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HOMOLYTIC REACTIONS OF POLYFLUOROAROMATIC COMPOUNDS. PART XI.
CONFIRMATION OF THE PROPOSED MECHANISM OF PHENYLATION OF POLY-
FLUOROAROMATIC SUBSTRATES

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SUMMARY

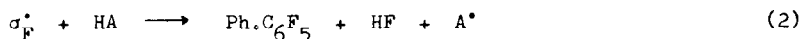
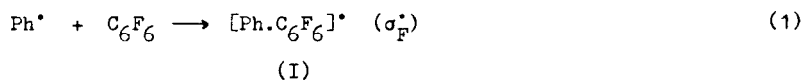
The derivatives of dihydrobiphenyl, which were predicted [1,2] to be formed in the thermolysis of benzoyl peroxide in polyfluoroaromatic compounds and which arose from transesterification, have been identified in the reactions of hexafluorobenzene and of octafluorotoluene with this peroxide. The presence of 1,4-dihydro-1,2,3,4,4,5,6-heptafluorobiphenyl (or its positional isomer, 1,2-dihydro-1,2,2,3,3,4,5,6-heptafluorobiphenyl) in such reaction mixtures also explains the formation of 3,4'-bis(phenyl)-octafluorobiphenyl in the dehalogenation products of the polynuclear residue from the reaction in hexafluorobenzene. Fluorine migration [3] does not need to be postulated.

The yield of 2,3,4,5,6-pentafluorobiphenyl from the thermal decomposition of phenylazotriphenylmethane (PAT) in hexafluorobenzene at 80° is generally increased by the presence of a variety of hydrogen donors. Larger amounts of additive increase the yield of biaryl with respect to PAT, but not usually with respect to the additive.

These results are consistent with the mechanism of arylation of polyfluoroaromatic compounds previously suggested [1,2].

INTRODUCTION

In previous papers [1,2] a mechanism of arylation of polyfluoroaromatic compounds was suggested, in which the formation of biaryl from the radical intermediate, σ_P^{\cdot} (I), involves attack by a hydrogen donor.



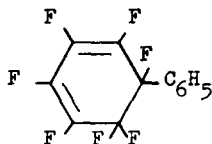
Benzoic acid was shown to increase the extent of formation of pentafluorobiphenyl from (I) generated when either benzoyl peroxide or PAT were decomposed in hexafluorobenzene [1]. The ready defluorination of (I) when benzoyl peroxide is the source of aryl radical arises from the formation of benzoic acid, initially either through phenylation of benzoyl peroxide -- which also leads, ultimately, to the formation of biphenyl radicals [4] -- or from the occurrence of a side-reaction in which 2,2',3,4,5,6-hexafluorobiphenyl is also formed [1,2,5,6]. Since the yield of pentafluorobiphenyl in these reactions was much more than that of benzoic acid, the regeneration of aroic acid was suggested to take place through a transesterification process. This in turn suggested the formation of derivatives of dihydrobiphenyl such as 1,4-dihydro-1,2,3,4,4,5,6-heptafluorobiphenyl ($\sigma_{\text{F}}^\bullet$; (II)).

We now report the identification of two such derivatives of dihydrobiphenyl in the products of decomposition of benzoyl peroxide in hexafluorobenzene and in octafluorotoluene, and a study of the efficiencies of various hydrogen donors in aiding the formation of pentafluorobiphenyl from the thermal decomposition of PAT in hexafluorobenzene.

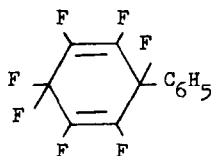
RESULTS AND DISCUSSION

Gas chromatography of the volatile products of the thermolysis of benzoyl peroxide in hexafluorobenzene at 80° showed the incomplete separation of a component eluted immediately after the solvent. Mass spectrometry of this showed the presence of a species of relative molecular mass 282 and a fragmentation pattern consistent with the structure $\text{Ph.C}_6\text{F}_7$. Similarly, the products of thermolysis of benzoyl peroxide in octafluorotoluene at 80° gave two peaks on the gas chromatogram, clearly separated from the solvent peak and occurring before the biaryl components. These two peaks were shown to arise from two isomeric C_{13} compounds of relative molecular mass 332. Again, their fragmentation patterns were consistent with the

dihydrobiphenyl structure $\text{Ph.C}_6\text{F}_6.\text{CF}_3$. These compounds were present in the same relative amounts (3:1) as the two major biaryl products (71:24 [6]); this ratio appears to be that of the relative concentrations of the two radical precursors ($\sigma_{\text{F}}^{\bullet}$). The structure of such derivatives of dihydrobiphenyl is still uncertain. The parent compound, $\text{Ph.C}_6\text{F}_7$ (II), may be either 1,2-dihydro-1,2,2,3,4,5,6-heptafluorobiphenyl (IIa) or 1,4-dihydro-1,2,3,4,4,5,6-heptafluorobiphenyl (IIb).

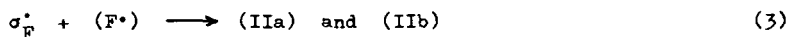


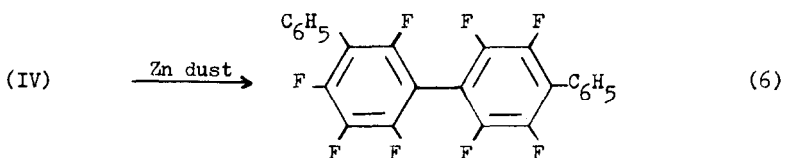
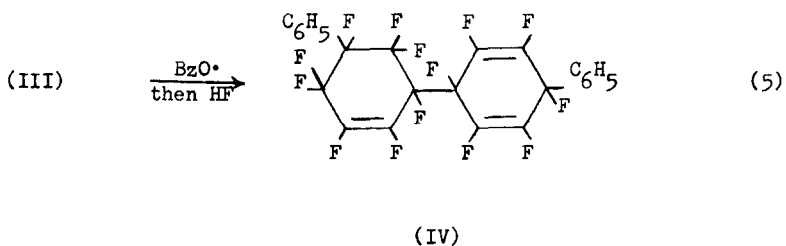
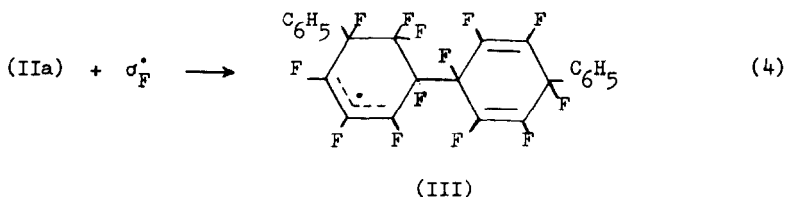
(IIa)



(IIb)

In a recent report [3], Kobrina et al. showed the thermal decomposition of the polynuclear residue in the phenylation of hexafluorobenzene to be a second source of pentafluorobiphenyl, confirming the earlier observation of Oldham and Williams [7]. The Russian workers also found that dehalogenation of this residue with zinc dust gave 2,4'-, 4,4'-, and 3,4'-quaterphenyl derivatives. The last product, which cannot arise from dimerisation of $\sigma_{\text{F}}^{\bullet}$, was thought to arise from a migration of fluorine in the intermediate radical. However, free-radical addition may take place to the olefinic systems (IIa) and (IIb). While there is no evidence of the products of phenyl radical addition to these compounds [4], the stationary concentration of the σ -intermediate ($\sigma_{\text{F}}^{\bullet}$) is much greater. Addition of $\sigma_{\text{F}}^{\bullet}$ to (IIa) or (IIb) would give radicals containing the 2,4'-, 3,4'- or 4,4'-quaterphenyl skeleton. Both benzoic acid and the benzoyloxy-radical would be expected to give trapping products from these radicals; these products would, in turn, give polyfluoro-derivatives of 2,4'-, 3,4'-, and 4,4'-quaterphenyl upon treatment under Kobrina's conditions. The formation of 3,4'-bis-(phenyl)-octafluorobiphenyl from such reaction of (IIa) is shown in eqns. (3) - (6). The analogous derivatives of 2,4'- and 4,4'-bis-(phenyl)-octafluorobiphenyl may be similarly obtained.





The effect of hydrogen donors upon the yield of pentafluorobiphenyl formed in the thermal decomposition of PAT in hexafluorobenzene at 80° is shown in Table 1. In the absence of hydrogen donors, the intermediate radical, $\sigma_{\text{F}}^{\bullet}$, does not give the biaryl [1]; nor does it abstract hydrogen from carbon or from nitrogen even when the resulting radical has considerable resonance stabilisation (e.g. aniline, dibenzyl disulphide, triphenylmethane). However, the hydroxyl groups in phenols and in carboxylic acids provide hydrogen for the aromatisation of the intermediate. Although trends may be found in a limited series of hydrogen donors, there is no simple relation between acidity of the additive and the effect upon the yield of biaryl. The influence of the hydrogen donor involves three factors: (i) the strength of the X-H bond which is broken, (ii) the stability of the radical resulting from hydrogen abstraction from the donor, and (iii) the extent to which the additive diverts phenyl radicals from reaction with hexafluorobenzene.

TABLE 1

Molar yields of pentafluorobiphenyl from the thermolysis of PAT in hexafluorobenzene in the presence of various hydrogen donors at 80°

Hydrogen donor	Moles donor Moles PAT	Moles PhC ₆ F ₅ Moles PAT	Moles PhC ₆ F ₅ Moles donor
None	-	0.000	-
C ₆ F ₅ NHNHCPPh ₃	0.10	0.000	0.000
PhNH ₂ , PhNHNH ₂	0.20	0.000	0.000
Ph ₃ CH	0.20	0.000	0.000
CH ₃ NO ₂	0.37	0.000	0.000
CH ₃ COCH ₂ COCH ₃	0.18	0.000	0.000
(PhCH ₂ S) ₂	0.18	0.000	0.000
p-CH ₃ C ₆ H ₄ SH	0.22	0.008	0.035
p-CH ₃ C ₆ H ₄ SH	1.00	0.014	0.014
2-C ₁₀ H ₇ OH	0.17	0.000	0.000
2-C ₁₀ H ₇ OH	1.00	0.012	0.012
p-NO ₂ C ₆ H ₄ OH	0.07	0.005	0.070
p-NO ₂ C ₆ H ₄ OH	1.00	0.023	0.023
C ₆ F ₅ OH	0.10	0.033	0.33
C ₆ F ₅ OH	0.87	0.033	0.038
PhCO ₂ H	0.22	0.003	0.014
PhCO ₂ H	1.00	0.004	0.004
C ₆ F ₅ CO ₂ H	0.22	0.015	0.067
CCl ₃ CO ₂ H	0.25	0.044	0.174
CCl ₃ CO ₂ H	0.83	0.137	0.164
CF ₃ CO ₂ H	0.16	0.011	0.066

EXPERIMENTAL

Solutions of benzoyl peroxide in the appropriate polyfluoroaromatic substrate (ca. 0.1M) were heated at 80° for 24 hours. The mixture was then distilled in steam, and the forerun, which contained mainly unreacted substrate, was separated from the biaryl fraction. Gas chromatography (Pye 104) linked with mass spectrometry (VG-Micromass 12 magnetic deflection mass spectrometer) was used to isolate and identify the new reaction products in this forerun. Table 2 gives the fragmentation patterns of the two isomeric dihydroonafluoromethylbiphenyls. Details of the fragmentation of the dihydroheptafluorobiphenyl

TABLE 2

Fragmentation pattern of dihydrononafluoromethylbiphenyls (70 eV)

Relative molecular mass (*)	Isomer (A) Relative intensity	Isomer (B) Relative intensity	Carbon atoms (**)
333	13.7	14.7	13 [±] 1
332 (M)	100	100	
314	3	3	14 [±] 4
313 (M-F)	19	19	
312	8	8	
295	3	3	
294 (M-2F)	6	6	
282 (M-CF ₂)	11	11	12 [±] 3
281	4	4	
264	5	9	11 [±] 3
263 (M-CF ₃)	33	88	
245	5	9	
244 (M-F-CF ₃)	13	16	
243	2	5	
232 (M-CF-CF ₃)	5	2	
225 (M-2F-CF ₃)	7	11	
217 (M-2F-Ph)	4	2	
213 (M-CF ₂ -CF ₃)	16	32	10 [±] 1
194 (M-2CF ₃)	6	10	
156 (M-2F-2CF ₃)	5	6	
77 (Ph)	47	53	6 [±] 1

(*) Assignments in parentheses

(**) Calculated from M/M+1 ratio

were obscured by the concomitant elution of large amounts of hexafluorobenzene. This allowed the identification of the molecular ion, and of some of its higher molecular weight fragmentation products, only.

Weighed amounts of commercial samples of hydrogen donor, and PAT (1.0 g.) were heated in hexafluorobenzene (10 ml.) at 80° overnight. The solvent was removed by distillation under slightly reduced pressure, known weights of 1,2,4,5-tetramethylbenzene were added as marker and calibrant, and the amount of 2,3,4,5,6-pentafluorobiphenyl present in the reaction mixture was found by gas chromatography (Pye 104).

ACKNOWLEDGEMENTS

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