Journal of Fluorine Chemistry, 5 (1975) 61 - 65

HOMOLYTIC REACTIONS OF POLYFLUOROAROMATIC COMPOUNDS. X. BIPHENYLYL RADICALS IN THE THERMOLYSIS OF AROYL PEROXIDES IN POLYFLUOROAROMATIC SOLVENTS*

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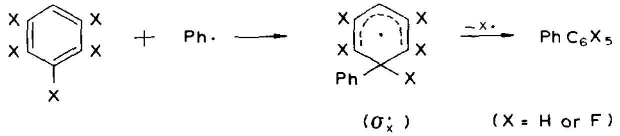
(Received February 22, 1974)

Summary

The thermolyses of a number of aroyl peroxides in hexafluorobenzene, and of benzoyl peroxide in octafluorotoluene, gave the corresponding biaryls which were isolated by steam distillation. Mass spectrometry of the residues showed evidence of biphenylyl radicals arising from the arylation of the peroxides themselves or, possibly, of the derived aroic acids. Terphenyls, and the corresponding σ-intermediate radicals, could be found, and the relative molecular masses of the latter components showed that subsequent arylation of the main binuclear products was not the main source of terphenyls.

Introduction

The decomposition of benzoyl peroxide in benzene at 80 °C gives biphenyl through a mechanism in which the σ intermediate undergoes a number of possible reactions, one of which is dehydrogenation to give the biaryl. While the analogous reaction with hexafluorobenzene gives the corresponding biaryl, the mechanism of this process is certainly different [2, 3].



(1)

In the decomposition of aroyl peroxides in benzene a number of other reaction products have been identified, including terphenyls which have been considered to arise from subsequent arylation of the biaryl [4]. These compounds may also arise from dehydrogenation of some products of radical–

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[*] For Part IX, see ref. 1.

radical combination (*e.g.* σ—Ar), or through initial arylation of benzoyl peroxide or benzoic acid to give sources of biphenylyl radicals. These new radicals would presumably undergo parallel reactions to those of the aryl radicals, and would thereby bring about the formation not only of terphenyls but also of a variety of radical–radical combination products which should parallel those resulting from phenylation.

We now report a mass spectrometric study in which evidence is found for the presence of such products, suggesting the intermediacy of such biphenylyl radicals.

Discussion

The decomposition of a number of aroyl peroxides in hexafluorobenzene, and of benzoyl peroxide in octafluorotoluene, gave products from which the corresponding biaryls could be isolated by steam distillation. The residues after this treatment contained a number a components; those of highest molecular weight appeared to undergo extensive fragmentation under mass-spectrometric conditions. Each residue from the decomposition of peroxides $(XC_6H_4COO)_2$ in hexafluorobenzene gave the ion-radicals $[XC_6H_4C_6F_5]^{\dot{+}}$, $[XC_6H_4C_6F_6]^{\dot{+}}$, $[XC_6H_4(XC_6H_3)C_6F_5]^{\dot{+}}$ and $[XC_6H_4(XC_6H_3)\cdot C_6F_6]^{\dot{+}}$ (see Table 1).

Since a change in the ionisation voltage from 70 eV to < 20 eV did not appreciably alter the relative intensities of these four mass peaks, these species did not result from electron bombardment of higher molecular weight precursors. It seems that the pyrolysis of the adducts, rather than electron bombardment, is the cause of such fragmentation.

An aryl radical which arises from the peroxide $(XC_6H_4COO)_2$ must add to a molecule of hexafluorobenzene to form the intermediate $\sigma_F^{\cdot}$, *i.e.* $[XC_6H_4C_6F_6]\cdot$, which is the necessary precursor of the isolated biaryl. Other fates of this intermediate include radical–radical combination, *e.g.*

$$2\sigma_F^{\cdot} \rightarrow (\sigma_F)_2 \qquad (2)$$

to give products which, upon pyrolysis, provide $\sigma_F^{\cdot}$ and hence the associated biaryl.

$$(\sigma_F)_2 \rightarrow 2\sigma_F^{\cdot} \qquad (3)$$

$$\sigma_F^{\cdot} \xrightarrow{-F\cdot} \text{biaryl} \qquad (4)$$

Such a decomposition has already been suggested to explain the variations in yield of 2,3,4,5,6-pentafluorobiphenyl with its conditions of isolation [5]. The present work confirms this suggestion.

The trinuclear species identified in the mass spectra may arise from subsequent arylation of the biaryl [reaction (5)], from radical–radical combination [reaction (6)] or from prior arylation of a source of aryl radicals [reaction (7)], followed by parallel processes (8) and (9) to those by which the biaryl is formed.

TABLE 1

Molecular weights of ion-radicals derived from the products of the thermolyses of aroyl peroxides in C_6F_6

X	$XC_6H_4C_6F_5$	$[XC_6H_4C_6F_6]\cdot$	$XC_6H_4(XC_6H_3)C_6F_5$	$[XC_6H_4(XC_6H_3)C_6F_6]\cdot$
H	244	263	320	339
CH_3	258	277	348	367
F	262	281	356	375
Cl	278, 280 (3:1)	297, 299 (3:1)	388, 390, 392 (9:6:1)	407, 409, 411 (9:6:1)
Br	322, 324 (1:1)	341, 343 (1:1)	476, 478, 480 (1:2:1)	495, 497, 499 (1:2:1)
NO_2	289	308	410	429
H[a]	294	313	370	389

[a] With octafluorotoluene, and not hexafluorobenzene, as the solvent.

$$C_6F_5C_6H_4X + XC_6H_4\cdot \rightarrow C_6F_5(C_6H_3X)C_6H_4X + XC_6H_4C_6F_4C_6H_4X \qquad (5)$$

$$[C_6F_6C_6H_4X]\cdot + XC_6H_4\cdot \rightarrow XC_6H_4C_6F_6C_6H_4X \qquad (6)$$

$$XC_6H_4\cdot + XC_6H_4COO\text{—}Z \rightarrow XC_6H_4(XC_6H_3)COO\text{—}Z \qquad (7)$$

$$(Z = H;\ OCOC_6H_4X;\ OCO(C_6H_3X)C_6H_4X)$$

$$XC_6H_4(XC_6H_3)COO\text{—}Z \rightarrow XC_6H_4(XC_6H_3)COO\cdot \rightarrow XC_6H_4(XC_6H_3)\cdot \qquad (8)$$

$$XC_6H_4(XC_6H_3)\cdot + C_6F_6 \rightarrow \underset{(I)}{[XC_6H_4(XC_6H_3)C_6F_6]\cdot} \qquad (9)$$

$$[XC_6H_4(XC_6H_3)C_6F_6]\cdot \xrightarrow{-F\cdot} XC_6H_4(XC_6H_3)C_6F_5 \qquad (10)$$

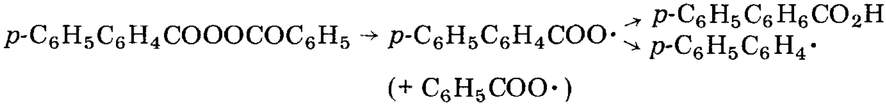
Arylation of the biaryl product would be expected to give two products, differing in their molecular masses by 18 units, arising from the displacement of hydrogen and of fluorine. For example, arylation of pentafluorobiphenyl would give 2,3,4,5,6-pentafluoroterphenyls as well as tetrafluoroterphenyls. Although there is no evidence of terphenyls arising from fluorine displacement, this does not constitute a proof of the absence of this step since fluorine displacement in general occurs less readily than does hydrogen displacement [5, 6].

The arylation of the biaryl, if it proceeds analogously to that of hexafluorobenzene or of benzene, ought to proceed through a σ-intermediate which, because of its divers reactions, should be apparent in the mass spectrum as a fragmentation product of dimers and similar by-products, just as the σ-radical precursor of biaryls occurs in the mass spectrum. There is, however, no evidence for the presence of the corresponding $\sigma_H^{\cdot}$ in any of the spectra. Specifically, the M/(M + 1) ratio for $[XC_6H_4(XC_6H_3)C_6F_5]^{+\cdot}$ could be entirely explained by contributions from ^{13}C at the natural level, since no more than 3% of the (M + 1) contribution could be attributed to the corresponding σ-intermediate and this is well within the experimental error. Subsequent arylation of the biaryl therefore cannot be a major source of the terphenyl fragments.

It is in principle possible that the product of radical–radical combination between $\sigma_F^{\cdot}$, the intermediate arising from arylation of hexafluorobenzene, and $XC_6H_4\cdot$, the aryl radical, might be the source of the observed mass spectra, for the adduct $XC_6H_4C_6F_6C_6H_4X$ (II) has a mass only one unit different from that of the putative σ-intermediates leading to terphenyls considered above. Absolute measurements of the molecular weights have a probable error of this order (although successive units could be clearly distinguished, the charge-to-mass ratio could not be measured with certainty without using internal calibrants, none of which were suitable for the present needs). However, such adducts are not the source of these peaks in the mass spectrum, since they would be expected to lose *two* fluorine atoms in succession to give an aromatic structure, and so would show three peaks corresponding to the parent adduct and to the successive loss of two fluorine atoms. The last of these, the ion-radical $[XC_6H_4C_6F_4C_6H_4X]^{\ddagger}$, is not present in any of the spectra.

Arylation of benzoyl peroxide would be expected to become significant either in concentrated solutions, where the ratio of solvent to peroxide is less, or in solutions in which the solvent is unusually inert. Since hydrogen is more readily displaced than fluorine in pentafluorobenzene [5], thermolysis of aroyl peroxides in fully fluorinated aromatic solvents would be expected to involve unusually large extents of attack by aryl radicals upon the peroxides themselves. *p*-Phenylbenzoic acid has been isolated during the decomposition of benzoyl peroxide in concentrated solutions [7] and might itself be a source of *p*-biphenylyl radicals [reaction (11)] or involve the presence of such a source (a peroxide) as an intermediate in its own formation [reaction (12)].

$$p\text{-}C_6H_5C_6H_4CO_2H \xrightarrow{-H\cdot} p\text{-}C_6H_5C_6H_4COO\cdot \qquad (11)$$



$$p\text{-}C_6H_5C_6H_4COOOCOC_6H_5 \rightarrow \underset{(+\,C_6H_5COO\cdot)}{p\text{-}C_6H_5C_6H_4COO\cdot} \begin{array}{l} \nearrow p\text{-}C_6H_5C_6H_6CO_2H \\ \searrow p\text{-}C_6H_5C_6H_4\cdot \end{array} \qquad (12)$$

Terphenyls identified in such reactions of benzoyl peroxide with benzene may arise through these aryl radicals by subsequent attack of the solvent. While the distinction between this route and phenylation of the biphenyl first formed cannot be made in this case, the distinction may be made when the decomposition is effected in hexafluorobenzene [reactions (7) - (10)].

The arylation of aroyl peroxides to give, ultimately, terphenyls must involve the formation of a σ-intermediate (I) which may, in the mass spectrograph, arise from fragmentation of its products of addition with other radicals, and which may also yield the corresponding terphenyl through loss of fluorine [reaction (10)]. However, the resulting aromatic compound would show considerable stability to fragmentation and would be associated with an ion-radical peak of high intensity. Two pairs of peaks are found in the mass spectrum corresponding with the biaryls and terphenyls, and their immediate σ-intermediate radical precursors. This is consistent only with the formation of biphenylyl radicals and their subsequent reaction with the solvent.

Experimental

Benzoyl peroxide, *o*- and *m*-fluorobenzoyl peroxide, *m*-toluoyl peroxide and *p*-chloro-, -bromo- and -nitro-benzoyl peroxides were each (1 g) heated in sealed tubes with hexafluorobenzene (20 cm^3) at 100 °C for 24 h.

The solvent, and subsequently the biaryl component, were removed by steam-distillation. The residue was dried and analysed as a solid by mass spectrometry using a VG-Micromass 12 magnetic-deflection mass spectrometer. Differential heating of the probe enabled components to be volatilised selectively; calibration of the instrument was carried out using 2,2′,4,4′,6,6′-hexabromodiphenylamine and polybromoethanes.

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