

chlordene was identified as a main product.

LITERATURE CITED

- Allmann, R., "The Chemistry of the Hydrazo-, Azo- and Azoxy-Groups", Part 2, Patai, S., Ed., Wiley-Interscience, New York, N.Y., 1975, pp 23-52.
- Cochrane, W. P., Parlar, H., Gäb, S., Korte, F., *J. Agric. Food Chem.* **23**, 882, 1975.
- De Lacy, T. P., Kennard, C. H. L., *J. Chem. Soc., Perkin Trans. 2*, 2153, 1972.
- Gäb, S., Cochrane, W. P., Parlar, H., Korte, F., *Z. Naturforsch., B*, **30**, 239, 1975.
- Gäb, S., unpublished results, 1975.
- Gäb, S., Parlar, H., Cochrane, W. P., Wendisch, D., Fitzky, H. G., Korte, F., *Justus Liebig's Ann. Chem.*, **1** (1976).
- Gäb, S., Parlar, H., Korte, F., submitted to *J. Agric. Food Chem.*, 1977.
- Germain, G., Main, P., Woolfson, M. M., *Acta Crystallogr., Sect. A* **27**, 368, 1971.
- Palmer, K. J., Wong, R. Y., Lundin, R. E., Khalifa, S., Casida, J. E., *J. Am. Chem. Soc.* **97**, 408, 1975.
- Polen, P. B., information supplied to the IUPAC Commission on terminal residues, Geneva, Switzerland, 1966.
- Sutton, L. E., Ed., "Tables of Interatomic Distances and Configuration in Molecules and Ions", Supplement 1956-1959, London, The Chemical Society, 1965.
- Velsicol Chemical Corp., Technical Bulletin, Standard for Technical Chlordane, 1971.
- Vollner, L., Parlar, H., Klein, W., Korte, F., *Tetrahedron* **27**, 501, 1971.
- Wilson, N. K., Sovocool, G. W., *Org. Magn. Reson.*, in press (1977).

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Photochemistry of Chlorinated Diphenyl Ethers

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The photoreactions of a series of chlorinated diphenyl ethers at wavelengths around 300 nm were investigated as to their photodecomposition rates and products formed. No significant differences in reaction rates were found between chlorodiphenyl ethers with up to four chlorine atoms per molecule which reacted slower than the pentachlorodiphenyl ethers investigated. The major products resulted from photodechlorination reactions but compounds with chlorine substituents in the 2 or 6 positions also gave rise to chlorinated dibenzofurans in about 10% yields. The yields of dibenzofurans were increased in most cases when photolysis was carried out in the presence of acetone. This reaction may also occur under natural conditions in the environment by influence from natural products which have photochemical characteristics similar to that of acetone.

The photoreactions of halogenated aromatic compounds have received considerable attention during recent years, one reason being the increased interest in the environmental chemistry of such compounds. Several groups of chlorinated aromatic compounds are ubiquitous environmental pollutants and a knowledge of the photochemical reactions of these compounds is necessary to gain understanding about the possible routes of activation (e.g., formation of toxic photoproducts) or deactivation (e.g., decomposition and mineralization) in the environment.

In our studies on the photoreactions of compounds of possible environmental significance we recently reported on the photochemistry of alkylated chlorobiphenyls (Ruzo et al., 1976a) and bromobiphenyls (Ruzo et al., 1976b). Both types of compounds are structurally closely related to the well-known pollutants polychlorinated biphenyls (PCB) whose photochemistry have been thoroughly investigated (cf. e.g., Ruzo et al., 1974a,b, 1975). The present paper deals with the photochemistry of polychlorinated diphenyl ethers, PDEs, compounds of obvious structural similarity to all above mentioned compounds. PDEs have

been found present in technical chlorophenol preparations (Firestone et al., 1972; Villanueva et al., 1973; Nilsson and Renberg, 1974; Buser, 1975) and they may therefore reach the environment through the use of these products.

Although the photochemistry of diaryl ether compounds has been extensively studied (cf. Elix and Murphy, 1975, and papers cited therein) only one investigation has been published on the photoreactions of PDEs. Norström et al. (1976) found that 2,2',4-trichloro- and 2,2',4,4'-tetrachlorodiphenyl ether gave dechlorinated diphenyl ether compounds and chlorinated dibenzofurans as major products upon photolysis in hexane solution. The formation of the latter type of products should give rise to concern since chlorinated dibenzofurans have been identified as very toxic by-products in a number of technical products like PCB (Vos et al., 1970; Bowes et al., 1973, 1975a,b; Roach and Pomerantz, 1974; Curley et al., 1975; Nagayama et al., 1976), chlorophenols (Firestone et al., 1972; Plimmer et al., 1973; Jensen and Renberg, 1973; Villanueva et al., 1973; Nilsson and Renberg, 1974; Buser, 1975, 1976; Buser and Bosshardt, 1976) and in hexachlorobenzene (Villanueva et al., 1974).

Ring formation of diaryl ethers to furan-type compounds have also been observed with 2-chlorophenyl 1-naphthyl ether (Henderson and Zweig, 1969) and polychloropyridyl phenyl ethers (Bratt and Suschitzky, 1972). The presence of photolabile chlorine atoms in the ortho position to the ether linkage thus seem to facilitate the ring-formation reactions. A related photochemical cyclodehydrogenation reaction of diaryl ethers and diaryl sulfides to dibenzofurans and dibenzothiophenes, respectively, was recently

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Table I. Photoreactivity of Chlorinated Diphenyl Ethers in Degassed Methanol Solution

No.	Substrate		Concn, M × 10 ²	% reacted ^a	Rel rate ^b	k, (mols × 10 ⁷) ^c
	Structure					
1	2-Chlorodiphenyl ether		7.0	1.3	0.7	0.31
2	4-Chlorodiphenyl ether		7.0	1.8	1.0	0.44
3	2,4-Dichlorodiphenyl ether		6.9	1.9	1.0	0.47
4	2,4'-Dichlorodiphenyl ether		7.5	9.1	5.2	2.4
5	4,4'-Dichlorodiphenyl ether		6.8	1.9	1.0	0.45
6	2,4,5-Trichlorodiphenyl ether		7.3	9.1	5.1	2.3
7	2,3,4-Trichlorodiphenyl ether		7.9	3.6	2.2	0.97
8	2,4,4',5-Tetrachlorodiphenyl ether		7.2	10.2	5.6	2.5
9	2,3',4,4'-Tetrachlorodiphenyl ether		7.1	0.3	0.15	0.07
10	3,3',4,4'-Tetrachlorodiphenyl ether		7.1	3.4	1.8	0.83
11	2,2',4,4',5-Pentachlorodiphenyl ether		7.2	22.2 ^d	12.2	5.5
12	2,3',4,4',5-Pentachlorodiphenyl ether		7.7	32.0 ^d	18.8	8.5
13	2,2',5,5'-Tetrachlorobiphenyl		7.2	0.1	0.05	0.02

^a 8-h photolysis. ^b 4,4'-Dichlorodiphenyl ether = 1.0. ^c Absolute rates calculated from the formula $M_0 - M_t = k \cdot t$.

^d Precipitates formed.

described by Zeller and Petersen (1975) and involved photolysis of the substrates in cyclohexane solution in the presence of iodine.

We have investigated the photochemical reactions of a number of PDEs with differences in substitution patterns and chlorine content and with emphasis on reaction rates and products formed.

EXPERIMENTAL SECTION

Polychlorinated Diphenyl Ethers (PDEs) were synthesized as recently described (Sundström and Hutzinger, 1976) and purified by column chromatography (aluminum oxide-hexane) until pure by gas chromatography (>99%).

Solvents. Spectrograde methanol and cyclohexane were obtained from J. T. Baker Chem. Co. Acetone for spectroscopic use was supplied by E. Merck. Technical hexane was distilled over potassium hydroxide before use.

Ultraviolet Spectra were recorded on a Cary-14 double-beam spectrophotometer.

Irradiation of Samples. Irradiations of solutions were performed in a Rayonet Reactor (The Southern New England Ultra Violet Co.) using a merry-go-round apparatus. The reactor was equipped with RUL 3000 lamps having an energy output of 90% between 290 and 310 nm. The solutions were contained in Pyrex tubes which transmit less than 1% of the radiation below 287 nm.

The samples for study of relative rates of photolysis of chlorinated DPEs (Table I) were irradiated for 8 h to have minimum effects of the photoproducts on the rates of the substrates. The solutions of compounds 4 and 7 containing lithium salts each (Table III) were photolyzed for 25 and 20 h, respectively. The samples described in Table IV about the photoproducts were irradiated for 88 h; such a long time was chosen in order to identify also minor products. The methanolic solutions of the compounds in the presence of acetone (0.45 M) (Table V) were photolyzed for 7 h. The times for irradiation in Table III and Table V were arbitrarily chosen.

Gas Chromatography was performed on a Hewlett-Packard 5830A instrument with a flame ionization detector connected to a 18850 GC terminal. Glass columns (290 × 0.2 cm) containing 3% purified Apiezon L (Jensen and Sundström, 1974) on 100-120 mesh Chromosorb W A/W DMCS were used. Injection port temperature was 270 °C and detector temperature 300 °C. The oven temperature was initially 140 °C which was kept for 2 min after injection, whereafter the oven was programmed to 250 °C at a rate of 8 °C/min. Carrier gas flow (He) was 26 mL/min.

Table II. Ultraviolet Spectra of Chlorinated Diphenyl Ethers

Substrate no.	Hexane solution			Methanol solution		
	λ_{\max} , nm	log ϵ_{\max}	log ϵ_{300}	λ_{\max} , nm	log ϵ_{\max}	log ϵ_{300}
1	268	3.30	0.82	268	3.28	1.29
	275	3.31		276	3.27	
2	272	3.22	1.25	272	3.25	1.56
	279	3.25		278	3.28	
	293	3.02				
3	262	3.23	2.20	268	3.24	2.16
	268	3.32		276	3.24	
	276	3.29		284	3.16	
	284	3.19				
4	294	2.97				
	274	3.28	1.50	274	3.28	1.60
	278	3.26				
	282	3.20				
5	288	3.12				
	274	3.35	1.64	273	3.34	1.25
	282	3.37		278	3.37	
	289	3.30		288	3.28	
6	268	3.23	3.17	268	3.18	3.09
	276	3.21		276	3.17	
	291	3.33		290	3.28	
	299	3.18				
7	273	3.29	1.80	274	3.30	2.15
	282	3.32		282	3.33	
	292	3.23		290	3.22	
	280	3.37	3.09	278	3.34	2.94
8	288	3.35		286	3.33	
	277	3.36	2.29	275	3.40	2.13
	282	3.41		282	3.45	
	292	3.32		290	3.34	
10	278	3.41	2.55	277	3.36	2.37
	283	3.46		283	3.51	
	293	3.41		295	3.35	
	284	3.46	3.04	282	3.40	2.87
11	292	3.42				
	283	3.42	2.87	282	3.38	2.76
	287	3.42		286	3.38	
	297	3.17				
13	277	3.20	1.08	276	3.20	1.14
	285	3.16		285	3.14	

Combined Gas Chromatography-Mass Spectrometry was carried out on a Hewlett-Packard 5982A system operating in the electron-impact mode at 70 eV. Chromatographic conditions were identical with those described above with the exception that nitrogen was used as carrier gas at a flow rate of 20 mL/min.

RESULTS AND DISCUSSION

Photoreactivity. In Table I the structures and photodecomposition rates of the PDEs in methanol are given.

Table III. Effect of Added Lithium Salts on the Photolysis of Chlorinated Diphenyl Ethers in Methanol Solution

Substrate		Salt added		% reacted	Rel rate ^a
No.	Concn, M × 10 ²	LiX	Concn, M × 10 ²		
4 ^b	1.5			31	1.00
		LiCl	8.3	24	0.77
		LiBr	8.0	11	0.36
7 ^c	1.5	LiI	6.4	8	0.26
				45	1.00
		LiCl	8.3	40	0.88
		LiBr	8.0	25	0.55
		LiI	6.4	11	0.25

^a Rate without salt 1.00. ^b 25-h photolysis. ^c 20-h photolysis.

Table II gives a comparison of the ultraviolet spectra in hexane and methanol solution.

As is evident from Table I there are no large differences in reaction rates between the PDEs containing three-four chlorine atoms or less and only the two pentachlorodiphenyl ethers 11 and 12 show significantly higher decomposition rates. One chlorobiphenyl compound, 13, was included in the series to obtain a comparison with a previously investigated compound (Ruzo et al., 1974a,b). The chlorobiphenyl reacted slower than any PDE which may partly be due to lower absorption at the wavelengths used (cf. Table II).

There is no clear correlation between reactivity and substitution pattern of the PDEs as was found in the chlorobiphenyl series where substitution in the 2 positions of the phenyl rings (ortho substitution) enhanced photoreaction rates although the molar extinction coefficients decrease with increasing ortho substitution (Ruzo et al., 1974a,b). This somewhat contradictory effect has been

explained by the fact that the achievement of a planar structure in the excited state of biphenyls is simplified by loss of any chlorine atoms in the ortho positions (Ruzo et al., 1974a). The small effect of such substitution in the PDEs is evident already from the ultraviolet spectra (Table II) since increasing substitution in the 2 positions does not decrease molar extinction coefficients of the absorption maxima around 270–280 nm.

In the present study no attempts were made to elucidate the reaction mechanisms or the nature of the excited states involved in the photolysis of PDEs. It is noteworthy, however, that the photoreactions of compounds 4 and 7 decrease upon addition of heavy atom salts like lithium bromide or lithium iodide (Table III). This has previously been shown to occur with a number of haloaromatic compounds and has been interpreted as an increase of the triplet decay rate relative to reaction rate which results in an overall decrease in yield of photoproducts (Ruzo et al., 1976c).

A slight increase in reaction rates was also observed in sensitizing experiments using acetone as sensitizer; however, a more surprising effect of the presence of acetone was found in the product composition after photolysis (see below).

Photoproducts. Initially the photolysis of PDEs were investigated in both hydrocarbon solvents and in methanol. However, no differences in product formation or distribution were observed between these solvents, and subsequent experiments were performed in methanol only. No methoxy-substituted products could be identified after photolysis in this solvent although the presence of small quantities of such compounds were monitored by mass spectrometry using the highly sensitive single ion monitoring technique. Such a photolytic substitution of chlorine atoms for methoxy groups does occur with similar aromatic chloro compounds, e.g., PCBs (Ruzo et al., 1974a).

Table IV. Photoproducts of Chlorinated Diphenyl Ethers in Degassed Methanol Solution

Substrate ^a			Photoproducts ^b			
No.	Ret. time, min ^c	% reacted ^d	Diphenyl ethers (DPE)	Ret. time, min	Dibenzofurans (DBF)	Ret. time, min
1	1.16	38	DPE	0.52	DBF	0.93
2	1.18	38	DPE	0.52		
3	2.24	35	4-Cl-DPE	1.17	2-Cl-DBF	2.19
4	2.79	53	4-Cl-DPE	1.17	2-Cl-DBF	2.19
5	3.00	52	4-Cl-DPE	1.17		
6	3.44	50	DPE	0.52		
			Cl ₂ -DPE	2.49	2,3-Cl ₂ -DBF	4.11
			2,4-Cl ₂ -DPE	2.21		
7	4.53	28	Cl ₂ -DPE	2.03		
			2,4'-Cl ₂ -DPE	2.80	1,2-Cl ₂ -DBF	3.79
			Cl ₂ -DPE	2.45	2-Cl-DBF	2.19
			4-Cl-DPE	1.17		
8	5.81	34	3,4,4'-Cl ₃ -DPE	4.85	2,3,7-Cl ₃ -DBF	6.35
			Cl ₃ -DPE	4.39		
			4,4'-Cl ₂ -DPE	3.00		
9	6.23	26	3,4,4'-Cl ₃ -DPE	4.85	Cl ₂ -DBF	6.23
			Cl ₃ -DPE	4.39	Cl ₂ -DBF (two isomers)	4.39
10	6.79	44	3,4,4'-Cl ₃ -DPE	4.85		
			3,3',4'-Cl ₃ -DPE	4.46		
			4,4'-Cl ₂ -DPE	3.00		
			2,3',4,4'-Cl ₄ -DPE	6.23	Cl ₄ -DBF	7.96
11	7.09	84	2,4,4,5-Cl ₄ -DPE	5.81	Cl ₄ -DBF	7.10
			Cl ₃ -DPE	4.73		
12	6.65	89	Cl ₄ -DPE	5.89	Cl ₄ -DBF	7.27
			Cl ₄ -DPE	5.55		
			Cl ₃ -DPE	4.58		
13	4.17	19	2,3',5-Cl ₃ -PCB	3.17	Cl ₂ -DBF (trace)	
			3,3'-Cl ₂ -PCB	2.53		

^a Concentrations as in Table I. ^b The photoproducts of oxygenated solutions were the same. ^c Retention times were recorded under the conditions given in the Experimental Section. ^d 88-h photolysis.

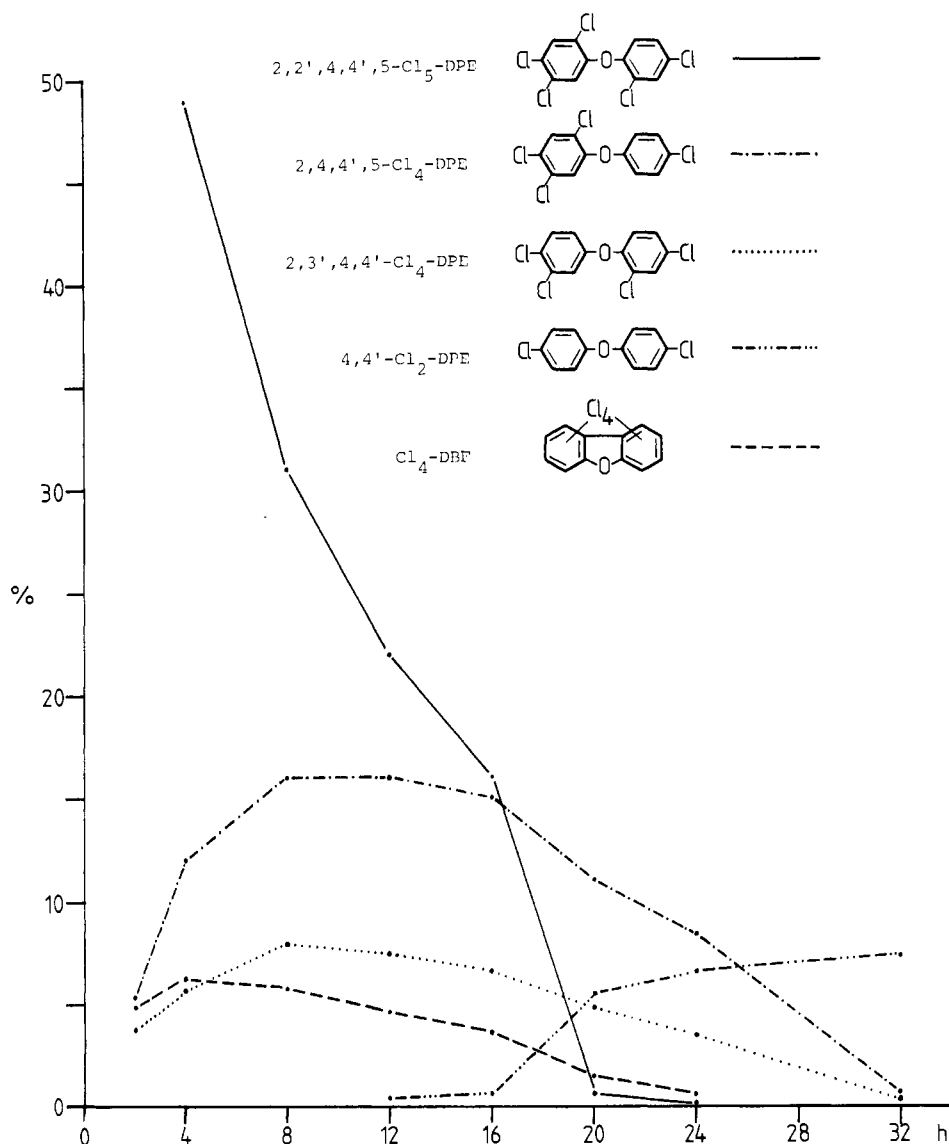


Figure 1. Schematic representation of the formation and photodecomposition of some photoproducts of 2,2',4,4',5-pentachlorodiphenyl ether in cyclohexane solution (10^{-2} M). Percentages of compounds present in the reaction mixture are given; the values are calculated from an internal, added, hydrocarbon standard; 0–32 h are photoreaction times; abbreviations for compounds next to structural formulae are explained in Table IV.

All compounds investigated gave upon photolysis dechlorinated diphenyl ethers as major products (Table IV). In cases where reference compounds were available it was also shown that in the photochemical dechlorination the chlorine atoms in the 2 positions of the phenyl rings were preferentially lost (cf. above). For example, the two major dechlorinated species formed from compound 11 (2,2',4,4',5-pentachlorodiphenyl ether) were 2,3',4,4'-tetrachloro- and 2,4,4',5-tetrachlorodiphenyl ether (cf. Figure 1).

The PDEs with chlorine substitution in the 2 positions also gave rise to substantial amounts of dibenzofuran compounds upon photolysis (see Table IV). The structure of some of the dibenzofurans formed were determined by comparison with standard compounds or by comparison of the individual photolysis mixtures with regard to retention times of the furans since it has been shown that no substantial rearrangements of the chlorine atoms occur during the photochemical ring-closure reaction (Norström et al., 1976). It is remarkable that, e.g., compound 7 gives rise to 1,2-dichlorodibenzofuran only, although formation of the 2,3-dichloro isomer is also possible. The only compound investigated with chlorine substitution in both 2 positions, compound 11, gave approximately equal

amounts of the two possible dibenzofurans (see below).

In the case of the PDE 11, the formation and disappearance rates of some photoproducts were more closely investigated by gas chromatography and gas chromatography-mass spectrometry. The products were quantitated by the use of synthetic compounds. Equal response for the dibenzofuran and for the diphenyl ethers was assumed on the flame ionization detector. The compound was photolyzed in cyclohexane at a 10^{-2} M concentration and with an internal hydrocarbon standard added. The results are given schematically in Figure 1. In the figure the level of only one of the tetrachlorodibenzofurans formed is given. Due to lack of suitable standards we were not able to determine the structure of this particular furan and the second isomer could not be accurately quantitated as it overlapped on gas chromatography with other components. However, on the basis of the ion chromatograms on mass spectrometry, the levels of the two tetrachlorodibenzofurans was estimated to be about equal at all times and thus never exceeding ca. 14% of the products formed. Similar levels of dibenzofurans were estimated to be formed upon photolysis of the other 2-chloro substituted PDEs. Norström et al. (1976) reported

Table V. Rates of Decomposition and Formation of Chlorinated Dibenzofurans (DBF) upon Photolysis of Chlorinated Diphenyl Ethers in the Presence of Acetone in Degassed Methanol Solution

No.	Substrate Concn, M × 10 ³	% reacted ^a		Relative disappearance rate (B/A)	Relative amount of DBF formation (B/A)
		Without acetone (A)	With acetone added ^b (B)		
4	3.7	49	58	1.2	3.9
5	3.4	35	32	0.96	
6	3.7	51	48	0.94	3.5
7	3.9	33	48	1.5	7.7
8	3.6	31	66	2.2	1.6
10	3.5	37	29	0.8	
11	3.6	65	73	1.1	0.8
12	3.8	50	67	1.3	1.4

^a 7-h photolysis. ^b 0.45 M acetone.

a 20% yield of 2,8-dichlorodibenzofuran upon photolysis of 2,4,4'-trichlorodiphenyl ether in hexane at a 3.7×10^{-3} M concentration.

The chlorinated dibenzofurans are further dechlorinated photochemically, and after about 26 h only traces of the tetrachlorodibenzofurans formed from PDE 11 could be found. The photochemical decomposition of some chlorinated dibenzofurans have previously been studied (Hutzinger et al., 1973; Crosby and Moilanen, 1973; Crosby et al., 1973), and it was shown that dechlorinated species are formed as major products upon photolysis in solution. In the present case it appears as if the photodecomposition of the chlorinated dibenzofurans is as fast as the photo-dechlorination of the diphenyl ethers and there is no accumulation of highly chlorinated dibenzofurans in the system.

Photochemical formation of dibenzofurans from chlorobiphenyls have previously been reported (Crosby and Moilanen, 1973; Crosby et al., 1973; Andersson et al., 1973, 1975), and we also detected trace amounts of a dichlorodibenzofuran after photolysis of the chlorobiphenyl 13 included in this investigation (Table IV).

Thus it seems as if the potentially toxic chlorinated dibenzofurans are relatively rapidly dechlorinated in pure hydrocarbon environments like cyclohexane and also in hydroxylic solvents like methanol. On the other hand, when we investigated the photodecomposition of PDEs in methanol with added acetone (0.45 M), we observed that the yield of dibenzofurans substantially increased from most compounds (ca. 4×10^{-3} M) and at the same time the dechlorination reactions were suppressed (Table V). Even more surprising, the photolysis of some 2-chloro substituted diphenyl ethers in neat acetone gave 80–90% yields of dibenzofurans without any concomitant reactions and the method could be used as a synthetic route to some chlorinated dibenzofurans of defined structure (Choudhry et al., 1977).

Some of the photoreaction mixtures were also investigated for products formed by cleavage of the ether bond, i.e., phenolic compounds, with negative results.

CONCLUSIONS

The results presented here and by Norström et al. (1976) clearly show that the photochemical cyclization of chlorinated diphenyl ethers occur easily under laboratory conditions. This reaction may also occur under natural conditions in the environment by influence from natural products which possess photochemical characteristics similar to that of acetone. It should be recommended that the photochemistry of the chlorinated dibenzofurans be further investigated especially in comparison with their precursors. However, in view of the present knowledge it seems that not only the levels of known neutral toxic

compounds like chlorinated dibenzodioxins and chlorinated dibenzofurans but also the levels of other neutral compounds like the chlorinated diphenyl ethers should be investigated in chlorophenol products and alike.

LITERATURE CITED

- Andersson, K., Nilsson, C.-A., Norström, Å., Rappe, C., "PCB Conference II", National Swedish Environment Protection Board Publications 1973:4E, 1973, p 115.
- Andersson, K., Norström, Å., Rappe, C., Rasmuson, B., Swahlin, H., in "Environmental Quality and Safety", Suppl. Vol. III, Coulston, F., Korte, F., Ed., Georg Thieme, Stuttgart, 1975, p 796.
- Bowes, G. W., Simoneit, B. R., Burlingame, A. L., de Lappe, B. W., Riseborough, R. W., *Environ. Health Perspect.* No. 5, 191 (1973).
- Bowes, G. W., Mulvihill, M. J., Simoneit, B. R. T., Burlingame, A. L., Riseborough, R. W., *Nature (London)* 256, 305 (1975a).
- Bowes, G. W., Mulvihill, M. J., DeCamp, M. R., Kende, A. S., *J. Agric. Food Chem.* 23, 1222 (1975b).
- Bratt, J., Suschitzky, H., *J. Chem. Soc., Chem. Commun.*, 949 (1972).
- Buser, H.-R., *J. Chromatogr.* 107, 295 (1975).
- Buser, H.-R., *Anal. Chem.* 48, 1553 (1976).
- Buser, H.-R., Bosshardt, H. P., *J. Assoc. Off. Anal. Chem.* 59, 562 (1976).
- Choudhry, G. G., Sundström, G., van der Wielen, F. W. M., Hutzinger, O., *Chemosphere* 6, 327 (1977).
- Crosby, D. G., Moilanen, K. W., Wong, A. S., *Environ. Health Perspect.* No. 5, 259 (1973).
- Crosby, D. G., Moilanen, K. W., *Bull. Environ. Contam. Toxicol.* 10, 372 (1973).
- Curley, A., Burse, V. W., Jennings, R. W., Villanueva, E. C., Kimbrough, R. D., *Bull. Environ. Contam. Toxicol.* 14, 153 (1975).
- Elix, J. A., Murphy, D. P., *Aust. J. Chem.* 28, 1559 (1975).
- Firestone, D., Ress, J., Brown, N. L., Barron, R. P., Damico, J. N., *J. Assoc. Off. Anal. Chem.* 55, 85 (1972).
- Henderson, W. A., Zweig, A., *Tetrahedron Lett.*, 625 (1969).
- Hutzinger, O., Safe, S., Wentzell, B. R., Zitko, V., *Environ. Health Perspect.* No. 5, 269 (1973).
- Jensen, S., Renberg, L., *Environ. Health Perspect.* No. 5, 37 (1973).
- Jensen, S., Sundström, G., *Ambio* 3, 70 (1974).
- Nagayama, J., Kuratsune, M., Masuda, Y., *Bull. Environ. Contam. Toxicol.* 15 9 (1976).
- Nilsson, C.-A., Renberg, L., *J. Chromatogr.* 89, 325 (1974).
- Norström, Å., Andersson, K., Rappe, C., *Chemosphere* 5, 21 (1976).
- Plimmer, J. R., Ruth, J. M., Woolson, E. A., *J. Agric. Food Chem.* 21, 90 (1973).
- Roach, J. A. G., Pomerantz, J. H., *Bull. Environ. Contam. Toxicol.* 12, 338 (1974).
- Ruzo, L. O., Zabik, M. J., Schuetz, R. D., *J. Am. Chem. Soc.* 96, 3809 (1974a).
- Ruzo, L. O., Zabik, M. J., Schuetz, R. D., *J. Agric. Food Chem.* 22, 199 (1974b).
- Ruzo, L. O., Safe, S., Zabik, M. J., *J. Agric. Food Chem.* 23, 594 (1975).

