Polyfluoroarenes. Part XIII.[1] Further Homolytic Reactions of Polyfluoroiodobenzenes

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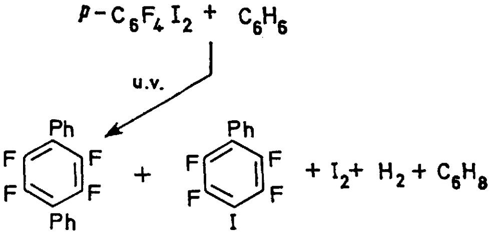
Pentafluorophenyl radicals, derived from the photolysis or thermal decomposition of pentafluoroiodobenzene, react with 1,2,4,5-tetrafluorobenzene to give 4*H*-nonafluorobiphenyl; similar homolytic reactions of the di-iodo-compounds, *p*-$C_6F_4I_2$ and *o*-$C_6F_4I_2$, with benzene afford good yields of polyfluoro-terphenyls and -biphenyls. Reaction of the iodo- and di-iodo-compounds with C–H bonds or with water leads to the replacement of iodine by hydrogen, and the di-iodo-compounds react with carbon tetrachloride to give the corresponding dichlorotetrafluorobenzenes.

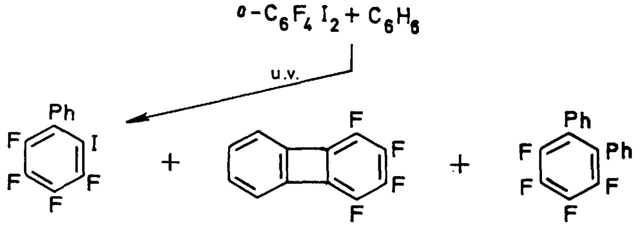
An earlier paper in this series describes the photochemical reactions of pentafluoroiodobenzene with some aromatic compounds and with carbon tetrachloride, and the thermal reactions (300°) of the iodo-compound with carbon tetrachloride, with copper-bronze, and with mercury.[2] Continuation of these investigations with pentafluoroiodobenzene, tetrafluoro-1,4-di-iodobenzene, and tetrafluoro-1,2-di-iodobenzene is now reported. Thermal reactions of pentafluoroiodo- and tetrafluoro-1,2-di-iodo-benzene with a number of metals and non-metals have recently been described.[3]

Reactions with Aromatic Substrates.—Irradiation of the *p*-di-iodo-compound in a large excess of benzene for a prolonged period (200 hr.) gives high yields of 2′,3′,5′,6′-tetrafluoro-*p*-terphenyl (I) (*ca.* 90%), a compound previously prepared by the reaction of phenyl-lithium with hexafluorobenzene.[4] Under these photochemical conditions, iodine (*ca.* 90%) is also formed, and the hydrogen displaced from the aromatic substrate appears partly as elemental hydrogen (*ca.* 9%) but mainly as cyclohexa-1,3- and -1,4-dienes (*ca.* 39% yield of each isomer). Irradiation for a shorter period (48 hr.) also leads to the formation of a tetrafluoroiodobiphenyl, almost certainly of structure (II) although its identification rests only on mass spectrometry. The reaction of the *p*-di-iodo-compound with benzene at 300° in the dark similarly gives the terphenyl in 69% yield [based on the di-iodo-compound consumed (55%)].



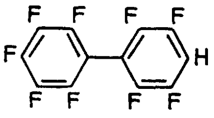
(I) (II)

The photochemical reaction (200 hr.) of the *o*-di-iodo-compound with benzene gives 3,4,5,6-tetrafluoro-2-iodobiphenyl (III) as the main product (43% yield); 1,2,3,4-tetrafluorobiphenylene (IV) (*ca.* 12%) and a little of the *o*-terphenyl (V) were identified among the products by mass spectrometry. The much slower formation of the terphenyl in this case is probably due partly to steric factors, which restrict the reactivity of the tetrafluoro-2-iodophenyl radical, and partly to the cyclisation of the biphenyl (III) to the biphenylene (IV).



(III) (IV) (V)

The photochemical reaction of pentafluoroiodobenzene with 1,2,4,5-tetrafluorobenzene is very slow, but a 65% yield of the 4*H*-nonafluorobiphenyl (VI) is obtained after irradiation for 400 hr. This reaction, and the thermal reaction between the *p*-di-iodo-compound and benzene, proceed much better than the related reactions with pentafluoroiodobenzene.[2] However, this is probably the result of comparatively minor changes in the reaction conditions, notably the use of much larger excesses of the aromatic substrates.



(VI)

The most likely mechanism for all these reactions remains the homolytic process discussed earlier,[2] the faster photochemical reactions with benzene being facilitated by preliminary complex formation with the polyfluoroiodoarenes. The continued failure to identify compounds of the type Ar_FH (Ar_F = polyfluoroaryl) as products from the reactions of the iodides Ar_FI with aromatic substrates supports the postulate that the hydrogen atom is removed from the σ-complex (VII)

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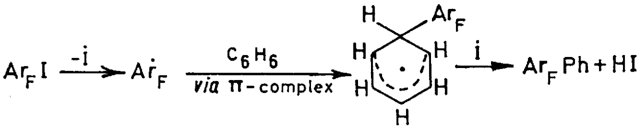
[1] Part XII, J. M. Birchall, R. N. Haszeldine, and J. E. G. Kemp, *J. Chem. Soc.* (*C*), 1970, 1519.

[2] J. M. Birchall, R. N. Haszeldine, R. Hazard, and A. W. Wakalski, *J. Chem. Soc.* (*C*), 1967, 47.

[3] S. C. Cohen, M. L. N. Reddy, and A. G. Massey, *Chem. Comm.*, 1967, 451; *J. Organometallic Chem.*, 1968, **11**, 563.

[4] M. T. Chaudhry and R. Stephens, *J. Chem. Soc.*, 1963, 4281.

mainly by an iodine atom, with subsequent decomposition of the hydrogen iodide leading to the iodine, elemental hydrogen, and cyclohexadienes produced.



(VII)

$$\begin{tikzcd}
HI \arrow[r] & \dot{I} \arrow[d, "\dot{I}"] & +\,\dot{H} \arrow[d, "HI"] \arrow[r, "C_6H_6"] & \dot{C}_6H_7 \arrow[r, "\text{disproportionation}"] \arrow[d, "\text{HI or (VII)}"] & C_6H_6 + C_6H_8 \\
 & I_2 & H_2 & C_6H_8 &
\end{tikzcd}$$

The formation of the tetrafluoroiodobiphenyls [(II) and (III)] suggests that the tetrafluorodi-iodobenzenes lose only one iodine atom at a time in these homolytic reactions. Whether diradicals or tetrafluorobenzyne (from *o*-$C_6F_4I_2$) are involved to some extent in the formation of the terphenyls or the biphenylene (IV) is not at present known.

Hydrogen-abstraction Reactions.—In connection with the stability of polymers containing polyfluoropolyphenylene units,[5] it was of interest to devise a simple method for the replacement of the reactive iodine in polyfluoroiodoarenes by the comparatively unreactive hydrogen atom. One promising method of effecting this conversion is provided by the reactions of the iodo-compounds with refluxing ethylene glycol (b.p. 198°), diethyl carbitol [bis-(2-ethoxyethyl) ether; b.p. 187°], or *N*-methyl-2-pyrrolidone (b.p. 202°), particularly with reaction periods of about 100 hr. (Table 1).

TABLE 1

Reactions of the polyfluoroiodoarenes with aliphatic solvents

Iodo-compound	Solvent *	Time (hr.)	Product	Yield †	Iodo-compound (%) recovered
C_6F_5I	NMP	15	C_6F_5H	67	89
C_6F_5I	DEC	15	C_6F_5H	58	91
C_6F_5I	EG	15	C_6F_5H	65	91
C_6F_5I	EG	48	C_6F_5H	78	85
o-$C_6F_4I_2$	EG	48	C_6F_4HI	74	51
o-$C_6F_4I_2$	EG	100	C_6H_4HI $C_6F_4H_2$	43 48	5
p-$C_6F_4I_2$	EG	48	C_6F_4HI	72	64
p-$C_6F_4I_2$	EG	100	C_6F_4HI $C_6F_4H_2$	35 53	19

* NMP = *N*-methyl-2-pyrrolidone; DEC = diethyl carbitol; EG = ethylene glycol. † Based on iodo-compound consumed.

N-Methyl-2-pyrrolidone produces quantities of tar even when heated alone, and ethylene glycol and diethyl carbitol are thus the preferred reagents. Good yields of pentafluorobenzene are obtained from pentafluoroiodobenzene, and the di-iodo-compounds give high yields of mixtures of the tetrafluorobenzene and the tetrafluoroiodobenzene; complete conversion into the tetrafluorobenzenes has not been achieved by this method.

Liberal quantities of free iodine are produced during the reactions, which are envisaged as simple hydrogen-abstractions from the solvent by the polyfluoroaryl radicals:

$$Ar_FI \rightleftharpoons \dot{Ar}_F + \dot{I}$$

$$\dot{Ar}_F + HO\cdot CH_2\cdot CH_2\cdot OH \longrightarrow Ar_FH + HO\cdot\dot{C}H\cdot CH_2OH$$

The slow rate of conversion is attributed to preferred cage-recombination of the polyfluoroaryl radical with the iodine atom.

More effective conversions of the iodo-compounds into the corresponding polyfluorobenzenes are achieved by autogenous reaction with water at *ca.* 300° (Table 2).

TABLE 2

Reactions with water

Iodo-compound	Temp.	Time (hr.)	Product	Yield * (%)	Iodo-compound (% recovered
C_6F_5I	280°	15	C_6F_5H	Trace	93
C_6F_5I	300	15	C_6F_5H	65	68
C_6F_5I †	300	15	C_6F_5H	88	0
o-$C_6F_4I_2$	270	90	$C_6F_4H_2$	86	0
o-$C_6F_4I_2$	300	10	C_6F_4HI $C_6F_4H_2$	15 61	3
p-$C_6F_4I_2$	270	90	$C_6F_4H_2$	81	0
p-$C_6F_4I_2$	300	10	C_6F_4HI $C_6F_4H_2$	27 54	3

* Based on iodo-compound consumed. † Mercury added.

Both di-iodo-compounds undergo complete conversion into the corresponding tetrafluorobenzenes in high yields (>80%), and short reaction periods (10 hr.) result in appreciable quantities of the tetrafluoroiodobenzenes. The addition of mercury has a marked effect on the rate of the reaction of pentafluoroiodobenzene with water; complete conversion into pentafluorobenzene (88% yield) is achieved after 15 hr. at 300° in the presence of mercury, whereas only 32% of the iodo-compound is converted under the same conditions in its absence. The effect of mercury on the reactions of the di-iodo-compounds has not been investigated.

Since nucleophilic attack of water on the iodo-compounds would be expected to give phenols by the displacement of fluoride ion,[6] it seems likely that abstraction of hydrogen atoms from the water by the polyfluorophenyl radicals is responsible for the formation of the polyfluorobenzenes. In the absence of mercury, the presence of iodate ion in the aqueous phase suggests the following:

$$C_6F_5I \rightleftharpoons \dot{C}_6F_5 + \dot{I}$$

$$\dot{C}_6F_5 + H_2O \longrightarrow C_6F_5H + \dot{O}H\ .$$

$$\dot{O}H + \dot{I} \longrightarrow HOI \longrightarrow I_2,\ HIO_3,\ H_2O$$

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[5] J. M. Birchall, R. N. Haszeldine, and J. G. Speight, forthcoming publication.

[6] L. A. Wall, W. J. Pummer, J. E. Fearn, and J. M. Antonucci, *J. Res. Nat. Bur. Stand.*, 1963, **67***A*, 481.

Mercury presumably accelerates the abstraction process by its rapid reaction with iodine atoms, since iodate is not formed when mercury is present. Mercury is known to react with pentafluoroiodobenzene at 200—300° to give bispentafluorophenylmercury,[2,3] a compound which is now shown to undergo 81% decomposition to pentafluorobenzene (76% yield) during 15 hr. in contact with water at 300°. It is thus possible that the mercurial is an intermediate in the reaction of pentafluoroiodobenzene with water and mercury.

Reactions with Carbon Tetrachloride.—Like pentafluoroiodobenzene,[2] both the di-iodo-compounds react with carbon tetrachloride at 310° to give the dichlorotetrafluorobenzenes in *ca.* 45% yield, *ca.* 20% of the di-iodo-compound being recovered. The chlorotetrafluoroiodobenzenes were not found, possibly since the greater volatility of these materials over that of the di-iodo-compounds enables them to react further in the gas-phase, where cage-recombination of the radicals produced will be much less prevalent.

EXPERIMENTAL

G.l.c. was carried out with Perkin-Elmer no. 154 and no. 451 instruments; columns were 2 m. long × 4 mm. internal diameter except when otherwise stated. I.r. spectra were recorded with a Perkin-Elmer no. 21 instrument and mass spectra with an A.E.I. MS2H spectrometer. Molecular weights, except where stated, were determined by Regnault's method, and volatile materials were manipulated in a conventional high-vacuum apparatus.

Reactions requiring u.v. irradiation were carried out in sealed silica tubes, secured to an efficient shaker 30—40 cm. from a Hanovia 500 w mercury discharge tube. Thermal reactions were carried out in sealed tubes of Dreadnought glass in a horizontal Carius furnace. Autoclaves were of stainless steel and were heated in a rocking furnace. Reagents were dried thoroughly and, where applicable, redistilled just prior to use. Molecular iodine was removed from organic solutions as described before,[2] and solvents were removed from all solutions containing polyfluoroaromatic compounds by distillation through a 20 × 1·5 cm. vacuum-jacketed column, packed with 2-mm. glass helices and fitted with a partial take-off head. Known compounds were identified by i.r. spectroscopy and (where applicable) m.p. and mixed m.p. determination, and yields are based throughout on starting material consumed.

The Iodo-compounds.—These were prepared by published methods [7-9] and their purities were confirmed by elemental analysis and i.r. spectroscopy. The *p*-di-iodo-compound (Found: C, 17·9; I, 62·9. Calc. for $C_6F_4I_2$: C, 18·0; I, 63·2%) had a lower, but sharper, m.p. (107—108°) than that quoted previously (109—111°);[8] repeated recrystallisation did not raise the m.p.

Reactions of the Di-iodo-compounds with Benzene.—(a) *Tetrafluoro*-1,4-*di-iodobenzene*. (i) The *p*-di-iodo-compound (4·02 g., 10 mmoles) and benzene (17·0 g., 220 mmoles) were irradiated in a 60-ml. tube with u.v. light for 48 hr. The products were dissolved in more benzene (50 ml.), washed to remove iodine, dried ($MgSO_4$), and distilled to give a fraction, b.p. 105—109°/2 mm., shown by mass spectrometry to contain 2,3,5,6-tetrafluoro-4-iodobiphenyl (*ca.* 0·1 g., 11%) and unchanged di-iodo-compound (*ca.* 0·2 g.). The solid residue was shaken with ethanol (15 ml.); recrystallisation of the insoluble material from light petroleum (b.p. 100—120°) gave 2′,3′,5′,6′-tetrafluoro-*p*-terphenyl (0·51 g., 68%) [Found: C, 71·4; H, 3·4%; *M* (mass spec.), 302. Calc. for $C_{18}H_{10}F_4$: C, 71·6; H, 3·3%; *M*, 302], m.p. 261·5—263° (lit.,[4] 259°). Addition of water to the ethanolic filtrate and recrystallisation of the precipitate from aqueous ethanol afforded white needles of unchanged tetrafluoro-1,4-di-iodobenzene (2·81 g., total recovery 75%).

(ii) An experiment on the same scale, but with irradiation for 200 hr. gave as volatile products hydrogen (*ca.* 0·45 mole, 9%) (Found: *M*, 3·1) and benzene (15·5 g.), which was washed to remove iodine, dried ($MgSO_4$), and shown by g.l.c. (4 m. column of dinonyl phthalate at 50°) to contain cyclohexa-1,3-diene (*ca.* 0·16 g., 39% yield) and cyclohexa-1,4-diene (*ca.* 0·16 g.). The solid products were dissolved in ether, washed to remove iodine, dried ($MgSO_4$), recovered by evaporation of the solvent, and recrystallised from light petroleum (b.p. 100—120°) to give white needles of 2′,3′,5′,6′-tetrafluoro-*p*-terphenyl (2·78 g., 94%) (Found: C, 71·6; H, 3·3%).

(iii) A third experiment on the same scale and with irradiation for 200 hr. gave iodine (91%, estimated by titration) and the *p*-terphenyl (2·74 g., 91%) (Found: C, 72·0; H, 3·3%).

(iv) The *p*-di-iodo-compound (4·02 g., 10 mmoles) and benzene (2·00 g., 25·6 mmoles), heated at 300° for 45 hr. in a 100-ml. tube, gave benzene (1·35 g., 68%) and solid products which were dissolved in benzene (80 ml.), washed to remove iodine, dried ($MgSO_4$), and recovered by evaporation of the solvent. Treatment of the residue with ethanol, as described for experiment (i), gave unchanged iodo-compound (2·15 g., 54%) and the terphenyl (0·96 g., 69%) (Found: C, 71·5; H, 3·4%).

(b) *Tetrafluoro*-1,2-*di-iodobenzene*. The *o*-di-iodo-compound (8·03 g., 20 mmoles) and benzene (35·0 g., 450 mmoles) were irradiated in a 300-ml. tube for 200 hr. Hydrogen (*ca.* 0·4 mmole) was formed, and the other products were dissolved in more benzene, washed free from iodine, and dried ($MgSO_4$). Distillation afforded an oil (3·02 g.), b.p. 161—166°/17 mm., and a tar (1·31 g.). Steam-distillation of the oil afforded 2,3,4,5-*tetrafluoro*-6-*iodobiphenyl* (2·18 g.) [Found: C, 41·1; H, 1·2%; *M* (mass spec.), 352. $C_{12}H_5F_4I$ requires C, 40·9; H, 1·4%; *M*, 352], colourless plates, m.p. 83—84·5° [from light petroleum (b.p. 40—60°)]. Evaporation of the mother liquors gave an oil (0·61 g.), which was shown by mass spectrometry to contain the tetrafluoroiodobiphenyl (*ca.* 0·24 g., total yield 43%), 2′,3′,4′,5′-tetrafluoro-*o*-terphenyl (*ca.* 0·03 g., 1%), and 1,2,3,4-tetrafluorobiphenylene (*ca.* 0·33 g., 12%).

Nonafluorobiphenyl.—Pentafluoroiodobenzene (3·00 g., 10 mmoles) and 1,2,4,5-tetrafluorobenzene (34·0 g., 227 mmoles), irradiated in an 80-ml. tube for 400 hr., gave liquid products which were dissolved in ether (40 ml.), washed to remove iodine, dried ($MgSO_4$), and distilled to yield 1,2,4,5-tetrafluorobenzene (29·3 g.) (Found: *M*, 150. Calc. for $C_6H_2F_4$: *M*, 150), b.p. 87—89°, pentafluoroiodobenzene (0·10 g., 3%), b.p. 74—74·5°/35 mm., and

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[7] E. Nield, R. Stephens, and J. C. Tatlow, *J. Chem. Soc.*, 1959, 166.

[8] A. J. Bilbo, M. Hellmann, and W. J. Pummer, *J. Amer. Chem. Soc.*, 1955, **77**, 3650.

[9] R. E. Florin, W. J. Pummer, and L. A. Wall, *J. Res. Nat. Bur. Stand.*, 1959, **62***A*, 113.

2,2′,3,3′,4,5,5′,6,6′-nonafluorobiphenyl (2·1 g., 65%) [Found: C, 45·4; H, 0·4%; *M* (mass spec.), 316. Calc. for $C_{12}HF_9$: C, 45·5; H, 0·3%; *M*, 316], b.p. 101—103°/18 mm., m.p. 73—75° (from ethanol) (lit.,[10] 77°). An intractable tar (0·96 g.) remained.

Reactions of the Iodo-compounds with Aliphatic Solvents.—(a) *Pentafluoroiodobenzene.* The iodo-compound (12·00 g.) and ethylene glycol (60 ml.) were stirred and heated under reflux for 48 hr. Steam-distillation afforded an oil, which was washed with water, dried ($MgSO_4$), and distilled to give pentafluorobenzene (0·81 g., 78%) (Found: *M*, 167), b.p. 83—83·5°, and pentafluoroiodobenzene (10·20 g., 85%), b.p. 76°/35 mm.

The other results shown in Table 1 were obtained from experiments carried out in an identical manner on the same scale.

(b) *Tetrafluoro*-1,4-*di-iodobenzene.* (i) *For* 48 *hr.* The *p*-di-iodo-compound (8·04 g.) and ethylene glycol (60 ml.) were stirred and heated under reflux for 48 hr. Steam-distillation gave an oil, which was washed free from iodine, dried (P_4O_{10}), and distilled to give 2,3,5,6-*tetrafluoroiodobenzene* (1·46 g., 72%) (Found: C, 26·2; H, 0·4. C_6HF_4I requires C, 26·3; H, 0·4%), b.p. 75°/27 mm., shown to be pure by g.l.c. (Silicone MS 550 at 175°). The aqueous residue was extracted with ether (3 × 40 ml.) to afford unchanged *p*-di-iodo-compound (5·10 g., 64%).

(ii) *For* 100 *hr.* The *p*-di-iodo-compound (5·10 g.) and ethylene glycol (60 ml.) were stirred and heated under reflux for 100 hr. The products were allowed to cool and poured on crushed ice (50 g.); extraction with ether and distillation afforded 1,2,4,5-tetrafluorobenzene (0·82 g., 53%) (Found: *M*, 149. Calc. for $C_6H_2F_4$: *M*, 150), b.p. 88·5—90°, and 2,3,5,6-tetrafluoroiodobenzene (0·99 g., 35%), b.p. 80°/28 mm., each identified by i.r. spectroscopy and by g.l.c. (Silicone MS 550 at 175°). The residue, purified by sublimation *in vacuo*, yielded unchanged di-iodo-compound (0·96 g., 19%).

(c) *Tetrafluoro*-1,2-*di-iodobenzene.* The procedures employed in these experiments were similar to those described for the reactions of the *p*-di-iodo-compound with ethylene glycol.

(i) *For* 48 *hr.* The *o*-di-iodo-compound (8·04 g.) and ethylene glycol (60 ml.) gave 2,3,4,5-tetrafluoroiodobenzene (2·02 g., 74%) (Found: C, 26·7; H, 0·6. Calc. for C_6HF_4I: C, 26·3; H, 0·4%), b.p. 79—80°/30 mm. (lit.,[10] 159—160°), pure by g.l.c. (Silicone MS 550 at 175°), and unchanged di-iodo-compound (4·07 g., 51%).

(ii) *For* 100 *hr.* The *o*-di-iodo-compound (4·07 g., 10·1 mmoles) and refluxing ethylene glycol (60 ml.) yielded 1,2,3,4-tetrafluorobenzene (0·65 g., 43%), b.p. 93—94°, 2,3,4,5-tetrafluoroiodobenzene (1·34 g., 48%), b.p. 81°/30 mm., and unchanged di-iodo-compound (0·19 g., 5%).

Reactions of the Iodo-compounds with Water.—(a) *Pentafluoroiodobenzene.* (i) *Alone.* The iodo-compound (12·00 g., 41 mmoles) and distilled water (7·21 g., 400 mmoles), heated in a 50-ml. autoclave at 300° for 15 hr., gave pentafluorobenzene (1·42 g., 65%) (Found: *M*, 167), b.p. 83—85°, and pentafluoroiodobenzene (6·95 g., 68%). The aqueous washings gave a positive test for iodate.

(ii) *With mercury.* Pentafluoroiodobenzene (12·00 g., 41 mmoles), distilled water (7·20 g., 400 mmoles), and mercury (8·16 g., 41 mg. atoms) were heated in a 50-ml. autoclave at 300° for 15 hr. to give pentafluorobenzene (6·06 g., 88%) (Found: *M*, 169), b.p. 84·5—86°. There were no other organic products and the aqueous phase gave a negative test for iodate.

(b) *Tetrafluoro*-1,4-*di-iodobenzene.* The *p*-di-iodo-compound (8·04 g., 20 mmoles) and distilled water (3·60 g., 200 mmoles), heated at 270° for 90 hr. in a 16-ml. autoclave, gave chromatographically pure 1,2,4,5-tetrafluorobenzene (2·44 g., 81%) (Found: *M*, 149. Calc. for $C_6H_2F_4$: *M*, 150), b.p. 88—89·5°.

An experiment on the same scale, but with heating at 300° for 10 hr., gave 1,2,4,5-tetrafluorobenzene (1·62 g., 54%), 2,3,5,6-tetrafluoroiodobenzene (1·47 g., 27%), b.p. 80°/30 mm., and unchanged di-iodo-compound (0·27 g., 3%), shown by i.r. spectroscopy to contain traces of the tetrafluoroiodobenzene.

(c) *Tetrafluoro*-1,2-*di-iodobenzene.* During 90 hr. in a 16-ml. autoclave at 270°, the *o*-di-iodo-compound (8·04 g., 20 mmoles) and distilled water (3·60 g., 200 mmoles) gave 1,2,3,4-tetrafluorobenzene (2·48 g., 86%) (Found: *M*, 151), b.p. 93—95°, identified by i.r. spectroscopy and g.l.c. (Silicone MS 550 at 175°), and no other organic product. Reaction at 300° for 10 hr. gave 1,2,3,4-tetrafluorobenzene (1·73 g., 61%) (Found: *M*, 148), 2,3,4,5-tetrafluoroiodobenzene (0·81 g., 15%), b.p. 85°/32 mm., and unchanged di-iodo-compound (0·21 g., 3%).

Reaction Between Bispentafluorophenylmercury and Water.—The mercurial (2·14 g., 4·3 mmoles)[2] and distilled water (7·20 g., 400 mmoles), heated at 300° for 15 hr. in a 50-ml. autoclave, gave pentafluorobenzene (0·89 g., 76%) (Found: *M*, 168) and unchanged mercurial (0·41 g., 19%).

Reactions of the Di-iodo-compounds with Carbon Tetrachloride.—(a) *Tetrafluoro*-1,4-*di-iodobenzene.* The *p*-di-iodo-compound (8·04 g., 20 mmoles) and carbon tetrachloride (12·7 g., 83 mmoles) were heated in a 50-ml. autoclave at 310° for 48 hr. The organic products were dissolved in carbon tetrachloride (60 ml.), washed free from iodine, and dried ($CaCl_2$). Distillation gave: (i) a fraction, b.p. 82—83·5°, (ii) 1,4-dichlorotetrafluorobenzene (1·49 g.) (Found: C, 32·9; Cl, 32·1. Calc. for $C_6Cl_2F_4$: C, 32·9; Cl, 32·4%), b.p. 155·5—156°, m.p. 51·5—52·5° (lit.,[11] b.p. 157—158°, m.p. 52—54°), pure by g.l.c. (Silicone MS 550 at 150°), (iii) a fraction (0·68 g.), b.p. 157—159°, shown by i.r. spectroscopy and mass spectrometry to be a mixture of the dichlorotetrafluorobenzene and the di-iodo-compound, and (iv) a residue, sublimation of which *in vacuo* gave the di-iodo-compound (1·19 g., 15%) and a tar (0·33 g.), which contained fluoroaromatic products (bands at 6·75 and 6·88 μm.) and hexachloroethane (bands at 12·76 and 14·75 μm.). Evaporation of carbon tetrachloride from fraction (i) gave 1,4-dichlorotetrafluorobenzene (0·19 g., total yield 45%).

(b) *Tetrafluoro*-1,2-*di-iodobenzene.* The *o*-di-iodo-compound (8·04 g., 20 mmoles) and carbon tetrachloride (12·7 g., 83 mmoles) similarly gave (i) a fraction, b.p. 84—86°, from which 1,2-dichlorotetrafluorobenzene (0·31 g.) was obtained on evaporation of carbon tetrachloride, (ii) 1,2-dichlorotetrafluorobenzene (1·21 g., total yield 42%) (Found: C, 33·1; Cl, 32·4. Calc. for $C_6Cl_2F_4$: C, 32·9; Cl, 32·4%), b.p. 154—156°, pure by g.l.c. (Silicone MS 550 at 150°), (iii) a fraction (0·72 g.), b.p. 157·5—160°, shown by i.r. spectroscopy to be a mixture of the dichloro- and di-iodo-compounds, and (iv) unchanged di-iodo-compound (1·41 g.,

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18%), sublimed *in vacuo* from a tar which contained fluoroaromatic products and hexachloroethane. The i.r. spectrum of the pure dichloro-compound was in only approximate agreement with that reported by Chambers, Heyes, and Musgrave [12] and showed strong bands at 6·13, 6·50, 6·63, 6·75, 6·82(sh), 8·81, 8·90, 9·50, 11·14, and 11·70 μm.

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