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COMMUNICATIONS

Photodecomposition of Unsymmetrical Polychlorobiphenyls

Cyclohexane solutions of several tri- and tetrachlorobiphenyls were photolyzed at 300 nm. The products obtained arose from dechlorination followed by hydrogen abstraction from the solvent. The reactivity of the compounds studied depended on the position of the chlorine substituents, ortho chlorines cleaving first and at a faster rate when para chlorines are present on the same ring. The quantum yields of the polychlorobiphenyls (PCB's) studied were determined.

Polychlorobiphenyls (PCB's) are known to react upon irradiation with ultraviolet light at 300 nm (Safe and Hutzinger, 1971; Hustert and Korte, 1972). Recently we have reported the products, quantum yields, and triplet lifetimes of a series of symmetrical PCB's (Ruzo et al., 1974). The reactivity at the ortho position was found to increase considerably when a para chlorine was present. Apparently electron donation from the para chlorine forces the excited state to be more planar and the driving force for cleavage of ortho chlorines, which hinder this planarity, is increased.

We now wish to report this effect in unsymmetrical PCB's and in a compound containing ortho and para chlorines in separate rings.

EXPERIMENTAL SECTION

Chlorobiphenyls. All PCB's used in photolysis or as standards were obtained from Analabs Inc. (North Haven, Conn.). The compounds were authenticated using nuclear magnetic resonance and mass spectra. They were purified by recrystallization from ethanol until >99.9% purity was achieved by gas chromatography (GC).

Reagents. Glass-distilled cyclohexane was obtained commercially (Burdick and Jackson Labs, Muskegon, Mich.). *cis*-1,3-Pentadiene (Chemical Samples) was used as received. Benzophenone (Baker Chemical Co.) was recrystallized from pentane until pure by GC. Alkanes used as internal standards were obtained from Aldrich Chemical Co. and used without further purification.

Photochemical Procedures. Solutions containing known concentrations of PCB's and internal standard were prepared in volumetric flasks. Then 3.0-ml portions of these solutions were syringed into separate, constricted, 100 × 13 mm Pyrex culture tubes. The tubes used did not transmit >1% of the radiation below 287 nm. The samples were degassed by three freeze-pump-thaw cycles and sealed in vacuo.

Irradiation of Samples. Irradiations were performed in a merry-go-round apparatus with a Rayonette Reactor (The Southern New England Ultra-violet Co.) fitted with RUL 3000 lamps having a peak (90%) output energy of 300 ± 10 nm. The merry-go-round ensures that the same intensity of radiation impinges on each sample of a set of simultaneously irradiated samples. The irradiation chamber temperature was 30°.

Quantum Yields. All quantum yields for the reaction of I–V were determined in cyclohexane in concentrations of 0.1–0.5 *M* to ensure 99.9% absorption of light in the 290–310-nm region. Benzophenone (0.2 *M*) sensitized cis → trans isomerization of 1,3-pentadiene (0.4 *M*) was used as an actinometer and samples were irradiated in parallel with those of I–V. Conversions were kept below 10%. In cases where quantum yields for PCB reaction were very low several different actinometer samples in staggered succession had to be used due to the length of time the irradiation was carried out (20–70 hr).

Gas Chromatography. All analyses for PCB disappearance were performed on a Beckman GC-4 gas chromatograph equipped with a flame ionization detector. A 50-ft stainless steel SE-30 SCOT column (Perkin-Elmer) was used for separations. The column oven was maintained isothermally at 170° with a nitrogen carrier gas flow of 8 ml/min. Detector and inlet temperatures were 300 and 250°, respectively.

For analyses of *cis*- to *trans*-1,3-pentadiene conversion a 25% 1,2,3-tris(cyano)ethoxypropane on a Gas-Chrom Q, 32 ft × ⅛ in. stainless steel column was used. Nitrogen carrier gas flow was 15 ml/min and an oven temperature of 40° was maintained isothermally.

Mass spectrometry was carried out with a DuPont 21-490 spectrometer interfaced with a Beckman GC-65 gas chromatograph equipped with a 15% QF1–10% DC200 on Gas-Chrom Q, 6 ft × ⅛ in. stainless steel column. The oven temperature was maintained at 220°, with a nitrogen carrier gas flow of 25 ml/min.

RESULTS

Photoproducts. Compounds I–V were observed to yield only dechlorination products upon irradiation. In each case the mass spectrum of the products indicated loss of one or two chlorines. Trichlorinated products showed m/e at 256 (M) with signals at M + 2, M + 4, M + 6, M − 35, M − 70, and M − 105. Dichlorobiphenyls had M at m/e 222 with M + 2, M + 4, M − 35, and M − 70 signals. Monochlorobiphenyls showed M at m/e 188 with M + 2 and M − 35 signals; the products were also identified by comparison of their GC retention time with authentic standards. In the case of compound III no standard was available for comparison of the trichlorinated product; however, the dichlorobiphenyl obtained could be identified as the 3,4-isomer. The trichlorobiphenyl retention time did not match that of authentic 2,4,5-trichlorobiphenyl.

Dechlorination in aromatic systems has been described extensively (Pinhey and Rigby, 1969; Barltrop et al., 1967). A free-radical mechanism has been postulated in dehalogenation reactions (Latowska and Latowski, 1966; Kharasch and Sharma, 1968); the radical abstracts hydrogen or dimerizes in poor hydrogen donors. During photolysis of I–V hydrogen chloride was detected in support of this mechanism.

Quantum Yields (Table I). In all cases ϕ_r was low, in the order of 10^{-3}. Compound IV showed a value lower than the rest. It could not be reproduced, but in all cases it was $<10^{-2}$. The small ϕ_r values have been explained (Ruzo et al., 1974) in terms of very fast decay rates (k_d) of the triplet. This is not surprising since the absorption in the 300-nm region has been characterized as π–π^*, this transition is allowed, and the chlorine substituents can exert at least a small heavy atom effect; return from the triplet to the ground-state singlet is more likely to be fast, thus the large ratios of k_d/k_r obtained previously. The only cases where the reaction rate (k_r) is of the same magnitude as k_d occurs when a para chlorine enhances the planarity of the triplet, thus forcing the ortho chlorine to cleave. Not only do products in I–V arise only from ortho cleavage, but the quantum yields also support this excited state steric effect.

The case of 2′,3,4-trichlorobiphenyl is informative in that it shows that only one chlorine each in the ortho and para positions is sufficient to accelerate the reaction. Both need not be in the same ring.

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Table I. Photoproducts and Quantum Yields of Unsymmetrical PCB's in Cyclohexane

PCB	ϕ_r	Product	T_r, min	% yield[a]
2,4,6-Trichloro-biphenyl (I)	0.02	2,4-Dichloro	1.25	85
		4-Chloro	0.85	15
2,4,5-Trichloro-biphenyl (II)	0.05	3,4-Dichloro	1.80	98
		4-Chloro	0.85	2
2,3,4,5-Tetrachloro-biphenyl (III)	0.04	3,4,5-Trichloro	3.60	95
		3,4-Dichloro	1.80	5
2,3,5,6-Tetrachloro-biphenyl (IV)	<0.01	2,3,5-Trichloro	2.20	50
		3,5-Dichloro	1.50	50
2',3,4-Trichloro-phenyl (V)	0.02	3,4-Dichloro	1.80	100

[a] Based on total product formation.

At the present time we are investigating the possibility that this effect may be transmitted from a para chlorine on ring 1 of a terphenyl to an ortho chlorine on ring 3, in order to elucidate the excited geometry of the terphenyl triplet.

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