Homolytic Reactions of Perfluoroaromatic Compounds. Part II.† Reactions of Perfluorobenzoyl Peroxide with Aromatic Compounds

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Perfluorobenzoyl peroxide decomposes in benzene and in nitrobenzene at 80° to give mainly pentafluorobiaryls and pentafluorobenzoic acid. In hexafluorobenzene the main product is a high-boiling residue, and in chloro- and bromo-benzene pentafluorobenzoic acid and phenyl pentafluorobenzoate are formed. The latter product must arise by benzoyloxylation of the halogenobenzenes at the 1-position. The results are discussed.

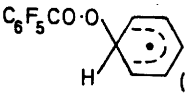
THE preparation of perfluorobenzoyl peroxide and its decomposition in benzene, hexafluorobenzene, chlorobenzene, bromobenzene, and nitrobenzene have been reported *in* preliminary communications.[1,2] Some reactions of this compound have also recently been reported elsewhere.[3,4] The peroxide decomposes homolytically in aromatic solvents at 80° and we have studied this decomposition in a large excess of each of the aforementioned solvents. The products of these reactions are given in Table 1.

TABLE 1

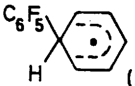
Mean yields of products of decomposition of perfluorobenzoyl peroxide (0·0025 mole, 1·055 g.) in solvents (80°)

Solvents	C_6H_6	C_6F_6	PhCl	PhBr	$PhNO_2$
Biaryl (moles per mole peroxide)	0·61	Trace	*ca.* 0	*ca.* 0	0·56
Pentafluorobenzoic acid (moles per mole peroxide)	0·82	0	0·55	0·75	0·82
Phenyl pentafluorobenzoate (moles per mole peroxide)	0·01		0·81	1·01	Trace
Residue (g.)	0·266	1·20	0·238	0·218	0·187

The reaction in benzene gave mainly pentafluorobenzoic acid and 2,3,4,5,6-pentafluorobiphenyl together with a small amount of phenyl pentafluorobenzoate and a high-boiling residue. The reaction probably proceeds by a mechanism analogous to that proposed by Gill and Williams[5] for the decomposition of benzoyl peroxide in benzene. Primary decomposition of the peroxide gives pentafluorobenzoyloxy- and pentafluorophenyl radicals and addition of these to the aromatic nucleus gives the σ-complexes (I) and (II), respectively. Dehydrogenation of (II) by reaction with pentafluorobenzoyloxy-radicals (1) or with perfluorobenzoyl peroxide (2) gives the biaryl together with pentafluorobenzoic acid. Reaction (2) also gives pentafluorobenzoyloxy-radicals and hence represents an induced decomposition of the peroxide. Kinetic results indicate that (2) makes a substantial contribution to the total reaction.[6] Similarly, dehydrogenation of (I) gives phenyl pentafluorobenzoate, a minor product of the reaction. Dimerisation of (II) gives tetranuclear hydroaromatic compounds which are probably the main constituents of the residue, while its disproportionation (3) would give the biaryl together with its 1,2- and 1,4-dihydro-derivates, aerial oxidation of which, during either the reaction or the work-up, would give biaryl. The contribution of (3) to the total reaction is, however, probably small, since the yield of biaryl does not exceed that of pentafluorobenzoic acid. Biaryls are therefore formed mainly in reactions (1) and (2).



(I)



(II)

$$\text{(II)} + C_6F_5{\cdot}CO{\cdot}O{\cdot} \longrightarrow C_6H_5{\cdot}C_6F_5 + C_6F{\cdot}_5CO_2H \quad (1)$$

$$\text{(II)} + (C_6F_5{\cdot}CO{\cdot}O)_2 \longrightarrow C_6H_5{\cdot}C_6F_5 + C_6F_5{\cdot}CO_2H + C_6F_5{\cdot}CO{\cdot}O{\cdot} \quad (2)$$

$$2\text{(II)} \longrightarrow C_6F_5{\cdot}C_6H_5 + C_6F_5{\cdot}C_6H_7 \quad (3)$$

The yields of biaryls and arenecarboxylic acids formed by the decomposition of aroyl peroxides in some aromatic solvents have been shown to be increased by the presence of additives such as oxygen,[7] nitro-compounds,[8] and iron(III) benzoate.[9] However these additives do not substantially affect the products of the reaction of perfluorobenzoyl peroxide with benzene, as is indicated in Table 2. The high apparent yield of pentafluorobenzoic acid formed in the reaction in the presence of iron(III) benzoate probably arises by contamination of this product with benzoic acid formed by hydrolysis of unchanged iron(III) benzoate during work-up since the biaryl yield is not increased. This apparent increase is therefore not significant.

The reaction in hexafluorobenzene gave very little decafluorobiphenyl, and no pentafluorobenzoic acid. Since the main product was a high-boiling residue, it is

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† Part I, P. A. Claret, G. H. Williams, and J. Coulson, *J. Chem. Soc.* (*B*), 1968, 341.

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[1] G. H. Williams, P. H. Oldham, and Mrs. B. A. Wilson, Fourth International Symposium on Fluorine Chemistry, Abstracts (Division of Fluorine Chemistry, American Chemical Society, and University of Denver), 1967, 100.

[2] G. H. Williams, 'Symposium on Free-radical Aromatic Substitution and Other Selected Free-radical Reactions,' *Intra-Science Chem. Reports* (Intra-Science Research Foundation, Santa Monica, California), 1969, **3**, 229.

[3] L. S. Kobrina and G. G. Yakobson, *Izvest. sibirsk Otdel. Akad. Nauk. S.S.S.R., Ser. khim. Nauk*, 1968, no. 5, 76.

[4] J. Burdon, J. G. Campbell, and J. C. Tatlow, *J. Chem. Soc.* (*C*), 1969, 822.

[5] G. B. Gill and G. H. Williams, *J. Chem. Soc.*, 1965, 995.

[6] R. Bolton, M. J. Coleman, and G. H. Williams, unpublished observations.

[7] R. T. Morrison, J. Cazes, N. Samkoff, and C. A. Howe, *J. Amer. Chem. Soc.*, 1962, **84**, 4152.

[8] D. H. Hey, M. J. Perkins, and G. H. Williams, *Chem. and Ind.*, 1963, 83.

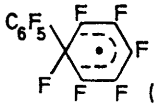
[9] B. N. Dailly and G. H. Williams, unpublished observations.

probable that addition of radicals to the hexafluorobenzene nucleus occurs but that no ready route exists for the defluorination of the σ-complexes (III). Consequently they either dimerise to give products which are stable under the conditions of the reaction and the subsequent distillation of binuclear products, or combine with pentafluorophenyl radicals to give trinuclear products. The latter reaction may well occur in this case, since the stationary concentration of pentafluorophenyl radicals would be expected to be unusually high; this is owing to the relative unreactivity of the electron deficient nuclear carbon atoms of hexafluorobenzene towards the pentafluorophenyl radical, which would be expected to be fairly electrophilic.

TABLE 2

Decomposition of perfluorobenzoyl peroxide in benzene (molar ratio 1 : 43) in the presence and absence of additives (80°)

Additive	Biaryl (moles per mole peroxide)	Pentafluorobenzoic acid (moles per mole peroxide)
None	0·61	0·82
Oxygen	0·66	0·92
Nitrobenzene	0·63	0·81
Iron(III) benzoate	0·60	1·16

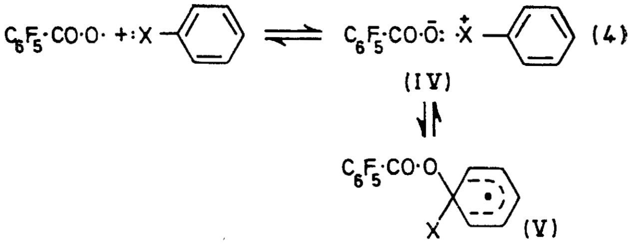


(III)

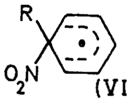
Burdon, Campbell, and Tatlow,[4] in studies of the decomposition in benzene and hexafluorobenzene, obtained results similar to those now reported except that these workers observed the formation of small quantities of pentafluorophenyl pentafluorobenzoate in both solvents.

Identical products, namely pentafluorobenzoic acid and phenyl pentafluorobenzoate, were formed in similar yields in the reactions in chlorobenzene and bromobenzene. The latter product can arise only by replacement of chlorine or bromine by pentafluorobenzoyloxy-radicals, and this process must supersede the decarboxylation of pentafluorobenzoyloxy-radicals. The products of the reaction in chlorobenzene were unaltered when the reaction was conducted at the b.p. of the solvent rather than at 80°, and also when a molar ratio of peroxide to solvent of 1 : 50 was used instead of 1 : 10.

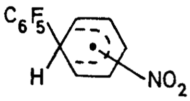
We suggest that, owing to their electrophilicity, pentafluorobenzoyloxy-radicals are stabilised by the formation of charge-transfer complexes such as (IV; X = Cl or Br) with the halogenobenzenes. The formation of such complexes has previously been postulated with the less electrophilic benzoyloxy-radicals in the reaction of benzoyl peroxide with bromobenzene,[10] and is more likely to occur in the reactions now described. The complexes such as (IV) are obviously readily convertible into the σ-complexes (V), which can give the observed product by loss of chlorine or bromine. This dehalogenation may occur by processes analogous to (1) and (2), giving the observed ester together with pentafluorobenzoyl hypohalites, which would give ultimately pentafluorobenzoic acid, possibly by reaction with the hydroaromatic compounds (residues) present.



The three isomeric products of pentafluorophenylation are formed in the reaction with nitrobenzene, although we were unable to estimate the proportions in which they were formed, owing to the difficulty of resolving the peaks in the gas chromatograms. A little phenyl pentafluorobenzoate was formed, and also a small quantity of 2,3,4,5,6-pentafluorobiphenyl. The combined yield of these two products constituted $\not>$ 10% of the total binuclear fraction. However, their formation indicates that both pentafluorobenzoyloxy- and pentafluorophenyl radicals are capable of addition to the 1-position of nitrobenzene, although addition to the 2-, 3-, and 4-positions is preferred in this solvent. Denitration of the σ-complexes (VI); (R = C_6F_5·CO·O· and C_6F_5·) gives phenyl pentafluorobenzoate and 2,3,4,5,6-pentafluorobiphenyl respectively.



(VI)



(VII)

We have no evidence concerning the reactions whereby (VI) becomes denitrated. However, reactions analogous to (1) and (2) would give the observed products together with pentafluorobenzoyl nitrate which, by further reactions, possibly with the residual hydroaromatic compounds, would be expected to give pentafluorobenzoic acid. In addition, 2,3,4,5,6-pentafluorobiphenyl might arise from disproportionation reactions involving (VI) or (VII).

EXPERIMENTAL

Decomposition of Perfluorobenzoyl Peroxide.—(a) *In benzene*. Perfluorobenzoyl peroxide (1 g.) was allowed to decompose in benzene (10 ml.) at 80° in a thermostat for 72 hr. Ether (10 ml.) was added to the cooled solution. Acidic material was extracted with sodium hydrogen carbonate (5 × 10 ml.), the aqueous and organic portions were washed with ether and water, respectively, and the washings were added to the organic and aqueous portions, respectively. Acidification of the aqueous portion with concentrated hydrochloric acid, followed by extraction with ether (3 × 20 ml.), and evaporation of the dried ($CaCl_2$) extracts gave pentafluorobenzoic acid (0·410 g.), m.p. and mixed

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[10] G. B. Gill and G. H. Williams, *J. Chem. Soc.*, 1965, 7127.

m.p. 103—104° (lit.,[11] 103—104°), i.r. spectrum identical with that of an authentic specimen.

The organic portion was dried ($MgSO_4$) and the solvents were distilled off at atmospheric pressure, then at 10 mm. The binuclear products (0·359 g.) were obtained from the residue by distillation at 0·01 mm. (bath temp. 110—130°), and were collected at −80°. An involatile residue (0·270 g.) remained. Gas chromatography of the distillate at 100° showed the presence of 2,3,4,5,6-pentafluorobiphenyl (99%) and phenyl pentafluorobenzoate (1%). The distillate gave 2,3,4,5,6-pentafluorobiphenyl, m.p. and mixed m.p. 111—112° (from methanol) (lit.,[12] 111—112°), i.r. spectrum identical with that of an authentic specimen.

Gas chromatography of the recovered solvent at 100° showed the presence of benzene with traces of 2,3,4,5,6-pentafluorobiphenyl and phenyl pentafluorobenzoate, but no pentafluorobenzene.

Similar experiments (i) with the passage of a slow stream of oxygen during the reaction, (ii) in the presence of nitrobenzene (0·30 g.), and (iii) in the presence of iron(III) benzoate (0·20 g.) gave the products indicated in Table 2. Duplicate experiments gave similar results.

(b) *In hexafluorobenzene.* Pentafluorobenzoyl peroxide (1·055 g.) was allowed to decompose in hexafluorobenzene (4·7 g.) at 80° for 72 hr. Gas chromatography of the solution then revealed the absence of pentafluorobenzoic acid. The solvent was distilled off at atmospheric pressure, then at 10 mm. A 'biaryl fraction,' (0·089 g.) which was shown to contain a little decafluorobiphenyl and an unidentified compound by gas chromatography at 150°, was distilled at 0·01 mm. An involatile residue (1·20 g.) remained. A second experiment, in which the reaction was allowed to proceed for 144 hr., gave a similar result.

(c) *In chlorobenzene.* In duplicate experiments, pentafluorobenzoyl peroxide (1·055 g.) was allowed to decompose in chlorobenzene (3·0 g.) at 80° for 72 hr. The resulting solutions were treated as described under (a).

The yields of products were, respectively: pentafluorobenzoic acid (0·280 g. and 0·255 g.); binuclear fraction (0·554 g. and 0·605 g.); involatile residue (0·259 g. and 0·217 g.). Gas chromatography at 150° of the binuclear fraction showed it to consist almost entirely (> 95%) of phenyl pentafluorobenzoate. The retention time was identical with that of an authentic specimen, but also with those of 3′- and 4′-chloro-2,3,4,5,6-pentafluorobiphenyl. However, since the gas chromatogram showed no peak which might correspond to 2′-chloro-2,3,4,5,6-pentafluorobiphenyl, it is unlikely that the 3′- and 4′-isomers were present. This conclusion was confirmed by analysis of the binuclear fraction (Found: C, 54·1; H, 1·73; Cl, 0·19; F, 32·8. Calc. for $C_{13}H_5F_5O_2$: C, 54·1; H, 1·74; Cl, 0; F, 33·0%). In addition, the i.r. spectrum of the binuclear fraction was identical with that of an authentic specimen of phenyl pentafluorobenzoate. Crystallisation of the biaryl fraction from aqueous methanol gave phenyl pentafluorobenzoate, m.p. and mixed m.p. 66—67°.

Gas chromatography at 110° of the solvent distilled from the mixture after reaction showed it to consist entirely of chlorobenzene.

Additional experiments in which (i) the reaction was conducted at the b.p. of chlorobenzene, and (ii) the quantity of chlorobenzene was increased to 15 g., gave similar results.

(d) *In bromobenzene.* Duplicate experiments conducted as under (c), in which perfluorobenzoyl peroxide was allowed to decompose in bromobenzene (3·9 g.), gave pentafluorobenzoic acid (0·363 g. and 0·393 g.), binuclear fractions (0·745 g. and 0·700 g.), and involatile residues (0·201 g. and 0·234 g.).

Gas chromatography of the binuclear fractions at 150° showed them to consist mainly (> 75%) of phenyl pentafluorobenzoate. A minor component was not identified. There were only minute peaks corresponding to 3′- and 4′-bromo-2,3,4,5,6-pentafluorobiphenyl (comparison with authentic specimens). The minor component was, therefore, neither of these two compounds nor, probably, the 2′-isomer. The i.r. spectrum of the binuclear fraction was identical with that of phenyl pentafluorobenzoate; crystallisation from aqueous methanol gave pure ester, m.p. and mixed m.p. 66—67°. The conclusion that the biaryl fraction consisted mainly of phenyl pentafluorobenzoate, with a small amount of a bromine-containing impurity, was confirmed by elemental analysis (Found: C, 53·2; H, 1·84; Br, 2·8; F, 29·1%. Calc. for $C_{13}H_5F_5O_2$: C, 54·1; H, 1·74; Br, 0; F, 33·0%.

Gas chromatography at 110° of the solvent distilled from the mixture after reaction showed it to consist entirely of bromobenzene.

(e) *In nitrobenzene.* In duplicate experiments perfluorobenzoyl peroxide (1·055 g.) was allowed to decompose in nitrobenzene (3·1 g.) at 80° for 72 hr. The resulting solutions were treated as described under (a), except that residual traces of solvent were removed by prolonged distillation at 0·01 mm. with an oil-bath temperature of 35°. The binuclear fractions were then distilled at 0·01 mm. with an oil-bath temperature of 110—130°. The yields of products were, respectively: pentafluorobenzoic acid (0·424 and 0·401 g.); binuclear fraction (0·369 and 0·398 g.); involatile residue (0·196 and 0·178 g.). Gas chromatography at 170° of the solvent distilled from the mixtures after reaction showed it to consist entirely of nitrobenzene.

Gas chromatography of the binuclear fractions at 200° showed the presence of four major components which were not well resolved (*ca.* 95%) and two minor components (*ca.* 5%). One minor component had the same retention time as phenyl pentafluorobenzoate; the other was not identified. Three of the major components had the same retention times, respectively, as authentic specimens of 2′-, 3′-, and 4′-nitro-2,3,4,5,6-pentafluorobiphenyl; the fourth had the same retention time as 2,3,4,5,6-pentafluorobiphenyl. The i.r. spectrum of the biaryl fraction contained, among others, absorptions corresponding to those of 3′- and 4′-nitro-2,3,4,5,6-pentafluorobiphenyl. The binuclear fraction was analysed (Found: C, 50·0; H, 1·55; F, 32·7; N, 4·7%. Calc. for $C_{12}H_4F_5NO_2$: C, 49·8; H, 1·38; F, 32·9; N, 4·9%).

The poor resolution in the gas chromatogram precluded estimation of the relative yields of the four biaryls.

Gas Chromatography.—For all analyses by gas chromatography (including those of mixtures of isomers), the stationary phase was Apiezon 'L' grease on Celite 545 (72—85 mesh), 15%w/w, the carrier gas was argon, and the flow rate 30 ml./min. A β-ionisation detector was used.

Reagents.—Benzene, chlorobenzene, bromobenzene, and nitrobenzene were purified by standard methods. Hexa-

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[11] G. M. Brooke, J. Burdon, M. Stacey, and J. C. Tatlow, *J. Chem. Soc.*, 1960, 1768.

[12] J. W. Birchall, R. N. Haszeldine, and A. R. Parkinson, *J. Chem. Soc.*, 1962, 4966.

fluorobenzene was purified as previously described.[13] Perfluorobenzoyl peroxide was prepared by slow addition of sodium peroxide (30 g.) in water (300 ml.) to a stirred solution of pentafluorobenzoyl chloride (Imperial Smelting Corporation Ltd.) (100 g.) in chloroform (100 ml.) at 0°. Filtration after 1·5 hr. gave a white residue which yielded perfluorobenzoyl peroxide (49 g.), m.p. 79·5° (from chloroform–methanol) (lit.,[4] 72°) (Found: C, 39·8; F, 45·2. Calc. for $C_{14}F_{10}O_4$: C, 39·8; F, 45·0%), $\nu_{max.}$ 1820 and 1770 cm.$^{-1}$ (C=O).

Phenyl pentafluorobenzoate was prepared by shaking a mixture of pentafluorobenzoyl chloride (10 g.). phenol (10 g.) and pyridine (90 ml.) for 1 hr. at room temperature. After addition of water (45 ml.), the crystalline product was filtered off and gave *phenyl pentafluorobenzoate*, m.p. 66—67° (from aqueous methanol). Found: C, 54·2; H, 1·90; F, 32·4. $C_{13}H_5F_5O_2$ requires C, 54·1; H, 1·74; F, 33·0%), $\nu_{max.}$ 1770 cm.$^{-1}$ (C=O).

Pentafluorobenzoic acid (I.S.C.) was crystallised from light petroleum (b.p. 40—60°) to constant m.p. 103—104° (lit.,[14] 103—104°).

Decafluorobiphenyl (I.S.C.) was crystallised from ethanol to constant m.p. 68—69° (lit.,[15] 68—69°). 2,3,4,5,6-Pentafluorobiphenyl and its 3′-chloro- and 3′-bromo-derivatives were prepared as described previously,[13] by decomposition of benzoyl peroxide and *m*-chloro- and *m*-bromo-benzoyl peroxide, respectively, in hexafluorobenzene. Similar reactions with *m*- and *p*-nitro-, *p*-chloro-, and *p*-bromo-benzoyl peroxide gave, respectively, 3′- and 4′-*nitro*-, 4′-*chloro*-, and 4′-*bromo*-2,3,4,5,6-*pentafluorobiphenyl*. Details of the isolation, analysis, and m.p.s of these compounds are given in Table 3.

Attempts to prepare 2′-chloro- and 2′-bromo-2,3,4,5,6-pentafluorobiphenyl by analogous methods from *o*-chloro- and *o*-bromobenzoyl peroxide gave only oils (4·5 and 3%, respectively) which could not be crystallised. Gas chromatography of these oils, however, showed that each contained one main component; retention times were measured under the same conditions as in the reactions of perfluorobenzoyl peroxide with chlorobenzene and bromobenzene, respectively.

TABLE 3

Derivatives of 2,3,4,5,6-pentafluorobiphenyl

Substituent	Solvent for crystallisation	Yield (%)	M.p.	Found (%)	Required (%)
3′-NO_2	Light petroleum (b.p. 60—80°)	9	111—112°	C, 51·2; H, 1·6; F, 32·8; N, 5·1	C, 49·8; H, 1·4; F, 32·9; N, 4·9
4′-NO_2	Aqueous methanol	4	89—90	C, 51·1; H, 1·25; F, 32·5; N, 5·1;	C, 49·8; H, 1·4; F, 32·9; N, 4·9
4′-Cl	Aqueous methanol	14	83—84	C, 52·0; H, 1·5; Cl, 12·7; F, 34·0	C, 51·6; H, 1·45; Cl, 12·7; F, 34·1
4′-Br	Aqueous methanol	17	84—85	C, 44·8; H, 1·4; Br, 24·8; F, 29·4;	C, 44·6; H, 1·4; Br, 24·8; F, 29·4

A similar attempt to prepare 2′-nitro-2,3,4,5,6-pentafluorobiphenyl from *o*-nitrobenzoyl peroxide also gave an oil (1·4%), crystallisation of which was difficult. Crystallisation to constant m.p. from aqueous methanol, however, gave a very small quantity, insufficient for analysis, of a pure substance, m.p. 82—83°, which was probably the required compound.

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[13] P. A. Claret, G. H. Williams, and J. Coulson, *J. Chem. Soc.* (*B*), 1968, 341.

[14] A. K. Barbour, M. W. Buxton, P. L. Coe, R. Stephens, and J. C. Tatlow, *J. Chem. Soc.*, 1961, 808.

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