

Photoreduction of 4,4'-Dichlorobiphenyl

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The photolysis of 4,4'-dichlorobiphenyl was performed using 3100 Å light. In degassed 2-propanol or methanol the reaction yielded exclusively HCl and 4-chlorobiphenyl, which was stable. The quantum yield (CH₃OH) for disappearance of reactant was 0.002. Photoreduction was not observed in ethyl ether, cyclohexane, or acetonitrile. Photolysis in CH₃OD did not lead to incorporation of deuterium. Oxygen slows the photo-reaction down substantially and leads to other

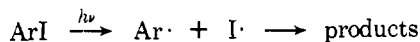
products in addition to 4-chlorobiphenyl. In ether containing 2% CF₃CO₂H or CH₃CO₂H, photoreduction to 4-chlorobiphenyl was also observed. A $k_H/k_D = 7.0$ was calculated when the rate of conversion in 2% CF₃CO₂ (ether) was compared to CF₃CO₂H(ether). Reaction under nitrogen or in air can be sensitized by the aromatic amines, tryptophan, and diethylaniline, but benzophenone, as expected, is ineffectual in air.

It has been shown that polychlorinated biphenyls (PCB's) have pervaded the environment and the paucity of knowledge about their chemistry is becoming increasingly apparent (Hammond, 1972). Although these compounds are quite resistant to degradation, photolysis by sunlight could be important in their environmental chemistry. Solar radiation could induce both degradation and unsuspected photoreactions between PCB's and naturally occurring organic compounds. A full understanding of the PCB's problem, therefore, requires a knowledge of their photochemistry. PCB's are such complex mixtures that we chose to study the photochemistry of a single model, 4,4'-dichlorobiphenyl (DCB).

Although several studies pertaining to photoreductive dechlorinations of aromatic pesticides (Crosby and Hamadmad, 1971; Crosby *et al.*, 1972; Moilanen and Crosby, 1972; Pinhey and Rigby, 1969; Plimmer, 1970) have appeared in the literature, little is known about the photochemistry of PCB's. Two groups have irradiated chlorinated biphenyls with sunlight or 3100 Å light in hexane (Bills *et al.*, 1972; Hutzinger and Safe, 1971). Although the structures of products were not elucidated, the mass spectra of several products indicated that dechlorination, polymerization, and isomerization took place.

Photolysis of 3,3',4,4'-tetrachlorobiphenyl in hexane with 3100 Å light produced a stepwise dechlorination process, *i.e.*, the tetrachloro compound led to 3,4,4'-trichlorobiphenyl which, in turn, produced 4,4'-dichlorobiphenyl and finally the very slow formation of the 4-chloro derivative (1% in 150 hr) (Zabik *et al.*, 1972). A similar pattern was observed for several hexa- and tetra-chlorinated biphenyls (Hustert and Korte, 1972).

Although chlorinated aromatics are much less reactive (Kharasch *et al.*, 1966) than the corresponding iodinated compounds, it has generally been hypothesized that the mechanism of photoreduction is the same (Pinhey and Rigby, 1969; Plimmer, 1970; Zabik *et al.*, 1972). Aryl iodides are reliable sources of aryl radicals (Kharasch and Sharma, 1968) and a homolytic cleavage mechanism adequately correlates the data available for aryl iodides.



The present study demonstrates that this mechanism requires revision for DCB and, by implication, perhaps for other aryl chlorides. Because of the restricted scope of reaction conditions under which photoreduction takes place, this study has only indirect implications for environmental chemistry. Indeed, other studies in nonaqueous solutions must now be regarded in a similar light.

EXPERIMENTAL SECTION

Gas Chromatography. A Bendix model 2110 gas chromatograph equipped with electron capture detector was used with a 6 ft × ¼ in. Teflon-lined aluminum column packed with 5% OV-1 on 60-80 mesh Chromosorb W. Operating conditions were: injection port, 170-180°; column oven, 180°; and flow rate, 35 ml/min. Preparative collection was performed on a F&M Hewlett-Packard model 5750 gas chromatograph equipped with thermal conductivity detector and splitter. The column employed was a 6 ft × ½ in. aluminum column packed with 5% SE 30 on 60-80 mesh Chromosorb W. Conditions were flow rate 30 ml/min, injection port 220°, and column oven, 250°.

Spectra. All ultraviolet spectra were obtained with a Cary 17 spectrometer. Mass spectra were measured with an AEI model MS-12 spectrometer using a direct probe.

Photolysis. A Rayonet photochemical reactor, equipped with merry-go-round and 16 3100 Å lamps, was used. DCB (111.6 mg, 0.5 mmol) was dissolved in the appropriate solvent (500 ml) to prepare a stock solution. Aliquots (5 ml) were placed in 15 × 160 mm Pyrex test tubes. Degassing was accomplished by 5-min nitrogen flush at 0° or six freeze-thaw cycles at 0.005 mm, followed by sealing *in vacuo*.

Following photolysis, product analysis was usually carried out by glc, where retention times were compared to authentic samples. In one experiment, MCB was isolated and identified spectroscopically. HCl was identified by following the pH with a pH meter and by the precipitation of AgCl when an AgNO₃ solution was added to the sample. The stability of 4-chlorobiphenyl was checked by dissolving it (9.4 mg, 0.05 mmol) in 2-propanol (50 ml) from which 5-ml samples were irradiated as above.

Quantum Yield. Benzophenone (0.91 g, 5.0 mmol) and benzhydrol (0.92 g, 5.0 mmol) were dissolved in benzene (50 ml), to be used as an actinometer as described by Moore and Ketchum (1962). DCB (11.2 mg, 0.05 mmol) was taken up to 50 ml with 2-propanol. Two 5-ml samples of each solution were placed in long-stemmed Pyrex tubes and degassed by three freeze-thaw cycles at 0.005 mm and sealed *in vacuo*. The samples were irradiated for 1 hr. The amount of DCB reacted, determined by glc, was found to be 7%. Using uv spectroscopy the amount of benzophenone reacted was found to be 65%. The quantum yield was calculated to be 0.002.

Kinetic Isotope Effect in Diethyl Ether-CF₃CO₂D. The deuterated acid was synthesized by adding D₂O (4.0 g, 0.2 mol) to (CF₃CO)₂O (21.0 g, 0.1 mol). The resulting mixture was distilled and the 68-70° fraction kept. Analysis by nmr showed the acid to have 96% deuterium incorporation.

DCB (56 mg, 0.25 mmol) was dissolved in 49 ml of diethyl ether and 1 ml of CF₃CO₂D. An identical solution was made up using CF₃CO₂H. Photolysis for 48 hr yielded

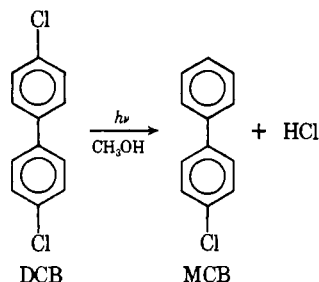
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35% MCB in the presence of the $\text{CF}_3\text{CO}_2\text{H}$ and 5% in the presence of $\text{CF}_3\text{CO}_2\text{D}$ ($k_{\text{H}}/k_{\text{D}} = 7.0$).

Photolysis of DCB in CH_3OD . DCB (25 mg, 0.22 mmol) was dissolved in 50 ml of CH_3OD (99.5%, Stohler isotope chemicals) and 5-ml samples were degassed by the freeze-thaw process and photolyzed for 48 hr. The MCB was collected from the glc. The mass spectrum was identical to the mass spectrum of an authentic sample of MCB, indicating no deuterium incorporation.

RESULTS AND DISCUSSION

The photolysis of DCB was performed in dilute non-aqueous solvents with 3100 Å light. In methanol and 2-propanol, 4-chlorobiphenyl (MCB) was formed in essentially quantitative yield. In a typical reaction 36% MCB was formed after 22 hr in degassed 2-propanol and 25% MCB was formed in degassed methanol. The quantum yield in degassed methanol was 0.002 for MCB formation. Photolysis in air gave a slower reaction (under oxygen 5% reaction in 24 hr) and complex products. The product MCB was found to be quite stable to the reaction conditions. Little change was observed even after 50 hr of photolysis in degassed methanol. This may be due to the low extinction coefficient of MCB at 3100 Å, $\epsilon_{3100} = 10$ for MCB and $\epsilon_{3100} = 289$ for DCB. The origin of the new hydrogen atom on MCB was explored by photolyzing DCB in CH_3OD . The MCB was isolated by preparative glc and analyzed by mass spectrometry. No deuterium was incorporated. This implies that a hydrogen atom is donated from the methyl group and is typical of free radical reactions where the weaker C-H bond is broken in preference to the O-H bond (Pryor, 1966).



As shown in Table I, all the other organic solvents gave a mixture of products. The presence of MCB could not be confirmed with confidence. Formation of MCB was found under one other condition. When either acetic or trifluoroacetic acid was added to an ethyl ether solution, smooth photoreduction of DCB to MCB was observed. Addition of trifluoroacetic acid to a cyclohexane solution did not give photoreduction. Furthermore, addition of trifluoroacetic acid to 2-propanol photolysis did not accelerate the reaction rate. The reduction using trifluoroacetic acid in ether involves a rather different mechanism than reduction in alcohol. In the former reaction the hydrogen comes from the O-H and is presumably a proton transfer. In agreement with this is a kinetic isotope effect on the overall rate of disappearance ($k_{\text{H}}/k_{\text{D}} = 7$) observed when $\text{CF}_3\text{CO}_2\text{D}$ was used in place of $\text{CF}_3\text{CO}_2\text{H}$. In alcohol, a hydrogen atom transfer from carbon is seemingly involved.

It is clear that photoreduction requires special conditions. The above results also suggest that a simple homolytic cleavage mechanism producing $\text{Ar}\cdot$ and $\text{Cl}\cdot$ is not correct, since both ether and cyclohexane should be sufficiently good hydrogen atom donors (in comparison with methanol) (Russell and Bridger, 1963) to scavenge these radicals and give overall photoreduction. The unusual acid-catalyzed photolysis also does not correspond with the simple homolytic mechanism.

Sensitization and quenching of DCB photolysis was also studied. Aromatic amines are of particular interest in this regard since they are effective sensitizers in air (Miller *et*

Table I. DCB Photolysis^a

Solvent	Additive	% DCB reaction	Products
2-Propanol		36	MCB
	2% $\text{CF}_3\text{CO}_2\text{H}$	36	MCB
Methanol		25	MCB
	2% $\text{CF}_3\text{CO}_2\text{H}$	15	Complex ^b
Diisopropyl ether		4	Complex
	2% $\text{CF}_3\text{CO}_2\text{H}$	25	MCB
Diethyl ether	2% $\text{CF}_3\text{CO}_2\text{H}^c$	35	MCB
	2% $\text{CF}_3\text{CO}_2\text{D}^c$	5	MCB
	2% $\text{CH}_3\text{CO}_2\text{H}$	39	MCB
		9	Complex
Cyclohexane	2% $\text{CF}_3\text{CO}_2\text{H}$	11	Complex
Hexane		16	Complex
Acetonitrile		30	Complex

^a 22 hr photolysis, 1.0×10^{-3} M/l. DCB. ^b Trace amounts of MCB detected by glc. ^c 48 hr photolysis, 5.0×10^{-3} M/l. DCB.

al., 1973). We found that tryptophan and diethylaniline induced the photodecomposition of DCB in both 2-propanol and cyclohexane. The rate of reaction with diethylaniline was slower in cyclohexane (10% in 24 hr) than in the alcohol (73% in 24 hr). The rate of disappearance of DCB was the same under either nitrogen or oxygen; however, only MCB was formed in the former case whereas several products besides MCB formed under oxygen. No attempt was made to identify these products. Tryptophan produced photodecomposition in 2-propanol (60% in 24 hr). Again no change in rate was seen between nitrogen or oxygen atmosphere, and the latter case produced several minor products other than MCB.

Quenching with biacetyl was achieved, but rather inefficiently. At the highest concentration of quencher employed (1×10^{-3} M) $\phi_0/\phi_Q = 0.92$ for a 24-hr photolysis in degassed isopropyl alcohol. If it is assumed that quenching is diffusion controlled, this indicates the lifetime of DCB* is about 10^{-6} sec. This seems too short for a triplet lifetime, but the nature of excited states in this process remains unresolved.

ACKNOWLEDGMENT

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