

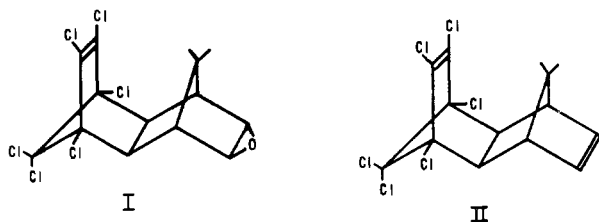
Photodecomposition of Dieldrin and Aldrin

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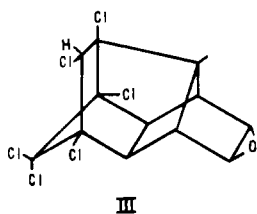
The ultraviolet irradiation of dieldrin solutions yields as a major product a pentachloro derivative that is less toxic than dieldrin to flies but more toxic to mice. Aldrin also is dechlorinated under these

conditions. This reaction requires irradiation at wavelengths lower than those found in sunlight, and the dechlorinated products have not been detected under field conditions.

The effect of sunlight and laboratory ultraviolet light on pesticides has recently received considerable attention. Rightly so, since any alteration of the compounds under field conditions may seriously affect their residual activity or toxicity. Mitchell (1961) reported that the important cyclodiene insecticides dieldrin (I) and aldrin (II) were decomposed by ultraviolet light at



2537 Å. Recently, Robinson *et al.* (1966) and Rosen *et al.* (1966) isolated and determined the structure of an unknown compound which had been reported earlier by Roburn (1963) as being present on grass treated with dieldrin and exposed to sunlight. Robinson prepared the photoproduct by irradiating at 2537 Å. a thin film of dieldrin deposited on filter paper, while Rosen's experiments involved solid films deposited on glass plates. The decomposition product was identified as an isomer of dieldrin in which intramolecular bridging had occurred to give compound III.



Our laboratory has examined the effect of ultraviolet light on dieldrin and aldrin in solution. Irradiation was accomplished with a variety of ultraviolet light sources as well as by exposure to spring and summer sunlight, with the purpose of isolating and identifying other decomposition products formed under these conditions,

determining their toxic properties, and seeking their presence under field conditions.

EXPERIMENTAL

Chemicals. Dieldrin (1,2,3,4,10,10-hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydro-1,4-*endo,exo*-5,8-dimethanonaphthalene), was obtained from the Shell Development Co., Modesto, Calif., and recrystallized from hexane to greater than 99.9% purity as determined by gas chromatography, m.p. 174–75° C.

Aldrin (1,2,3,4,10,10-hexachloro-1,4,4a,5,8,8a-hexahydro-1,4-*endo,exo*-5,8-dimethanonaphthalene), m.p. 104–05° C., also was obtained from the Shell Development Co. and purified in the same manner as dieldrin.

Hexane, acetone, and benzene were of nanograde quality from the Mallinckrodt Chemical Works, St. Louis, Mo.

The chromogenic reagent used for the detection of chlorinated compounds on thin-layer chromatograms was prepared from reagent grade silver nitrate and 2-phenoxyethanol (Distillation Products Industries, Rochester, N. Y.) according to the directions of Mitchell (1961).

Irradiation Apparatus. Irradiations in solution were carried out in an immersion-type ultraviolet irradiation vessel (Figure 1) which consisted of a water-jacketed flask (A) fitted with a quartz sleeve (B) into which a spiral low-pressure mercury arc lamp (C) was inserted and attached to a 0–5000-volt a.c. power supply (Nester and Faust, Inc., Newark, Del.). Nitrogen or air could be bubbled through the vessel from the inlet (D), and the side arm (E) could be connected to a gas trap containing aqueous silver nitrate solution. Solutions were stirred during irradiation with a magnetic stirrer and stirring bar. A borosilicate glass sleeve (30-mm. O.D.) could be substituted for the quartz sleeve to filter out light of wavelengths shorter than 2800 Å.

Corn leaf surfaces were irradiated with a 360-watt Raymaster high-pressure mercury lamp (George W. Gates and Co., Franklin Square, N. Y.), and thin-layer chromatographic plates were irradiated with a low pressure germicidal lamp (George W. Gates and Co.) containing a Westinghouse G8T5 tube. All three lamps produced a peak intensity at 2537 Å.

A Fluorispec fluorescence spectrophotometer Model SF-1 (Baird-Atomic, Inc.) was used as a monochromatic light source. The xenon lamp excitation monochromator provided an irradiation source with a 32-m μ bandwidth.

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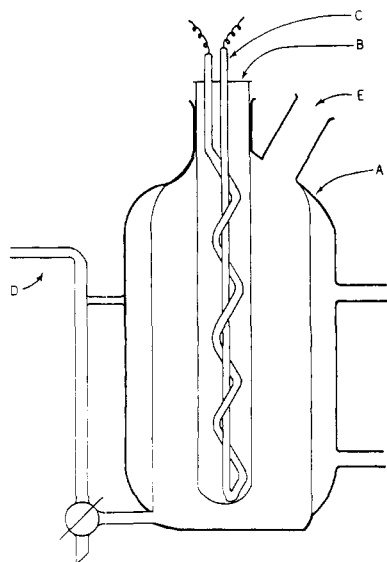


Figure 1. Irradiation apparatus with water jacket (A), quartz sleeve (B), arc lamp (C), gas inlet (D), and side arm (E)

Gas Chromatography. Several types of gas chromatographic equipment were employed during this investigation. The F and M Model 720 gas chromatograph was equipped with a thermal conductivity detector, a 2-foot \times $\frac{1}{4}$ -inch O.D. stainless steel column packed with 10% SE-30 gum rubber on 60- to 80-mesh Chromosorb P. The Aerograph 680 Pestilyzer gas chromatograph (Varian-Aerograph Corp., Walnut, Calif.) utilized an electron-capture detector, a 5-foot \times $\frac{1}{8}$ -inch O.D. glass column packed with 5% Dow 11 silicone oil on 60- to 70-mesh Chromosorb W treated with HMDS. The Aerograph Model 204 gas chromatograph employed an electron-capture detector, 6-foot \times $\frac{1}{8}$ -inch O.D. glass column packed with 10% DC-200 silicone oil on 110- to 120-mesh Anakrom ABS, while the Aerograph Autoprep Model A-700 equipped with a 50:1 stream splitter, flame ionization detector, and an electrostatic precipitator, contained a 6-foot \times $\frac{3}{8}$ -inch O.D. stainless steel column packed with 5% Dow 11 silicone oil on 60- to 80-mesh Chromosorb P.

Thin-Layer Chromatography. A slurry containing 40 grams of silicic acid mixed with 95 ml. of distilled water was applied to the surface of 200 \times 200 mm. glass plates with a commercial spreader set to provide a layer thickness of 0.5 mm. The plates were allowed to stand for 15 minutes and then were dried overnight in an oven at 110° C., allowed to cool, and stored in a desiccating cabinet.

Aliquots of the undiluted irradiated solution and reference solutions of dieldrin and aldrin were applied as spots with a microliter syringe about 3 cm. from the lower edge of the plate. The chromatograms were developed in the ascending direction with a variety of solvents and solvent mixtures. The developed plates were dried, sprayed with silver nitrate chromogenic solution (Mitchell, 1961), and then exposed for 3 minutes under the ultraviolet lamp. Chlorine-containing compounds appeared as dark brown or black spots.

Irradiation of Dieldrin and Aldrin Solutions. Purified samples of dieldrin were irradiated at room temperature in solution in the irradiation apparatus. Hexane served as solvent when the photoreaction was carried out on the preparative scale. Irradiations also were carried out in cyclohexane and in methanol, and the same photoproduct was formed regardless of which of the three solvents was used.

An amount of the photodecomposition products of dieldrin and aldrin sufficient for structure elucidation was obtained by irradiating solutions containing 2 grams of the insecticide dissolved in 1 liter of hexane in the irradiation apparatus. Nitrogen was bubbled through the solution and then passed through a gas trap containing an aqueous solution of silver nitrate; silver chloride precipitated as the irradiation proceeded. The nitrogen gas served only as an aid in trapping volatile chlorine-containing compounds and played no apparent role in the photolysis reaction. Irradiations carried out in the presence of air gave the same product composition, although solvent loss through evaporation was reduced. Discoloration of the liquid was observed, and the solution became yellow as the irradiation progressed. The irradiated solution also was observed to have a sharp, pungent odor.

Greater than 50% conversion to the photoproduct was accomplished with an irradiation time of 8 hours. For preparative work, the solution was irradiated for 24 hours, after which the volume was reduced to 100 ml. with a rotary evaporator. An aliquot (10-ml.) was removed for chromatographic analysis, and the remaining 90 ml. of solution was concentrated on a rotary evaporator to a thick, viscous yellow liquid.

An aliquot (1.0-ml.) of the 10-ml. sample of the irradiated solutions saved for chromatographic analysis was diluted to 10 ml. with acetone, and 100- μ l. portions of the dilute solution were injected into the F and M Model 720 gas chromatograph (helium flow 40 ml. per minute, temperature 176° C.). Dieldrin had a retention time of 9.5 minutes under these conditions, and the photoproduct, which was the only other compound detected in significant quantity, had a retention time of 7.2 minutes. Under these conditions, aldrin had a retention time of 3.5 minutes and the aldrin photoproduct had a retention time of 2.8 minutes.

Isolation and Identification of the Photoproducts. The concentrated, irradiated solution of dieldrin was allowed to stand at room temperature for one week. The photoproduct crystallized as a white precipitate, while the dieldrin remained as a viscous oil. The photoproduct was removed by filtration and recrystallized from hexane; the resulting white needles were similar in appearance to dieldrin and had a melting point of 104° C. (dieldrin m.p. 174–75° C.).

ANALYSIS. Calculated for $C_{12}H_9Cl_3O$: C, 41.6; H, 2.6; Cl, 51.2. Found: C, 41.8; H, 2.3; Cl, 49.6.

The irradiated solution of aldrin also was concentrated to a yellow viscous liquid and allowed to stand at room temperature for a week. Crystals appeared in the liquid at this time, but were found to be unchanged aldrin; the photoproduct remained behind in the solution and could not be made to precipitate. It was separated by preparative gas chromatography, using the Aerograph

Autoprep Model A-700; 100- μ l. portions of a solution containing 20 mg. of the irradiation aldrin concentrate per milliliter were injected into the gas chromatograph, and the effluents corresponding to the photoproduct peak on the chromatogram were collected repeatedly. The collected white solid showed only one peak when reinjected into the gas chromatograph. The product was recrystallized from hexane and further purified by vacuum sublimation at room temperature (0.075 torr.). The resulting white crystals exhibited a melting point of 87–89° C. (as compared to 104–05° C. for aldrin).

ANALYSIS. Calculated for $C_{12}H_9Cl_3$: C, 43.6; H, 2.8; Cl, 53.6. Found: C, 44.3; H, 2.8; Cl, 52.9.

The pure photodecomposition products were subjected to a variety of spectral measurements. Infrared spectra were determined in potassium bromide disks on Perkin-Elmer Model 421 and Model 337 spectrophotometers. Ultraviolet spectra were measured in hexane or ethanol solutions on a Beckman DK-2A recording spectrophotometer. Mass spectra were recorded on a Perkin-Elmer Hitachi Model RMU-6D single-focusing instrument by direct introduction into ion source. Nuclear magnetic resonance (NMR) spectra were determined with a Varian DP-60 instrument as solutions in deuteriochloroform with a tetramethylsilane internal standard.

Solar Irradiation of Corn Leaves Treated with Dieldrin.

Corn seeds were planted in a 35 \times 50-cm. flat by broadcasting them to give a dense carpet of leaves upon germination. After a growing period of 9 days in the greenhouse, the young corn plants, now 6 inches high, were sprayed with 40 ml. of a solution containing 0.2 gram of dieldrin, 40 ml. of acetone, 20 ml. of water, and 0.5 ml. of Tween 20. Care was taken to coat the leaves evenly by using a fine spray from an aspirator-type reagent sprayer. After drying, a white residue was visible, and about 20% of the leaves were harvested immediately and used as a control. The flat was placed out of doors in the intense sunlight of late spring and early summer in an area that received little or no shade. The plants were watered daily at their base so as not to wash off any of the applied insecticide.

Equal portions of the flat were harvested at 6, 17, and 64 days and analyzed. The harvested leaves were washed, with agitation, for 5 minutes with 250 ml. of benzene in a 1-liter flask; the leaves were stripped quickly with benzene, rather than extracted at length with a polar solvent, to avoid interference by plant materials. The benzene extract was filtered, dried over anhydrous magnesium sulfate, filtered again, and analyzed with the Aerograph Model 680 gas chromatograph equipped with an electron-capture detector. The temperature was maintained at 196° C. and the nitrogen carrier gas flow rate set at 40 ml. per minute.

Laboratory Irradiation of Corn Leaves Treated with Dieldrin. A single blade of a 4-week-old corn plant was tied securely with thread and taped at each end to a piece of cardboard that was supported by clamps from ring stands. The leaf was sprayed with 2 ml. of a solution containing 10 mg. of dieldrin, 10 ml. of acetone, 4 ml. of water, and 2 drops of Tween 20. The sprayed leaf was allowed to dry and then was irradiated for 15 minutes by a high pressure mercury arc lamp placed 6 inches above its

surface. The leaf subsequently was cut into 2-inch pieces and placed in a 1-liter flask to which 250 ml. of benzene was added. The flask was agitated on a rocker table for 5 minutes and the solution was then decanted, dried over anhydrous magnesium sulfate, filtered, and analyzed with the Aerograph Model 680 gas chromatograph (temperature 180° C. and nitrogen carrier gas flow rate 40 ml. per minute).

Irradiation of Dieldrin with Monochromatic Light. A round quartz cuvette of 5-ml. capacity was filled with a solution of dieldrin (1 mg. per ml.) in hexane. The quartz cell was placed in the spectrophotofluorometer and irradiated for 24 hours at a selected wavelength. There was no significant increase in temperature, but the irradiation was interrupted briefly every 4 hours to replenish solvent lost to evaporation. Irradiations were conducted at 100-A. intervals beginning at 3000 A. and decreasing to 2500 A. The entrance spectral slit was opened to the widest position for maximum incident radiation and provided a spectral bandwidth of 320 A.

After irradiation, aliquots of the irradiated solution were removed and analyzed with the Aerograph Model 204 gas chromatograph (electron-capture detector, temperature 195° C., and nitrogen flow rate 50 ml. per minute). Dieldrin had a retention time of 16 minutes, and the photoproduct had a retention time of 12 minutes under these conditions.

Toxicity Measurements. To determine the toxicity of dieldrin and the dieldrin photoproduct to houseflies, 1- μ l. drops of an acetone solution containing a measured amount of the compound were applied topically to the pronotum of insecticide-sensitive female flies at one to three days of age. The amount of dieldrin applied to the flies increased in increments from 0.00175 to 0.042 μ g. per fly, the former providing 0% mortality and the latter 100% mortality. The amount of photoproduct applied increased in increments of 0.014 to 0.063 μ g. per fly. Ten flies were exposed at each dosage level, a total of 10 dosage levels was employed (including the control) for each test, and four replications for dieldrin and three replications for the photoproduct were made. The flies were anesthetized briefly with CO_2 prior to the application and after treatment were provided with a standard housefly diet and maintained at a temperature of 27° C. After 24 hours, the per cent mortality was determined, and the LD_{50} for each compound was determined by means of the computer program for probit analysis developed by Spratt (1966).

The acute oral toxicities of dieldrin and the photoproduct were measured with young adult male mice of the Swiss strain. Weighed amounts of the compounds were dissolved in corn oil and introduced orally via stomach tube (1.27-mm. O.D.). The amount of dieldrin administered ranged from 31 to 187 mg. per kg., and the amount of photoproduct ranged from 5 to 125 mg. per kg. A total of 53 animals was treated with dieldrin, and a total of 38 animals received the photoproduct. After treatment, the animals were provided with food and water *ad libitum* and maintained at 26° C. The percentage mortality was determined after 48 hours, and the LD_{50} for each compound was determined with the computer program for probit analysis.

RESULTS AND DISCUSSION

Analysis by gas chromatography of solutions irradiated with 2537-A. light revealed that dieldrin and aldrin were photolyzed in solution to form, in each case, a single major degradation product in a significant quantity. A sufficient amount of these photoproducts was prepared for structure elucidation by irradiating hexane solutions of the parent insecticides in an immersion-type irradiation apparatus. The solubility characteristics, gas chromatographic retention times, and thin-layer chromatographic R_f values of the decomposition products were so similar to those of the parent compounds that detection and isolation by these means generally proved to be extremely difficult. Furthermore, the photoproducts differed only slightly in chemical reactivity from dieldrin and aldrin, and so principal reliance was placed on spectrometric methods for the determination of their structures.

The infrared spectra of dieldrin and its photoproduct were very complex, but the principal functional group, the epoxide, was represented in each instance by a strong band at 840 cm^{-1} . The similarity of the spectra (Figure 2) indicated no loss of major structural features or addition of new functional groups during irradiation.

The mass spectrum showed a parent peak at m/e 344, corresponding to a likely empirical formula of $\text{C}_{12}\text{H}_9\text{Cl}_5\text{O}$. A trace of dieldrin, mass 378, also was present as an impurity. Although not entirely satisfactory because of this impurity, elemental (combustion) analysis of the photoproduct likewise indicated an empirical formula of $\text{C}_{12}\text{H}_9\text{Cl}_5\text{O}$, suggesting that dieldrin simply had undergone monodechlorination during photolysis. The NMR spectrum of the photoproduct (Figure 3) supported this conclusion with a multiplet centered at $8.8\ \tau$, a doublet at $7.30\ \tau$, a singlet at $6.95\ \tau$, and a singlet at $4.0\ \tau$. The peak

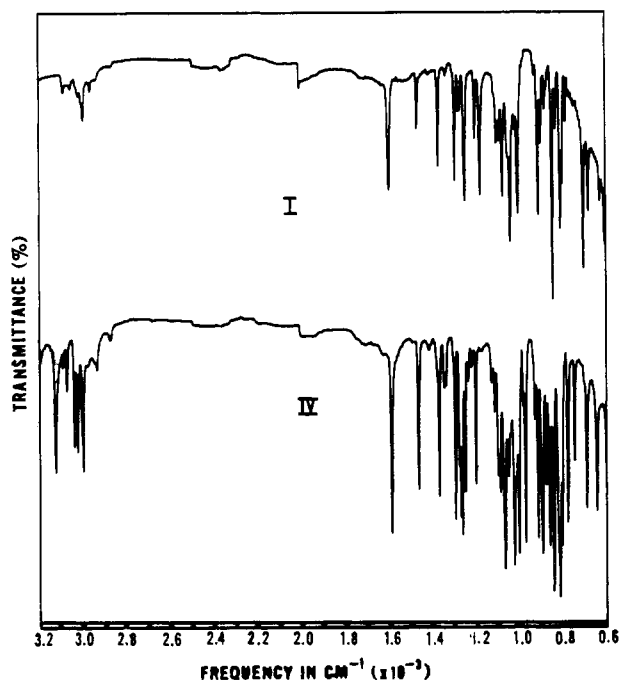
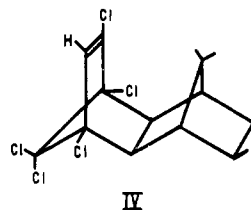
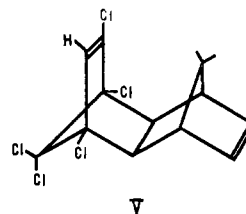


Figure 2. IR spectrum of dieldrin (I) and photoproduct (IV)

areas were in a ratio of 2:4:2:1. A comparison of the NMR spectrum of the photoproduct with that of dieldrin showed only the net addition of one vinyl proton. Thus, the endo, exo configuration of dieldrin appeared to have remained unchanged and one of the vinyl chlorine atoms was replaced by a hydrogen atom. On the basis of this physical evidence, the photodecomposition product of dieldrin was assigned structure IV.



The elemental analysis of the purified photoproduct of aldrin indicated an empirical formula of $\text{C}_{12}\text{H}_9\text{Cl}_5$, which suggested that aldrin had been dechlorinated as in the case of dieldrin. The infrared spectrum was consistent with this interpretation. The mass spectrum of the photoproduct did not show a clear parent peak at m/e 328 which would correspond to the proposed formula, but the cracking pattern was consistent with the proposed structure. The NMR spectrum of the compound (Figure 4) contained a doublet at $8.74\ \tau$, a doublet at $7.85\ \tau$, and singlets at 7.3 , 7.12 , 4.07 , and $3.7\ \tau$, the peak areas representing a ratio of 1:1:2:2:1:2. This NMR spectrum represents the net addition of one vinyl proton and, as was the case with dieldrin, the endo, exo configuration was retained. This physical evidence supports the proposed structure V for the major photolysis product of aldrin.



Although the correlation of insecticidal activity and molecular structure of the cyclodiene insecticides has been the subject of intensive research for many years (Soloway, 1965), the synthesis of compounds possessing a hydrogen atom at positions 2 or 3 has not previously been successful. Most modifications of the chlorinated ring of dieldrin (and aldrin) result in greatly reduced insecticidal activity (Table I), but substitution of hydrogen for both the 2- and 3-chlorines causes an almost 4-fold increase in the toxicity to houseflies. The LD_{50} of IV was found to be 29.6×10^{-9} gram per fly (dieldrin LD_{50} 17.8×10^{-9} gram per fly), giving it a relative toxicity of 60 compared to the parent insecticide.

Dieldrin is one of the more toxic of the chlorinated hydrocarbon insecticides to mammals and exhibits an unusually steep toxicity gradient. The photoproduct (IV) was found to be about 5 times more toxic to mice

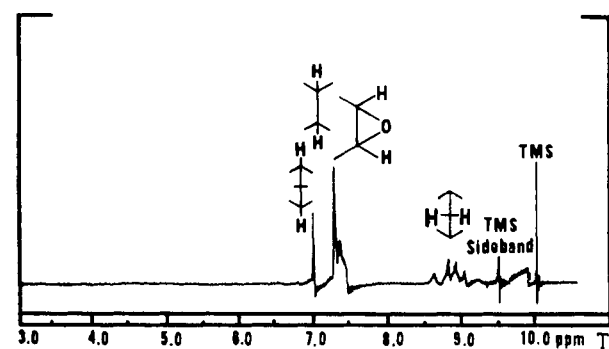
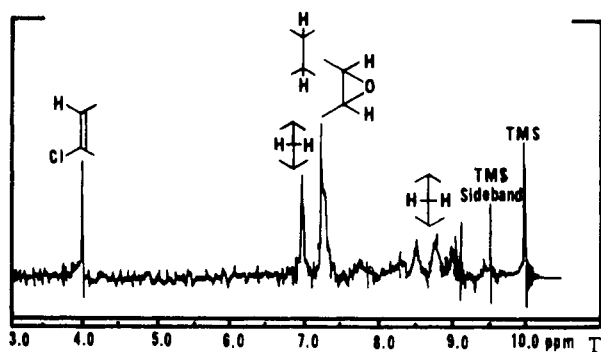


Figure 3. NMR spectra of dieldrin (bottom) and photoproduct IV (top)

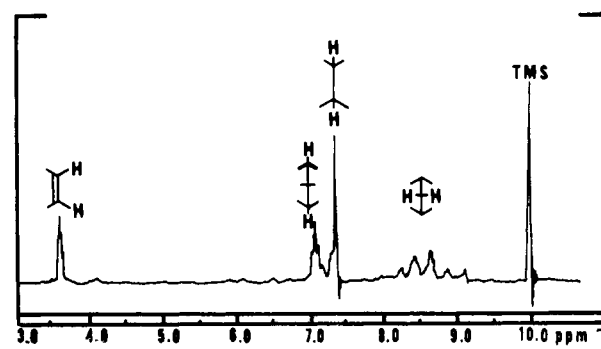
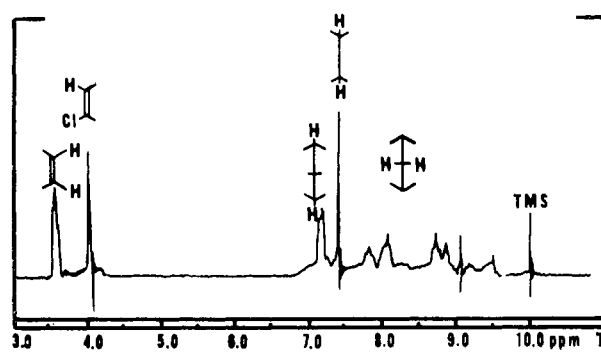


Figure 4. NMR spectra of aldrin (bottom) and aldrin photoproduct V (top)

(LD_{50} 15.9 mg. per kg.) than was dieldrin (LD_{50} 74.1 mg. per kg.), and its toxicity gradient was equally steep.

This increased mammalian toxicity and the striking similarity of the solubility and chromatographic properties of I and IV prompted a search for the photoproduct under field conditions. Gas chromatographic analysis of the residue remaining on corn plants which had been treated with dieldrin and exposed to sunlight showed that none of the pentachloro compound was formed. Instead, another substance appeared which was identified as the photoisomerization product (III) by comparison with an authentic specimen. However, when the dieldrin-treated leaves were exposed to 2537-A. ultraviolet light in the laboratory, considerable amounts of IV were found after only 15 minutes of irradiation.

To determine at which wavelengths the photodechlorination occurred, hexane solutions of dieldrin were irradiated in a spectrophotofluorometer which served as a source of monochromatic light. Examination of the solutions irradiated at wavelengths between 2500 and 3000 A. showed maximum conversion of I to IV at 2500 A.; no conversion occurred at wavelengths above 2600 A. Likewise, when dieldrin was irradiated in the immersion vessel with the light source shielded by a borosilicate glass sleeve which filtered out light of wavelengths below 2900 A., no formation of IV was detected. The monodechlorination of dieldrin apparently requires short-wavelength, high-energy ultraviolet light—that is, light of 2600-A. wavelength or lower. Since the earth's atmosphere is effective in absorbing all light of wavelengths less than about 2863 A. (Koller, 1965), this particular reaction

Table I. Insecticidal Activity of Dieldrin Analogs (Soloway, 1965)

Compound	Relative Toxicity to <i>Musca domestica</i> (Dieldrin = 100)
(I)	100
(II)	35
(IV)	60
(VI)	380
(VII)	8
(VIII)	2
(IX)	2

would not be expected to occur in the field during exposure to natural sunlight.

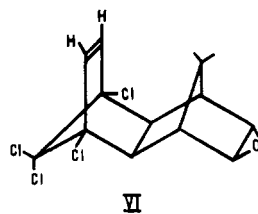
That the dechlorination of dieldrin is wavelength-dependent is also suggested by the ultraviolet spectrum of the compound. Absorption of light energy must take place before a photochemical reaction can occur, and the spectrum of a hexane solution of dieldrin shows only a

single absorption band appearing at 2600 Å. and reaching a maximum extinction at 2150 Å. According to this spectrum, dieldrin is essentially transparent to light of wavelengths greater than 2600 Å. and, in accord with the spectrophotofluorometer studies, should be photochemically inert to the longer wavelengths represented by normal sunlight.

However, dieldrin apparently actually is converted to III in sunlight. Although the 2150-Å. absorption may be attributed to the carbon-carbon double bond, possibly only very small amounts of energy may be required to bring about such photochemical reactions as the intramolecular cyclization of dieldrin in which steric factors are highly favorable. The wavelengths and intensities common to sunlight may then be sufficient to cause such chemical changes directly.

Despite its presence under field conditions, III could not be detected after irradiation of dieldrin solutions at wavelengths between 2500 and 3000 Å., although IV was formed below 2600 Å. as described. The occurrence of III always has been observed under conditions of high concentration, in solution, or in the solid state (Robinson *et al.*, 1966; Rosen *et al.*, 1966), which should favor the intramolecular reaction of carbon 2 with the closely adjacent hydrogen on the methylene bridge. In dilute solutions such as those employed here, which provide a very large molar excess of a hydrogen donor such as hexane, the replacement of chlorine by hydrogen appears to predominate.

The energy absorbed at 2150 Å. by the double bond of dieldrin may be redistributed to bring about rupture of the carbon-chlorine bond. Compound IV likewise contains a carbon-carbon double bond adjacent to a carbon-chlorine bond, and its ultraviolet absorption spectrum is very similar to that of dieldrin; however, no trace of the known compound VI containing hydrogens on both carbons 2 and 3 was ever detected. At present, then, the photodechlorination can be applied only to compounds possessing chlorines on both carbons adjacent to the double



bond. However, a number of chlorinated hydrocarbon insecticides, including heptachlor, chlordan, endrin, telodrin, and thiodan probably will undergo this reaction.

ACKNOWLEDGMENT

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