

HOMOLYTIC REACTIONS OF POLYFLUOROAROMATIC COMPOUNDS PART VI.* THE MECHANISM OF THE PHENYLATION OF HEXA- FLUOROBENZENE**

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Summary

The decomposition of phenylazotriphenylmethane in hexafluorobenzene gives very little 2,3,4,5,6-pentafluorobiphenyl, since no mechanism exists for the defluorination of the radical intermediate. The yield of biaryl is raised by added benzoic acid, although this also introduces a competition with the substrate for the radicals and their precursor. The decomposition of benzoyl peroxide in hexafluorobenzene gives pentafluorobiphenyl, the yield of which increases considerably when the reaction is carried out in the presence of *p*-fluorobenzoic acid; in the latter case, 2,3,4,4',5,6-hexafluorobiphenyl is also found.

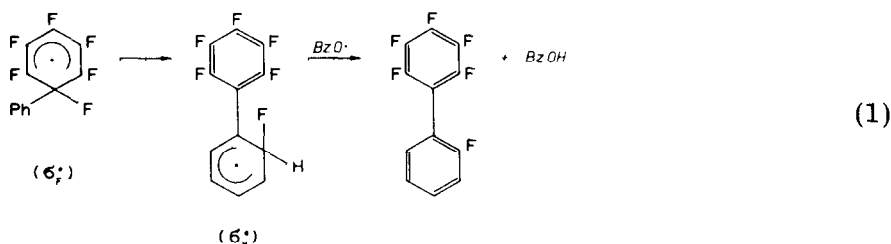
A mechanism incorporating these observations is suggested.

Introduction

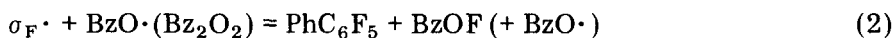
Hexafluorobenzene gives some 2,3,4,5,6-pentafluorobiphenyl when attacked by phenyl radicals generated by the thermolysis of benzoyl peroxide [2] or by the interaction of aniline and pentyl (amyl) nitrite [3]. Only the thermal decomposition of benzoyl peroxide gives good yields of the biaryl; these are subject, to some extent, to the conditions of isolation and are highest when the most drastic distillation conditions are used [3,4]. As with the hydrogen-containing analogues, the decomposition of benzoyl peroxide in hexafluorobenzene shows kinetic evidence of an induced decomposition process as well as the expected, spontaneous, homolysis of the oxygen-oxygen bond [4,5]. These kinetic suggestions are paralleled by the formation, in small yield (0.05 - 10 mol per mole of peroxide), of 2,2',3,4,5,6-hexafluorobiphenyl and benzoic acid [5,6]. These products could arise from the reaction between benzoyl peroxide and the rearrangement product ($\sigma_{\text{H}}\cdot$) of the initially-formed radical intermediate ($\sigma_{\text{F}}\cdot$):

* For Part V, see ref. 1.

** See also R. Bolton and J. P. B. Sandall, *J. Chem. Soc. (Chem. Commun.)*, (1973) 286.



The formation of 2,3,4,5,6-pentafluorobiphenyl from $\sigma_{\text{F}}\cdot$ involves the concomitant production of fluorine benzoate if the strict analogy with the benzene system is maintained:



Such mechanisms of defluorination of $\sigma_{\text{F}}\cdot$ are thermodynamically unsatisfactory explanations of the formation of pentafluorobiphenyl. We now report a study of the reactions of hexafluorobenzene with some sources of phenyl radicals.

Results and Discussion

While the thermolysis of phenylazotriphenylmethane (PAT) in benzene gives biphenyl, triphenylmethane and isomeric 1,4-dihydro-4-triphenylmethylbiphenyls [7] in hexafluorobenzene, it gave only very small amounts ($> 0.1\%$) of 2,3,4,5,6-pentafluorobiphenyl. This is not the result of using an inert solvent; 35% of the generated phenyl radicals gave species other than pentafluorobiphenyl which showed absorptions in the ^{19}F NMR spectrum. Triphenylmethyl fluoride, the analogue of triphenylmethane (found in decompositions in benzene), was also absent in all but vanishingly small ($> 0.01\%$) amounts.

The ^{19}F NMR spectra of the reaction products are shown in Table 1.

The spectrum of the products of decomposition of PAT in hexafluorobenzene (Table 1, Row 1) shows no absorptions due to pentafluorobiphenyl, but falls into two parts, each comprising four broad peaks whose structures suggest that they arise from stereoisomers. Such compounds most probably result from those reactions of $\sigma_{\text{F}}\cdot$ which do not involve defluorination to give pentafluorobiphenyl, and may include the products of radical-radical addition between $\sigma_{\text{F}}\cdot$ and either itself or $\text{Ph}_3\text{C}\cdot$.



Although the presence of water or the access of air during the thermolysis did not change the spectrum of the reaction product appreciably, the decomposition of PAT in the presence of benzoic acid gave some 2,3,4,5,6-pentafluorobiphenyl (Table 1, Row 4).

TABLE 1

¹⁹F NMR spectra^a of phenylation products of hexafluorobenzene by PAT

Added compound	Spectrum
None	135.7, 136.2, 137.3, 137.8, 146.9, 147.4, 148.8, 149.3
Air	135.7, 136.3, 137.2, 137.8, 146.9, 147.4, 148.8, 149.3
Water	135.7, 136.2, 137.3, 137.8, 146.9, 147.0, 148.8, 149.3
BzOH	135.7, 136.2, 137.3, 137.8, 143.9, 148.8, 149.3, 158.5
Bz ₂ O ₂ ^b	143.8 ^c , 147.0, 148.8, 153.1, 156.8, 158.5 ^c

^a Shifts upfield from CFCl₃ in ppm.^b Products of decomposition of 0.1 mol l⁻¹ benzoyl peroxide in hexafluorobenzene.^c Signal arising from *ortho*- and *para*-fluorine atoms of pentafluorobiphenyl.

The thermolysis of benzoyl peroxide in hexafluorobenzene gives mainly pentafluorobiphenyl, the other major fluorine-containing component being thought to be the dimer [equation (4)] of $\sigma_F\cdot$ formed in chain-termination processes [4 - 6]. The spectrum of such a reaction mixture (Table 1, Row 5) suggests that the group of four peaks centred around 137 ppm and unique to the PAT decomposition products probably arises from stereoisomers of Ph₃C- σ_F [equation (5)]. Since none of these addition products could be obtained pure, and since the solvent masked any other absorptions in the region 160 - 166 ppm, the relative numbers of fluorine atoms observed could not be assessed, and so the relative yields of products could not be determined. The common absorption in both sets of spectra is presumably due to the dimer, (σ_F)₂, [equation (4)]. The possible presence of phenylheptafluorocyclohexadienes (σ_F -F) was discounted, for if no interaction occurred between incipient fluorine atoms and triphenylmethyl radicals, no such interaction should occur with the slightly more reactive but less abundant $\sigma_F\cdot$. Gas chromatography, and preliminary studies using gas chromatography linked with mass spectrometry, confirmed this deduction.

In the thermolysis of PAT in hexafluorobenzene, the high stationary concentration of triphenylmethyl radicals evidently hinders the production of pentafluorobiphenyl. Although triphenylmethyl radicals might be expected to defluorinate $\sigma_F\cdot$ to form this biaryl, the abstraction reaction, *i. e.*



is in competition with a radical-radical combination process [equation (5)] of virtually zero activation energy and hence will not contribute measurably.

Benzoic acid improves the yield of pentafluorobiphenyl in this reaction; equimolecular amounts of benzoic acid and PAT gave up to 8% yields of 2,3,4,5,6-pentafluorobiphenyl. This yield depended upon a number of factors, since acids also attack PAT itself. This observation suggested that benzoic acid may bring about the formation of pentafluorobiphenyl from $\sigma_F\cdot$ and that its formation in the thermolysis of benzoyl peroxide in hexafluorobenzene may be an essential step in the production of this biaryl.

TABLE 2

^{19}F NMR spectra^a of phenylation products of hexafluorobenzene by benzoyl peroxide with added *p*-fluorobenzoic acid

Concentration of added acid/mol l ⁻¹	Spectrum
0.00	— 143.8, 147.0, 148.8, 153.1, 156.8, 158.5
0.10	111.4 ^b , 143.9, 147.0, 148.8, 153.1, 156.8, 158.5
0.42	111.4 ^b , 143.9 ^c , 147.0, — 153.1, 156.8, 158.5 ^c

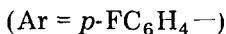
^a Shifts upfield from CFCl_3 in ppm.

^b 4'-F in 2,3,4,4',5,6-hexafluorobiphenyl; identical with authentic sample.

^c Signal arising from *ortho*- and *para*-fluorines of pentafluorobiphenyl.

In the latter reaction we have confirmed the production of 2,3,4,5,6-pentafluorobiphenyl in quantity, and the concomitant formation of small amounts of 2,2',3,4,5,6-hexafluorobiphenyl. The addition of *p*-fluorobenzoic acid, however, raised the yield of pentafluorobiphenyl [1]. The relative amounts of some of the adducts changed, and no 2,2',3,4,5,6-hexafluorobiphenyl could be found either by ^{19}F NMR spectroscopy or gas chromatography (Table 2). 2,3,4,4',5,6-Hexafluorobiphenyl, however, was now formed in quantities approximately proportional to the amount of added acid (Table 3). The presence of this compound suggests the formation of *p*-fluorophenyl radicals, apparently arising from the added *p*-fluorobenzoic acid. Since no other *p*- FC_6H_4 - system, apart from *p*- $\text{FC}_6\text{H}_4\text{C}_6\text{F}_5$, was found in the reaction product after the removal of acids by dilute aqueous sodium carbonate, these *p*-fluorophenyl radicals could not arise from interchange between benzoyl peroxide and aroic acid except in the unlikely event that the resulting mixed peroxide decomposed much more rapidly than benzoyl peroxide itself.

The amount of hydrogen fluoride evolved was also increased when the decompositions were carried out in the presence of added aroic acid. It is therefore probable that the two new reaction products, 2,3,4,4',5,6-hexafluorobiphenyl and hydrogen fluoride, had a common origin in the defluorination of $\sigma_{\text{F}}\cdot$, *i. e.*



Although the decomposition of benzoyl peroxide is susceptible to acid catalysis under some conditions [8], autocatalysis has not been observed in kinetic studies of the arylation of aromatic compounds by benzoyl peroxide [9] although aroic acid is formed in the reactions. Integration of the ^{19}F NMR spectra shows that the biaryls are formed at the expense of the other fluorine-containing species, confirming that the *p*-fluorobenzoic acid diverts $\sigma_{\text{F}}\cdot$ and does not merely aid its formation.

TABLE 3

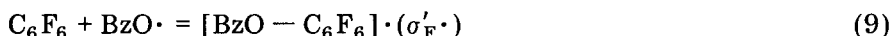
Yields of biaryls from the thermolysis of benzoyl peroxide (0.1 mol l^{-1}) in hexafluorobenzene at 80°C in presence of added *p*-fluorobenzoic acid

Concn. of added acid/mol l^{-1}	0.00	0.10	0.42
	Yield of biaryl/mg		
2,3,4,5,6-Pentafluorobiphenyl	20	29	30
2,2',3,4,5,6-Hexafluorobiphenyl	2	0	0
2,3,4,4',5,6-Hexafluorobiphenyl	0	2	9
Benzoyl peroxide decomposed	28	(*)	31

(*) = Not measured.

Fields and Meyerson [10], who also observed the rearrangement of $\sigma_{\text{F}}\cdot$ to give hexafluorobiphenyl ultimately, found that rearrangement was favoured over defluorination at higher temperatures, suggesting that the former process has a higher activation energy. Added *p*-fluorobenzoic acid in facilitating defluorination of $\sigma_{\text{F}}\cdot$ simultaneously minimises its extent of rearrangement by assisting the process of lower activation energy.

We suggest that the benzoic acid produced during the thermolysis of benzoyl peroxide in hexafluorobenzene is the essential source of hydrogen in the defluorination process of the radical intermediate, $\sigma_{\text{F}}\cdot$. Benzoic acid is initially formed either from attack upon the reagent itself by aryl or aryloxy radicals [11] or from rearrangement of $\sigma_{\text{F}}\cdot$ which leads to 2,2',3,4,5,6-hexafluorobiphenyl [equation (1)]. The acid may then cause the defluorination of another $\sigma_{\text{F}}\cdot$ radical to give benzoyloxy radical, pentafluorobiphenyl and hydrogen fluoride [equation (7)]. Benzoyloxy radicals may decarboxylate to give phenyl radicals and, ultimately, $\sigma_{\text{F}}\cdot$; alternatively, they may add to hexafluorobenzene to give a new radical intermediate ($\sigma_{\text{F}}'\cdot$), *i. e.*



or undergo radical-radical addition [*e.g.* equation (10)]:



Since no pentafluorophenyl benzoate is found, $\sigma_{\text{F}}'\cdot$, if it is formed at all, does not lose fluorine. The formation of tertiary esters [*e. g.* equation (10)] allows the ready regeneration of benzoic acid by trans-esterification with hydrogen fluoride. This allows benzoic acid to be returned to the defluorination stage, the process being limited by the availability of tertiary esters to supply benzoic acid or of $\sigma_{\text{F}}\cdot$ radicals to be defluorinated. The process is summarized in Figure 1.

In this scheme, disproportionation is not put forward as a possible source of biaryl. In the arylation of hexafluorobenzene, this requires the process



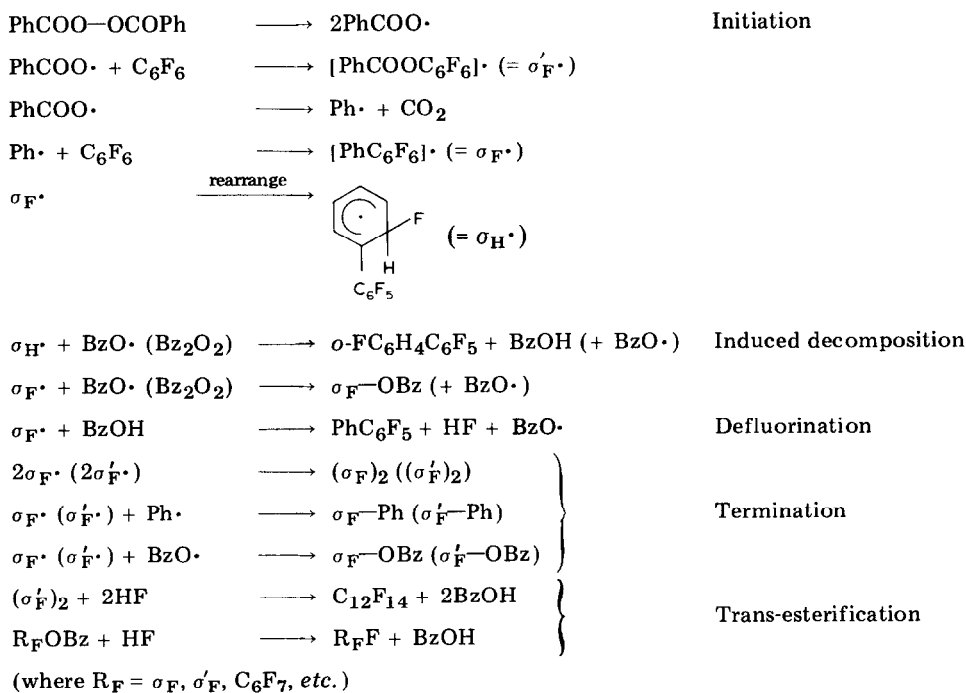


Fig. 1. Phenylation of hexafluorobenzene by benzoyl peroxide.

which, if it occurs at all, must compete with the dimerisation process [equation (4)]. The comparable defluorination of $\sigma_\text{F}\cdot$ by triphenylmethyl radicals has already been shown to be insignificant compared with the rapid radical-radical combination process with which it competes [equation (5)]. The comparable reactivities of $\sigma_\text{F}\cdot$ and of $\text{Ph}_3\text{C}\cdot$ implies that the combination process [equation (4)] will also prevail over the disproportionation [equation (11)]. This is found in the products of thermolysis of PAT in hexafluorobenzene, where there was evidence for the presence of $(\sigma_\text{F})_2$, but not of pentafluorobiphenyl; in contrast, while both the biaryl and $(\sigma_\text{F})_2$ were found in the products of thermolysis of benzoyl peroxide in hexafluorobenzene, only small amounts of phenylheptafluorocyclohexadienes could be found.

Disproportionation cannot therefore be a significant process in either of these systems.

The proposed scheme has the following advantages:

(i) The formation of pentafluorobiphenyl is explained by a thermodynamically probable route, the reaction products of which are in fact found in contrast with the previously proposed benzoyl hypofluorite which was necessary to explain defluorination of $\sigma_\text{F}\cdot$.

(ii) The effects of added aroic acid upon the yield of pentafluorobiphenyl, and the subsequent fate of the acid molecules which participate, are now explained.

(iii) It provides an explanation of the induced decomposition of benzoyl peroxide by σ -radical intermediates when the displaced atom is fluorine and not hydrogen.

(iv) It provides an explanation of the relative ease of displacement of substituents in the homolytic attack of pentafluorophenyl derivatives. The order of displacement is $F > NO_2 > Cl, Br$ [3] which is the order in which these substituents will form hydrogen bonds with an acid, and which is also the order in which they are displaced in nucleophilic aromatic substitution [12].

Against these advantages the scheme predicts the formation of some tertiary fluorides arising from the regeneration reactions. We have preliminary evidence of the existence of some of these; this will be presented subsequently.

Even in the phenylation of hexafluorobenzene by benzoyl peroxide, aroic acid did not completely divert $\sigma_F\cdot$ to biaryl formation; radical-addition processes could not be completely suppressed even in the presence of large amounts of added acid. The pentafluorophenylation of hexafluorobenzene by pentafluorobenzoyl peroxide gave low yields of decafluorobiphenyl [13] which were not improved by added pentafluorobenzoic acid, although this acid was effective in raising the yield of pentafluorobiphenyl in the phenylation of hexafluorobenzene by benzoyl peroxide. This suggests that the defluorination of the radical intermediate produced in the pentafluorophenylation of hexafluorobenzene cannot compete with the alternative radical-combination processes, implying a comparatively high stationary concentration of radicals in this system. The alternative implication, that the decafluorobiphenyl and pentafluorophenyl pentafluorobenzoate observed [13] as the only identifiable products arise from collapse of radical pairs generated solely from the peroxide, is rejected by the formation of much high-boiling residue indicating the other fates of the radical intermediate.

Experimental

Phenylazotriphenylmethane [14] was prepared by the ferricyanide oxidation of *N*-phenyl-*N'*-triphenylmethylhydrazine. Benzoyl peroxide, m.p. 105 - 106 °C (from chloroform/methanol mixtures) and *p*-fluorobenzoic acid, m.p. 182 - 183 °C (from hexafluorobenzene) were commercial samples which were purified by recrystallisation. Hexafluorobenzene (I.S.C.: 99.1% pure, glc) was used without further purification.

The decomposition of PAT (0.20 g) in hexafluorobenzene (5.00 cm³) was carried out by firstly freezing the suspension by the addition of solid carbon dioxide and subsequently warming the mixture slowly to the boiling point, when the reagent dissolved and gas was evolved. During the 10 min required for total decomposition of the reagent an inert (CO₂) atmosphere was maintained; however, when air was allowed access to the reaction mixture, triphenylmethyl peroxide was slowly precipitated. The presence of triphenylmethyl radicals did not interfere seriously with either of the analytical methods since the same results were obtained whether these radicals were

removed from the solution (iodine, or oxygen as reagents) or not. In all cases the solvent was removed by distillation under reduced pressure and the residue was dissolved in fluorochloroform.

The decomposition of benzoyl peroxide in hexafluorobenzene (0.100 mol l^{-1}) was carried out using three 5 cm^3 samples, two of which also contained *p*-fluorobenzoic acid. The three solutions were heated at 80°C in the same heating bath for 5 h during which $25 \pm 2\%$ of the peroxide had decomposed. This treatment ensured that the possible presence of mixed aroyl peroxides arising from exchange between the added *p*-fluorobenzoic acid and the benzoyl peroxide could be determined by ^{19}F NMR spectroscopy. The three samples were each shaken with aqueous sodium carbonate to remove acids, and the solvent was removed under reduced pressure from the dried (MgSO_4) organic layers. The acid recovered from the reaction mixture which was originally 0.42 mol l^{-1} in *p*-fluorobenzoic acid had m.p. $179 - 181^\circ \text{C}$; that recovered from the reaction mixture without added acid had m.p. $118 - 120^\circ \text{C}$. These seemed to be samples of reasonably pure *p*-fluorobenzoic acid and benzoic acid, respectively.

Gas chromatography of reaction products was carried out using a Perkin-Elmer F21 instrument. Under our conditions, 2,3,4,4',5,6-hexafluorobiphenyl and 2,3,4,5,6-pentafluorobiphenyl were indistinguishable, but 2,2',3,4,5,6-hexafluorobiphenyl was always well separated. ^{19}F NMR spectroscopy involved the use of a Varian HA-60 machine operated at 56.4 MHz with fluorochloroform as solvent and internal standard. Solutions were adjusted to approximately 10 mol%. Spectra were intensified, when required, using a digital signal averager (E. G. and G. Nuclear Ltd., model 546V).

Acknowledgements

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