

Chlordane Photoalteration Products: Their Preparation and Identification

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Photolysis of technical chlordane and some of its pure components afforded rearranged products. The compounds were irradiated in acetone solution by mercury vapor lamps equipped with filters, and as thin films by sunlight or germicidal lamps. Chlordene, *cis*-chlordane, heptachlor, and heptachlor epoxide were converted to cage and half-cage

photoisomers which were isolated as crystalline compounds. Similar photolyses were carried out on *trans*-nonachlor, *trans*-chlordane, and β -dihydroheptachlor, but no crystalline photoproducts were isolated. Structures are proposed for the photoisomers, and ms, nmr, glc, and tlc data are presented.

Photolytic reactions have recently attracted the attention of pesticide chemists, since sunlight plays a significant role in the weathering of pesticides. A number of toxicologically important photoalteration products are produced in this manner. While studying the chemistry of chlordane, the authors learned that Korte's group had irradiated some components of chlordane, and that crystalline photoproducts had been isolated (Korte, 1968). These compounds were synthesized in this laboratory with two objectives: to determine whether they exist in residues derived from chlordane, and to learn more about the structures of the components of chlordane by determining whether they could be converted to cage and half-cage compounds. During the course of this investigation, Rosen *et al.* (1969) reported that benzophenone-sensitized irradiation of heptachlor gave a photoproduct more toxic to houseflies and mosquito larvae than heptachlor.

Chlordene, heptachlor, heptachlor epoxide, and *cis*-chlordane were converted to their corresponding photoisomers but *trans*-chlordane and *trans*-nonachlor did not give analogous products. These results are consistent with the postulated structures for these components of technical chlordane.

EXPERIMENTAL

Solution Irradiation with uv Lamp. A 450-W quartz mercury vapor lamp (Hanovia 679A36) housed in a water-

cooled, double-walled quartz immersion well (Ace Glass Inc.) was used. The assembly was immersed in a vessel containing the solution to be irradiated. Acetone was used both as solvent and photosensitizer. Kimax KG-33 (Kimble) and Corex 9700 (Corning) sleeves could be placed around the lamp to exclude undesired wavelengths of light.

The heptachlor used in this study was 99.9% pure; it was supplied by Velsicol Chemical Co.

A solution of heptachlor (1 g, 0.0027 mol) in 600 ml of acetone was irradiated through the Kimax sleeve, which excluded wavelengths shorter than about 300 nm. The reaction was monitored by glc; after 32 hr the photoisomer peak was predominant while other peaks were very small. Evaporation gave a tan solid which was washed with cold methanol to give 800 mg (80% yield) of a white solid. Recrystallization from methanol afforded purified photoheptachlor, mp 119.5–121.5° C.

Several other pure components and technical chlordane were irradiated in the same manner through the Kimax filter. Photochlordene and photo-*cis*-chlordane were purified by recrystallization from hexane; photoheptachlor epoxide was crystallized from acetone-methanol. These irradiations initially gave clean conversions to the corresponding photoisomers, but when some of the photolysis experiments were repeated, the conversion times became extremely long, and side products which colored the reaction solutions were produced. The use of a new lamp did not improve the reaction rates significantly. A Corex filter, which cut off uv radiation at about 280 nm, was substituted for the Kimax filter and the primary reaction rate increased markedly, as did the side reactions. The results of the

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Table I. Solution Photolyses

No.	Compound	Filter	Concn, mmol/l.	Hr	Photoisomer, % by glc	Reacted, % by glc
(I)	Chlordene	Kimax	30	155	45	85
		Corex	5	3	65	95
		None	30	5	30	98
(III)	Heptachlor	Kimax	5	32	90	99
		Corex	5	2	70	95
(V)	<i>cis</i> -Chlordane	Kimax	3	27	80	99
		Corex	5	1	65	90
(VII)	<i>trans</i> -Chlordane	Kimax	0.4	50	0	60
(VIII)	<i>trans</i> -Nonachlor	Kimax	2	64	0	80
(XI)	β -Dihydroheptachlor	Kimax	0.4	20	0	0
		None	0.4	7	10	98
(XIII)	Heptachlor epoxide	Kimax	4	11	90	99
		Corex	5	1	50	99

Table II. Thin-Film Photolyses

No.	Compound	Light source	Hr	Photoisomer, % by glc	Pre-cursor lost, % by glc
(I)	Chlordene	uv	1	<1	40
		uv	5	1	50
		uv	24	7	60
		Sun	410 ^a	3	40
(III)	Heptachlor	uv	1	2 ^b	25
		uv	5	5 ^b	40
		uv	24	8 ^b	70
		Sun	510 ^a	2	30
(V)	<i>cis</i> -Chlordane	uv	1	2	7
		uv	5	5	20
		uv	24	10	40
		Sun	460 ^a	1	10
(VII)	<i>trans</i> -Chlordane	uv	1	0	7
		uv	5	0	20
		uv	24	0	25
(XIII)	Heptachlor epoxide	uv	1	5	20
		uv	5	13	30
		uv	24	23	40
		Sun	250 ^a	40	45

^a Based on 10 hr sunlight daily. ^b 1-2% heptachlor epoxide was also found.

photolyses of the components of chlordane are presented in Table I.

Thin-Film Irradiation with Germicidal Lamps. Two 36-in., 30-W GE-G30T8 germicidal lamps were mounted in an overhead assembly. Samples weighing approximately 75 mg were dissolved in a minimum of anhydrous ether and distributed uniformly on 3.25 × 4-in. glass plates. When dry, the plates were placed in Petri dishes and covered with the 1/8-in. polished quartz sheets. After having been irradiated at a distance of 4 cm from the lamps, the plates were stripped with ethyl acetate. The percentage lost by vaporization ranged from 2 to 9%, and was smaller when larger samples were used. The products were examined by glc, with the results summarized in Table II. The photoisomers referred to are the same as those obtained by solution photolysis (Figures 1 and 2).

Thin-Film Irradiation with Sunlight. Petri dishes containing 75-mg samples on glass plates were covered with 1/8-in. quartz sheets and exposed to summer sun. These results are included in Table II. Volatility losses ranged from 1% for *cis*-chlordane to 29% for chlordene.

Gas Chromatography. A Barber-Colman series 5000 gas chromatograph equipped with an electron capture detector was used. The glass columns (6 ft × 4 mm i.d.) were packed with an equal mixture of 10% DC-200 and 15% QF-1 (mixed column), or with 10% DC-200 on 80/100 mesh Gas Chrom Q.

Table III. Physical Properties of Chlordane Components and Photoisomers

No.	Compound	Melting point, °C	Gas chromatography		Thin-layer chromatography, <i>R_f</i> of <i>n</i> -heptane	Mass spectra	
			DC-200 column	Mixed column		Base peak, <i>m/e</i>	% total ionization ^a
(I)	Chlordene	200 dec	0.58	0.56	0.42	66	34.2
(II)	Photochlordene	310 dec	0.92	1.25	0.13	66	15.7
(III)	Heptachlor	96.1-96.4	0.79	0.81	0.32	100	8.5
(IV)	Photoheptachlor	119.5-121.5	1.08	1.24	0.22	100	6.6
(V)	<i>cis</i> -Chlordane	107.0-108.0	1.59	1.70	0.19	371	2.9
(VI)	Photo- <i>cis</i> -chlordane	148.0-151.5	2.55	2.97	0.14	371	6.4
(VII)	<i>trans</i> -Chlordane	103.0-105.0	1.43	1.54	0.19		
(VIII)	<i>trans</i> -Nonachlor	117.0-122.0	1.68	1.70	0.26		
(XI)	β -Dihydroheptachlor	136.0-137.0	1.01	1.08	0.32		
(XIII)	Heptachlor epoxide	157.5-159.0	1.24	1.48	0.06	81	4.7
(XIV)	Photoheptachlor epoxide	211.3-213.3	1.68	2.20	0.05	323	2.6

^a Summed from *m/e* 45 to molecular ion.

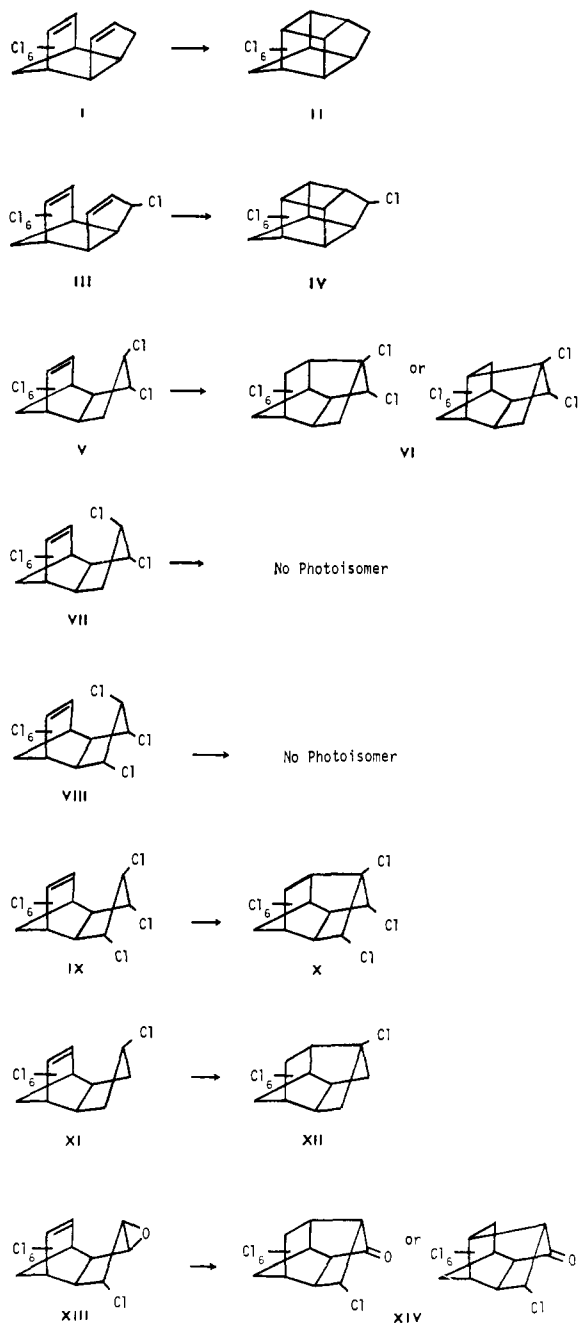


Figure 1. Photoisomers of chlordane components

The columns were operated at 200° C and 120 ml/min N₂; the other operating parameters are described in the Pesticide Analytical Manual (1968).

Thin-Layer Chromatography. Precoated silica gel G plates (250 μ, Analabs) were used as received. The plates were developed with *n*-heptane and treated with silver nitrate reagent, and the spots were visualized with uv light (Mitchell, 1961).

Infrared Spectra. A Perkin-Elmer 337 infrared spectrophotometer was used for the preliminary examination of the photoisomers. The infrared spectra of the photoisomers (KBr pellet) were consistent with the structures proposed, as the photoisomers lack the olefinic absorption in the 1600 cm⁻¹ region that is present in the spectra of the parent compounds. Detailed analysis of the infrared spectra will be published separately.

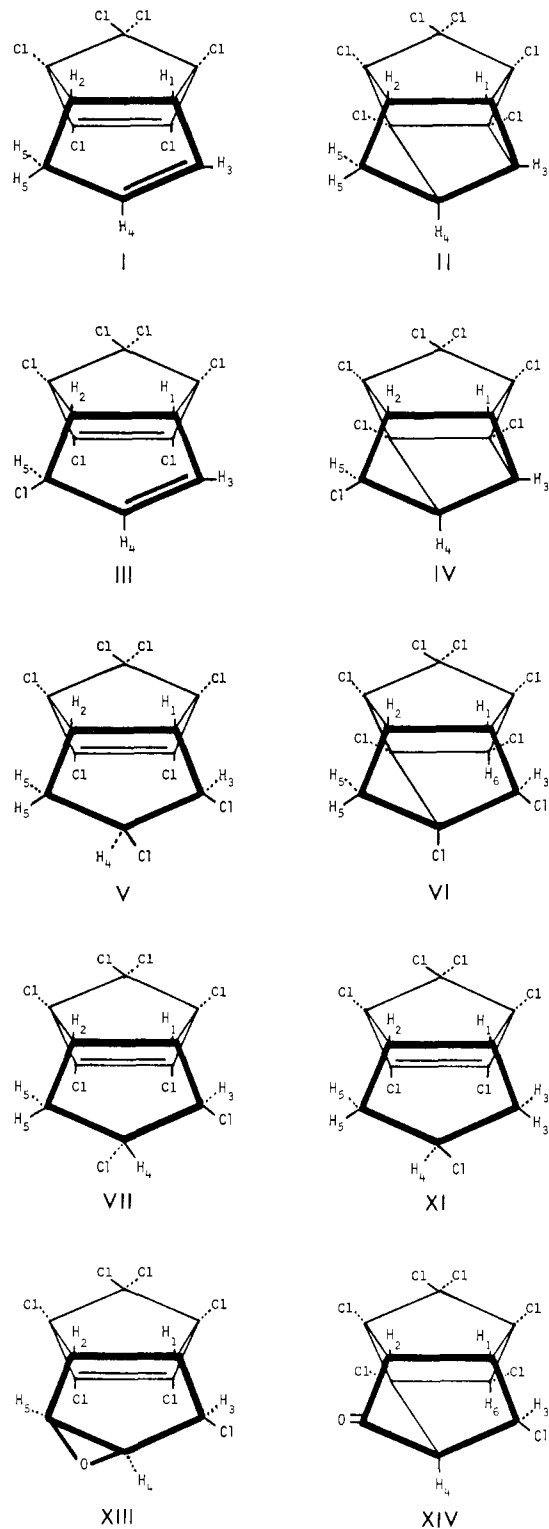


Figure 2. Photoisomers of chlordane components

Physical Properties. Inspection of Table III shows that the photoisomers have melting points which are significantly higher than those of the parents, tlc R_f's which are lower, and glc retention times which are about 1.5 times as long.

Elemental Analyses. Photochlordene (II), C₁₀H₆Cl₆: carbon, calcd 35.44, found 35.78; hydrogen, calcd 1.78, found 1.74. Photoheptachlor (IV), C₁₀H₅Cl₇: carbon, calcd 32.17, found 32.12; hydrogen, calcd 1.35, found 1.21. Photo-*cis*-chlordane (VI), C₁₀H₆Cl₈: carbon, calcd 29.31, found

Table IV. Nmr Data for Chlordane Components and Photoisomers^a

No.	Compound	H ₁	H ₂	H ₃	H ₄	H ₅	H ₆
(I)	Chlordene	Complex 3.73-4.00	Complex 3.27-3.62	Complex 5.50-5.93	Complex 5.50-5.93	Complex 2.28-2.57	
(II)	Photochlordene	Complex 3.18-3.43	Complex 3.18-3.43	Complex 3.18-3.43	Complex 3.18-3.43	Complex 1.48-2.58	"AB pattern"
(III)	Heptachlor	"Doublet of doublets" 3.53-3.71	"Doublet of doublets" 3.96-4.18	"Singlet" 5.86-5.95	"Singlet" 5.86-5.95	"Triplet" 4.70-4.85	
(IV)	Photoheptachlor	Complex 3.25-3.68	Complex 3.25-3.68	Complex 3.25-3.68	Complex 3.25-3.68	Complex 4.63-4.73	
	Photoheptachlor ^b	Multiplet 3.45	Multiplet 3.45	Multiplet 3.45	Multiplet 3.45	4.70	
(V)	<i>cis</i> -Chlordane	Complex 3.33-4.06	Complex 3.33-4.06	Complex 4.13-4.41	Complex 4.63-4.86	Complex 1.40-2.68	
(VI)	Photo- <i>cis</i> -chlordane ^c	Complex 2.16-3.58	Complex 2.16-3.58	Doublet 5.40-5.53		Complex 2.16-3.58	Singlet 5.65
(VII)	<i>trans</i> -Chlordane ^d	3.52	3.52	2.88 endo 2.02 exo		2.88 endo 2.02 exo	
(XI)	Dihydroheptachlor	Complex 3.30-3.75	Complex 3.30-3.75	Complex 1.63-2.58	Complex 4.16-4.51	Complex 1.63-2.58	
(XIII)	Heptachlor epoxide	"Doublet of doublets" 3.16-3.41	"Triplet" 3.58-3.80	"Triplet" 4.20-4.36	"Triplet" 3.58-3.80	"Triplet" 3.58-3.80	
(XIV)	Photoheptachlor epoxide ^e	Complex 3.27-3.82	Complex 3.27-3.82	"Triplet" 4.78-4.88	Complex 3.27-3.82		Singlet 4.97

^a For the numbering of protons see Figure 2. The ranges of bands are given in ppm (δ) as read from spectral charts. All spectra were run at 60 MHz except those of I and V, which were obtained at 100 MHz. Samples were run in CDCl₃ unless noted otherwise. ^b Literature values, in CCl₄ (Rosen *et al.*, 1969). ^c Acetone-*d*₆. ^d Literature values, solvent unspecified (Büchel *et al.*, 1966). ^e Dimethylsulfoxide-*d*₆.

29.60; hydrogen, calcd 1.48, found 1.37. Photoheptachlor epoxide (XIV), C₁₀H₆Cl₇O: carbon, calcd 30.85, found 31.16; hydrogen, calcd 1.29, found 1.33.

Nmr Spectroscopy. The nmr spectra were obtained on Varian A-60 and HA-100 spectrometers; spin decoupling was performed with the HA-100. Table IV gives nmr data and literature values for the compounds shown in Figure 2. Where possible CDCl₃ was used as the solvent so that the solvent-dependent chemical shifts could be meaningfully compared. (The poor solubilities of compounds VI and XIV in CDCl₃ required the use of different solvents.) The proton numbering in Figure 2 is arbitrary, but appeared to be the most convenient for comparison of the nmr data. When possible, bands are described in terms of their first-order appearance (*e.g.*, "doublet"), although additional fine structure might have been present because of long-range coupling or second-order effects. Assignments were based primarily on multiplicity, integration, and the results of spin decoupling experiments, although known ranges of chemical shifts for certain types of protons were also considered. In general, however, chemical shifts were rationalized in terms of the proposed structures.

Mass Spectrometry. An Atlas CH-4B mass spectrometer was used. It was equipped with a molecular beam inlet system (Brunnee, 1966) to permit the sample temperature to be maintained independently of the ion source temperature while only 2 mm from the ionization chamber. Samples were heated until a sufficient quantity was vaporized to obtain a spectrum; the temperatures ranged from 20 to 50° C. The following conditions were used: ion source, 250° C; electron energy, 70 V; 100 μ A emission; magnetic scanning; accelerating potential 3 kV; and ion source potentials adjusted for maximum beam current. The mass spectra of several photoisomers and the previously unreported spectra of *cis*- and *trans*-chlordane were prepared and are available from the authors. The spectra and fragmentation pathways of

chlordene, heptachlor, and heptachlor epoxide have been reported earlier (Damico *et al.*, 1968). The interpretation of the mass spectral data was therefore focused on those features that permitted the photoisomer to be distinguished from the isomeric starting material.

RESULTS AND DISCUSSION

Chlordene (I) is a minor component in technical chlordane, but it serves as a good model system. Its photoisomerization is similar to that of isodrin (Cookson and Crundwell, 1958) where the two double bonds open and form two new bonds to give a cage structure. The proposed structure for photochlordene (II) is supported by comparison of its nmr spectrum with that of chlordene. The chlordene spectrum shows a complex band at 5.50-5.93 ppm (δ) for the vinyl protons H₃ and H₄ (Figure 2). The spectrum of the photoisomer is quite similar to that of its parent except for the lack of a band in the vinyl region and absorption at 3.18-3.43 ppm, as would be expected for protons H₃ and H₄ of photochlordene.

The mass spectra of chlordene and photochlordene exhibit fragment ions of such low intensity that the two isomers may not be distinguished with any confidence unless percent total ionization is used to express ion abundances (Biemann, 1962). Two distinctions are then apparent: the chlordene molecular ion accounts for 60 times and its base peak two times as much of the total ionization as do the corresponding photochlordene ions (Table III). The fact that the chlordene molecular ion (*m/e* 336) is much more abundant than that of photochlordene indicates that chlordene is more stable to electron bombardment, probably due primarily to the stabilization of the positive charge on its molecular ion by its π -electron systems.

Heptachlor (III) has an allylic chlorine atom that is not present in chlordene, but it is photolyzed similarly to a cage compound (IV). Our nmr spectrum of photoheptachlor is

identical with that reported by Rosen *et al.* (1969). As in the case of photochlordene, the vinyl band (5.86–5.95 ppm) present in the heptachlor spectrum is absent in the photoisomer spectrum, and there is additional absorption at 3.25–3.68 ppm. These observations are consistent with the proposed structure.

The general comments made on the mass spectra of chlordene and photochlordene apply to the mass spectra of heptachlor (Damico *et al.*, 1968) and photoheptachlor in that the compounds may be distinguished only by comparing ion abundances in terms of percent total ionization. The ion current at m/e 270 attributed to retro Diels–Alder collapse of the photoheptachlor molecular ion is lower (its formation would require reversal of the photoisomerization), and photoheptachlor produces ions of greater abundance at m/e 335 and 299 by successive losses of Cl and HCl.

The photoisomerization of *cis*-chlordane (V) is similar to that of dieldrin, *i.e.*, it gives a half-cage compound (VI) through hydrogen migration and carbon–carbon bond formation (Benson, 1971; Harrison *et al.*, 1967; Ivie and Casida, 1970; Robinson *et al.*, 1966; Rosen *et al.*, 1966). Rate studies on the dehydrochlorination of *cis*-chlordane (Chau and Cochrane, 1969) indicate that the two chlorine atoms on the cyclopentane ring are *cis* to each other and *exo* to the CCl_2 bridge. This *cis* structural assignment is supported by the photorearrangement, since the chlorine atoms do not interfere with ring closure and hydrogen transfer. Two isomeric products are possible, but the data obtained in this study do not permit choosing between them. The nmr spectra of *cis*-chlordane and photo-*cis*-chlordane support a cage structure for the photoisomer. Little consideration is given to chemical shifts because the compounds were examined in different solvents. The *cis*-chlordane spectrum shows complex bands for H_3 and H_4 . In the photoisomer spectrum one of these complex bands collapses to a doublet (H_3), the other is absent, and a downfield singlet (H_6) appears. This indicates that H_4 has been replaced by an nmr-inactive nucleus and that a proton has appeared in a position isolated from nuclei with which it can couple.

As in the case of the other mass spectra, *cis*-chlordane is difficult to distinguish from its photoisomer except by comparing their percent total ionizations. *cis*-Chlordane gives a relatively intense m/e 66 ion (C_5H_6^+) which is extremely weak in the photoisomer, where its formation would require the reversal of the photoisomerization by bond rupture and migration of H_6 back to the cyclopentane ring (Figure 2, No. VI). The ion current at m/e 270 due to retro Diels–Alder collapse of the photoisomer molecular ion is also weaker; its formation would also require reversal of the photoisomerization.

trans-Chlordane (VII) should not photolyze to a half-cage compound, as the chlorine atom on the center carbon of the cyclopentane ring is directed toward the double bond. *trans*-Chlordane does, indeed, disappear very slowly on irradiation, and products which do not gas chromatograph are obtained.

trans-Nonachlor (VIII) disappears slowly on irradiation, and the products which predominate do not gas chromatograph. Vollner *et al.* (1969) proposed an *exo*–*endo*–*exo* arrangement of the chlorine atoms on the cyclopentane ring; it is therefore not surprising that *trans*-nonachlor does not isomerize to a half-cage compound, as the center chlorine atom is directed toward the double bond. (The *trans*-nonachlor used in this study had the same melting point and glc properties as reported by Büchel in 1966; he proposed

that the three chlorines on the cyclopentane ring were probably all *cis* to each other and *exo* to the CCl_2 bridge.) The synthesis of the all-*cis*-nonachlor (IX) has been reported (Cochrane *et al.*, 1970). This nonachlor isomer has a much higher melting point than *trans*-nonachlor, and apparently photolyzes to the half-cage compound (X) (Cochrane, 1969).

β -Dihydroheptachlor (XI) should also isomerize to a half-cage compound. This photoisomer (XII) was isolated by Vollner *et al.* (1969). The acetone-sensitized irradiation in the present study, using the Kimax filter, gave essentially no reaction, while irradiation for 7 hr through quartz gave a small additional glc peak. Removal of solvent left a dark oil from which no crystalline product could be isolated. This reaction was not investigated further.

Heptachlor epoxide (XIII) photolyzes to a ketone (XIV), probably in a manner similar to the photorearrangement of endrin (Rosen *et al.*, 1966). This involves hydrogen migration, rearrangement of the epoxy to a carbonyl group, and carbon–carbon bond formation. As in the case of photo-*cis*-chlordane, two isomeric compounds are possible. The nmr spectrum of heptachlor epoxide shows a complex band (“triplet”) at 3.58–3.80 ppm for H_2 , H_4 , and H_5 . Integration of the spectrum of photoheptachlor epoxide indicates that there is one less proton above 4 ppm than in the parent spectrum. A downfield singlet (H_6) appears, while H_2 and H_4 still give complex bands. As in the case of *cis*-chlordane and its photoisomer, the data suggest that H_5 has migrated to a position isolated from nuclei with which it can couple. Little information can be obtained from a consideration of chemical shifts because these compounds were examined in different solvents. The ir spectrum of the photoisomer shows a strained-ring carbonyl band at 1780 cm^{-1} .

Photoheptachlor epoxide is the only photoisomer whose mass spectrum differs greatly from that of its precursor, allowing simple and unequivocal differentiation. The most striking feature is the shift of the base peak from m/e 81 ($\text{C}_9\text{H}_9\text{O}^+$) in the parent spectrum to m/e 325 ($\text{C}_9\text{H}_5^{35}\text{Cl}_5^{37}\text{Cl}^+$) in the photoisomer spectrum. This ion is probably formed by successive losses of a chlorine radical and CO molecule from the molecular ion. In contrast, no loss of CO from the heptachlor epoxide M–Cl ion is observed. The heptachlor epoxide molecular ion undergoes retro Diels–Alder collapse to give a m/e 270 ion not observed in the photoisomer spectrum; this indicates a significant structural difference. The spectra also differ in that the photoisomer produces intense ions at m/e 287 and 251 by consecutive losses of HCl.

All three methods of photolysis (solution/uv, thin-film/uv, thin-film/sunlight) give the same photoisomers as determined by glc. It is clear that solution photolysis is the synthetic method of choice, as large amounts of product can be obtained easily. Irradiation of thin films with the “hard” uv (254 nm) of the germicidal lamps gives a low conversion to photoisomer and produces many side products. Exposure of the parents to summer sunlight seems to give cleaner reactions, since the parent and photoisomer glc peaks predominate. Irradiation of heptachlor with “hard” uv apparently produced some heptachlor epoxide (glc), while none was detected in the sunlight experiments. This conversion to the epoxide by light has been reported (Gannon and Decker, 1958). As was mentioned previously, other photoproducts, some of which do not gas chromatograph, are also formed in these photolyses. It is apparent that competitive reactions are taking place, since, once the photoisomers are formed, they are relatively stable to Corex- or Kimax-filtered uv

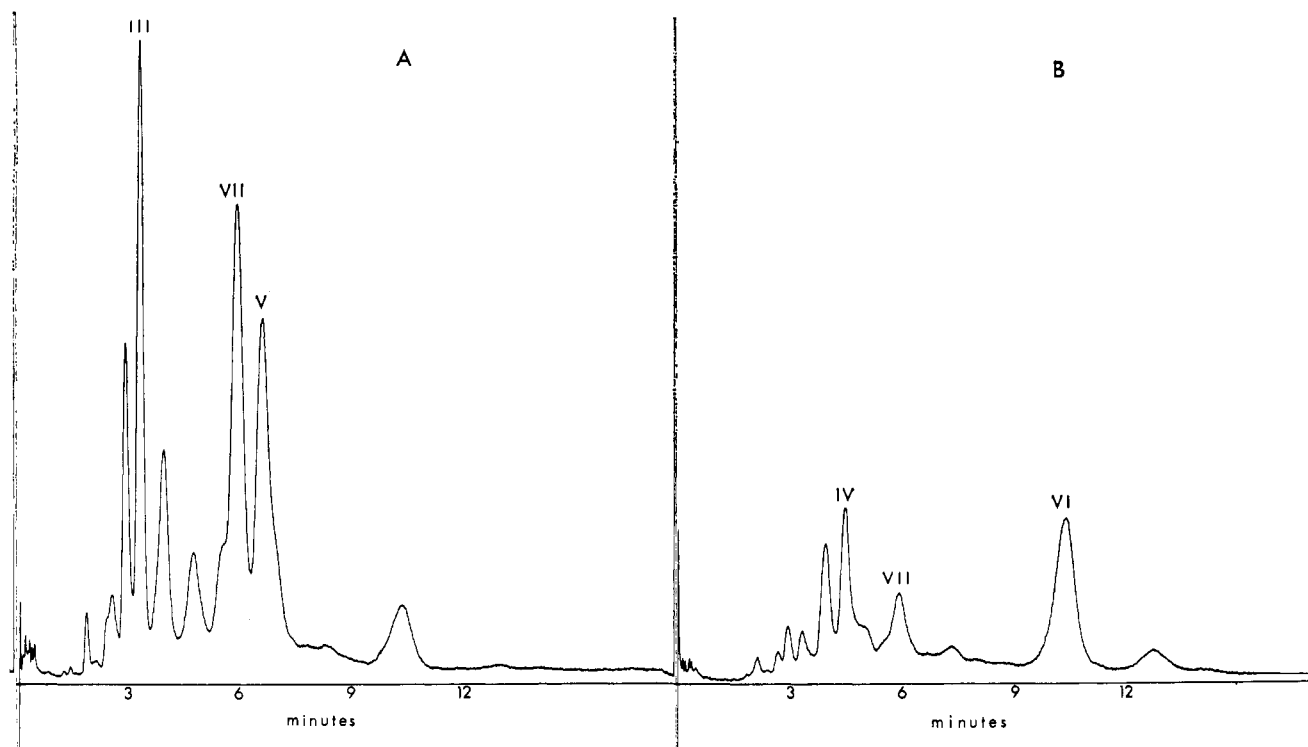


Figure 3. Gas chromatograms of technical chlordane. A. Before irradiation; B. After 70 hr irradiation. (III) Heptachlor; (IV) Photoheptachlor; (V) *cis*-Chlordane; (VI) Photo-*cis*-chlordane; (VII) *trans*-Chlordane

light. These other products may be formed through processes such as photooxidation and polymerization.

Photolysis of technical chlordane in acetone solution using Kimax-filtered uv light gives a complex mixture of products. Figure 3 illustrates gas chromatograms of technical chlordane (DC-200 column) before and after 70 hr of irradiation. The heptachlor, *cis*-chlordane, and *trans*-chlordane components disappear at rates similar to the rates observed for the pure compounds, and the corresponding photoheptachlor and photo-*cis*-chlordane peaks appear. The total glc response of the photolyzed mixture is quite low, which indicates that many products are formed which do not gas chromatograph. It may be noted that a small amount of *trans*-chlordane still remains after 70 hr.

It is possible that sunlight may produce photoalteration products under field conditions; the findings reported here will help the residue analyst determine whether or not these photoisomers exist as residues. If these residues do indeed exist, their biological significance should be determined.

Nomenclature. The photoisomers were named according to the von Baeyer system: photochlordene (II): 1,7,8,9,10,10-hexachloropentacyclo[5.3.0.0^{2,6}.0^{3,9}.0^{5,8}]decane; photoheptachlor (III): 1,4,7,8,9,10,10-heptachloropentacyclo[5.3.0.0^{2,6}.0^{3,9}.0^{5,8}]decane; photo-*cis*-chlordane (VI): 1,3,4,7,8,9,10,10-octachlorotetracyclo[5.2.1.0^{2,6}.0^{4,9}]decane; photoheptachlor epoxide (XIV): 1,5,7,8,9,10,10-heptachlorotetracyclo[5.2.1.0^{2,6}.0^{4,9}]decane-3-one.

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