Polyfluoroarenes. Part VIII.¹ Some Homolytic Reactions of Pentafluoroiodobenzene

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Pentafluorophenyl radicals from the photolysis of pentafluoroiodobenzene react with benzene and toluene to give high yields of pentafluorobiphenyls. Much slower reactions occur with nitrobenzene, hexafluorobenzene, and pentafluorobenzene. Photolysis with carbon tetrachloride yields chloropentafluorobenzene, formed in much higher yield from the same reactants in the dark at 290°. The thermal decomposition of pentafluoroiodobenzene is not a satisfactory route to the pentafluorophenyl radical, but reactions of the iodo-compound with copperbronze and with mercury at 300° give high yields of decafluorobiphenyl and bispentafluorophenylmercury, respectively.

INVESTIGATION of the utility of pentafluoroiodobenzene as a synthetic intermediate in polyfluoroarene chemistry has hitherto been confined mainly to its use as a precursor of pentafluorophenylmagnesium iodide.² The present Paper describes a study of the photochemical and thermal decomposition of the iodo-compound as potential routes to the pentafluorophenyl radical, previously obtained by the oxidation of pentafluorophenylhydrazine³ and by the photolysis of pentafluorobenzenesulphonyl chloride.⁴ The value of trifluoroiodomethane as a source of the trifluoromethyl radical is well established,⁵ and the photolysis of a number of hydrocarbon aryl iodides has recently been shown to give aryl radicals.6

Photochemical Reactions.—The photochemical decomposition of pentafluoroiodobenzene [absorption maxima in hexane at 227 and 265 mµ (c, 12100 and 760, respectively)], under the influence of ultraviolet light from a high-intensity mercury vapour lamp, proceeds slowly. After 150 hr. 56% of the iodo-compound remains unchanged and the remainder appears only as intractable tar and surface coating on the silica vessel. The failure to detect decafluorobiphenyl as a product suggests that, as for trifluoroiodomethane,⁵ recombination of the radicals assumed to be produced in the primary process is preferred. Even in the presence of copper-bronze or mercury, which should react with the iodine atoms produced, dimerisation of the pentafluorophenyl radicals during the photolysis does not become a significant process. Presumably the radicals react with the iodocompound itself in a way which leads ultimately to the formation of the tarry products. Pentafluorophenyl radicals produced by photolysis of pentafluoroiodobenz-

¹ Part VII, J. M. Birchall, W. M. Daniewski, R. N. Haszeldine,

ene in carbon tetrachloride abstract chlorine to give chloropentafluorobenzene in 21% yield.

In the presence of certain aromatic compounds, the rate of the photolysis is markedly increased, and the reaction can give rise to high yields of pentafluorobiphenyls. Thus, irradiation with benzene gives an 89% vield of 2,3,4,5,6-pentafluorobiphenyl; 40% of the theoretical yield of hydrogen is produced, and the reaction is 84% complete after 80 hr. Toluene gives pentafluorobenzene and the pentafluoromethylbiphenyls:



The pentafluoromethylbiphenyls have also been synthesised (33-62% yield) from hexafluorobenzene and the corresponding tolyl-lithiums; smaller amounts of the tetrafluorodimethyl-p-terphenyl (12-35% yield) were also obtained in each case:

$$C_6F_6$$
 + MeC₆H₄Li
ether -15°
 $C_6F_5 \cdot C_6H_4Me$ + MeC₆H₄ $\leftarrow F_F$
 F_F

⁴ P. J. Bain, E. J. Blackman, W. Cummings, S. A. Hughes, E. R. Lynch, E. B. McCall, and R. J. Roberts, *Proc. Chem. Soc.*, 1962, 186.

⁵ R. N. Haszeldine, J. Chem. Soc., 1949, 2856.

⁶ J. M. Blair and D. Bryce-Smith, *J. Chem. Soc.*, 1960, 1788; W. Wolf and N. Kharasch, *J. Org. Chem.*, 1961, **26**, 283; N. Kharasch, W. Wolf, T. J. Erpelding, P. G. Naylor, and L. Tokes, *Chem. and Ind.*, 1962, **81**, 1720; N. Kharasch and L. Göthlich, *Angew. Chem., Internat. Edn.*, 1962, **1**, 459.

and L. S. Holden, J. Chem. Soc., 1965, 6702.
 ² E. Nield, R. Stephens, and J. C. Tatlow, J. Chem. Soc., 1959, 166; W. J. Pummer and L. A. Wall, J. Res. Nat. Bur. Stand., 1959, 63Å, 167.

³ J. M. Birchall, R. N. Haszeldine, and A. R. Parkinson, J. Chem. Soc., 1962, 4966.

Two processes probably facilitate the decomposition of pentafluoroiodobenzene in the presence of the aromatic hydrocarbons. Freezing point-composition curves for mixtures of pentafluoroiodobenzene with benzene and with toluene (Figure) reveal that appreciable association occurs between the iodo-compound and the hydrocarbon, particularly at molar compositions ranging from 1:2 to 2:1. Association between polyfluoroarenes and aromatic hydrocarbons has been observed



Freezing point-composition curves for mixtures of pentafluoroiodobenzene with benzene and with toluene. $A = C_6 H_6/$ $C_{6}H_{5}I; B = C_{6}H_{6}/C_{6}F_{5}I; C = C_{6}H_{5}Me/C_{6}F_{5}I.$

previously, and is attributed to partial π -electron transfer between the two.7 It is now suggested that association of this type (I) may assist the primary photochemical fission of the iodo-compound, and that the ready acceptance of the resultant aryl radical by the hydrocarbon, perhaps via direct formation of the π -complex (II) during the photolysis, prevents ready recombination with the iodine atom. The latter probably serves to remove the hydrogen atom from the resulting σ-complex (III):



More recent work has shown that some of the hydrogen

7 C. R. Patrick and G. S. Prosser, Nature, 1960, 187, 1021.

⁸ J. M. Birchall, R. N. Haszeldine, and J. G. Speight, unpublished results.

displaced from the aromatic substrate can eventually attack another molecule of the hydrocarbon, to yield cyclohexenes and cyclohexadienes as by-products.⁸

The virtual absence of pentafluorobenzene (<0.05%yield) from the products of the photolysis in benzene shows that removal of the hydrogen atom from the complex (III) by a pentafluorophenyl radical is not a significant process, probably because a sufficiently high concentration of free pentafluorophenyl radicals is not attained during the reaction. The pentafluorobenzene formed in the reaction with toluene is probably the result of abstraction from the methyl group. The proportion of such abstraction (ca. 8% of the total attack on the toluene), the ratio of the isomers produced during the pentafluorophenylation of toluene (o: m: p = 1.81: 0.95: 1.00), and the relative rates of the reactions with benzene and toluene (established by a competition experiment as $1:2\cdot3$) are of the same order as those obtained from the reactions of these hydrocarbons with phenyl radicals from benzoyl peroxide (side-chain abstraction from C₆H₅Me, 13%; isomer distribution for C_6H_5Me , o:m:p=4.6:1.4:1.0; relative rate C_6H_6 : C_6H_5Me , 1.0: 1.7; values obtained at 80°).9 The photochemical reactions described in the present communication were conducted under conditions where the heat generated by the lamp raised the temperature of the reaction tube to $ca. 50-60^\circ$, and a detailed comparison with the data for phenyl radicals is therefore not justified. However, an enhanced electrophilicity of the pentafluorophenyl radical is suggested by the slightly reduced proportion of side-chain abstraction with this radical and by a substantial decrease in the m: p ratio. The reduction in the proportion of attack at the ortho-position in toluene when the pentafluorophenyl radical is employed may be attributed to the larger steric requirements of this entity.

The slow rate of photolysis of pentafluoroiodobenzene with nitrobenzene is probably due partly to absorption of the irradiation by the nitrobenzene itself (λ_{max} , 252 mµ; ε , 10,000¹⁰) and partly to weaker association between the reactants, the nitro-group substantially reducing the electron-donor characteristics of the benzene ring; only a low yield (6%) of a mixture of the isomeric pentafluoronitrobiphenyls is produced. The slow reactions with hexafluorobenzene or pentafluorobenzene may be explained similarly; the small amounts of decafluorobiphenyl which are formed may be the result of dimerisation of the pentafluorophenyl radicals or of slow substitution in the polyfluoroarene rings. The latter seems more likely in view of the failure to detect decafluorobiphenyl as a product of the other reactions studied; free-radical displacement of fluorine from the hexafluorobenzene ring has been observed previously.1,11

⁹ D. H. Hey, B. W. Pengilly, and G. H. Williams, J. Chem. Soc., 1955, 6; 1956, 1463.

¹⁰ R. A. Morton and A. McGookin, J. Chem. Soc., 1934, 901.
 ¹¹ P. A. Claret, J. Coulson, and G. H. Williams, Chem. and Ind., 1965, 228; J. M. Birchall, J. D. Davison, and R. N. Haszeldine, unpublished results.

Thermal Reactions .- The thermal decomposition of pentafluoroiodobenzene does not appear to be a useful source of pentafluorophenyl radicals. Pentafluoroiodobenzene shows little sign of decomposition after prolonged heating (50 hr.) in glass at 250°; 80% decomposition occurs during 50 hr. at 300°, and the compound completely decomposes at 350° (10 hr.) without the formation of decafluorobiphenyl. Only small amounts of biphenyls are formed in reactions at 300° in the dark with benzene, hexafluorobenzene, or pentafluorobenzene, indicating that pentafluorophenyl radicals are produced only slowly even at this temperature.

However, pentafluoroiodobenzene reacts with carbon tetrachloride at 290° to give a 93% yield of chloropentafluorobenzene, and it is probable that this is a chain reaction initiated by decomposition of either or both of the reactants:

$$CCI_{4} \longrightarrow CCI_{3} + CI^{*}$$

$$C_{6}F_{5}I \longrightarrow C_{6}F_{5}^{*} + I^{*}$$

$$CCI_{3}^{*} + C_{6}F_{6}I \longrightarrow CCI_{3}I + C_{6}F_{5}^{*}$$

$$C_{6}F_{5}^{*} + CCI_{4} \longrightarrow C_{6}F_{5}CI + CCI_{3}^{*}$$

The trichloroiodomethane formed in this sequence would decompose at 300°, and its ultimate fate has not been established during the present work.

Copper-bronze facilitates the thermal decomposition of the iodo-compound and changes its course, since a 72% yield of decafluorobiphenyl is obtained at 300° (10 hr.) and no iodo-compound is recovered. Bv contrast, mercury at 300° gives bispentafluorophenylmercury in 75% yield.

The conditions used for the reaction with copperbronze resemble those of the conventional Ullmann reaction, which has been applied previously to the synthesis of decafluorobiphenyl from bromopentafluorobenzene.² The mechanism of the Ullmann reaction is still uncertain,¹² but it may involve participation of the copper in free-radical formation:¹³

$$C_{6}F_{5}I + Cu(0) \longrightarrow C_{6}F_{5} + Cu^{+} + I^{-}$$
$$2C_{6}F_{5} - C_{6}F_{5} + Cu^{+} + I^{-}$$

It is also possible that pentafluorophenylcopper is formed in this process and subsequently decomposes to give the biphenyl.¹⁴ The reaction with mercury probably proceeds in a similar way, loss of iodine being facilitated by the mercury and the resulting pentafluorophenyl radical reacting with the metal to form the mercurial. Whether such processes could be used to facilitate radical formation in the presence of other substrates is not yet clear.

EXPERIMENTAL

Thermal reactions were carried out without agitation in evacuated 300-ml. Dreadnought tubes, and photochemical reactions were carried out with vigorous shaking in evacuated 300-ml. silica tubes. The lamp employed was a Hanovia 500-watt mercury discharge tube (principal emission at 254, 265, 302, 313, 366, 405, 436, 546, and 578 $m\mu$). Indine was removed from the products in each case by washing with aqueous sodium hydrogen sulphite, aqueous sodium hydrogen carbonate, and water. Gasliquid chromatography (g.l.c.) was carried out as described previously with a Perkin-Elmer No. 452 instrument; columns were 2 m. long \times 4 mm. internal diameter except when otherwise stated. Infrared spectra were recorded on a Perkin-Elmer No. 137 instrument and ¹⁹F n.m.r. spectra on a Perkin-Elmer No. R10 instrument at 56.458 Mc./sec.

Photochemical Reactions of Pentafluoroiodobenzene.—(a) With carbon tetrachloride. Pentafluoroiodobenzene (5.0 g., 17 mmole) and carbon tetrachloride (15.0 g., 96 mmole) were irradiated for 160 hr. The products were dissolved in ether (60 ml.), which was washed and dried (Na₂SO₄). Distillation gave carbon tetrachloride (14.5 g.), identified by infrared spectroscopy, and a fraction distilling at 80-163° (4.8 g.). Analysis by g.l.c. (Apiezon "L" grease at 128°) showed that the latter contained carbon tetrachloride (0.39 g., bringing the total recovery to 98%), pentafluoroiodobenzene (4.31 g., 86%), and chloropentafluorobenzene (0.10 g., 21% based on C_6F_5I consumed).

(b) With benzene. Pentafluoroiodobenzene (5.0 g., 17 mmole) and benzene (4.3 g., 55 mmole) were irradiated for 80 hr. Hydrogen (ca. 3 mmole) (Found: M, 2.7) was obtained, and the condensable products were allowed to distil in vacuo into a receiver cooled to -196° . Analysis by g.l.c. (4-m. column; Silicone MS 550 at 70°) showed this material to consist of benzene (2.8 g.), pentafluoroiodobenzene (0.8 g., 16% recovery), and a trace of pentafluorobenzene (<0.05% yield). The solid remaining in the tube was dissolved in ether (50 ml.), and the solution was washed to remove iodine, dried (Na₂SO₄), and evaporated. The residue was recrystallised from aqueous ethanol and sublimed in vacuo to give 2,3,4,5,6-pentafluorobiphenyl (3.1 g., 89% based on C₆F₅I consumed), m. p. 112° (mixed m. p. with an authentic specimen,³ 112°), identified by infrared spectroscopy.

Pentafluoroiodobenzene (10.0 g., (c) With toluene. 34 mmole) and toluene (20.0 g., 218 mmole) were irradiated for 150 hr. Hydrogen (ca. 6 mmole) was obtained, and the remaining products were dissolved in ether $(2 \times 40 \text{ ml.})$, which was washed, dried (Na₂SO₄), and divided into two equal parts, (a) and (b). Distillation of part (a) gave toluene (7.5 g.) and left a semi-solid, which was dried on a porous tile and recrystallised from aqueous ethanol to give 2,3,4,5,6pentafluoro-4'-methylbiphenyl (0.70 g.) (Found: C, 60.4; H, 3.0. $C_{13}H_7F_5$ requires C, 60.5; H, 2.8%), m. p. 118°, identified by mixed m. p. (118°) and comparison of its infrared spectrum with that of the specimen described below. Ether was distilled from part (b), and the concentrated solution was analysed by g.l.c. (Silicone MS 550 at 225°). Calibration of the instrument with standard mixtures of the components showed that the solution contained pentafluorobenzene (0.19 g., 7% yield), toluene (3.98 g., 79% recovery), 2,3,4,5,6-pentafluoro-2'-methylbiphenyl (1.64 g., 37% yield), 2,3,4,5,6-pentafluoro-3'-methylbiphenyl (0.86 g., 19%), and 2,3,4,5,6-pentafluoro-4'-methylbiphenyl (0.91 g., 20%). No pentafluoroiodobenzene was detected.

14 H. Gilman and J. M. Straley, Rec. Trav. chim., 1936, 55, 821.

P. E. Fanta, Chem. Rev., 1964, 64, 613.
 W. A. Waters, "The Chemistry of Free Radicals," Oxford University Press, 2nd edn. 1948, p. 171.

(d) Competition with benzene and toluene. Pentafluoroiodobenzene (6·2 g., 21 mmole), benzene (17·2 g., 220 mmole), and toluene (20.2 g., 220 mmole) were irradiated for 160 hr. Hydrogen (ca. 2 mmole) was obtained, and the remaining products were washed and dried (Na₂SO₄). A mixture of benzene, pentafluorobenzene, and toluene (15.0 g.), b. p. 77-109°, was distilled off, and the remaining solution was analysed by g.l.c. (Silicone MS 550 at 225°). Calibration of the instrument showed that the ratio of pentafluoromethylbiphenyls to pentafluorobiphenyl in the solution was $2 \cdot 3 : 1 \cdot 0$.

(e) With nitrobenzene. Pentafluoroiodobenzene (5.0 g., 17 mmole) and nitrobenzene (18.0 g., 148 mmole) were irradiated for 150 hr. No gaseous material was detected, and the products were dissolved in ether (20 ml.), which was then washed, dried (Na₂SO₄), and distilled. A mixture of pentafluoroiodobenzene and nitrobenzene (21.4 g), b. p. $84-120^{\circ}/40$ mm., was obtained, and the residue was sublimed in vacuo to give a mixture of 2,3,4,5,6-pentafluoronitrobiphenyls (0.3 g., 6%) (Found: C, 50.7; H, 1.5. Calc. for $C_{12}H_4F_5NO_2$: C, 49.8; H, 1.4%), m. p. 100–103°, identified by comparison of its infrared spectrum with those of authentic samples of the three isomers.15

Thermal Reactions of Pentafluoroiodobenzene.-(a) With copper-bronze. Pentafluoroiodobenzene (5.0 g.) and copperbronze (2.4 g.) were kept in a 60-ml. tube at 300° for 10 hr. No gaseous material was obtained; the tube was rinsed out with ether (2 imes 20 ml.) and the ethereal solution was filtered and distilled. The residue (2.7 g.) from the distillation was recrystallised from methanol to give decafluorobiphenyl (2.2 g., 72%), m. p. 66.5° (lit.,² 68-69°), identified by infrared spectroscopy.

(b) Reaction with mercury. Pentafluoroiodobenzene (5.0)g.) and mercury (10.0 g.) were heated in a 60-ml. tube at 300° for 30 hr. A small amount (0.09 mmole; M, 102) of gas was identified by infrared spectroscopy as a mixture of carbon dioxide and silicon tetrafluoride, and the less volatile products were dissolved in ether (40 ml.). The ethereal solution was filtered and distilled, and the residue (4.4 g.), m. p. 126-134°, from the distillation was recrystallised from carbon tetrachloride, sublimed in vacuo at 140°/10 mm., and then recrystallised from light petroleum (b. p. 60- 80°) to give bispentafluorophenylmercury (3.4 g., 75%) (Found: C, 26.9. Calc. for C₁₂F₁₀Hg: C, 27.0%), m. p. 138-139°. This compound was identified by comparison of its infrared spectrum with that of a sample prepared by the oxidation of pentafluorophenylhydrazine with mercuric oxide.3 The melting point of the mercurial prepared from pentafluorophenylhydrazine was previously reported as 164-165°,³ but repetition of this experiment has given a product of m. p. 140-141.5°. No explanation for this discrepancy has been discovered. Chambers, Coates, Livingstone, and Musgrave have reported m. p. 142.3° for a sample of the mercurial prepared from pentafluorophenylmagnesium bromide and mercury (II) chloride.16

(c) With carbon tetrachloride. Pentafluoroiodobenzene (7.9 g., 27 mmole) and carbon tetrachloride (8.7 g., 56 mmole) were kept at 290° for 70 hr. The products were

¹⁵ J. M. Birchall, R. N. Haszeldine, and H. Woodfine, unpublished results.

dissolved in ether (45 ml.), to leave a small amount of carbonaceous residue, and the ethereal solution was washed and dried (Na₂SO₄). Distillation and g.l.c. (dinonyl phthalate at 110°) showed the product to consist of carbon tetrachloride (6.47 g.) and chloropentafluorobenzene (5.17 g., 93%). A fraction (5.2 g.), b. p. 114-116°, was purified by g.l.c. (column, $2 \text{ m.} \times 12 \text{ mm.}$ internal diameter) and yielded chloropentafluorobenzene (4.0 g., 70%) (Found: C, 35.7. Calc. for C₆ClF₅: C, 35.7%), b. p. 121-123° (lit., 122-123°, 17 117.5° 18).

Pentafluoromethylbiphenyls and Tetrafluorodimethyl-p-terphenyls.—(a) o-Tolyl-lithium (82.7 mmole) in ether (59 ml.), prepared from o-bromotoluene and lithium in ether.19 was added with continuous stirring during 60 min. to a cold (-15°) solution of hexafluorobenzene (11.0 g., 59.7 mmole) in ether (75 ml.) under nitrogen. The mixture was stirred for 15 min. at -10° after the addition, then allowed to warm to room temperature and poured, with vigorous stirring, into ice-cold water (250 ml.) containing 5N-hydrochloric acid (30 ml.). The ethereal layer was separated and the aqueous layer was extracted with ether (4×50) ml.). The combined ethereal solutions were dried $(MgSO_4)$ and the ether was removed by distillation to leave a solid residue, recrystallised from ethanol to give 2',3',5',6'-tetrafluoro-2,2"-dimethyl-p-terphenyl (2.7 g., 14%) (Found: C, 72.6; H, 4.4. $C_{20}H_{14}F_4$ requires C, 72.8; H, 4.3%), m. p. 169—170.5°, the structure of which was confirmed by the appearance of only a single ¹⁹F n.m.r. band at +68.4 p.p.m. from trifluoroacetic acid. Addition of water to the ethanolic mother-liquor gave an immiscible oil. This was separated, dried (P_4O_{10}) , and distilled to give 2,3,4,5,6-pentafluoro-2'-methylbiphenyl (5.0 g., 33%) (Found: C, 60.5; H, 2.7. C₁₃H₇F₅ requires C, 60.4; H, 2.7%), b. p. 200-203°, m. p. 38-39.5°.

(b) An identical procedure, in which m-tolyl-lithium (119 mmole) in ether (85 ml.) was added to hexafluorobenzene (11.0 g., 59.7 mmole) in ether (90 ml.), gave 2',3',5',6'-tetrafluoro-3,3''-dimethyl-p-terphenyl (6.7 g., 35%) (Found: C, 73.1; H, 4.2%), m. p. 144-145° (from ethanol), and 2,3,4,5,6-pentafluoro-3'-methylbiphenyl (6.8 g., 45%) (Found: C, 60.5; H, 2.5%), b. p. 236-238°, m. p. 43.5-45°. The terphenyl gave a single ¹⁹F n.m.r. band at +66.8 p.p.m. from trifluoroacetic acid.

(c) A similar procedure, in which p-tolyl-lithium (120) mmole) in ether (80 ml.) was added to hexafluorobenzene (11.0 g., 59.7 mmole) in ether (100 ml.), gave an ethereal extract and a solid which was insoluble in ether. The latter was recrystallised from benzene and gave 2',3',5',6'tetrafluoro-4,4"-dimethyl-p-terphenyl (2.3 g., 12%) (Found: C, 73.0; H, 4.5%), m. p. 226-227°, showing a single ¹⁹F n.m.r. band at +67.2 p.p.m. from trifluoroacetic acid. The ethereal extract yielded a solid residue, which was recrystallised from ethanol and gave 2,3,4,5,6-pentafluoro-4'-methylbiphenyl (9.4 g., 62%) (Found: C, 60.2; H, 2.7%), m. p. 119-120°.

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18 R. D. Chambers, J. Heyes, and W. K. R. Musgrave, Tetrahedron, 1963, 19, 891. ¹⁹ H. Gilman, E. A. Zoellner, and W. M. Selby, J. Amer.

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 ¹⁶ R. D. Chambers, G. E. Coates, J. G. Livingstone, and
 <sup>W. K. R. Musgrave, J. Chem. Soc., 1962, 4367.
 ¹⁷ E. T. McBee, W. B. Ligett, and V. V. Lindgren, U.S.P.
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