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PHOTOLYTIC LABILITY OF BROMO, CHLORO AND FLUORO SUBSTITUENTS IN DIALKYL PHENYLPHOSPHONATES

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The formation of aryl radicals by the photolytic homolyses of carbon-halogen bonds in aryl iodides,[1-3] bromides[2,4-6] and chlorides[4,5,7] has been demonstrated and it has been shown that the ease of homolysis parallels the carbon-halogen bond strengths of the aryl halides.[5] Synthetic utilization of radicals generated from aryl iodides was first achieved by Kharasch in the synthesis of biphenyls[1a]; the reaction now constitutes the basis of procedures for the arylation of aromatic systems[1,3] and organophosphorus compounds.[2] Similar synthetic procedures based on aryl bromides have been reported,[2b,5b,6] although product yields are lower than for aryl iodides. A further drop in reactivity is observed with aryl chlorides[4,5,7] and attempted synthetic reactions with these halides are generally unsuccessful.[3,5b] Recent studies have shown that aryl fluorides are essentially unreactive under these photolytic conditions.[5]

We now wish to report three examples of aryl halide photolyses in which synthetically important carbon-chlorine and carbon-fluorine bond lability is observed. Studies in this laboratory have shown that photolyses of iodo- and bromo-benzenes in the presence of trialkyl phosphites result in the formation of dialkyl phenylphosphonates in good yield[2]; the reaction has

$$C_6H_5X + P(OR)_3 \xrightarrow{h\nu} C_6H_5P(O)(OR)_2 + RX$$

also been shown to be effective with substituted iodobenzenes.[2c] In an extension of these synthetic studies, the photolyses (Table I) of a series of dihalobenzenes in trimethyl phosphite have been examined. As expected, photolyses of the isomeric bromoiodobenzenes (Ia-c) led to the formation of mixtures of the bromophenyl (IIa-c) and phenylenebisphosphonates (III). The reaction is presumed to be sequential with II serving as precursor to III and it was shown that photolysis (53 hr.) of the *meta*-bromophenylphosphonate (IIb) in trimethyl phosphite yielded the bisphosphonate (*meta*-III, 85%). The results obtained with *ortho*-chloroiodobenzene (Id) were unexpected; the carbon-chlorine bond of the anticipated product (IId) proved to be quite labile and the bisphosphonate (*ortho*-III) was the major product. In a control experiment, IId was converted to *ortho*-III (17%) by photolysis (24 hr.) in trimethyl phosphite. The corresponding *para*-isomer (If) also gave bisphosphonate, although the chlorophenylphosphonate (IIf) was the major product. The anticipated lack of reactivity of the carbon-chlorine bond was observed in the case of the *meta*-isomer (Ie) and the chlorophenylphosphonate (IIe) was the sole product. The results of the photolysis of *para*-bromofluorobenzene (Ig) were also unanticipated. The expected *para*-fluorophenylphosphonate (IIg) was the major product, but a significant degree of carbon-fluorine bond lability was observed with the formation of the bisphosphonate (*para*-III). A longer reaction time was employed in the photolysis of Ig, since the carbon-bromine bond is less labile than the carbon-iodine bonds of Ia-f.

The unexpected degree of carbon-chlorine and carbon-fluorine bond lability shown by IId,f,g must be attributed to an activating influence of the dimethoxyphosphono group. Under comparable conditions, chloro- and fluoro-benzenes fail to react with trimethyl phosphite. The yields of bisphosphonates obtained in the bromoiodobenzene series also provide evidence for an activation effect. The yields of photolysis products from IIa-c range from 23 to 87%; under comparable conditions, photolysis of bromobenzene

TABLE I

Photolytic Formation of Halophenylphosphonates and Phenylenebisphosphonates[a]

$$\underset{\text{I}}{C_6H_4XY} + P(OCH_3)_3 \longrightarrow \underset{\text{II}}{YC_6H_4P(O)(OCH_3)_2} + \underset{\text{III}}{C_6H_4[P(O)(OCH_3)_2]_2}$$

		X	Y	%II	%III	Hr.
(a)	ortho	I	Br	<4	87	23.5
(b)	meta	I	Br	57	23	24
(c)	para	I	Br	17	39	24
(d)	ortho	I	Cl	11	28	24
(e)	meta	I	Cl	92	0	24
(f)	para	I	Cl	72	10	24
(g)	para	Br	F	39	29	117

[a] Conditions: 0°, 450 watt Hanovia high pressure lamp, five-fold excess of trimethyl phosphite, no solvent, quartz apparatus. Yields cited are based on isolation.

in trimethyl phosphite gives only a 23% yield of phenylphosphonate.[2b] This activation is also dependent upon substituent orientation with carbon-halogen bond lability decreasing in the order *ortho* > *para* > *meta* for IIa-f. Similar orientational effects have been observed in the photolyses of other substituted halobenzenes.[4,5a,7,8]

The products obtained in these photolyses have not been previously described in the literature, but the structures were fully supported by elemental analyses, infrared and NMR spectra. The following physical constants were observed: IIa, b.p. 113-115° (0.2 mm.); IIb, b.p. 104-105° (0.2 mm.); IIc, b.p. 95-96° (0.1 mm.); IId, b.p. 106-107° (0.3 mm.); IIe, b.p. 109-110° (0.5 mm.); IIf, b.p. 95-96° (0.1 mm.); IIg, b.p. 80-81° (0.2 mm.); *ortho*-III, m.p. 80-81°; *meta*-III, high boiling liquid; *para*-III, m.p. 100-101°. Further work in this area is in progress and full details of these and other reactions with substituted aryl halides will be reported.

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