

Gas Chromatographic Determination of Several Cyclodiene Insecticides in the Presence of Polychlorinated Biphenyls by Photoisomerization Reactions

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The gas chromatographic determination of cyclodiene insecticides and their conversion products is often rendered difficult by the presence of PCB residues in environmental samples. This problem can be satisfactorily overcome by inducing photoisomerization reactions ($\lambda > 290$ nm) of some cyclodiene insecticides, thus producing the corresponding photoisomers in high yields. The photoisomers have longer retention times than their parent compounds and can therefore be identified and quantitatively determined by gas chromatography. The method can be improved by a subsequent UV irradiation of the samples with wavelengths above 230 nm in methanol. This procedure yields photodechlorinated products of the PCBs with shorter retention times but leaves the photoisomerization products of cyclodiene insecticides unaffected.

An important problem in analytical environmental chemistry is the determination of pesticides in the presence of ubiquitous contaminants (e.g., PCBs). Routine gas chromatographic (GC) procedures are usually troublesome because the GC peaks corresponding to the pesticides are overlapped by those of the contaminants. Several methods have been developed for the elimination of PCB interferences in the determination of organochlorine pesticides in environmental samples. (Leavitt et al., 1973; Lewis et al., 1976). However, these procedures are not suitable for the determination of cyclodiene insecticides. This work deals with the GC and GC-MS determination of aldrin (1), dieldrin (2), heptachlor (3), and heptachlor epoxide (4) in the presence of interfering polychlorinated biphenyls. A commercially available sample of PCB (A 40, Bayer AG, Germany) was chosen as a representative ubiquitous contaminant which to some extent resembles the usual PCB residues found in environmental samples (Sachsenbrecker et al., 1972; Rohleder et al., 1977).

The UV irradiation of compounds 1, 2, 3, and 4 in acetone with wavelengths above 290 nm yields, along with other compounds, the photoisomerization products 5, 6, 7, and 8 (Fischler and Korte, 1969; Vollner et al., 1971; Parlar and Korte, 1972; Ivie et al., 1972) (Figure 1), which have longer retention times than the parent compounds (Table I). Since the PCBs are not affected under these reaction conditions (Hustert and Korte, 1972; Safe and Hutzinger, 1971), an indirect method for the routine qualitative and quantitative determination of cyclodiene insecticides such as 1, 2, 3, and 4 is possible. This procedure is improved by UV irradiation of the compounds in methanol with wavelengths above 230 nm. Under these conditions the PCBs are dechlorinated yielding compounds with shorter retention times (Hustert and Korte, 1974). The photoisomerization products (5, 6, 7, and 8) formed by the UV irradiation ($\lambda > 290$ nm) in acetone remain stable and can therefore easily be determined by GC and GC-MS (Figure 2).

MATERIALS AND METHODS

Chemicals. Aldrin (1,2,3,4,10,10-hexachloro-1,4,4a-,5,8,8a-hexahydro-*exo*-1,4-*endo*-5,8-dimethanonaphthalene (1) was synthesized by condensing hexachlorocyclo-

pentadiene with bicyclo[2.2.1]heptadiene (Lidov, 1953); dieldrin (1,2,3,4,10,10-hexachloro-6,7-epoxy-1,4,4a,5,6,7-,8,8a-octahydro-*endo*-1,4,5,8-dimethanonaphthalene) (2) was produced by careful oxidation of aldrin (1) with peracids (Soloway, 1965).

Both compounds were purified by repeated recrystallization from *n*-hexane. Heptachlor (1-*exo*-4,5,6,7,8,8-heptachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene) (3) and heptachlor epoxide (1-*exo*-4,5,6,7,8,8-heptachloro-*exo*-2,3-epoxy-3a,4,7,7a-tetrahydro-4,7-methanoindane) (4) were kindly supplied by the Velsicol Chemical Company, Chicago, Ill. The photoisomers 5, 6, 7, and 8 were produced by UV irradiation of parent compounds (1 g) in 150 mL of oxygen-free acetone (3–6 h). Separation of pure photoproducts was carried out on a 30-g deactivated silica gel column, (diameter, 3 cm; length, 30 cm; grain size 0.06 to 0.20 mm, Merck Co.), which were eluted with high-boiling petroleum ether (60–90 °C)/acetone (5:1) and collected with a fraction collector. Crystallizations were made from *n*-hexane. Solvents used were 99.5% methanol, acetone, *n*-hexane, and petroleum ether.

Chromatography and Spectroscopy. A Packard gas chromatograph Model 417 (glass column length, 2 m; 4 mm (i.d.); injection port temperature, 250 °C; carrier gas nitrogen; flow rate 40 mL/min) equipped with a linearized ⁶³Ni electron-capture detector (ECD) and Hewlett Packard 3380 A integrator was employed for qualitative and quantitative analysis. The following different column materials were used: (a) 3% OV-17 on Gas-Chrom Q (80–100 mesh); (b) 10% Igepal Co 880 on Chromosorb W AW DMCS (80–100 mesh); (c) 3% SE 30 on Chromosorb W AW DMCS (80–100 mesh); (d) 3% QF 1 on Chromosorb W AW DMCS (80–100 mesh). The mass spectra of single compounds (determined by GC-ECD to be pure) were obtained by direct solid probe analysis on an LKB 9000 S mass spectrometer. GC-MS analyses of mixtures were performed on the same instruments interfaced with a LKB gas chromatograph (glass column, 4 mm (i.d.) 2m, 3% OV-1 on Chromosorb W AW DMCS). The electron energy was 70 eV. The MS data were processed by a digital computer IBM 1130 via an interface made by WDV Company (Munich, West Germany).

Irradiation Procedure. The samples were dissolved in 100 mL of acetone or methanol, and a Pyrex or quartz water-jacketed cooling finger containing a Hg high-pressure lamp (HPK 125 W Philips, with wavelengths above 230 nm) was immersed in the solution. The solvents were purged with nitrogen to remove dissolved oxygen. Irradiation times were normally 2–3 h for isomerization and

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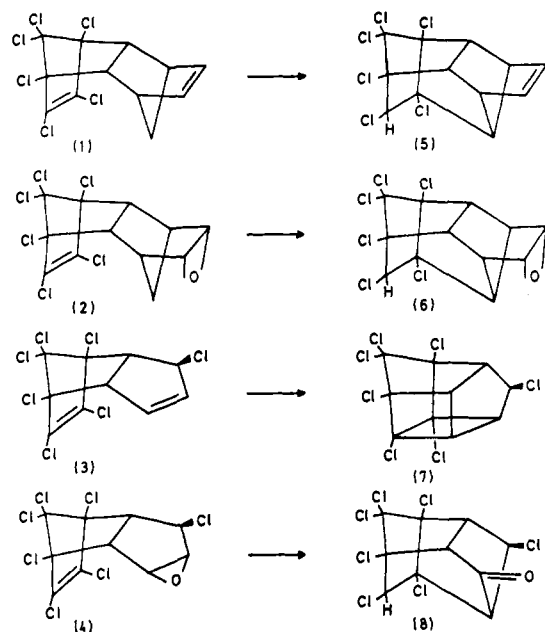


Figure 1. Photoisomerization reactions of cyclodiene insecticides (1, 2, 3, and 4)

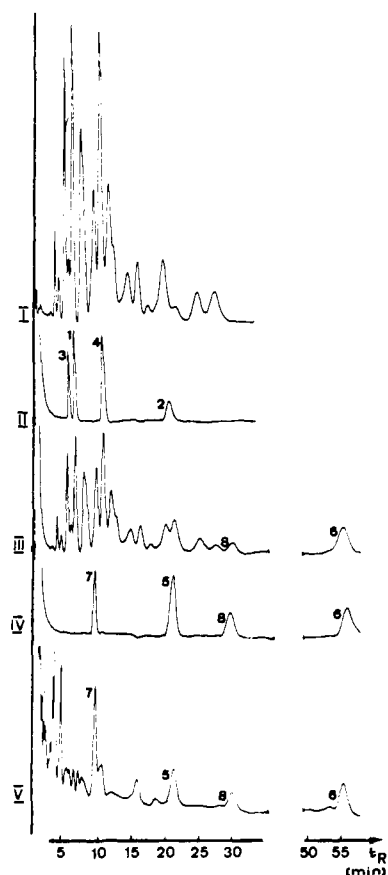


Figure 2. Gas chromatograms (3% QF 1 on Chromosorb W AW DMCS; column temperature, 150 °C; flow rate, 40 mL/min): (I) sample before irradiation; (II) cyclodiene insecticides aldrin (1), dieldrin (2), heptachlor (3) and heptachlor epoxide (4); (III) after irradiation at wavelengths above 290 nm in acetone; (IV) photoisomerization products photoaldrin (5), photodieldrin (6), photoheptachlor (7), and photoheptachlor ketone (8); (V) after irradiation at wavelengths above 230 nm in methanol.

3–4 h for dechlorination reactions. The concentration of the irradiated compounds was 10^{-7} – 10^{-5} mol/L.

Determination of Aldrin (1), Dieldrin (2), Heptachlor (3), and Heptachlor Epoxide (4) in the Presence

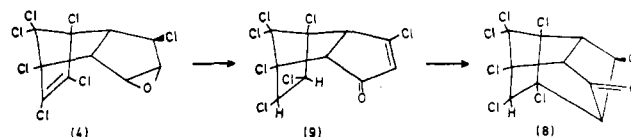


Figure 3. Photoreaction of heptachlor epoxide (4) at wavelengths above 290 nm in acetone.

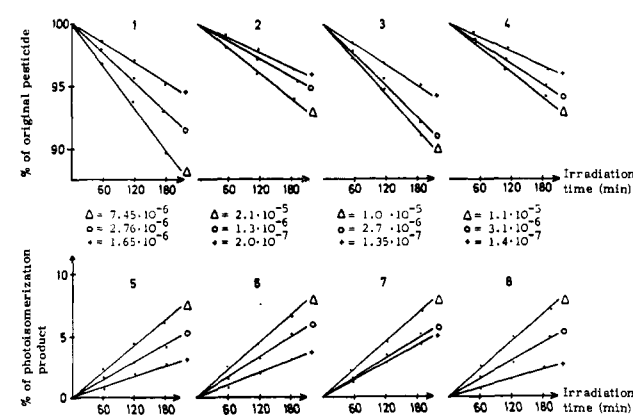


Figure 4. Variation of cyclodiene insecticides (1, 2, 3, and 4) and the formation of the corresponding photoisomerization products (5, 6, 7, and 8) with time for the irradiation with UV light ($\lambda > 290$ nm). Units of the initial concentrations (Δ , O, and +) in mol/L.

of PCBs in Environmental Samples. Solid and liquid samples (100 g) were four times extracted with 500 mL of *n*-hexane (24 h). A Soxhlet apparatus was used for solid samples and a liquid–liquid extractor with sintered glass disc tube and Dimroth condenser made by Wertheim Company (Wertheim, West Germany) for liquid samples. The extracts were concentrated to 10 mL under reduced pressure and purified by column chromatography; (500 mL of high-boiling petroleum ether–acetone 5:1, deactivated silica gel column: 3 cm (i.d.); length, 50 cm; grain size 0.06 to 0.20-mm, Merck Co.). The eluates were evaporated to dryness and dissolved in 100 mL of nitrogen-purged acetone and irradiated at wavelengths above 290 nm (Pyrex glass). The extent of the reaction was monitored by gas chromatography every 15 min. Irradiation times from 2 to 3 h were sufficient for quantitative determinations, while an irradiation time of 1 h was adequate for qualitative determinations. This method could be improved, especially for the determination of aldrin (1) and heptachlor (3), by further irradiation at wavelengths above 230 nm in quartz). For this purpose, acetone was removed from the solution by evaporation, the sample was irradiated at wavelengths above 230 nm.

RESULTS

The UV irradiation of some cyclodiene insecticides (1, 2, and 3) and their metabolites (e.g., 4) in the presence of PCBs (acetone, $\lambda > 290$) results in the formation of the corresponding photoisomers after short irradiation times. (It is known that irradiation of compounds 4, results in a hydrogen-transfer product (9) which reacts rapidly to compound 8) (Parlar et al., 1975; Knox et al., 1973) (Figure 3).

The photochemical conversion of the cyclodiene insecticides (1, 2, 3, and 4) with three different initial concentrations and the formation of the photoisomerization products (5, 6, 7, and 8) are compared with irradiation time in Figure 4. It is evident from the irradiation experiments with PCB mixtures (A 30, A 40, and A 60, Bayer AG, Germany) that the PCBs react slowly at wavelengths above 290 nm, since trace amounts of the

Table I. GLC Characteristics of Cyclodiene Insecticides (1-4) and Its Photoisomers (5-8)

Compound	Rel. retention time			
	3% OV-17	10% Igepal	3% SE 30	3% QF 1
Aldrin (1,2,3,4,10,10-hexachloro-1,4,4a,5,8,8a-hexahydro- <i>exo</i> -1,4- <i>endo</i> -5,8-dimethanonaphthalene) (1)	0.40	0.30	0.48	0.37
Dieldrin (1,2,3,4,10,10-hexachloro- <i>endo</i> -6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydro- <i>endo</i> -1,4,5,8-dimethanonaphthalene) (2)	1.00	1.00	1.00	1.00
Heptachlor (1- <i>exo</i> -4,5,6,7,8-heptachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene) (3)	0.31	0.25	0.36	0.29
Heptachlor epoxide (1- <i>exo</i> -4,5,6,7,8-heptachloro- <i>exo</i> -2,3-epoxy-3a,4,7,7a-tetrahydro-4,7-methanoindane) (4)	0.66	0.70	0.65	0.53
Photoaldrin (1,1,2,3,3a,7a-hexachloro-2,3,3a,4,6a,7,7a-octahydro-2,4,7-metheno-1 <i>H</i> -cyclopenta[<i>a</i>]pentalene) (5)	0.65	0.98	1.04	1.17
Photodieldrin (1,1,2,3,3a,7a-hexachloro-5,6-epoxy-2,3,3a,3b,4,5,6,6a,7,7a-decahydro-2,4,7-metheno-1 <i>H</i> -cyclopenta[<i>a</i>]pentalene) (6)	2.28	2.10	2.70	2.83
Photoheptachlor (1,3,4,5,5a,6-heptachlorooctahydro-1,2,4-metheno-1 <i>H</i> -cyclobuta[<i>cd</i>]pentalene) (7)	0.48	0.50	0.63	0.53
Photoheptachlor ketone (2,3,3,3a,4,6,8-heptachloro-1,2,3,3a,4,5,6,6a-octahydro-1,5,2,4-dimethano-1 <i>H</i> -pentalen-7-one) (8)	0.96	1.41	1.92	1.64

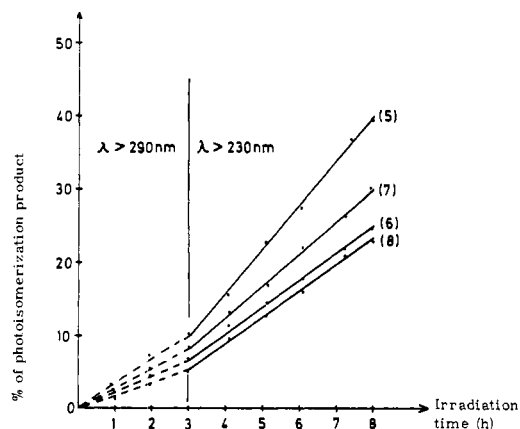


Figure 5. Formation of the photoisomerization products 5, 6, 7, and 8 at wavelengths above 290 nm in acetone and above 230 nm in methanol.

corresponding dechlorination products seem to appear after longer irradiation times (over 40 h) with yields of between 0.1 and 0.2% of the PCB amount. These results are also confirmed by UV-irradiation experiments ($\lambda > 290$ nm) of several pure representative PCB isomers. 2,2'-Dichlorobiphenyl, 2,4'-dichlorobiphenyl, 4,4'-dichlorobiphenyl, and 2,4,6,2',4',6'-hexachlorobiphenyl are not dechlorinated even after UV irradiation lasting several days. As seen in Figure 2, photodieldrin (6) and photoheptachlor ketone (8) can easily be determined after UV irradiation using wavelengths above 290 nm, in acetone due to their longer retention times, although the identification of photoaldrin (5) and photoheptachlor (7) is not satisfactory. The subsequent UV irradiation ($\lambda > 230$ nm) of the samples in methanol makes a determination of these compounds possible (Figure 2). It should be noted that the cyclodiene insecticides form the same photoisomers. The yields of the photoproducts (5, 6, 7, and 8) should be taken into consideration for quantitative determinations (Figure 5).

CONCLUSIONS

A simple method is presented for the identification and quantitative determination of some cyclodiene insecticides in the presence of PCBs. This method may be very useful when accompanying contaminants are stable to UV irradiation at wavelengths above 290 nm. Although this work has dealt only with a representative PCB mixture, the method can also be applied to determine cyclodiene insecticides in environmental samples containing other ubiquitous contaminants such as chlorinated paraffins, chlorinated aromatics, or other chlorinated pesticide mixtures.

LITERATURE CITED

- Fischler, H. M., Korte, F., *Tetrahedron Lett.* **32**, 2793, 1969.
 Hustert, K., Korte, F., *Chemosphere* **1**, 7 (1972).
 Hustert, K., Korte, F., *Chemosphere* **3**, 153 (1974).
 Ivie, G. W., Knox, J. R., Khalifa, S., Yamamoto, I., Casida, J. E., *Bull. Environ. Contam. Toxicol.* **7**, 376 (1972).
 Knox, J. R., Khalifa, S., Ivie, G. W., Casida, J. E., *Tetrahedron* **29**, 3869 (1973).
 Leavitt, R. A., Su, G. C. C., Zabik, M., *J. Anal. Chem.* **45**, 2130 (1973).
 Lewis, R. G., Hanisch, R. C., MacLeod, K. E., Sovocool, G. W., *J. Agric. Food Chem.* **24**, 1030 (1976).
 Lidov, R. E., U. S. Patent 2 635 977 (to Shell Development Co.), 1953; *Chem. Abstr.* **48**, 2769 (1954).
 Parlar, H., Gäb, S., Lahaniatis, E., Korte, F., *Chem. Ber.* **108**, 3692 (1975).
 Parlar, H., Korte, F., *Chemosphere* **1**, 125 (1972).
 Parlar, H., Korte, F., *Chemosphere* **2**, 169 (1973).
 Rohleder, H., Vollner, L., Korte, F., Gesellschaft für Strahlen- und Umweltforschung mbH München, FRG, PCB residues in environmental samples, unpublished results, 1977.
 Safe, S., Hutzinger, O., *Nature (London)* **232**, 641 (1971).
 Saschenbrecker, P. W., Funnel, H. S., Platonow, N. S., *Vet. Rec.* **90**, 100 (1972).
 Soloway, S. B., *Adv. Pest Control Res.* **6**, 85, 1965.
 Vollner, L., Parlar, H., Klein, W., Korte, F., *Tetrahedron* **27**, 501 (1971).

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