–10°, an almost quantitative evolution of nitrogen occurs, and crystalline 2,3,4,5,6-pentafluorobiphenyl is produced in 63% yield. When bleaching powder is used as the oxidising agent, a 74% yield of the biphenyl is obtained. The formation of the pentafluorophenyl radical probably takes place through the diazo-compound (I) by a homolytic route similar to that envisaged for oxidation in aqueous media.

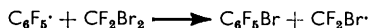
Removal of the hydrogen atom from the intermediate  $\sigma$ -complex (II) is effected by the oxidising agent or by another radical. Abstraction by a second pentafluorophenyl radical would give pentafluorobenzene and this is not formed during the reaction, but

<sup>21</sup> Hardie and Thompson, *J.*, 1957, 2512.

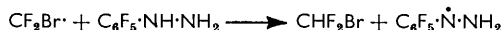
<sup>22</sup> Dermer and Edmison, *Chem. Rev.*, 1957, 57, 77; Augood and Williams, *ibid.*, p. 123; Williams, "Homolytic Aromatic Substitution," Pergamon Press, London, 1960.



for the versatility of this type of reaction as a route to polyfluoroarene derivatives. With silver oxide in dibromodifluoromethane, pentafluorophenylhydrazine gives bromopentafluorobenzene (22%) and pentafluorobenzene (6%), the former by abstraction of bromine from the solvent, and the latter, presumably, mostly by hydrogen abstraction from the unchanged hydrazine:

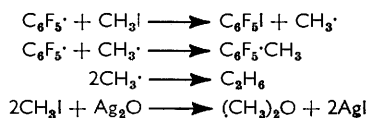


The fate of the bromodifluoromethyl radical is uncertain, but it probably abstracts hydrogen and is lost as the volatile bromodifluoromethane (b. p.  $-14.5^\circ$ <sup>24</sup>):



The low yield of bromopentafluorobenzene and the formation of pentafluorobenzene in this oxidation show that dibromodifluoromethane is not particularly reactive towards the pentafluorophenyl radical. More reactive solvents, which would lead to an increased yield of bromopentafluorobenzene, could clearly be chosen, and the selection of dibromodifluoromethane for these initial experiments was based on availability and ease of separation from the products on the scale employed.

Pentafluorophenylhydrazine reacts with silver oxide in methyl iodide to give pentafluoroiodobenzene (60%), pentafluorobenzene (7%), and a trace of 2,3,4,5,6-pentafluorotoluene. The nitrogen evolved during the reaction contains ethane and dimethyl ether. The formation of these products is best explained as follows:



The high yield of pentafluoroiodobenzene obtained from this reaction now enables this useful compound to be prepared from hexafluorobenzene in good yield in only two stages.

#### EXPERIMENTAL

Gas-liquid chromatography was carried out by the technique described previously;<sup>1</sup> analytical columns were of 4 mm. internal diameter, packed with 30% by wt. of the stationary phase on Celite. Volumes of gases are corrected to N.T.P.

*Pentafluorophenylhydrazine.*—Hexafluorobenzene (40.0 g., 0.22 mole), hydrazine hydrate (25.0 g., 0.63 mole), and ethanol (150 ml.) were heated under reflux for 12 hr. The solvent and unchanged hexafluorobenzene were distilled out, and hexafluorobenzene (8.0 g., 20%) was recovered from the distillate by the addition of water. Addition of water to the less volatile brown liquid residue gave crystals, which were washed repeatedly with water, dried, and recrystallised from light petroleum (b. p. 80–100°), to give white plates of pentafluorophenylhydrazine (24.0 g., 57%, 71% based on hexafluorobenzene consumed) (Found: C, 36.3; H, 1.8; N, 14.0. Calc. for  $\text{C}_6\text{H}_3\text{F}_5\text{N}_2$ : C, 36.4; H, 1.5; N, 14.2%), m. p. 77–78° (lit.,<sup>3</sup> m. p. 76.0–77.5°). The aromatic ring vibration of this compound is at 1529  $\text{cm}^{-1}$ , and the N–H stretching vibrations are at 3356 and 3279  $\text{cm}^{-1}$ .

Pentafluorophenylhydrazine is soluble in most common organic solvents, slightly soluble in cold water, and moderately soluble in hot; it is readily soluble in concentrated mineral acids, from which it is reprecipitated by base. Treatment of the hydrazine in anhydrous ether with gaseous hydrogen chloride gave the hydrochloride (97%) (Found: C, 30.8; H, 1.7; N, 12.2. Calc. for  $\text{C}_6\text{H}_4\text{ClF}_5\text{N}_2$ : C, 30.7; H, 1.7; N, 12.0%), m. p. 238–240° (lit.,<sup>3</sup> m. p. 239–241°).

*Ionisation Constant of Pentafluorophenylhydrazine.*—This was determined by potentiometric titration of 0.02N-solutions of the hydrazine, purified by repeated recrystallisation and sublimation *in vacuo*, in carbonate-free distilled water against 0.02N-hydrochloric acid. The apparatus has been described earlier.<sup>6</sup> Repeated determinations at the "half-neutralisation" point at 20° gave  $\text{pH} = \text{pK}_a = 4.15$ , whence  $\text{pK}_b = 9.85$ ,  $K_b = 1.4 \times 10^{-10}$ .

<sup>24</sup> Swarts, *Bull. sci. Acad. roy. Belg.*, 1910, 113.

*Pyrolysis of Pentafluorophenylhydrazine.*—The hydrazine (10.0 g., 50.5 mmoles) was pyrolysed in a flask fitted with a double-surface reflux condenser leading, *via* two wash-bottles containing 0.2N-hydrochloric acid, to a gas-burette. The flask was heated in an oil-bath, and the hydrazine began to decompose at a bath-temperature of 180°. During 4 hr. at 180–190°, ammonia (20 mmoles, 40%, determined by back-titration of the contents of the wash-bottles) and nitrogen (535 ml., 46%) were evolved. Distillation of the residual liquid gave pentafluorobenzene (3.14 g., 37%), b. p. 85°, identified by infrared spectroscopy. The solid residue was fractionally sublimed *in vacuo*, to give pentafluoroaniline (3.90 g., 42%), m. p. 33° (lit.,<sup>3</sup> m. p. 33.5–34.5°), identified by infrared spectroscopy, and pentafluorophenylhydrazine (0.50 g., 5%), m. p. and mixed m. p. 77–78°. An involatile tar (0.4 g.) remained after the sublimation.

*Reaction of Pentafluorophenylhydrazine with Bromine.*—(a) *In ethanol.* Bromine (3.25 g., 20 mmoles) in ethanol (15 ml.) was added during 30 min. to a vigorously stirred solution of pentafluorophenylhydrazine (2.0 g., 10 mmoles) in ethanol (15 ml.). The mixture was cooled to –60° throughout the addition and for 2 hr. afterwards, during which time the colour of the bromine completely disappeared. Addition of a portion of the solution (*ca.* 2 ml.) to dry ether (5 ml.) failed to give a precipitate of a diazonium salt, the absence of which was confirmed by failure to produce a precipitate with alkaline, neutral, and acid solutions of  $\beta$ -naphthol. The ethanolic solution was distilled, to give a yellow oil (1.4 g.), b. p. 55°/50 mm., shown to contain bromopentafluorobenzene (*ca.* 0.6 g., 24%) and pentafluorophenyl azide (*ca.* 0.8 g., 38%) by infrared spectroscopy. Addition of aqueous 2N-sodium hydroxide to the tarry residue, followed by steam-distillation, gave pentafluoroaniline (0.1 g., 5%), m. p. 32.5–34°, identified by infrared spectroscopy.

(b) *In aqueous hydrochloric acid.* Bromine (*ca.* 20 g., 125 mmoles) was added gradually to a vigorously stirred solution of the hydrazine (9.5 g., 48 mmoles) in 5N-hydrochloric acid (30 ml.) at 60–70°. A rapid evolution of nitrogen (1075 ml., 99%) commenced after a short induction period, and the addition of bromine was continued until effervescence ceased and the colour was no longer discharged. A red oil, which was precipitated during the reaction, was separated, washed with 10% aqueous sodium metabisulphite and water, and dried (MgSO<sub>4</sub>). The colourless product (6.3 g.) was analysed by gas-liquid chromatography and shown to contain at least eleven components. The aqueous phase from the reaction gave a positive test for fluoride ion, and extraction with ether gave only a viscous black tar (*ca.* 1.0 g.).

(c) *In aqueous hydrobromic acid.* Bromine (16.0 g., 100 mmoles) was added slowly to a stirred solution of the hydrazine (9.0 g., 46 mmoles) in constant-boiling hydrobromic acid (40 ml.) at 60–70°. Nitrogen (950 ml., 92%) was evolved, and the organic layer was washed, dried, and distilled, to give a liquid (7.95 g.), boiling 100°/760 mm. to 150°/50 mm., shown to contain at least five components by gas-liquid chromatography. The aqueous phase contained fluoride ion and yielded a black tar (2.1 g.) on extraction with ether.

*Reaction of Pentafluorophenylhydrazine with Hydriodic Acid and Iodine.*—Iodine (18.0 g., 71 mmoles) was added during 30 min. to pentafluorophenylhydrazine (7.0 g., 35 mmoles) in 55% aqueous hydriodic acid (50 ml.) at 70–80°, and the mixture was heated under reflux for a further hour. No nitrogen was evolved and the colour of iodine was not discharged. Solid sodium metabisulphite was added to remove the iodine, and steam-distillation gave a white solid (4.3 g.), m. p. 32°. This was dried by melting it with magnesium sulphate, and sublimed *in vacuo* at 20° to give pentafluoroaniline (4.2 g., 65%) (Found: C, 39.2; H, 1.1; N, 7.2. Calc. for C<sub>6</sub>H<sub>2</sub>F<sub>5</sub>N: C, 39.4; H, 1.1; N, 7.6%), m. p. 33.5–34.5°, identified by comparison of its infrared spectrum with that of an authentic specimen prepared by the reaction of hexafluorobenzene with sodamide.<sup>2</sup>

In a second experiment, the hydrazine (10.0 g., 50.5 mmoles) was heated under reflux with 55% aqueous hydriodic acid (60 ml.) for 3 hr. The products were treated as before and gave pentafluoroaniline (6.9 g., 75%), m. p. 34–34.5°.

*Action of Sodium Azide on Hexafluorobenzene.*—Hexafluorobenzene (5.0 g., 27 mmoles), sodium azide (10 g., 154 mmoles), acetone (30 ml.), and water (20 ml.) were heated under reflux for 72 hr., but gave only hexafluorobenzene (4.6 g., 90%), shown to be pure by gas-liquid chromatography (2 m.; dinonyl phthalate; at 85°).

*Pentafluorophenyl Azide.*—(a) *From pentafluorophenylhydrazine and nitrous acid.* The hydrazine (4.85 g., 24.5 mmoles) in 5N-aqueous hydrochloric acid (50 ml.) was cooled to 0–5°, and ether (10 ml.) was added. Sodium nitrite (1.8 g., 26 mmoles) in water (6 ml.) was slowly added to the vigorously stirred mixture, which was kept at 0–5° for a further hour and then



extracted with ether ( $3 \times 10$  ml.). The combined extracts were dried ( $\text{MgSO}_4$ ) and the solvent was removed at room temperature and reduced pressure (380 mm.) in a stream of dry nitrogen. When the bulk of the solvent had been removed, a violent reaction took place and the residue became deep red. The residue was distilled at 5 mm., to give a yellow oil (2.5 g.), shown to contain pentafluoroaniline by infrared spectroscopy. Dry hydrogen chloride was passed into an ethereal solution (25 ml.) of the oil for 15 min., the ether was filtered and removed as before, and distillation of the residue gave yellow *pentafluorophenyl azide* (1.50 g., 30%) (Found: C, 34.8; N, 19.5.  $\text{C}_6\text{F}_5\text{N}_3$  requires C, 34.5; N, 20.1%), b. p.  $35^\circ/5$  mm. This compound shows strong absorption at 2128 and 2198  $\text{cm}^{-1}$ , attributed to the azide function, and the aromatic ring vibration is at 1515  $\text{cm}^{-1}$ .

(b) *From pentafluorophenylhydrazine and nitrosyl chloride.* A slow stream of nitrosyl chloride (ca. 2.0 g.) was passed into stirred glacial acetic acid (20 ml.) containing pentafluorophenylhydrazine (6.0 g.). Reaction began immediately and continued for about 2 hr., the solution gradually becoming deep red. The solution was left open to the atmosphere for 14 hr., then heavily diluted with water and steam-distilled. The organic distillate was washed with water and 2*N*-aqueous sodium carbonate, dried ( $\text{MgSO}_4$ ), and distilled to give pentafluorophenyl azide (3.3 g., 52%), b. p.  $35^\circ/5$  mm., identified by its infrared spectrum. Attempts to establish the purity of this compound by gas-liquid chromatography failed, owing to extensive decomposition at the temperatures (ca. 110–120°) necessary to elute the azide from the column.

*Decomposition of Pentafluorophenyl Azide.*—The azide (2.0 g., 10 mmoles) was heated in a small flask fitted with a reflux air-condenser. Decomposition began at 80° (bath) and proceeded smoothly at 120°. The nitrogen evolved (203 ml., 95%) was passed over sodium hydroxide pellets and through concentrated sulphuric acid, and collected in a gas burette. The dark brown solid residue (1.5 g.), m. p. 85–107°, was not identified, but gave a strong aromatic band at 1517  $\text{cm}^{-1}$ .

*Oxidation of Pentafluorophenylhydrazine in Aqueous Media.*—(a) *With Fehling's solution at 80°.* Fehling's solution (125 ml. each of solutions "A" and "B") was added dropwise during 30 min. to a fine, stirred, suspension of pentafluorophenylhydrazine (7.0 g., 35.4 mmoles) in water (50 ml.) at 80° (bath). Nitrogen (760 ml., 96%), evolution of which ceased shortly after all the oxidising agent had been added, was led through a trap at  $-78^\circ$  to a gas-burette. The mixture was heated under reflux for a further 30 min., a small quantity of liquid which condensed in the trap was returned to the reaction flask, and the mixture was steam-distilled. The organic product (3.5 g.) was washed with 5*N*-aqueous hydrochloric acid and water, dried ( $\text{MgSO}_4$ ), and shown by gas-liquid chromatography (2 m.; dinonyl phthalate; at 85°) to contain only two components. Distillation failed to give a significant separation, but specimens of the two components were isolated by preparative-scale chromatography (dinonyl phthalate column; 4 m.  $\times$  22 mm. internal diameter; at 85°) and identified by infrared spectroscopy as pentafluorobenzene (Found: C, 43.1; H, 0.8%; *M*, 167. Calc. for  $\text{C}_6\text{HF}_5$ : C, 42.9; H, 0.6%; *M*, 168), b. p. (micro-capillary)  $85^\circ$  (lit.,<sup>25</sup> b. p.  $85^\circ$ ), and 1,2,4,5-tetrafluorobenzene (Found: C, 48.2; H, 1.4%; *M*, 149. Calc. for  $\text{C}_6\text{H}_2\text{F}_4$ : C, 48.0; H, 1.3%; *M*, 150), b. p. (micro-capillary)  $88^\circ$  (lit.,<sup>26</sup> b. p.  $88^\circ$ ). Calibration of the chromatographic instrument with a mixture of the pure compounds showed that the yields were: pentafluorobenzene, 1.5 g., 25%; tetrafluorobenzene, 2.0 g., 38%. The aqueous residue from the steam-distillation was shown to contain fluoride ion: acidification with 5*N*-aqueous hydrochloric acid and extraction with ether ( $3 \times 50$  ml.) gave a brown tar (1.2 g.), having a strong phenolic odour and giving a violet colour with aqueous ferric chloride.

A second experiment with pentafluorophenylhydrazine (10 g.) and Fehling's solution at 80° gave pentafluorobenzene (2.2 g., 26%) and 1,2,4,5-tetrafluorobenzene (4.0 g., 53%).

(b) *With Fehling's solution at 65°.* *Effect of temperature and concentration.* Two experiments involving a similar procedure to that described above were conducted concurrently. In one of these, pentafluorophenylhydrazine (5.0 g., 25.3 mmoles) and Fehling's solution (90 ml. each of solutions "A" and "B") were used, and, in the other, these reactants in the same quantities were diluted with water (540 ml.). The reactants were mixed at room temperature and heated in the same bath to 65°; this temperature was maintained for 1 hr. and nitrogen

<sup>25</sup> Nield, Stephens, and Tatlow, *J.*, 1959, 166.

<sup>26</sup> Finger, Reed, Burness, Fort, and Blough, *J. Amer. Chem. Soc.*, 1951, 73, 145.

was evolved quantitatively in each case. Separation and analysis of the products as before gave (results in concentrated solution first) pentafluorobenzene (1.95 g., 46%; 1.80 g., 43%) and 1,2,4,5-tetrafluorobenzene (1.41 g., 37%; 1.43 g., 38%).

(c) *With copper sulphate.* Copper sulphate (25.0 g., 100 mmoles) in water (100 ml.) was added to a stirred suspension of the hydrazine (10.0 g., 50.5 mmoles) in water (250 ml.) at 80° (bath). The reaction, which commenced immediately, was controlled by careful addition of the oxidant and, after the addition, the reactants were heated under reflux for 1 hr. with more copper sulphate (5.0 g.). Nitrogen (1100 ml., 97%) was evolved, and steam-distillation of the liquid products gave a yellow oil, which was dried ( $\text{MgSO}_4$ ) and distilled to give a clear colourless product (6.8 g.). This was analysed by infrared spectroscopy and gas-liquid chromatography (2 m.; dinonyl phthalate; at 85°) and shown to consist of pentafluorobenzene (6.5 g., 77%) and 1,2,4,5-tetrafluorobenzene (0.3 g., 4%).

(d) *With hypobromite.* An alkaline solution of sodium hypobromite [from bromine (8.1 g., 50 mmoles), sodium hydroxide (8.1 g., 200 mmoles), and ice-cold water (50 ml.)] was added during 1 hr. to a suspension of pentafluorophenylhydrazine (5.0 g., 25 mmoles) in water (100 ml.) at 80° (bath). A vigorous reaction ensued and nitrogen (300 ml., 53%) was evolved. Steam-distillation of the products gave an oil, which was dried ( $\text{P}_4\text{O}_{10}$ ) and purified by fractional condensation *in vacuo* to give pentafluorobenzene (1.8 g., 43%) (Found: *M*, 168. Calc. for  $\text{C}_6\text{HF}_5$ : *M*, 168), b. p. (micro-capillary) 85°, shown to be pure by infrared spectroscopy and gas-liquid chromatography (2 m.; dinonyl phthalate; at 85°). Extraction of the alkaline aqueous residue with ether (3 × 20 ml.) gave an intractable tar (1.4 g.), and acidification of the aqueous layer followed by a further extraction gave traces of a tarry residue with a phenolic odour.

*Reaction of Pentafluorophenylhydrazine with Stannous Chloride.*—Pentafluorophenylhydrazine (5.0 g., 25 mmoles), stannous chloride (11.3 g., 50 mmoles), and concentrated hydrochloric acid (150 ml.) were heated to 70–80° (bath) under a reflux condenser for 4.5 hr. The products were poured on to ice, made alkaline with 5*N*-aqueous sodium hydroxide, and steam-distilled. The organic distillate was washed with water, dried ( $\text{MgSO}_4$ ), and distilled to give only 1,2,4,5-tetrafluorobenzene (2.5 g., 66%) (Found: *M*, 149. Calc. for  $\text{C}_6\text{H}_2\text{F}_4$ : *M*, 150), b. p. 85–89°, identified by infrared spectroscopy and shown to be pure by gas-liquid chromatography (2 m.; dinonyl phthalate; at 90°).

2,3,4,5,6-Pentafluorobiphenyl.—(a) *From the hydrazine and silver oxide.* Silver oxide (12 g., 52 mmoles) was added gradually with vigorous stirring to pentafluorophenylhydrazine (10 g., 50.5 mmoles) in chromatographically pure benzene (150 ml.). An induction period of 2–3 min. followed addition of the initial small portion of silver oxide, after which the reaction became vigorous and was controlled by cooling in ice. When the addition was complete, the mixture was heated slowly to 80° and refluxed for 1 hr. with more silver oxide (6.0 g.). Nitrogen (1100 ml., 98%) was evolved during the reaction. The mixture was filtered, the filtrate was dried ( $\text{MgSO}_4$ ), and the solvent was distilled out and shown to be pure benzene by gas-liquid chromatography (4 m.; dinonyl phthalate; at 85°). The residual brown solid was recrystallised from ethanol to give 2,3,4,5,6-pentafluorobiphenyl (7.75 g., 63%) (Found: C, 58.8; H, 1.8.  $\text{C}_{12}\text{H}_5\text{F}_5$  requires C, 59.0; H, 2.0%) as white plates, m. p. 110.5–112°.

(b) *From the hydrazine and bleaching powder.* Pentafluorophenylhydrazine (9.9 g., 50 mmoles) in chromatographically pure benzene (50 ml.) was added gradually to a stirred suspension of commercial bleaching powder (25 g.) in benzene (100 ml.). No reaction occurred at room temperature, but the oxidation proceeded smoothly at 70–80° to give an almost quantitative yield of nitrogen (1110 ml., 98%) in 2 hr. The mixture was then heated under reflux with more bleaching powder (5 g.) for 30 min., the products were filtered, and benzene was distilled from the filtrate to leave a brown solid (10.0 g.). Recrystallisation of this from aqueous ethanol and treatment with charcoal failed to remove the coloured impurity, but sublimation *in vacuo* at 90° (bath) gave pure 2,3,4,5,6-pentafluorobiphenyl (9.0 g., 74%), m. p. and mixed m. p. 111–112°, identified by infrared spectroscopy.

*Oxidation of Pentafluorophenylhydrazine in Hexafluorobenzene.*—Pentafluorophenylhydrazine (10.0 g., 50.5 mmoles) was added during 2 hr. to a suspension of silver oxide (23.4 g., 100 mmoles) in chromatographically pure hexafluorobenzene (94.0 g.). The mixture was cooled in ice during the addition, nitrogen (1080 ml., 96%) was evolved, and a silver mirror was deposited on the walls of the vessel. The products were filtered and dried ( $\text{MgSO}_4$ ), leaving a deep red solution which was distilled through a 40 cm. column packed with 1 mm. Dixon rings. The liquid

distilling up to 84° (86.2 g.) was collected as a number of fractions, which were shown by gas-liquid chromatography (2 m.; dinonyl phthalate; at 85°) to contain only hexafluorobenzene (80.8 g.) and pentafluorobenzene (5.4 g., 63%). The residue was distilled in a semimicro-unit and gave a fraction (0.2 g.), b. p. 100°/20 mm., from which a white solid crystallised on storage. This was dried on a porous tile and recrystallised from aqueous methanol to give decafluoro-biphenyl (0.11 g., 2%), m. p. 68° (lit., m. p. 68—69°,<sup>25</sup> 67.5—68°<sup>27</sup>), identified by infrared spectroscopy.

*Bispentafluorophenylmercury*.—Finely divided mercury (together with some mercuric oxide) was prepared by the addition of dilute aqueous ammonia to mercurous nitrate (50 g.) in water (200 ml.). The mixture was heated to the b. p. with an excess of glucose, and the black precipitate was washed with water, acetone, and ether, and dried. The droplets coalesced when ground in a mortar, to give the more familiar form of the metal.

Pentafluorophenylhydrazine (11.0 g., 55 mmoles) was added in small portions to mercuric oxide (25 g., 60 mmoles) and finely divided mercury (*ca.* 30 g.) suspended in perfluoropentane (100 ml.). The reaction was initiated by gentle warming, after which nitrogen (1200 ml., 97%) was evolved smoothly while the temperature was kept at 0—5°. The mixture was then heated under reflux for 1 hr., the solvent was distilled off, and the black residue was extracted with ether (200 ml.). Removal of the ether by distillation gave a mass of large colourless crystals which crumbled to an amorphous powder (10.1 g.), presumably losing solvent of crystallisation, in a vacuum-desiccator. Recrystallisation from light petroleum (b. p. 60—80°) and sublimation *in vacuo* at 130° (bath) gave *bispentafluorophenylmercury* (9.5 g., 64%) (Found: C, 27.2. C<sub>12</sub>F<sub>10</sub>Hg requires C, 27.0%), m. p. 164—165°. The aromatic ring vibrations in this compound are at 1511 cm.<sup>-1</sup>.

*The Pentafluorophenyl Radical and Dibromodifluoromethane*.—Pentafluorophenylhydrazine (10 g., 50 mmoles) in dibromodifluoromethane (50 ml.) was added during 90 min. to a stirred suspension of silver oxide (17.6 g., 76 mmoles) in dibromodifluoromethane (150 ml.) at 0°. The mixture was heated under reflux for a further 30 min., nitrogen (840 ml., 74%) being evolved during the reaction. The resulting solution was filtered, dried (MgSO<sub>4</sub>), and distilled; the residue was an intractable tar (*ca.* 6 g.), and the distillate could not be separated into pure components on this scale. Analysis of the distillate by gas-liquid chromatography (2 m.; dinonyl phthalate) and infrared spectroscopy showed it to contain pentafluorobenzene (0.5 g., 6%) and bromopentafluorobenzene (2.7 g., 22%). The latter was identified by comparison with an authentic specimen prepared by bromination of pentafluorobenzene.<sup>25</sup>

*The Pentafluorophenyl Radical and Methyl Iodide*.—Pentafluorophenylhydrazine (13.6 g., 69 mmoles) was added during 2 hr. to a stirred suspension of silver oxide (24.0 g., 104 mmoles) in methyl iodide (150 ml.). The violent reaction, which commenced after a short induction period, was controlled by cooling in ice, and the mixture was heated under reflux for 30 min. after completion of the addition. Nitrogen (1520 ml., 98%), shown by infrared spectroscopy to contain ethane and dimethyl ether, was evolved, and a silver mirror was formed on the wall of the vessel. The liquid products were filtered, dried (MgSO<sub>4</sub>), and distilled, to give pentafluorobenzene (0.80 g., 7%), b. p. 80—90°, identified by infrared spectroscopy, a fraction (0.56 g.), b. p. 65—107°/150 mm., and chromatographically pure pentafluoroiodobenzene (11.7 g., 60%) (Found: C, 24.7. Calc. for C<sub>6</sub>F<sub>5</sub>I: C, 24.5%), b. p. 107°/150 mm., identified by comparison with an authentic specimen.<sup>25</sup> Infrared spectroscopy and gas-liquid chromatography (2 m.; Apiezon "L" grease; at 130°) showed the fraction of b. p. 65—107°/150 mm. to contain 2,3,4,5,6-pentafluorotoluene and pentafluoroiodobenzene.

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<sup>27</sup> Pummer and Wall, *J. Res. Nat. Bur. Stand.*, 1959, **63A**, 167.