

## Photoreaction of Benzene with Hexafluorobenzene

By Derek Bryce-Smith,\* Andrew Gilbert, and Peter J. Twitchett, Department of Chemistry, University of Reading, Whiteknights, Reading, Berkshire

Hexafluorobenzene reacts photochemically with benzene to produce mainly 2,3,4,5,6-pentafluorobiphenyl, and with toluene analogously gives a mixture of *o*-, *m*-, and *p*-pentafluorophenyltoluenes. A particularly unusual feature is that naphthalene markedly sensitises these photoreactions in preference to causing the formation of pentafluorophenyl naphthalenes, but not apparently *via*  $T_1$  naphthalene since heavy-atom solvents strongly inhibit the sensitised processes. In contrast, these solvents promote the unsensitised processes.

Although some of the evidence suggests that intermediacy of  $C_6F_5$  radicals, the reactions show certain polar characteristics, particularly promotion by polar solvents and proton donors, and are considered to involve a dipolar intermediate formed *via* attack on ground state benzene by triplet  $C_6F_6$  functioning as a diradical.

THE benzene ring undergoes numerous types of photoreaction with ethylenes, acetylenes, amines, and other species, and these have recently been the subject of summarising reports.<sup>1,2</sup> Photoaddition rather than photosubstitution processes tend to predominate, in contrast with the classical behaviour of aromatic compounds in their electronic ground states. Benzene itself is not known to undergo photoaddition to other aromatic species, with the exception of pyrrole<sup>3</sup> and furan.<sup>4</sup> In the former case, the pyrrole ring rather than the more aromatic benzene ring is rather surprisingly retained in the photoadduct (1), whereas with furan, the major

comparison with an authentic sample. Only the u.v. spectrum in ethanol ( $\lambda_{max}$ , 236 nm,  $\epsilon$  13 000 l mol<sup>-1</sup> cm<sup>-1</sup>) was at variance with that recorded ( $\lambda_{max}$ , 273 nm,  $\epsilon$  7 600 l mol<sup>-1</sup> cm<sup>-1</sup>)<sup>10</sup> but a sample of (4) synthesised by phenylation of hexafluorobenzene had a spectrum identical with that of the present photoproduct, and with that of a sample kindly provided by Professor R. N. Haszeldine.

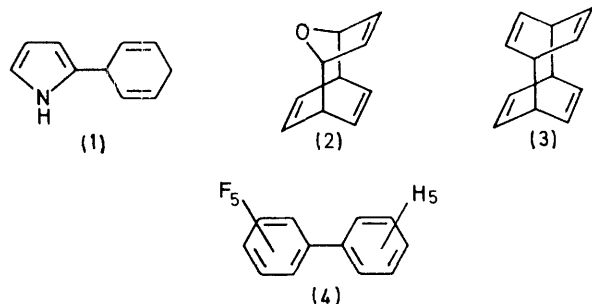
Hydrogen fluoride is evolved during the irradiation, together with traces of biphenyl and decafluorobiphenyl [3 and 1%, respectively, of the major product (4) from an equimolar mixture of the starting materials]. The efficiency of the reaction showed a strong concentration dependence: thus for 80 mole % benzene the chemical yield of (4) was approximately three times that for 50 mole % benzene under otherwise comparable conditions. In view of the formation of hydrogen fluoride during the reaction, it should be noted that quantum yields are acid-dependent, an effect which is discussed below.

The mechanism for the formation of these aryl coupling products was at first thought likely to involve production of  $C_6F_5\cdot$  and/or  $C_6H_5\cdot$  radicals and their subsequent attack on  $C_6F_6$  and/or  $C_6H_6$  *via* the pathways of conventional homolytic aromatic substitution. Certainly formation of phenyl radicals from homolysis of a benzene C-H bond (bond strength 95 kcal mol<sup>-1</sup>) is consistent with the quantal energy of the light used (112.5 kcal einstein<sup>-1</sup> at 254 nm). But we have been obliged to question simple mechanisms of this type for the following reasons.

Generation of phenyl radicals in equimolar mixtures of benzene and hexafluorobenzene (*a*) thermally from dibenzoyl peroxide, and (*b*) photochemically from iodobenzene led to ratios of (4) to biphenyl of 1 : 14 and 1 : 9.5, respectively,\* whereas from the irradiation the ratio is 100 : 3. Clearly the intermediacy of free phenyl radicals can be discounted.

The participation of free pentafluorophenyl radicals initially appeared much more likely. Thus thermal decomposition of perfluorobenzoyl peroxide in an equimolar mixture of benzene and hexafluorobenzene gave

\* The greater relative yield of (4) in the light-induced generation of phenyl radicals may arise from a concurrent photoreaction between benzene and hexafluorobenzene, or less probably from a related direct reaction between iodobenzene and hexafluorobenzene.



primary product (2) arises from 1,4-/2',5'-cycloaddition.

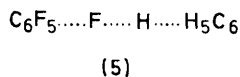
The existence of well defined crystalline 1 : 1 molecular complexes of hexafluorobenzene with benzene and other aromatic hydrocarbons<sup>5,6</sup> suggested the possibility that irradiation of these might give rise to a product analogous to the furan adduct (2), that is, a derivative of the long elusive benzene dimer (3). As reported in a preliminary communication,<sup>7</sup> the reaction in practice takes a different course, which we now describe in fuller detail.

We note in advance that the present reactions of hexafluorobenzene with benzene, toluene, and naphthalene are wholly unlike the corresponding reactions of this compound with ethylenes,<sup>8</sup> although there is a superficial similarity to the reactions with cycloalkanes.<sup>9</sup>

Irradiation (low- or medium-pressure Hg lamps) of mixtures of hexafluorobenzene and benzene at 25 °C under air or nitrogen yields a white crystalline compound, m.p. 110–112°, as the major product: this was identified as 2,3,4,5,6-pentafluorobiphenyl (4) by <sup>19</sup>F and <sup>1</sup>H n.m.r. spectra, i.r. spectrum, and by m.p.

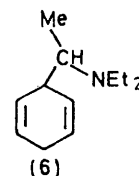
(4) and decafluorobiphenyl in the approximate ratio of 100:0.7; *cf.* 100:1 for the photoprocess. To investigate this matter further, the products from irradiation of an equimolar mixture of hexafluorobenzene and toluene were compared with those from thermal decomposition of perfluorobenzoyl peroxide in toluene. The latter process gave a mixture of *o*-, *m*-, and *p*-pentafluorophenyltoluenes (but no bibenzyl) in the ratios 1.38:1.03:1.00, and the photoreaction gave the same products plus bibenzyl in the closely similar corresponding ratios 1.30:1.05:1.00:0.2. These findings appear further to suggest the involvement of  $C_6F_5\cdot$  radicals. We have not studied independent photochemical methods for the generation of pentafluorophenyl radicals in view of the report by Haszeldine *et al.* that photochemically generated  $C_6F_5\cdot$  radicals in toluene give *o*-, *m*-, and *p*-pentafluorophenyltoluenes in the ratios 1.81:0.95:1.00.<sup>11</sup> No pentafluorophenylphenylmethane was detected as a product from any of these reactions in toluene. The isomer ratios reported by these workers are not identical with those which we have found, but are sufficiently close to suggest the involvement either of a common intermediate, or more probably of closely related intermediates having rather similar reactivity characteristics: we return to this point below.

Apart from the experimental findings, the involvement of free pentafluorophenyl radicals in the photoreactions of hexafluorobenzene with benzene and toluene is in fact rendered questionable by the following considerations. First, the quantal energy ( $112 \text{ kcal einstein}^{-1}$ ) of the exciting radiation is appreciably below that ( $124.5 \text{ kcal mol}^{-1}$ ) required for simple photo-homolysis of the aromatic C-F bond, although a transition state (5)



having F partly bonded to H can be envisaged which would reduce the energy requirement: *cf.* ref. 9. A more serious difficulty arises from the observation that the quantum efficiency of the reaction is very sensitive to solvent polarity and the presence of proton donors. Thus the rate of formation of (4) was increased some forty-fold in acetonitrile or methanol solutions 1M in benzene and hexafluorobenzene, in comparison with the corresponding rate in cyclohexane. Even trace amounts of such polar solvents markedly accelerated the process. Thus the incorporation of 0.085M-acetonitrile, methanol, or trifluoroacetic acid into equimolar mixtures of the reactants increased the chemical yield of (4) by 30, 100, and 400%, respectively, under comparable irradiation conditions: the reaction involving trifluoroacetic acid had a quantum yield of 0.001. Examples of acid catalysis in other photoreactions of benzene have previously been reported.<sup>12,13</sup> For example, the benzene-triethylamine photoadduct (6) is formed at a greatly increased rate in the presence of methanol. The use of MeOD led to incorporation of deuterium both in the adduct (6) and in photoreduction products of the

arene: in this case the reaction appears to proceed *via* a radical anion-radical cation pair.<sup>13</sup> In contrast, no



deuterium was incorporated into (4) when benzene and hexafluorobenzene were irradiated in the presence of MeOD.

In the case of benzene-hexafluorobenzene, the overlapping absorption spectra make selective excitation of either component virtually impossible, so one cannot establish *a priori* which of the two arenes is the initially excited species fruitful of reaction. The increase in quantum yield associated with increased proportions of benzene should however be noted in this connection. On the other hand, irradiation of a solution of naphthalene in hexafluorobenzene under conditions where only the naphthalene was excited ( $\lambda > 290 \text{ nm}$ ) led to the formation of a mixture of 1- and 2-pentafluorophenyl-naphthalenes in the ratio 5:1, respectively: as with benzene, the reaction was promoted by trifluoroacetic acid or methanol. Thus direct absorption by hexafluorobenzene is not essential, in this case at least.

An even more interesting observation has been that naphthalene sensitises the formation of (4) from hexafluorobenzene and benzene under conditions where only naphthalene is excited. The heavy-atom solvents dibromomethane and 1,2-dibromoethane strongly inhibited this sensitisation, so the involvement of  $T_1$  naphthalene in product formation can be ruled out with some confidence. In contrast, the unsensitised process leading to product (4) is markedly promoted by heavy-atom solvents, so this evidently does involve triplet species. The proposal of a triplet mechanism for the unsensitised process is supported by the observation that oxygen causes marked inhibition (although we recognise that the interpretation of oxygen effects in isolation is fraught with ambiguities: see for example the cases of oxygen-enhancement of intersystem crossing discussed by Fischer and Fischer<sup>14</sup>).

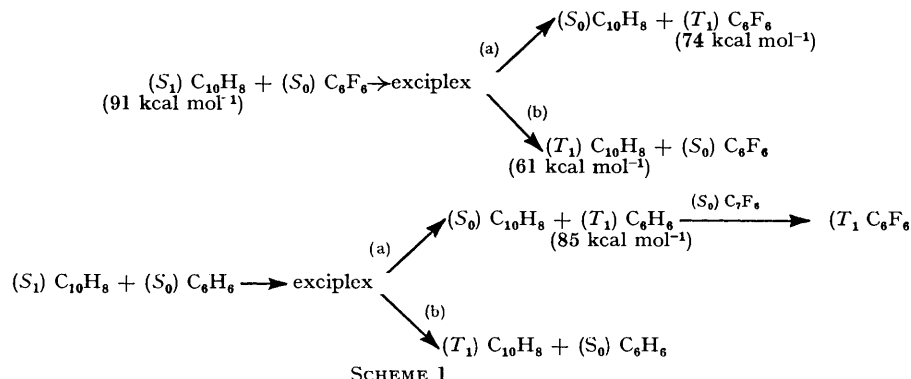
It therefore appears necessary to postulate that naphthalene sensitisation involves energy transfer from free or complexed  $S_1$  naphthalene to produce  $T_1$  benzene and/or  $T_1$  hexafluorobenzene. There are in fact precedents<sup>15</sup> for the proposal that an exciplex of  $S_1$  naphthalene with benzene or hexafluorobenzene would dissociate to form triplet species. In principle, the exothermic processes shown in Scheme 1 could occur.

It is evident from the above-mentioned effects of heavy-atom solvents that interactions of type (b) would be energy-wasting through physical processes, and would not lead to product (4). Therefore the sensitisation by naphthalene would appear to involve processes of type (a). A problem here, however, is that processes of type (a) would be less exothermic than those of type

(b); but one must bear in mind that the quantum yield for formation of (4) is very low, and that any competing processes of type (b) would not be detected under our experimental conditions. The differences in exothermicity between competing processes of types (a) and (b) are however such that for type (a) processes to occur to any detectable extent it is necessary to postulate that the

than the reactants. Occam's razor encourages us to depict this as the  $\sigma$ -bonded species (7), essentially a polarised diradical susceptible to stabilisation by a polar medium. Product (4) could reasonably arise from this by a reaction sequence involving protonation, deprotonation, and loss of hydrogen fluoride (Scheme 2).

Factor (b) concerning free  $C_6F_5\cdot$  radicals remains to be



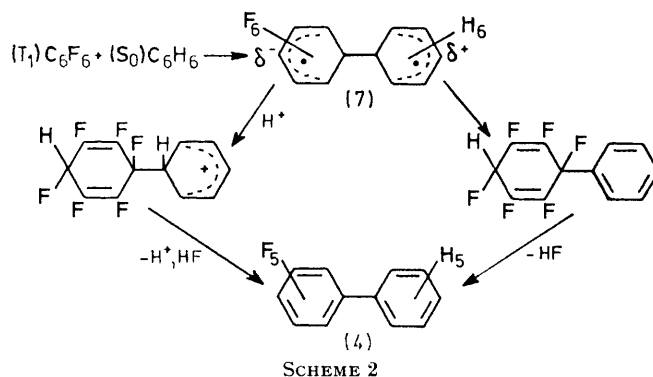
relative rates are governed more by kinetic than by thermodynamic factors. This seems reasonable in view of the low dissociation energies to be expected for the exciplexes involved.

In short, the effects of heavy-atom solvents and oxygen indicate that factors which would be expected to promote the formation of  $T_1$  naphthalene in the sensitised process are unproductive of the product (4), whereas factors favouring the formation or survival of triplet species in the unsensitised process favour the formation of (4).

A further important point is that naphthalene and benzene respond in opposite ways to the effects of heavy-atom solvents in their *separate* reactions with hexafluorobenzene. Thus the formation of pentafluorophenyl naphthalenes from hexafluorobenzene and naphthalene in the absence of benzene is inhibited by such solvents. This seems to require the conclusion that the common key intermediate in both naphthalene-sensitised and unsensitised formation of (4) is  $T_1$  hexafluorobenzene: the formation of this from  $T_1$  naphthalene would be endothermic by 13 kcal mol<sup>-1</sup>, whereas the formation from  $T_1$  benzene in the unsensitised process would be exothermic by 11 kcal mol<sup>-1</sup>; and of course its more direct formation by intersystem crossing from  $S_1$  hexafluorobenzene should be promoted by heavy atom solvents. By analogy with the behaviour of ground state hexafluorobenzene, it seems likely that the  $T_1$  hexafluorobenzene will readily form a complex with benzene.

Any mechanistic scheme for the remaining steps onward from  $T_1$  hexafluorobenzene to pentafluorobiphenyl (4) must encompass the further following features: (a) the promoting effects of polar solvents and proton donors, and (b) the apparent involvement of  $C_6F_5\cdot$  radicals. The former effects are consistent with the intermediacy of an intermediate which is more polar

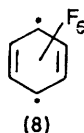
considered. It will be recalled that the isomer ratios for the photochemical formation of *o*-, *m*-, and *p*-pentafluorophenyltoluenes from hexafluorobenzene and toluene were very similar to those from thermally generated



free  $C_6F_5\cdot$  radicals in toluene, and less close to, though of the same order as, those reported by Haszeldine *et al.*<sup>11</sup> for  $C_6F_5\cdot$  radicals generated by photolysis of  $C_6F_5I$  in toluene. The question arises as to how  $C_6F_5\cdot$  radicals could arise from ( $T_1$ )  $C_6F_6$ . As previously mentioned, simple homolysis seems unlikely on energy grounds, and at the very least would require the absorption of a second photon under conditions highly unfavourable for such absorption. The only route which we can conceive would involve a homolytic process of type (5). In the case of benzene, this process might well occur *via* a somewhat polar transition state to produce a radical pair, primary recombination of which would give pentafluorobiphenyl (4). But in the case of toluene, the transition state involving hydrogen abstraction would in no way resemble any intermediate addition stage of the type normally considered to be involved in homolytic aromatic substitution, and no even approximate similarity in isomer ratios between such processes is to be

expected. Moreover, any radical-producing processes of type (5) which led to diffusion of radicals from the solvent cage would be expected to give rise to products resulting from solvent attack by both  $C_6F_5\cdot$  and  $C_6H_5\cdot$  radicals (or  $C_7H_7\cdot$  radicals from toluene). In fact, any significant involvement of  $C_6H_5\cdot$  radicals can be decisively ruled out for reasons already given. It follows that the concomitant formation of  $C_6F_5\cdot$  radicals must also be rejected as anything more than a minor side-reaction.

On balance therefore, we feel obliged to conclude that free  $C_6F_5\cdot$  radicals are not significantly involved as intermediates, notwithstanding the rather persuasive evidence from isomer ratios. We are left with  $(T_1)C_6F_6$  as the key intermediate, in accordance with the reaction scheme depicted above. By analogy with  $T_1$  benzene, it would be reasonable to depict  $T_1$  hexafluorobenzene essentially as the diradical (8),<sup>16</sup> a species which in its



reactions with benzene and toluene might well behave rather similarly to the pentafluorophenyl radical.

#### EXPERIMENTAL

Preparative-scale photolyses were carried out using either (a) an immersion cell of total capacity 300 ml illuminated by a water-cooled 100 W medium-pressure mercury arc, or (b) a fused silica tube of capacity 65 ml illuminated by a 15 W low-pressure spiral mercury arc. The latter apparatus was cooled by means of a fan. Small-scale irradiations were performed using the lamp described in (b) and fused silica tubes of capacity 1.5 ml mounted in a holder which was rotated at approximately 15 rev. min<sup>-1</sup>.

*Irradiation of Benzene and Hexafluorobenzene.*—A mixture of hexafluorobenzene (25 ml, 0.29 mol) and benzene (180 ml, 2.0 mol) was saturated with dry nitrogen and irradiated using the apparatus described in (a) for 100 h. A slight deposit of pale polymeric material was observed on the lamp-jacket and acid vapours of HF were present above the irradiated solutions. Distillation of the pale yellow solution under reduced pressure gave starting materials and a dark residual liquor which solidified on cooling (0.5 g). Recrystallization from toluene gave a buff coloured product which was sublimed (90 °C; 2.6 mmHg) to yield a white solid which after further crystallization (ethanol) gave 2,3,4,5,6-pentafluorobiphenyl (4), m.p. and mixed m.p. 110–112°.

The effects of concentration, solvent, and the presence of proton donors on the photoreaction of hexafluorobenzene and benzene were examined by means of experiments performed in the small fused silica tubes mentioned above. G.l.c. of the solutions was performed on a column packed with 8% Carbowax 20M on 80–100 mesh Chromosorb W; the apparatus was calibrated with solutions of known concentrations of the products. The mechanistic significance of the concentration effect cannot be assessed without knowledge of the rate constants for the various competing processes which could in principle be involved. The effect

of atmosphere on the yield of (4) was studied using equimolar solutions of the arenes containing 0.085M- $CF_3$ - $CO_2H$ ; these were degassed by four freeze-pump-thaw cycles under either argon or oxygen. The solutions were then irradiated with a low-pressure lamp and the reaction was monitored by g.l.c.

*Generation of Phenyl Radicals in Benzene and Hexafluorobenzene.*—(a) *Photochemical method.* To a mixture of benzene (8.9 ml, 0.1 mol) and hexafluorobenzene (11.5 ml, 0.1 mol) were added freshly distilled iodobenzene (1.02 g, 0.005 mol) and silver powder (1.6 g, 0.0125 mol). The mixture was irradiated for 11 h in a water-jacketed fused silica cell using a medium-pressure mercury arc. The inner surface of the cell was kept free of silver deposits by a rotating pad of quartz wood inside the cell.<sup>17</sup> Filtration of the photolysate gave a yellow solution which was found to contain biphenyl and pentafluorobiphenyl in the ratio 9.3 : 1.

(b) *Thermal method.* Dibenzoyl peroxide (0.03 g,  $2.5 \times 10^{-4}$  mol  $C_6H_5\cdot$ ) was added to a mixture of benzene (1.95 g, 0.025 mol) and hexafluorobenzene (4.65 g, 0.025 mol). The mixture was heated under reflux for 2 h to give biphenyl and pentafluorobiphenyl in the ratio 14 : 1.

*Generation of Phenyl Radicals in the Presence of Benzene and Hexafluorobenzene.*—Perfluorobenzoyl peroxide (0.102 g,  $2.5 \times 10^{-4}$  mol) was dissolved in a mixture of benzene (4.95 ml, 0.05 mol) and hexafluorobenzene (5.75 ml, 0.05 mol), and the solution was heated under reflux for 3 h. G.l.c. (5% cyanosilicone oil column) indicated that the ratio of pentafluorobiphenyl to decafluorobiphenyl was approximately 100 : 0.7.

*Irradiation of Hexafluorobenzene and Toluene.*—Toluene (321 ml, 3.0 mol), hexafluorobenzene (38 ml, 0.3 mol), and trifluoroacetic acid (3.25 g, 0.085 mol) were mixed and irradiated for 50 h under nitrogen using a 100 W medium-pressure mercury arc. Acid vapours were observed on opening the vessel and g.l.c. (Carbowax 20M) of the pale yellow liquid showed the presence of four products (A–D) at  $t_R$  0.17, 0.24, 0.27, and 1.00 in the ratios 1.30 : 1.05 : 1.00 : 0.2, respectively. Distillation of the irradiated solution at water-pump pressure gave starting materials and an orange oil, which solidified on cooling. Trituration with light petroleum (b.p. 60–80°) gave an intractable tarry residue together with an orange solution. Evaporation of the solution and recrystallization of the resulting solid from ethanol gave white crystals (0.97 g) which following vacuum sublimation melted at 115–117°. Spectroscopic analysis of the product identified it as 2,3,4,5,6-pentafluoro-4'-methylbiphenyl (lit.,<sup>11</sup> m.p. 118°) and g.l.c. showed this to be product C in the original mixture. Pure samples of compound A, as a colourless oil, and D, as a white solid, were obtained by preparative g.l.c. and identified by spectroscopic analysis as 2,3,4,5,6-pentafluoro-2'-methylbiphenyl and bibenzyl, respectively. Preparative t.l.c. on a 20 cm wide plate coated with silica (Merck) provided a 60 mg sample of product B of 60% purity as a white crystalline solid. Further purification of B proved extremely difficult, but it was identified as 2,3,4,5,6-pentafluoro-3'-methylbiphenyl by comparison of the i.r. spectrum with that given in the literature.<sup>18</sup>

*Generation of Pentafluorophenyl Radicals in the Presence of Toluene.*—Perfluorobenzoyl peroxide (0.5 g,  $1.25 \times 10^{-3}$  mol) was heated under reflux in toluene (4.5 g,  $50 \times 10^{-3}$  mol) for 2 h. G.l.c. showed the resulting solution to contain as major products the hexafluorobenzene–toluene photo-

products the hexafluorobenzene-toluene photoproducts A, B, and C in the ratios given in the text.

*Irradiation of Hexafluorobenzene and Naphthalene.*—Saturated solutions of naphthalene in hexafluorobenzene (50 ml) with and without trifluoroacetic acid (0.085M) were irradiated for 24 h at 20 °C using a low-pressure mercury arc. The resulting red-brown solutions were found to contain two products of *m/e* 294 in the ratio 5 : 1 at *t<sub>R</sub>* 5.9 and 9.7 relative to naphthalene (Apiezon L). The photo-reaction also proceeded in a Pyrex vessel illuminated by a medium-pressure mercury arc.

*Sensitisation by Naphthalene of the Photoreaction of Benzene with Hexafluorobenzene.*—Naphthalene (20 mg) was added to an equimolar mixture (0.5 ml) of benzene and hexafluorobenzene (with and without 0.085M-trifluoroacetic acid). The Pyrex tube was warmed slightly to melt the naphthalene-hexafluorobenzene molecular complex and was irradiated using a Pyrex-sheathed 100 W medium-pressure mercury arc. An identical Pyrex tube containing hexafluorobenzene and trifluoroacetic acid but no naphthalene was irradiated alongside the first as a blank experiment. G.l.c. on both Carbowax 20M and Apiezon L columns showed the formation of pentafluorobiphenyl only when naphthalene was present.

The effects of the heavy atom solvents dibromomethane and 1,2-dibromoethane on the foregoing reactions were examined in the small fused silica tubes using solutions of hexafluorobenzene (1.0M), and benzene (1.0M) with and without naphthalene (0.1M) in the solvent, and compared with those using acetonitrile as solvent. In the sensitised experiments the presence of the heavy-atom solvent inhibited formation of pentafluorobiphenyl (decrease *ca.* 40 fold) whereas in the unsensitised case formation of this product was promoted (*ca.* 3 fold) by the same solvents.

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