4. *Polyfluoroarenes. Part I. Pentafluorophenol.*

By J. M. Birchall and R. N. Haszeldine.

Hexafluorobenzene, readily prepared by pyrolysis of tribromofluoromethane, has been converted into pentafluorophenol under mild conditions and in good yield; derivatives and properties of pentafluorophenol are described. Infrared spectroscopy reveals a characteristic ring vibration near 1520 cm.$^{-1}$ for pentafluorophenyl derivatives and suggests that appreciable aromatic character is associated with the ring. The decreased basicity of oxygen in pentafluorophenol causes less intermolecular hydrogen bonding than with phenol, and is reflected in its relatively low b. p. (143°); the possibility of intramolecular hydrogen bonding to the *ortho* fluorine atoms is considered.

Although many per- and poly-fluoroalkyl compounds are now known, very few compounds of type Ar_FX, where Ar_F is a perfluoroaryl group and X is a functional group, have been synthesised. Hexafluorobenzene was prepared by McBee *et al.*[1] but the route followed is unsatisfactory for synthesis on a larger scale. Earlier work by Désirant, only recently published,[2] provides the best method for the synthesis of hexafluorobenzene:

$$CFBr_3 \xrightarrow[\text{Pt tube}]{630\text{–}640^\circ} C_6F_6$$

Hexafluorobenzene has since been obtained[3] by dehydrofluorination of a nonafluoro*cyclo*hexane, but the preparation of suitable pure precursors of this type is tedious.

---

[1] McBee, Lindgren, and Ligett, *Ind. Eng. Chem.*, 1947, **39**, 378.

[2] Désirant, *Bull. Acad. roy. Belg.*, 1955, **41**, 759.

[3] Godsell, Stacey, and Tatlow, *Nature*, 1956, **178**, 199.

Like Wall *et al.*,[4] we have used Désirant's method and find it well suited to continuous preparation of hexafluorobenzene. Carbon tetrabromide, readily prepared from acetone,[5] was converted by activated antimony trifluoride into tribromofluoromethane in 65—75% yield. Pyrolysis at atmospheric pressure in a nickel tube lined with platinum gave readily-reproducible results leading to the establishment of optimum conditions. The pyrolysis was catalysed by platinum gauze; nickel tubes or nickel packings were much less effective than platinum. Under optimum conditions the conversion into hexafluorobenzene was 35% with a 48% net yield.

The formation of hexafluorobenzene by pyrolysis of tribromofluoromethane probably involves difluoroacetylene as intermediate ($CFBr_3 \longrightarrow CFBr_2{\cdot}CFBr_2 \longrightarrow C_2F_2 \longrightarrow C_6F_6$); it is well known that dichloroacetylene trimerises to hexachlorobenzene.[6]

Hexafluorobenzene, like other perfluoro-olefins, is sensitive towards nucleophilic attack, but only in a non-aqueous solvent. Thus hexafluorobenzene is resistant to aqueous sodium hydroxide at atmospheric pressure, and although reaction occurs under autogenous pressure, pentafluorophenol is produced in low yield, if at all. This contrasts with hexachlorobenzene which gives pentachlorophenol in 80% yield under similar conditions.[7] Similarly, methanolic sodium hydroxide converts hexachlorobenzene into pentachlorophenol in 99% yield,[8] whereas hexafluorobenzene under comparable conditions in ethanol reacts only slowly and yields 2 : 3 : 4 : 5 : 6-pentafluorophenetole. The apparent ease of nucleophilic attack by ethoxide ion is confirmed by the ready conversion of hexafluorobenzene into 2 : 3 : 4 : 5 : 6-pentafluorophenetole by ethanolic potassium ethoxide; small amounts of ethoxide ion are known to be present in ethanolic potassium hydroxide.

Pentafluorophenol was prepared in good yield under mild conditions by heating hexafluorobenzene with potassium hydroxide in *tert.*-butyl alcohol. The phenol has a typical phenolic odour and, as expected, is markedly acidic. Pentafluorophenol has a b. p. (143°) much lower than that of phenol (182°), indicating a decrease in intermolecular hydrogen bonding accompanied by some intramolecular hydrogen bonding (see discussion of infrared spectra below).

It readily forms a crystalline potassium salt and yields such crystalline esters as benzoate and 3 : 5-dinitrobenzoate without difficulty.

Infrared Spectra of Pentafluorophenyl Derivatives.—An interesting point is whether hexafluorobenzene shows aromatic character with full conjugation of the three double bonds. Hexafluorobuta-1 : 3-diene, for example, is quite different from buta-1 : 3-diene; its chemical reactivity and its infrared spectrum show that there is little conjugation

TABLE 1.

		Ring vibration (cm.$^{-1}$)	C–F stretching vibrations (cm.$^{-1}$)
C_6F_6	Vap.†	1536	1021, 1003
,, ...	Liq.	1531	1018, 994
$C_6F_5{\cdot}OEt$	Liq. film	1515	1037, 997
$C_6F_5{\cdot}OH$	Liq. film	1515, 1534 (doublet)	1016, 996, 979
,, ...	Vap.	1522, 1543 (doublet)	1016, 994, 978
$C_6F_5{\cdot}OK$	Mull *	1479, 1497	1009, 974
$C_6F_5{\cdot}O{\cdot}COPh$	Mull *	1520	1044, 1024, 1009, 996
$C_6F_5{\cdot}O{\cdot}CO{\cdot}C_6H_3(NO_2)_2$ ...	Mull *	1524	1014, 995

* In Nujol or hexachlorobutadiene.

† Delbouille, *J. Chem. Phys.*, 1956, **25**, 182, reports bands at 1529, 1018, and 1003 cm.$^{-1}$ for a sample prepared by Désirant.

---

[4] Hellmann, Peters, Pummer, and Wall, *J. Amer. Chem. Soc.*, 1957, **79**, 5654.

[5] Hunter and Edgar, *ibid.*, 1932, **54**, 2025; Berthelot and Jungfleisch, *Annalen*, 1870, *Supplement*, 7, 252.

[6] Nicodemus, *J. prakt. Chem.*, 1911, **83**, 312; Ott and Dittus, *Ber.*, 1943, **76**, 80; Goodall and Howlett, *J.*, 1954, 2599.

[7] Troitskii and Voronina, *Org. Chem. Ind.* (*U.S.S.R.*), 1940, **7**, 240.

[8] Smith and Livak, U.S.P. 2,107,650/1938; *Chem. Abs.*, 1938, **32**, 2548.

between the double bonds.[9] Examination of the infrared spectra of hexafluorobenzene and its derivatives strongly indicates aromatic character in the cyclic triene system. All the spectra show strong C–F stretching bands near 1000 cm.$^{-1}$, and another strong band near 1520 cm.$^{-1}$ (Table 1) that is attributed to the C:C ring vibration. The extent of conjugation is revealed by comparison with other C:C stretching vibrations, shown in Table 2, which are at much higher frequency.

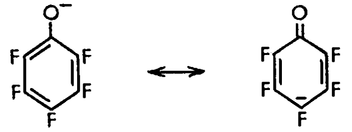
TABLE 2. C:C *Stretching vibration* (*cm.*$^{-1}$).

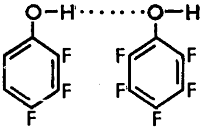
cis–trans-HCF:CFH ...	*a*	Vap.	1736, 1715	$CF_2\cdot CF:CF\cdot CF_2$	*e*	Vap.	1802
cis-$CF_3\cdot CF:CF\cdot CF_3$ ...	*b*	Vap.	1733	$CF_2\cdot CF_2\cdot CF:CF\cdot CF_2\cdot CF_2$	*f*	Vap.	1754
cis-$C_2F_5\cdot CF:CF\cdot C_2F_5$	*c*	Vap.	1712	$CF_2\cdot CF:CF\cdot CF_2\cdot CF:CF$ ...	*g*	CCl_4 Soln.	1739
$CF_2:CF\cdot CF:CF_2$	*d*	Vap.	1770	$CF_2\cdot CF_2\cdot CF:CF\cdot CF:CF$	*g*	CCl_4 Soln.	1754, 1712

[a] Haszeldine and Steele, *J.*, 1957, 2800. [b] Haszeldine, *J.*, 1952, 4423. [c] Haszeldine and Steele, *J.*, 1953, 1592. [d] Haszeldine, *J.*, 1952, 4423. [e] Unpublished work. [f] Haszeldine, *Nature*, 1951, **168**, 1028. [g] Evans and Tatlow, *J.*, 1954, 3779; 1955, 1184.

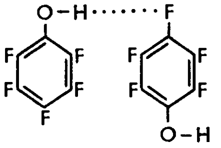
The ring vibration of the pentafluorophenoxide ion at 1502 cm.$^{-1}$ is at lower frequency than that in the covalent pentafluorophenyl derivatives, indicating increased resonance of type shown inset.

The spectrum of pentafluorophenol in the 3500 cm.$^{-1}$ region was studied in more detail to determine the effect of hydrogen bonding. The liquid film shows a sharp band at 3571 cm.$^{-1}$ and a broad band of approximately equal intensity centred on 3425 cm.$^{-1}$; the former is the typical " free " hydroxyl stretching vibration band and the latter the typical hydrogen-bonded hydroxyl group band. The spectrum of pentafluorophenol vapour shows a sharp strong band at 3623 cm.$^{-1}$ and no band in the 3400 cm.$^{-1}$ region. A 1% solution in carbon tetrachloride shows a single sharp band at 3571 cm.$^{-1}$ with a weak shoulder at 3676 cm.$^{-1}$ and a weak broad bonded hydroxyl band at 3257 cm.$^{-1}$. These facts show that intermolecular hydrogen bonding of type (I) [or, less likely, (II)] occurs in the liquid, and is absent from the vapour and much reduced in solution in a non-polar solvent. The situation is similar to that found with perfluoroalkyl alcohols[10] where the decreased basicity of the oxygen caused by the adjacent electron-attracting fluorocarbon group decreases its participation in intermolecular hydrogen bonding. Judged by the relative intensities of the " bonded " and " free " hydroxyl group bands, intermolecular hydrogen bonding is weaker in pentafluorophenol than in phenol. As with the perfluoro- and perchloro-alcohols, intramolecular hydrogen bonding of type (III) is possible, and the band at 3623 cm.$^{-1}$ could be ascribed to a " free " hydroxyl group appearing again at 3676 cm.$^{-1}$ in the solution, with the 3571 cm.$^{-1}$ band caused by bonding of type (III). Alternatively, the shift from 3623 to 3571 cm.$^{-1}$ is to be ascribed to the dielectric constant of the medium. The marked difference in b. p. between phenol and pentafluorophenol

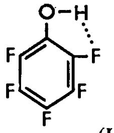




(I)



(II)



(III)

---

[9] Haszeldine, *J.*, 1952, 4423.

[10] *Idem*, *J.*, 1953, 1757.

is caused by decrease in intermolecular hydrogen bonding rather than by increase in intramolecular hydrogen bonding, *i.e.*, the change in basicity of the oxygen atom is responsible rather than the presence of fluorine in the *ortho* position to give structures of type (III); the difference in b. p. between *o*-fluorophenol (152°) and *p*-fluorophenol (189°) is to be explained similarly.

EXPERIMENTAL

Preparation of Tribromofluoromethane.—Dry carbon tetrabromide (1 mole), antimony trifluoride (0·5 mole), and bromine (0·05 mole) were heated to 120—130° during 1 hr. so that the tribromofluoromethane distilled out as it was formed. The temperature was later raised to 150—160° for 0·5 hr. to ensure complete removal of the product. The crude product was washed with 5% aqueous tartaric acid, 10% aqueous sodium sulphite, 2% aqueous sodium hydroxide, and water; it was then dried (P_4O_{10}) and distilled to give tribromofluoromethane (65—75%), b. p. 106—107°. Dibromodifluoromethane, b. p. 23·5°, was also formed (5—10%). Rathsburg[11] obtained a 19% yield of tribromofluoromethane by this method.

Preparation of Hexafluorobenzene.—The pyrolysis apparatus consisted of a tube of platinum foil (50 cm. long × 1·8 cm. i.d.), encased in nickel, and heated electrically over 40 cm. of its length. The nickel inlet and outlet tubes were water cooled by means of lead coils. The tube was packed with a 3 in. square of platinum gauze of 80-mesh 0·003 in. diameter wire. Under optimum conditions, tribromofluoromethane (130 g./hr.) was dripped at constant rate into the furnace at 630—640°; nitrogen (60 ml./hr.) was added simultaneously. The apparatus was operated continuously. The products, condensed in two cooled traps, were washed with ice-cold 10% aqueous sodium sulphite, aqueous 5N-sodium hydroxide, and water, then dried (P_4O_{10}) and distilled through a Podbielniak column of 25—30 plates to give hexafluorobenzene (35%; 48% on tribromofluoromethane actually used) (Found: C, 38·8%; *M*, 187. Calc. for C_6F_6: C, 38·7%; *M*, 186), b. p. 80—81°, n_D^{20} 1·3777, which solidified at 0°. Under these conditions some tribromofluoromethane (26%) was recovered, and 65% of the theoretical amount of bromine was liberated. Investigation of the products of b. p. > 110° (20 g./hr. on the above scale) will be described later. With apparatus of the dimensions stated, higher rates of flow left much tribromofluoromethane unchanged whereas lower rates gave more by-products. Typical results at 640° are shown in the annexed Table.

$CFBr_3$, g./hr.	Br liberd. %	$CFBr_3$ recd. %	C_6F_6		$CFBr_3$, g./hr.	Br liberd. %	$CFBr_3$ recd. %	C_6F_6	
			Yield %	Net yield %				Yield %	Net yield %
72·5 *	74	23	28	36	130 †	88	11	33	37
101 *	70	24	28	37	170	54	41	26	44
310	45	50	21	42	130	60	27	34	47
530	26	66	13	37	130	65	26	35	48

* Tube without gauze packing. † Furnace at 680°.

Pyrolysis in a nickel tube gave a 25% yield of hexafluorobenzene; use of nickel wire as packing reduced the yield substantially.

The purity of the hexafluorobenzene is shown by gas chromatography, analysis, molecular-weight determination, and infrared spectroscopy. The infrared bands reported by Stacey *et al.*[3] at 1702, 1761, and 1802 cm.$^{-1}$ were not present in our material, and must be attributed to impurity.

Action of Aqueous Sodium Hydroxide on Hexafluorobenzene.—The action of aqueous sodium hydroxide on hexafluorobenzene was studied at atmospheric pressure and in an autoclave; the conditions of concentration, temperature, reactant ratios, etc., were varied. Hexafluorobenzene was resistant to attack by aqueous alkali at atmospheric pressure; reaction occurred at higher pressures but gave no readily identifiable product.

2 : 3 : 4 : 5 : 6-*Pentafluorophenetole.*—Hexafluorobenzene (5·0 g.) was heated under reflux with N-potassium ethoxide in anhydrous ethanol (25 ml.) for 1 hr. The mixture was poured into an excess of water and the organic layer was washed with water. dried, and distilled to give

---

[11] Rathsburg, *Ber.*, 1918, **51**, 669,

hexafluorobenzene (1·1 g., 22%) and 2 : 3 : 4 : 5 : 6-*pentafluorophenetole* (3·2 g., 56%) (Found: C, 45·1; H, 2·5%. $C_8H_5OF_5$ requires C, 45·3; H, 2·4%), b. p. 152—153°, n_D^{20} 1·4109.

Action of Ethanolic Potassium Hydroxide on Hexafluorobenzene.—Hexafluorobenzene (2·0 g.) and 10% ethanolic potassium hydroxide (10 ml.) were heated in a sealed tube at 120° for 30 min.; the mixture was poured into water. The dried ($MgSO_4$) ether extract was distilled to give hexafluorobenzene (0·9 g., 45%) and 2 : 3 : 4 : 5 : 6-pentafluorophenetole (1·1 g.; 48%), identical with the compound described above.

Pentafluorophenol.—Hexafluorobenzene (10·0 g.; 0·054 mole), potassium hydroxide (7·6 g.; 0·135 mole), andt *ert.*-butyl alcohol (100 ml.; 1·1 moles) were heated under reflux for 1 hr. Water (200 ml.) was added to the cooled reactants and the *tert.*-butyl alcohol distilled off. The residual aqueous solution was filtered and extracted with ether (2 × 50 ml.). The aqueous layer was then acidified with 5N-hydrochloric acid (80 ml.), a colourless oil separating. This was extracted with ether (4 × 50 ml.), and the ethereal layer washed with water, dried ($MgSO_4$), and distilled to give *pentafluorophenol* (7·0 g.; 71%) (Found: C, 39·3; H, 0·9%; equiv., 183·6. C_6HOF_5 requires C, 39·1; H, 0·5%; equiv., 184·1), m. p. 25—30°, b. p. 143°, n_D^{20} 1·4270. It proved difficult to dry ethereal pentafluorophenol thoroughly, and analysis for hydrogen was carried out after the distilled liquid had been dried by azeotropic distillation with benzene immediately before analysis. The equivalent weight was determined by titration in ethanolic solution against standard sodium hydroxide with phenolphthalein as indicator.

Pentafluorophenol, a crystalline solid with marked phenolic odour, gives a deep violet colour with aqueous ferric chloride and liberates carbon dioxide from cold aqueous sodium hydrogen carbonate. It is hygroscopic but not freely soluble in water.

Potassium Pentafluorophenoxide.—Hexafluorobenzene (2·0 g.) was heated under reflux with potassium hydroxide (1·5 g.) in *tert.*-butyl alcohol (20 ml.) for 1 hr. An excess of water was added and the alcohol was distilled off. The residual aqueous solution was filtered and cooled, white needles were deposited of *potassium pentafluorophenoxide* (1·5 g.; 69%) (Found: C, 32·2; H, 0·2. C_6OF_5K requires C, 32·4; H, 0%), m. p. 246° (slight decomp.) (from water); it is hygroscopic, soluble in acetone, but insoluble in ether. Potassium pentachlorophenoxide, similarly prepared, deposits pentachlorophenol as a solid when its aqueous solution is acidified.[12]

Pentafluorophenyl Benzoate and 3 : 5-*Dinitrobenzoate.*—These were prepared by treatment of pentafluorophenol in pyridine with the appropriate acid chloride. The *benzoate* (Found: C, 52·4; H, 1·7. $C_{13}H_5O_2F_5$ requires C, 54·2; H, 1·7%) crystallised from aqueous ethanol as white needles, m. p. 74—75°; it shows carbonyl absorption in the infrared at 1773 cm.$^{-1}$.

The 3 : 5-*dinitrobenzoate* (Found: C, 41·5; H, 0·8; N, 7·4. $C_{13}H_3O_6N_2F_5$ requires C, 41·3; H, 0·8; N, 7·4%) crystallised from light petroleum as plates, m. p. 107°; its carbonyl absorption is at 1776 cm.$^{-1}$.

The authors thank Mlle. Y. Désirant for providing details of her method for preparing hexafluorobenzene. One of them (J. M. B.) is indebted to the D.S.I.R. for a Research Studentship.

MANCHESTER COLLEGE OF SCIENCE AND TECHNOLOGY. [*Received, June 16th*, 1958.]

[12] Bartlett, U.S.P. 2,644,015/1953; *Chem. Abs.*, 1954, **48**, 5216.