

The photolysis of dieldrin (I, mp 175–176° C) in the solid state has been followed as a function of time. Over 50% of the dieldrin was converted to photodieldrin (II) after exposure to ultraviolet light (2537 Å) for 1 hr with 25% of the dieldrin remaining unchanged. Evaporative losses were negligible, and two other unidentified products were formed. A preparative method for II is given. Radiolabeled ¹⁴C-photodieldrin was synthesized in 30% yield by

similar methods, beginning with solid ¹⁴C-dieldrin. The rate of formation of pentachlorodieldrin (IV) as well as II by photolysis of I in ethyl acetate solution is also presented. The identities of II and IV are discussed. Solids II and IV were found to be relatively stable for less than 5 hr of exposure to uv light, but after 24 hr II and IV were decreased 42% and 29%, respectively. At least two new compounds were formed from II.

Several unknown compounds are formed from the weathering of formulated "dieldrin" under field conditions (Harrison *et al.*, 1967; Roburn, 1963). [In this paper the term dieldrin refers to HEOD, 1,8,9,10,11,11-hexachloro-4,5-epoxytetracyclo[6.2.1.1.1^{0,2}.7]dodec-9-ene, mp 175–176° C, Compound I of Figure 1. The term dieldrin is used to refer to a compound for which the cited literature does not state the purity. A fuller discussion of nomenclature is given elsewhere (Benson, 1969).] Starting with purified dieldrin, several unknown compounds are also formed from the solid and from solution under the influence of sunlight (Roburn, 1963; Rosen *et al.*, 1966) and artificial light (Rosen and Carey, 1968). Some of these products are at least as toxic as dieldrin (Harrison *et al.*, 1967) or more toxic (Brown *et al.*, 1967; Rosen and Sutherland, 1967). Khan *et al.* (1969) have reported that one photoproduct may be converted to an even more toxic metabolite (V) in insects.

Known and postulated structures are shown in Figure 1 and physical data on conversion products of dieldrin photolysis are given in Table I.

Photodieldrin (II or III) can be prepared by solid state photolysis. The alteration of solid dieldrin by artificial light was first reported by Mitchell (1961), and Roburn (1963) reported its decomposition by sunlight. Subsequently, II was prepared from solid dieldrin in larger quantities on filter paper (Robinson *et al.*, 1966; Kawashiro *et al.*, 1966) and on glass (Rosen *et al.*, 1966; Harrison *et al.*, 1967). Benson and Raszewski (1969), using ¹⁴C-labeled dieldrin on glass, prepared and isolated radiolabeled II for metabolism studies by a tlc streaking technique.

Photodieldrin is also obtained by photolysis of dieldrin in solution. Parsons and Moore (1966) photolyzed dieldrin in ethyl acetate for 20 days, obtaining mainly II (52% yield). Compound I was no longer detectable and a minor component was not identified. Henderson and Crosby (1967) photolyzed dieldrin and aldrin for 24 hr in cyclohexane to yield pentachlorodieldrin (IV) and a structurally similar pentachloroaldrin in conversions greater than 50%. Henderson and Crosby (1968) found that sunlight converted I to II in water.

Contrary to earlier reports, Rosen *et al.* (1967) found that aldrin could be photolyzed in ethyl acetate by exposure to uv light for 7 days to form the photoaldrin (VI) and a penta-

chloroaldrin. Compound VI was converted to II with peracids. These authors did not state whether pentachloroaldrin was convertible to IV in a similar manner. Rosen and Carey (1968) used benzene, uv light, and a photosensitizer to convert aldrin and dieldrin to VI (77%) and II (75%) respectively, in 21 hr.

The occurrence of at least three photodieldrins on grass and crops has been observed (Harrison *et al.*, 1967) and several photoconversion products appear to be toxic (Rosen and Sutherland, 1967). However, no work has been published on the rate of formation of II from solid I or solutions of I, or on the rate of degradation of II.

This study was undertaken to prepare compounds II (or III) and IV, together with some of the polymeric material, for use in toxicological tests, metabolism studies, and development of analytical methods. Using material prepared in this study, Burke (1969) of these laboratories has determined and described the analytical behavior of two photodieldrins in a widely used analytical method for chlorinated pesticide residues.

This paper describes the formation of photodieldrins from dieldrin, studies of the rates of formation, and further examination of the identity of the compounds. Identity was established by gas-liquid chromatography, melting point measurements, thin-layer chromatography, mass spectrometry, infrared spectrometry, and nuclear magnetic resonance.

The investigation established that a photodieldrin, formed from dieldrin by solid state and solution photolysis, probably has the structure II and that, in addition to II, a second photodieldrin, pentachlorodieldrin (IV), is formed by photolysis of dieldrin in solution.

EXPERIMENTAL

Reference Materials. Dieldrin (I), mp 175–176° C, was obtained through repeated recrystallization from ethanol of dieldrin (mp ~140–145° C) and also from Shell Chemical Company, Modesto, Calif. ¹⁴C-dieldrin (at least 85% HEOD and no more than 15% related chlorinated compounds) was obtained from Nuclear-Chicago: 1.0 mCi, specific activity 70.4 mCi/mole, mp 144–148° C (uncorrected). The stated purity was 102–98% dieldrin by tlc, paper chromatography, and dilution analysis (received in two ampoules).

Photodieldrin was obtained by repeated recrystallization of the solid state reaction mixture until the product was pure by glc and tlc analyses (impurities <0.1%), mp 194–195° C (lit. 188°, 192°, 195°, 201° C).

Pentachlorodieldrin (IV) was obtained from a preparation similar to that described by Henderson and Crosby (1967) but

Residue Chemistry Branch, Division of Pesticide Chemistry and Toxicology, Food and Drug Administration, Washington, D.C. 20204

¹ Present address: BD-420 Chief, Phys. Chem. Br., Div. of Drug Chemistry, Oprt. Bur. of Drugs, FDA, Wash., D.C. 20204

Table I. Physical Data and Nomenclature of Two Identified Products from the Photolysis of Dieldrin

A. Product II or III											
Paper	Method of Preparation	C, H, Cl, Analysis, %	M.S.	I.R.	Nmr	Mol. Weight	Structure	Names Used	Melting Point	Tlc	Glc
Robinson, Richardson, Bush, and Elgar (1966)	uv irradiation of solid	C-37.5% H-1.8% Cl-55.6%	<i>a</i>	<i>a</i>	<i>a</i>	377	II	Photoproduct of dieldrin, photoisomer of dieldrin photochemical product, photoconversion product, dieldrin U.V.C.P.	188	<i>a</i>	<i>a</i>
Rosen, Sutherland, and Lipton (1966)	uv irradiation of solid	...	<i>a</i>	<i>a</i>	<i>a</i>	378	II	10-oxa-3,6- <i>exo</i> -4,5,13,13-hexachlorohexacyclo-[6,3,1,1 ^{3,6} ,1 ^{9,11} ,0 ^{2,7} ,0 ^{5,12}] tridecane
Harrison, Holmes, Roburn, and Tatton (1966)	uv irradiation of solid	...	<i>a</i>	<i>a</i>	<i>a</i>		III	Dieldrin irradiation product	195-6	<i>b</i>	...
Parsons and Moore (1966)	uv irradiation of solid	C-37.8% H-2.1% Cl-55.8%	<i>a</i>	<i>a</i>	<i>a</i>	378	II	1,9,10,10,11- <i>exo</i> -12-hexachloro-4,5-epoxy-pentacyclo[7,3,0 ^{1,9} ,0 ^{2,6} ,0 ^{3,8} ,0 ^{7,11}] dodecane	200-201	<i>b</i>	...
Rosen and Carey (1968)	uv irradiation of solution	<i>a</i>	II	1,1,2,3,3a,7a-hexachloro-5,6-epoxydecahydro-2,4,7-methano-1H-cyclopenta[<i>a</i>]pentalene	192	...	<i>b</i>
This work	uv irradiation of solid	...	<i>b</i>	<i>b</i>	<i>b</i>	378	II	1,9,10,10,11- <i>exo</i> -12-hexachloro-4,5- <i>exo</i> -epoxy-8,3-7,6- <i>endo</i> -8,9-7,11- <i>exo</i> -pentacyclo-[7,3,0,0 ^{2,6} ,0 ^{3,8} ,0 ^{7,11}] dodecane	194-195	<i>b</i>	<i>b</i>
B. Product IV											
Henderson and Crosby (1967)	uv irradiation in hexane solution	C-41.8% H-2.3% CP-49.6%	<i>a</i>	<i>b</i>	<i>b</i>	344	IV	Photoproduct of dieldrin	104 (164)	<i>b</i>	...
This work	uv irradiation in EtOAc solution	...	<i>b</i>	<i>b</i>	<i>b</i>	344	IV	1,8,10,11,11-pentachloro-4,5-epoxytetracyclo-[6,2,1,1 ^{3,6} ,0 ^{2,7}]dodec-9-ene	162.5-163.5	<i>b</i>	<i>b</i>
This work	uv irradiation in hexane solution	...	<i>b</i>	<i>b</i>	<i>b</i>	344	IV	Same as above	162.5-163.5	<i>b</i>	<i>b</i>

^a Selected lines and/or bands given. ^b Gave sufficient data but may not be the same data as other workers found.

under different conditions; mp 163-164° C (lit. 104° corrected to 163-164° C; see PHOTOLYSIS OF DIELDRIN IN ETHYL ACETATE SOLUTION). Melting points were taken on a Thomas-Hoover Uni-melt and are corrected. Spectra were obtained as follows: mass spectra, Bendix time-of-flight mass spectrometer, Model 14; nmr spectra, Varian A-60 and Varian HA-100 spectrometers; infrared spectra, Beckman IR-10.

For irradiation of solids, two G.E. G30T8 germicidal lamps were used; they were mounted in an office overhead fluorescent light fixture. For solutions, the apparatus consisted of a 100-ml short-neck, round-bottom Pyrex flask, # 24/40, fitted with a Pen Ray lamp (2753 Å, Model SC-1 with power supply, Ultra-violet Products, Inc., San Gabriel, Calif.) seated on a magnetic stirrer.

Gas chromatography was performed using a Barber-Colman Model 5360 gas chromatograph with a concentric electron capture tritium foil detector. The glass column (6 ft × 4 mm i.d.) was packed with 10% DC-200 on 100/120 mesh Gas Chrom Q. Conditions were as follows: chart speed 1/2 in./min, N₂ flow 120 ml/min, and injection port, column and detector temperatures 200° C. Injection volumes were 5 μl (see Figure 2).

Except where stated otherwise, all thin-layer chromatography was performed in the following manner. Batches of five 20 × 20 cm glass plates were prepared according to Kovacs (1963), except that 40 g of Silica Gel G was added to 70 ml of distilled water to prepare the slurry, which was spread with a commercial spreader to a thickness of 0.25 mm. Pre-washing of the plates was unnecessary. The plates were dried in an oven for 30 min at 100° C. For spotting, dilution of concentrated solutions of the compounds with ethyl acetate, ethanol, or acetone was equally satisfactory; ethyl acetate was used to prepare 1 mg/ml solutions. Plates were developed with a 1:3 solution of ethyl acetate:*n*-heptane. The plate was saturated with silver nitrate chromogenic spray solution until the coating was translucent, dried in an oven for 5 min at 75° C, and exposed to ultraviolet light for 10 min or until the spots were permanent.

SOLID STATE PHOTOLYSIS OF DIELDRIN

Effect of Time on Formation of Photodieldrin. To measure the effect of time on conversion of solid dieldrin (I) to photodieldrin (II), various periods of irradiation were used,

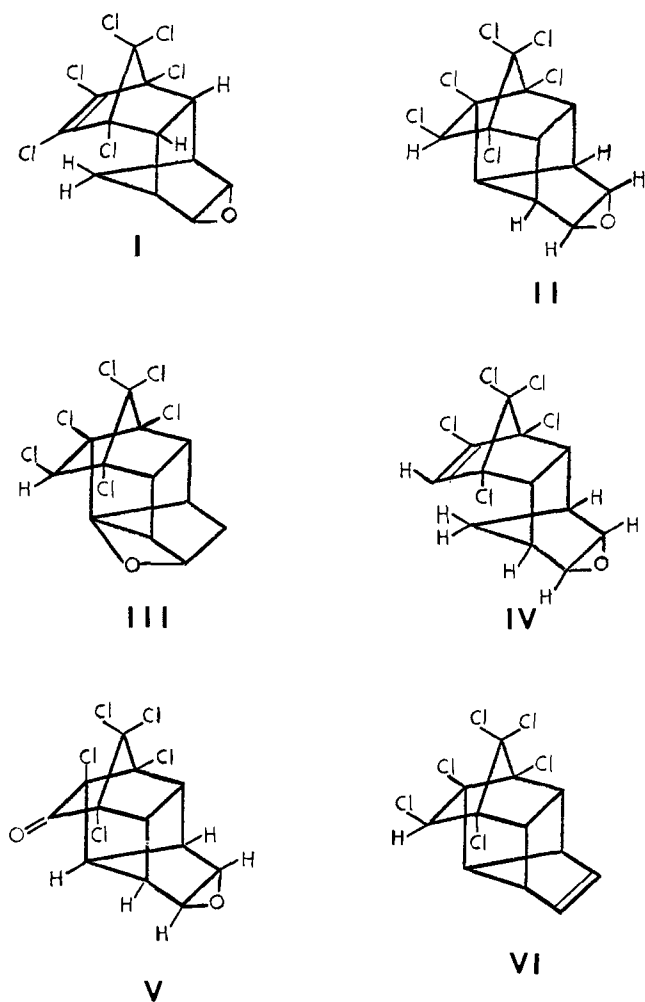


Figure 1. Stereochemical structures of compounds discussed. I: HEOD or dieldrin (mp 175–176°C). II: Photodieldrin. III: Photodieldrin. IV: Pentachlorodieldrin. V: Klein's Metabolite. VI: Photoaldrin

Table II. Rate Conversion of Solid Dieldrin (I) to Photodieldrin (II) as Analyzed by Glc

Batch ^a	Exposure (Hr)	% Photo-dieldrin ^b	% Dieldrin ^b	Total Photo-dieldrin + Dieldrin	By Difference Others
1	1/2	32.3	50.7	83.0	17.0
2	1	51.8	25.5	77.3	22.7
3	2	52.5	25.1	77.6	22.4
4	3	49.6	19.5	69.1	30.9
5	65	44.4	12.0	56.4	43.6

^a Each batch consists of three plates. ^b Average of three plates.

as shown in Table II. For each period, three clean 20 × 20 cm glass plates were weighed on a Mettler balance and sprayed as follows: Compound I (1.60 g) was dissolved in 50 ml of ethyl ether, transferred to a 100-ml tlc spray bottle, and sprayed onto the plates with the spray nozzle held about 2–3 in. from the surface of the plate to minimize loss of dieldrin (in 15 previous trials, dieldrin losses averaged 25%). Air pressure was set at about 3 psi, and the bottle was moved horizontally and vertically in such a way as to keep the spray about 3 cm inside each edge and to form a fairly uniform coating. Clogging was common if spraying was done too fast. When spraying even into a box situated in the hood did not

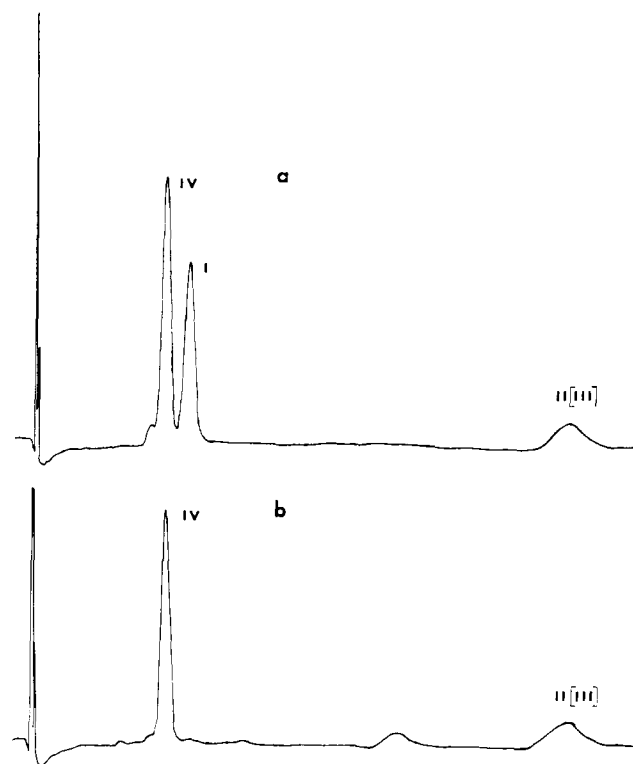


Figure 2. Gas chromatograms of diluted solutions containing photolyzed dieldrin in ethyl acetate (mm units at base)

prevent the laboratory from being contaminated, the spraying of dieldrin was discontinued.

Each of the three sprayed plates was air dried, weighed separately, placed 4 cm from the light source, irradiated for the chosen period of time, and reweighed. About 1.4 to 2.3% of the weight was lost, apparently due to evaporation. Each plate was then washed with ethyl acetate; the solution was transferred to a 250-ml volumetric flask and diluted to volume with ethyl acetate. A portion of this solution was then diluted with *n*-hexane to a concentration of 1 µg/ml for injection into the gas chromatograph under the conditions described above. Results are shown in Table II.

Effect of Different Methods of Preparing Plates on Conversion of Dieldrin to Photodieldrin. Large quantities of photodieldrin were prepared by spraying many plates, photolyzing them for 1 hr, dissolving the remaining material with ethyl acetate, combining all ethyl acetate solutions and evaporating them under vacuum, heating the remaining white solid with hexane three times to dissolve out most of the dieldrin, and recrystallizing the remaining solid from 95% ethanol. Some photodieldrin was lost in the hot hexane. Typical conversions are given in Table II.

Other methods of preparing plates included pouring and streaking. In the pouring technique, 1.60 g of dieldrin was dissolved in 10 ml of ethyl ether and gradually poured onto a 20 × 20 cm preweighed clean glass plate. The solvent evaporated rapidly, leaving relatively large dieldrin crystals, which were somewhat more concentrated at the edges than in the center of the plate. The plate was placed under the lamp for 1 hr and then washed with ethyl acetate to dissolve the light yellow crystals. The solution was diluted to 250 ml (6.08 mg/ml), and this stock solution was used to prepare a solution (1.22 µg/ml) which was analyzed by gas chromatography.

Two major peaks were observed. The first had a retention time of 5.5 min (69 mm) and the second had a retention time

of 12.5 min (159 mm). These peaks corresponded exactly to the retention times of dieldrin (I) and photodieldrin (II), respectively.

The conversion to photodieldrin by the pouring technique was 28.1%; unconverted dieldrin remaining was 52.1%. The remaining 19.8% was not detected by glc but was still present on the plate; there was, relatively speaking, no loss in weight.

In the streaking technique, 20 × 20-cm coated tlc plates were prepared as before. About 500 mg of recrystallized dieldrin was dissolved in 10 ml of ethyl acetate, and 2 ml of this solution (100 mg) was streaked onto a tlc plate in a line about 4 cm from the bottom, using a 5-ml Yale Luer-Lok syringe. After the ethyl acetate had evaporated, the plate was placed under the ultraviolet lamps and irradiated for 1 hr; it was removed and developed with 1:3 ethyl acetate:*n*-heptane for a distance of 100 mm and dried in an oven at 100° C for 10 min. The areas to which dieldrin and photodieldrin migrated were light brown.

The photodieldrin streak (near $R_d = 0.58$) (R_d = relative to dieldrin) was scraped off the plate and placed in a beaker, to which 50 ml of hot ethyl acetate was added. The suspension was swirled vigorously for a few minutes while warm, and then filtered; this process was repeated. The combined ethyl acetate solutions were evaporated to dryness with a Rinco evaporator. The white photodieldrin solid recovered (45.1 mg) was used to prepare a dilute solution for glc analysis (1.80 µg/ml). The chromatogram showed one major peak at the retention time corresponding to II and one very minor peak (<3%) corresponding to the peak of I. Photodieldrin was produced in 44.7% conversion and in a relatively pure state.

When the dieldrin was applied to the tlc plate as an ethyl ether solution in place of ethyl acetate, the conversion was much lower, possibly because of the tight, concentrated streak formed on the tlc plate by the rapid evaporation of ethyl ether.

FORMATION AND PURIFICATION OF RADIOLABELED PHOTODIELDRIN (II)

The contents of the two ampoules containing ^{14}C -dieldrin were transferred to a 50-ml centrifuge tube and two 1-ml washings of ethyl ether from each vial were added, followed by 67.0 mg of unlabeled I. This solution was evaporated to dryness in 15 min with a gentle stream of air with warming. The sides of the centrifuge tube were washed with two 1-ml portions of ethyl ether. The resulting solution was then placed on a glass plate within an area of 9 in.² restricted by masking tape. The tube was washed with five 0.5-ml portions of ethyl ether and the washings were placed within the same areas of the plate to help disperse the solid dieldrin uniformly over the 3 × 3 in. surface. This plate was placed 4 cm from the surface of a uv light (General Electric G30T8 Germicidal Lamp) and photolyzed for 1 hr. (CAUTION! Protect eyes. Do not look directly at uv light.) The masking tape was removed and the photolyzed product was dissolved in ethyl acetate. The ethyl acetate was removed under vacuum with warming on a water bath and recollected by inserting a trap. This process also yielded a white solid residue (A). No radioactivity was noted in the collected ethyl acetate as determined by a hand counter (Model Pac 4 G, Eberline Instrument Corp., Santa Fe, New Mexico; with Model Ac-2B hand probe).

Thin-layer chromatographic plates were prepared according to Kovacs (1963), as described earlier.

The solid A was transferred to a beaker, dissolved in 1 ml of

ethyl ether, and streaked near the bottom of the tlc plate. In the marginal area of this same tlc plate, three spots were added: 10 µg of I, 10 µg of II, and about 1 µl of A dissolved in 1 ml of ethyl ether, *i.e.*, the equivalent of about 72 µg of I.

The plate was developed with 1:3 ethyl acetate:*n*-heptane and dried, and the streaked portion was covered so that little or no light or chemicals could fall on this area. The spotted portion was sprayed with a chromogenic spray reagent consisting of 0.05% AgNO_3 , 10% 2-phenoxyethanol, and 0.1% H_2O_2 (30% solution) in acetone (Kovacs, 1963), and exposed to uv light for 5 min. Two of the R_f values found were 0.68 (I) and 0.35 (II). A number of spots from A were visible, including spots with R_f values for I and II.

The developed, unsprayed portion of the plate was divided into three sections: origin section, photodieldrin section (0.5 to 4.5 cm) and dieldrin section (4.5 to 10 cm). The silica gel from each section was scraped into a separate beaker and 50 ml acetone was added to each. The mixture was stirred, filtered through a 30-ml medium porosity sintered glass funnel, and washed several times with acetone. The recovered solution was placed in a weighed flask and the acetone removed. Each section was treated in the same way. The following recoveries were found: origin, 12.3 mg (mp 133–145° C); photodieldrin, 47.7 mg (mp 135–138° C); and dieldrin, 10.7 mg (mp 125–128° C). Each section was examined by glc, and the two lower sections were found to be highest in II content.

The material from the photodieldrin section was recrystallized from ethanol and water, and then fractions were analyzed by glc using ethyl acetate for dilution to approximately 1 ng/µl. Those high in II were combined with the material from the origin area and the process was repeated, *i.e.*, the material was restreaked, chromatographed on tlc, etc. Although tlc showed polar materials at the origin, only a few small unidentified peaks came through the glc analysis. The final yield of ^{14}C -labeled II was 16.4 mg; 16.0 mg of purified ^{14}C -labeled I was also recovered. The purity of II was evidenced by final tlc and glc analyses; mp 195–196° C (lit. 188–201° C; Rosen and Carey, 1968). This gave a yield of 30% based on total I consumed. The activity of both compounds was 5.3 mCi/mmmole, as measured by a liquid scintillation counter.

PHOTOLYSIS OF DIELDRLIN IN ETHYL ACETATE SOLUTION

Solutions of dieldrin, prepared by adding 2.00 g of I to a measured volume of ethyl acetate, were irradiated at room temperature. To facilitate free movement of the stirrer, the flask was placed at an angle of about 15° from a vertical position. The apparatus was surrounded by a box to protect the operator's eyes from harmful rays.

After irradiation for various periods of time, as shown in Table III, the volumes of the solutions were measured. Each solution was then diluted to 100 ml with ethyl acetate and an aliquot diluted with hexane to a concentration suitable for injection into the gas chromatograph. By comparison of retention times and peak areas with those of standards run at the same time, dieldrin (I), pentachlorodieldrin (IV), and photodieldrin (II) were determined quantitatively.

To confirm its identity, IV was prepared by irradiating 2.00 g of dieldrin in about 90 ml of ethyl acetate for 24 hr. The brownish-yellow solution obtained was concentrated in a rotary evaporator heated with a water bath. After 1 hr the solution was dark brown and oily. The tan crystals which formed after the solution had stood at room temperature for 24 hr were washed with hexane and ethanol; they melted at 161.6–163.5° C. Further washing with acetone, ethyl acetate,

Table III. Rate of Photolysis of Dieldrin (2.00 g) in Ethyl Acetate (approx. 2% solution)

Exp. No.	Hr Exposed	Glc Analysis Products Formed ^a			Total	Volume Recovered
		I	II	IV		
1	1	75.0%	N.D.	8.0%	83.0%	97 ml
2	2	37.4%	7.5%	16.0%	60.9%	70 ml
3	5	17.0%	12.0%	33.0%	62.0%	92 ml
4	15.5	3.8%	25.4%	32.0%	61.2%	92 ml
5	24	N.D.	11.6%	30.8%	42.4%	92 ml
6	24	1.8%	17.0%	28.0%	48.8%	80 ml
7 ^b	24	4.0%	9.7%	31.4%	45.1%	84 ml

^a N.D. = none detected. ^b H₂O₂ (2% concentration) added.

and ether, and a recrystallization from hot ethanol yielded white crystals (mp 160.5–162.5° C). In addition, IV was prepared by irradiation in hexane, somewhat similar to the manner used by Henderson and Crosby (1967) but with 10-fold more concentrated solutions. Nmr and ir studies showed that both crystalline products were the same (IV), as reported by Henderson and Crosby (1967). The final melting point of IV prepared from ethyl acetate after several recrystallizations was 163–164° C; Henderson and Crosby (1967) reported the melting point of their product to be 104° C, but Crosby (1968) has stated that this was a typographical error and should be 164° C.

Thin-layer chromatography of IV prepared in this manner yielded only one spot, with essentially the same *R_f* as the dieldrin standard. The solutions used for tlc (2 g/100 ml ethyl acetate) were diluted with ethyl acetate to a concentration compatible with standards for injection into the gas chromatograph. The solution of IV showed two glc peaks: a small peak at the retention time of dieldrin, which represented less than 3%; and a larger peak at 0.85 of the retention time of dieldrin which is attributed to IV.

The longer the solutions of dieldrin in ethyl acetate were irradiated, the yellower they became (Experiments 1–5, Table III). When 2.00 g of dieldrin was irradiated with 80 ml of ethyl acetate for 24 hr (Experiment 6), the solution formed was a lighter color than that obtained by 24 hr of irradiation with 92 ml of ethyl acetate. A possible explanation is that less ultraviolet light and heat reached the solution because the finger of the lamp was not immersed as fully as when larger volumes of ethyl acetate were used. However, glc data indicated that nearly as much pentachlorodieldrin was formed as in Experiment 5 (Table III). In an attempt to form compound V by reaction of H₂O₂ with some short-lived intermediate, 6 ml of 30% H₂O₂ was added to 84 ml of ethyl acetate containing 2.00 g of dieldrin. However, there was no major change in the formation of IV (see Experiment 7, Table III) although a polar, colorless material (as per tlc) was formed which, as in the solid state experiments, does not appear to pass through the gas chromatographic column. Thus, even the use of this 2% hydrogen peroxide solution in aqueous ethyl acetate did not appreciably interfere with the formation of IV. For further identification of the products indicated by glc and tlc analyses, the final solutions were combined and evaporated to a thick oil, from which IV crystallized.

SOLID STATE PHOTOLYSIS OF PHOTODIELDRIN (II)

A 20 × 20-cm glass plate was weighed; 575 mg of photodieldrin was dissolved in 50 ml of ethyl ether and sprayed onto the surface of the plate, using a 50-ml spray bottle with a fine spray nozzle. The plate was allowed to dry for 10 min,

weighed, and exposed to ultraviolet light for 68 hr. Similarly prepared plates were irradiated for 1 and 5 hr.

The dark yellow solid which formed in 68 hr was washed off the plate with ethyl acetate into a 250-ml volumetric flask and diluted to volume. The concentration of this solution was 1.88 mg/ml; it was used to spot tlc plates, along with a reference solution of photodieldrin (II). The developed plates were dried, sprayed with silver nitrate chromogenic solution, and exposed for 10 min under ultraviolet lamps. Dark brown spots were formed. The *R_f* value for dieldrin on this plate was 0.80.

The *R_f*'s relative to dieldrin (*R_d*) were: for standard photodieldrin, 0.55; spot 1 (photodieldrin), 0.58; spot 2 (unknown), 0.35; yellow spot at origin, 0.0 (unknown and designated VII).

The glc analysis of the solution yielded only one peak with the same retention time as that of unreacted II. About 58% of II appeared to be unconverted; by difference, 42% was converted to unknown products. As usual, any loss of weight after photolysis was minor.

SOLID STATE PHOTOLYSIS OF PENTACHLORODIELDRIN (IV)

Photolysis. Seventy-two mg of pentachlorodieldrin (IV) was placed in a small beaker and 1 ml of ethyl ether was added. The solution was transferred by a 1-ml syringe to a weighed, 3½ × 4 in. glass plate. The beaker was washed six times with ethyl ether, and each washing was transferred to the plate with the syringe. The dried plate was weighed again and the weight of pentachlorodieldrin was determined by difference. The plate was then exposed to ultraviolet light for the required time and reweighed, and the weight of the material remaining on the plate was determined by difference. The surface of the plate was washed with redistilled acetone and the acetone solution diluted to 100 ml. Plates 1, 2, and 3, treated in this manner and exposed for 1, 5, or 24 hr, showed weight losses of 0.6, 0.7, and 0.6%, respectively. The color of plate 1 was unchanged; plate 2 was a very pale yellow, and plate 3 was yellowish-tan.

Thin-Layer Chromatographic Analysis. Standards (19 µg) of dieldrin (I), pentachlorodieldrin (IV), and photodieldrin (II) were spotted on a silica gel G plate. Approximately 14 µg of material from solutions prepared from plates 1, 2, and 3 was also spotted. After development and AgNO₃ visualization, four spots were formed from each plate sample. For each plate, one of the spots (a) had an *R_f* similar to that of pentachlorodieldrin, another spot (c) had an *R_f* similar to that of photodieldrin, one spot (d) remained at the origin, and the fourth spot (b) represented an unknown compound, with an *R_d* of 0.65, 0.66, and 0.61 for plates 1, 2, and 3, re-

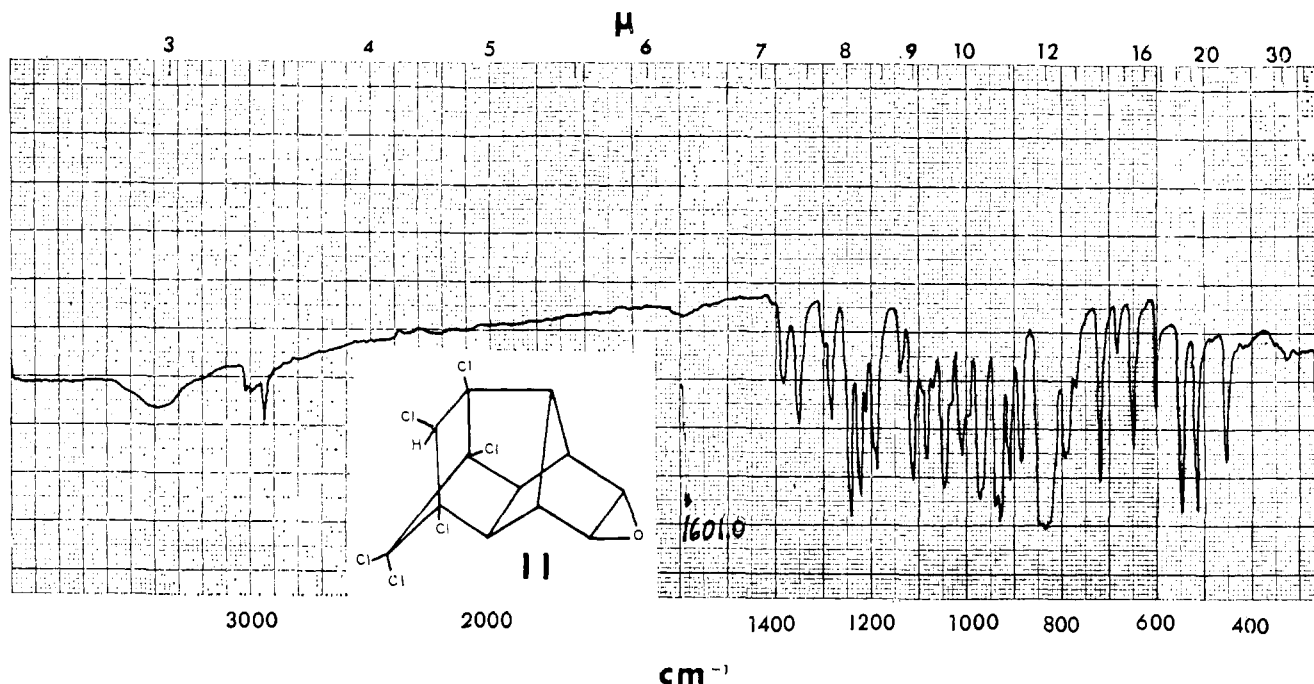


Figure 3. Infrared spectrum of II (photodieldrin)

spectively. In each case spot (a) was dark and intense, and did not appear to change with time of irradiation. Spot (b) became slightly darker as the time of exposure to ultraviolet light was increased, spot (c) remained at about the same intensity, and spot (d) became much darker with increased exposure.

Gas Chromatographic Analysis. Using the same conditions as before, 1.5 ng of pentachlorodieldrin standard was injected. The equivalent of about 1.5 ng of photolyzed pentachlorodieldrin was also injected. No other peak besides pentachlorodieldrin was observed. Comparison of peak areas of standard and of solutions from plates 1 and 2 showed that nearly all of the original pentachlorodieldrin (97–100%) was still present as such; plate 3 showed that only 71% of the starting material remained as pentachlorodieldrin.

RESULTS AND DISCUSSION

Solid State Photolysis. When solid dieldrin (I) was exposed to ultraviolet light for 1 hr, approximately 50% was converted to photodieldrin (II) and about 25% remained as unchanged dieldrin (I) (Table II).

The percentage that was converted to photodieldrin (II) was dependent on many factors, *e.g.*, the quantity of I on the glass plates, distribution on the plate, the evaporating solvent used, type of surface, light intensity, distance of light from surface, time of exposure, etc. Every effort was made to keep all factors constant except the one being studied.

Identities of II (or III) and IV. The structure of photodieldrin (see Figure 1, structures II and III) is disputed. Harrison *et al.*, who favor structure III, may not have had the benefit of examining the detailed nmr analysis of photodieldrin (Parsons and Moore, 1966). The material the latter used was prepared by photolysis of I in solution, and its nmr spectrum is identical to the high resolution (100 MHz) (in CDCl_3) nmr spectrum of photodieldrin prepared by solid state photolysis, which was obtained in this laboratory. However, the author's nmr spectrum of II in deuterated

acetone ($\delta = 5.33$ is a singlet and 2.48, 2.85, 3.20, 3.45 and 3.60 represent a multiplet involving 7 protons) is different from the published spectrum. Thus, the nmr spectrum of II has a strong dependence on solvent.

With regard to the remaining data on structures II and III, the mass spectrum of II (Table IV available from FDA) is indeed different from that of I, contrary to the reports of Harrison *et al.* (1967) and Robinson *et al.* (1966). Although various workers have disagreed on interpretation of the ir spectrum of II (Figure 3), the authors found it useful in establishing identity. Rosen (1967) has demonstrated that VI is converted to II. The melting point of compound II obtained in this laboratory agrees with that of Harrison *et al.* (1967) but not with others; these melting points have recently been corrected (Rosen and Carey, 1968). These discrepancies may be explained by different crystal formations (Lombardo *et al.*, 1969). The nmr and mass spectra data for II or III indicate that one hydrogen remains on the methano bridge and that, within the limitations of these considerations, II is a better representation of the structure of photodieldrin than III.

Dieldrin was converted not only to photodieldrin but also to two other materials. One substance, designated VII, was a yellow, polar, chlorinated organic material which did not respond under our glc conditions and remained at the origin under our tlc conditions. Compound VII could not be eluted from the silica gel. Some Compound II could be eluted from this material which remained at the origin. Evidently II was partly held by VII. Rosen and Sutherland (1967) have reported a polymeric material for which they gave two different average molecular weights, depending on the light source. The second material which did migrate under the tlc conditions used in this study (R_f 0.35) also responded to glc analysis. By tlc, ms, glc, and independent synthesis, this product appears to be the chlorohydrin of II (Benson *et al.*, 1970).

The possibility that Compound I might be lost by volatilization during the exposure to uv was considered. Lichtenstein *et al.* (1968) showed that aldrin and dieldrin were volatil-

ized to a great extent from inside and outside agar and from glass surfaces. However, these investigators used only 10 μ g over a 24-hr period. Roburn (1963), who also worked with small quantities (50–100 μ g), did not report yields of II because he thought that a portion of the product and starting material was lost through volatilization. The work reported here generally represents approximately 1×10^5 times as much material, used over short periods of time. Losses due to volatilization were small relative to the amounts involved. The lamps used gave little buildup of heat. Temperatures for 1-hr exposures were near room temperature; in the 68-hr exposures the temperatures reached 40° C.

To determine whether photodieldrin was an intermediate in the formation of the polar materials similar to Compound VII, photodieldrin was sprayed onto three glass plates and exposed for 1, 5, and 68 hr, respectively. At 1 and 5 hr of exposure there appeared to be little or no reaction with light, but at 68 hr of exposure about 42% of II (by difference) was converted to compounds which were not detected by glc, although little if any loss in weight occurred. Analysis by tlc indicated that two products were formed—a polar yellow material (R_d 0.0) and an unknown material with a relative R_d value of 0.35 (dieldrin = 1.00); thus, II may be the intermediate between I and the other two photoproducts.

Conversion rate of I to II on photolysis was higher when I was sprayed onto a glass plate than when it was poured. By the pouring technique, 28.1% of the dieldrin was converted to photodieldrin, and 52.1% remained unconverted. Streaking small quantities on a tlc plate gave about a 45% conversion to photodieldrin II.

It was necessary to pour solutions 14 C-dieldrin onto plates before photolyzing in the solid state to avoid contaminating the hood. This method of preparation appears to be rapid (1 hr of photolysis) and could also be used to prepare the unidentified side products of the photolysis which separate during tlc development and which do not pass rapidly through the gas chromatographic procedure. This procedure also uses low cost materials which can be discarded after 14 C-contamination with little economic loss.

To determine whether IV (pentachlorodieldrin) would undergo a reaction similar to the formation of II from I, three glass plates were coated with IV and exposed to uv light. Compound IV appeared to be relatively stable in the solid state up to 5 hr. After 24 hr of exposure, glc showed only 1 peak, that of IV; however, only 71% of IV remained, while a yellow, polar component was observed in the tlc analysis (R_f 0.0). Apparently the formation of two possible cage structures similar to II did not occur. As with I, very little of IV or the reaction products appeared to evaporate from the plate; whether exposure lasted 1 hr or 24 hr, total "loss" was about 0.6% and approached the weighing error for the small coated plates.

Glc data (Figure 2) indicate that IV could be resolved from I by this system but not by the systems reported elsewhere; the molecular weight corresponded to that reported by Henderson and Crosby (1967). An analysis of the mass spectrum of IV indicates m/e of 79 (100%) and 81 (65%), which are typical of dieldrin, *viz.*, 79 (100%) and 81 (30%), whereas the ratio for photodieldrin II is different, *viz.*, 79 (22%) and 81 (100%). IV also shows strong peaks for M-Cl (309). The mass spectral data for IV are consistent with the m/e 309 ion fragmenting in a retro Diels-Alder reaction to the m/e 227 (39%) representing the tetrachlorobicycloheptadiene ion ($C_7H_3Cl_4$) and m/e 81 (100%) representing C_5H_5O . These data are consistent with the literature on the mass spectrum of dieldrin (Damico *et al.*,

1968a), and thus, all the data of this study confirm the structural assignment of IV.

Two attempts were made to convert II to V, to confirm the structures of II and V (Damico *et al.*, 1968b) by reaction with silver tetrafluoroborate in DMSO, and by reaction with NaOEt and DMSO. Both attempts were inconclusive, but loss of one Cl atom was indicated. Before this work could be completed, Adams and Mackenzie (1969) found that isodrin, aldrin, and related fused polychloro-norbornenes are stereospecifically dechlorinated with sodium methoxide in methanol-dimethyl sulfoxide. This appeared to be happening under the present conditions as well. Infrared, nmr, X-ray analysis, and chemical studies on related strained model systems would allow more positive assignments.

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