Photoreaction between Benzene and Hexafluorobenzene

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Summary Hexafluorobenzene undergoes a photoreaction with benzene to give 2,3,4,5,6-pentafluorobiphenyl: the process is unusual in that it can be sensitised by naphthalene, is susceptible to polarity effects, and may not involve free $C_6F_5^{\cdot}$ radicals.

MANY photoreactions of benzene and hexafluorobenzene with various addends have been reported.[1,2] We now describe the photoreaction between these two aromatic compounds. A 1:1 molecular complex, m.p. 23—27°, is already known.[3]

Irradiation (low- or medium-pressure Hg lamps) of equimolecular mixtures of hexafluorobenzene and benzene at 25° under nitrogen or air gives 2,3,4,5,6-pentafluorobiphenyl (m.p. and mixed m.p., ^1H and ^{19}F n.m.r. spectra: $\psi = 0{\cdot}00025$), biphenyl, and decafluorobiphenyl in the molecular ratio 100:3:1. Neither mono- nor penta-fluorobenzene was detected among the products in this reaction nor in the more efficient variants of it described below. Hydrogen fluoride is evolved. The u.v. spectrum of the pentafluorobiphenyl in ethanol (λ_{max} 236 nm, ϵ 13,000 mol^{-1} l cm^{-1}) differed from that recorded in ref. 4 (λ_{max} 273 nm, ϵ 7600 mol^{-1} l cm^{-1}), but was identical with that of reference samples. The formation of this compound exemplifies a novel procedure for linking aromatic rings.

Mechanistically the reaction is puzzling. The intermediacy of phenyl radicals has been discounted by the observation that generation of such radicals in an equimolecular mixture of C_6H_6 and C_6F_6, (a) thermally from dibenzoyl peroxide and (b) photochemically from iodobenzene, yields biphenyl and pentafluorobiphenyl in the ratios 14:1 (a) and 9·5:1 (b).† The question whether $C_6F_5^{\cdot}$ radicals are involved leads to an apparent conflict of evidence. On the one hand it has been found that the thermal generation of $C_6F_5^{\cdot}$ radicals from perfluorobenzoyl peroxide in an equimolecular C_6H_6—C_6F_6 mixture produces pentafluoro- and decafluoro-biphenyl in the molecular ratio 100:0·7 in comparison with the ratio 100:1 found following irradiation of the C_6H_6–C_6F_6 mixture. Further, similar thermal generation of $C_6F_5^{\cdot}$ radicals in toluene gave *o*-, *m*-, and *p*-pentafluorophenyltoluenes in the ratio 1·38:1·03:1·00 in good agreement with the corresponding ratio 1·30:1·05:1·00 found after irradiation of an equimolecular mixture of toluene and hexafluorobenzene.

These findings might provide convincing evidence for the intermediacy of free $C_6F_5^{\cdot}$ radicals, but for the following considerations.

Firstly, the dissociation energy of the aromatic C–F bond (520 kJ mol^{-1} in C_6F_6) is considerably higher than the quantal energy of the exciting radiation (468 kJ mol^{-1} at 254 nm). Although irradiation of C_6F_6 in cyclohexane and cyclo-octane is known to produce products indicative of intermediate $C_6F_5^{\cdot}$ radicals,[5] addition of cyclohexane was without effect on the formation of the present photoproducts. In contrast, the polar solvents acetonitrile and methanol led to a 40-fold greater rate of formation of pentafluorobiphenyl (C_6H_6 and C_6F_6 being each 1M) than did cyclohexane. Even trace (0·085M) amounts of acetonitrile, methanol, and CF_3CO_2H increased the rate of reaction by factors of 30 ± 5, 100 ± 10, and 400 ± 50% respectively.

Although the necessary initially excited species has not been definitely identified for the reaction of C_6H_6 and C_6F_6, it has been shown by use of a Pyrex filter that C_6F_6 undergoes analogous reactions with naphthalene (giving a mixture of 1- and 2-pentafluorophenylnaphthalenes) *via* initial excitation of the naphthalene. Surprisingly, naphthalene has been found to photosensitise the reaction of C_6H_6 with C_6F_6 using radiation of wavelength $>$ 290 nm (which gives rise to no reaction in the absence of naphthalene): polar solvents promote this process. Yet naphthalene has a lower triplet energy (255 kJ mol^{-1}) than either benzene (355 kJ mol^{-1}) or hexafluorobenzene (311 kJ mol^{-1}) and singlet–singlet energy transfer is ruled out on similar grounds. The only exothermic energy transfer process available appears to involve S_1 naphthalene (380 kJ mol^{-1}) and either T_1 benzene or T_1 hexafluorobenzene. This would imply a novel phenomenon whereby complexing of S_1 naphthalene in an exciplex with, say, S_0 hexafluorobenzene promotes intersystem crossing to produce T_1 hexafluorobenzene, possibly through spin–orbit perturbation induced by the combined effects of six fluorine atoms (*cf.* Cundall and Robinson[6]).

The reactions are influenced by the heavy-atom solvents CH_2Br_2 and $BrCH_2CH_2Br$. For example, under comparable conditions, the rates of formation of pentafluorobiphenyl from benzene and hexafluorobenzene in diethyl ether, acetonitrile, 1,2-dibromoethane, and dibromomethane

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† This difference is under investigation but is probably irrelevant to the present issue.

were 1:5:24:45, respectively. A quenching effect of oxygen was also noted. In contrast, these heavy-atom solvents strongly inhibited the naphthalene-sensitised process, doubtless by promoting the formation of T_1 naphthalene.

On balance, the evidence seems to point to the necessary involvement of T_1 hexafluorobenzene, and the formation of this *via* one or more exciplexes having marked dipolar character. In the absence of any obvious route from T_1 C_6F_6 to $C_6F_5^{\cdot}$, it seems necessary to postulate that these two species may have closely similar patterns of reactivity in homolytic aromatic substitution processes.

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[1] See for example, D. Bryce-Smith, *Pure Appl. Chem.*, 1968, **16**, 47; K. E. Wilzbach and L. Kaplan, *J. Amer. Chem. Soc.*, 1971, **93**, 2073; D. Bryce-Smith, B. E. Foulger, A. Gilbert, and P. J. Twitchett, *Chem. Comm.*, 1971, 794; D. Bryce-Smith, G. B. Cox, and A. Gilbert, *ibid.*, p. 914.

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[5] D. Bryce-Smith, B. E. Connett, A. Gilbert, and T. E. Kendrick, *Chem. and Ind.*, 1966, 855.

[6] R. B. Cundall and D. A. Robinson, *J.C.S. Faraday II*, 1972, **68**, 1691.