A Mechanism of Formation of Biaryls in the Thermolysis of Benzoyl Peroxide in Polyfluorinated Aromatic Solvents

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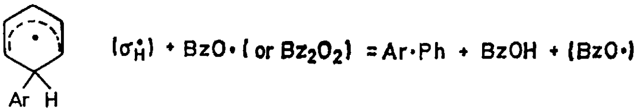
Summary The yield of 2,3,4,5,6-pentafluorobiphenyl formed by thermolysis of benzoyl peroxide in hexafluorobenzene is increased in the presence of *p*-fluorobenzoic acid, while the yields of radical–radical combination products and of 2,2′,3,4,5,6-hexafluorobiphenyl are decreased.

Benzoyl peroxide decomposes at 80° in hexafluorobenzene to give varying[1–3] yields of 2,3,4,5,6-pentafluorobiphenyl, together with smaller quantities of hydrogen fluoride, benzoic acid, and 2,2′,3,4,5,6-hexafluorobiphenyl.[1,3] The parallel between the products[1–4] and the kinetics[3,4] of decomposition of benzoyl peroxide in benzene and in hexafluorobenzene suggested analogous mechanisms. As the pentafluorobiphenyl seems to arise mainly from defluorination of the radical intermediate during the course of the decomposition[2] and not through decomposition of adducts, and as the analogous process to the reaction is thermodynamically improbable in the attack of hexafluorobenzene,[1] we attempted to define the mechanism of this reaction more closely.



$$(\sigma_H^\bullet) + \mathrm{BzO}\bullet\ (\text{or } \mathrm{Bz_2O_2}) = \mathrm{Ar{\cdot}Ph} + \mathrm{BzOH} + (\mathrm{BzO}\bullet)$$

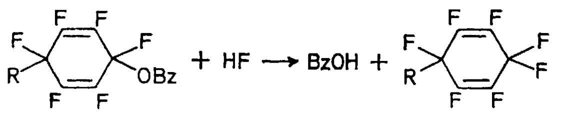
We now confirm that the decomposition of benzoyl peroxide in hexafluorobenzene (0·1M; 80°) gives 2,3,4,5,6-pentafluorobiphenyl, together with *ca.* 5% of 2,2′,3,4,5,6-hexafluorobiphenyl and products arising from radical–radical combination (analysed by g.l.c. and ^{19}F-n.m.r. spectrometry). Addition of *p*-fluorobenzoic acid, under otherwise identical conditions, raises the yield of pentafluorobiphenyl by *ca.* 50%, at the expense of both 2,2′,3,4,5,6-hexafluorobiphenyl and of the radical combination products. Depending upon the concentration of added acid (0·1–0·4M) the increased yield of pentafluorobiphenyl is accompanied by 6–25% of this amount of 2,3,4,4′,5,6-hexafluorobiphenyl, and hydrogen fluoride is also evolved. These results suggest the following sequence (1)—(3) for the defluorination of $\sigma_{\dot{\mathrm{F}}}$ ([Ph–C_6F_6]·), particularly since the formation of a 4′-fluoro-biaryl requires the presence of *p*-fluorophenyl radicals as intermediates.

$$\sigma_{\dot{\mathrm{F}}} + \mathrm{HO{\cdot}CO{\cdot}C_6H_4{\cdot}F} \rightarrow \mathrm{Ph{\cdot}C_6F_5} + \mathrm{HF} + \mathrm{{\cdot}OOC{\cdot}C_6H_4{\cdot}F} \quad (1)$$

$$\mathrm{{\cdot}OOC{\cdot}C_6H_4{\cdot}F} \rightarrow \mathrm{CO_2} + [p\text{-}\mathrm{C_6H_4F}]{\cdot} \quad (2)$$

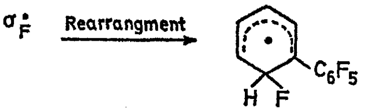
$$\mathrm{C_6F_6} + [p\text{-}\mathrm{C_6H_4F}]{\cdot} \xrightarrow[\text{analogous steps}]{\text{several}} p\text{-}\mathrm{F{\cdot}C_6H_4{\cdot}C_6F_5} \quad (3)$$

An analogous reaction can clearly occur with benzoic acid, which is formed in the decomposition of benzoyl peroxide in this solvent,[1] and it is suggested that this is the main route for the defluorination of $\sigma_{\dot{\mathrm{F}}}$ in the absence of added acids. A low, though sufficient, concentration of benzoic acid may be maintained as a result of its regeneration by reaction of hydrogen fluoride with tertiary benzoate esters formed as the ultimate products of benzoylation processes, *e.g.* reaction (4).



(4)

Sufficient benzoic acid may be formed originally by reaction of (I), arising from rearrangement of $\sigma_{\dot{\mathrm{F}}}$,[3,5] with benzoyl peroxide in the chain transfer stage of its induced decomposition leading to 2,2′,3,4,5,6-hexafluorobiphenyl.



(I)

$$\mathrm{(I)} + \mathrm{Bz_2O_2} \longrightarrow o\text{-}\mathrm{F{\cdot}C_6H_4{\cdot}C_6F_5} + \mathrm{BzOH} + \mathrm{BzO{\cdot}}$$

Each stage of the proposed sequence is energetically feasible, and the process as a whole explains the unexpectedly high yields of pentafluorobiphenyl, the isolation of benzoic acid as a side product, and the relative ease of displacement of groups (F > NO_2 > Cl,Br) from pentafluorobenzene derivatives during homolytic substitution.[6] Although an analogous series of reactions can be proposed for the defluorination of the product of benzoyloxylation of hexafluorobenzene ($\sigma_{\dot{\mathrm{F}}}'$), the absence of pentafluorophenyl benzoate shows that such processes proceed to a very slight extent.

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