Photochemistry of Bioactive Compounds

## Studies of a Major Photolytic Product of Endrin

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Endrin (1,2,3,4,10,10-hexachloro-6,7-epoxy-1,4,4a,- 5,6,7,8,8a-octahydro-1,4-*endo,endo*-5,8-dimethano- naphthalene) was found to be cleanly converted by irradiation at 253.7 nm, 300 nm, and in sunlight in cyclohexane and hexane solution to a half-cage ketone compound, 1,8-*exo*-9,11,11-pentachloropen- tacyclo[6.2.1.1^{3,6}.0^{2,7}.0^{4,10}]dodecan-5-one, in yields up to 80%. This photoproduct (XI) was found to be highly resistant to the usual oxidation and reduc- tion procedures. Compound XI has been detected in fields where Endrin has been applied.


The fate and persistence of organic pesticides have been given considerable attention recently. The widespread application of pesticides has preceded their in-depth studies of the potential long-range health hazards to man and effects on his environment. The chemical fate, especially under field conditions, of many of these pesticides is still unknown. The need and importance of such photo- chemical research are dramatic when one considers the unexplored risks of the present applications of organic pesticides to our environment.

Effects of sunlight and laboratory ultraviolet light on pesticides have been investigated with renewed interest in the past decade, due in part to the exciting advances in the field of organic photochemistry (Dilling, 1966). Mitchell (1961) reported that two cyclodiene insecticides, Dieldrin (I) and Aldrin (II), were decomposed by irradiation at 253.7 nm. Roburn (1963) later reported a photoproduct of Dieldrin present on grass exposed to sunlight. Robinson *et al.* (1966) and Rosen *et al.* (1966) isolated and determined the structure of this Dieldrin photoproduct. Both prepared the same photolysis product by irradiation (253.7 nm) of thin films of solid Dieldrin. The product was identified as an isomer of Dieldrin in which intramolecular bridging had occurred to give compound III.


I

II

III
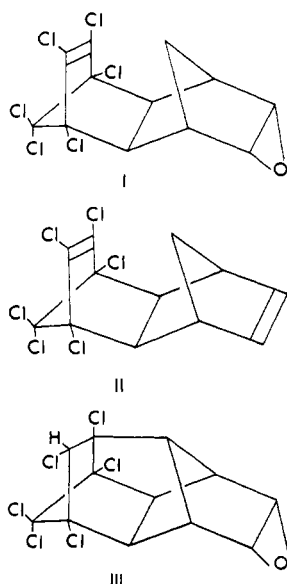
Henderson and Crosby (1967, 1968) studied the photo- decomposition of I and II in solution. Irradiation of I and

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II in hexane, cyclohexane, or methanol at 253.7 nm resulted in the formation of their respective photodechlorination products IV and V. Photolysis did not occur under labora- tory conditions at wavelengths greater than 280 nm. These photodechlorination products IV and V have not been detected under field conditions.

IV

V
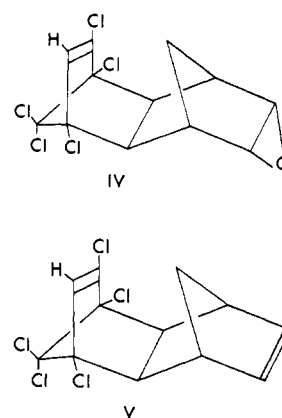
A widely used member of the class of chlorinated hydro- carbon insecticides is Endrin (1,2,3,4,10,10-hexachloro-6,7- epoxy-1,4,4a,5,6,7,8,8a-octahydro-1,4-*endo,endo*-5,8-dimetha- nonaphthalene) (VI). Interest in Endrin has arisen for two reasons: its use as an effective broad spectrum and low cost pesticide; and its unique stereochemistry which allows it to undergo a variety of reactions, from simple addition to complex transannular rearrangements (Bird *et al.*, 1961; Bruck *et al.*, 1960; Cookson and Crundwell, 1958, 1959; DeVries and Winstein, 1960; Phillips *et al.*, 1962; Soloway, 1960).


VI
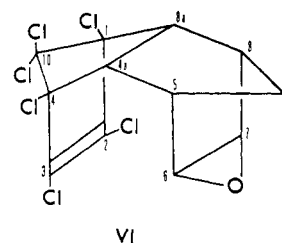
A reasonable avenue for the disappearance of Endrin under field conditions is by photochemical reactions and rearrangements as the result of irradiation by sunlight.

Roburn (1963) reported qualitatively that Endrin was converted to new compounds by irradiation of the deposited solid at 253.7 nm. Rosen *et al.* (1966) and Rosen and

Sutherland (1967) isolated the ketone VII and the aldehyde VIII in 37 and 9% yields, respectively, after irradiation of

VII
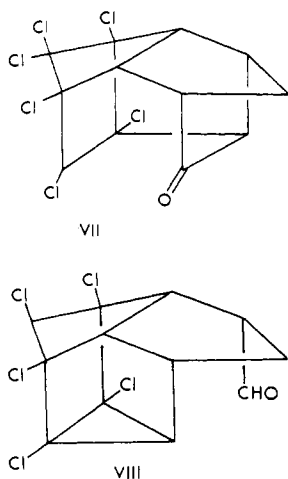
VIII

Endrin at 253.7 nm. Compounds VII and VIII had been reported by Phillips *et al.* (1962).

A different initial approach would be to study the photolysis of Endrin in solution. More exacting conditions can be attained in solution-phase *vs.* solid-phase irradiation. Since Endrin is usually applied in the form of 20% active ingredients in a hydrocarbon solvent, two such inert solvents were chosen: hexane and cyclohexane. Therefore photolysis experiments were carried out in these laboratories to ascertain whether Endrin undergoes photochemical rearrangements in solution.

EXPERIMENTAL MATERIALS AND METHODS

Purification of Endrin. Endrin was obtained from the commercial Endrin Emulsible Concentrate (20% Endrin in 73% petroleum hydrocarbons). Solvent was evaporated and the residue recrystallized from absolute ethanol until no variation in the melting point was observed and gas chromatography gave a single peak. Chemical authenticity was supported by infrared (ir) and nuclear magnetic resonance (nmr) spectra.

Solvents. The hexane and cyclohexane solvents used in the photolysis reactions were classified as nanograde-distilled in glass (Burdick and Jackson Laboratories, Inc., Muskegon, Mich.). At all other times, analytical grade solvents were used.

Photochemical Equipment. Reaction vessels were of borosilicate glass and fitted with Teflon stopcocks and accessories. Standard taper (60/50) Asco Quorn sleeves (Arthur F. Smith Co., Inc., Pompano Beach, Fla.) were used as seals between the ground glass tapers of the reaction vessel and the inserted immersion well. There was a usable volume of approximately 550 ml after the standard reaction vessels were fitted with an immersion well. Photochemical lamps, immersion wells, and absorption sleeves were obtained from Hanovia Lamp Division, Engelhard Hanovia, Inc., Newark. In all experiments, clear, fused quartz immersion wells (water-cooled) were used to hold the ultraviolet (uv) source inside the reaction vessel. A 250-W type S and a 450-W type L laboratory photochemical lamp were used as the uv sources. These lamps emitted a continuous spectrum from 1367.3 nm in the ir to at least 222.4 nm in the far uv region, with a primary uv emission at 253.7 nm. Absorption sleeves consisted of three types of glass: 7910 Vycor, 9700 Corex, and 7740 Pyrex (with uv cut-offs at 210, 250 and 280 nm, respectively).

Photolysis was also carried out in a Rayonet Southern N.E. photochemical reactor (The Southern N.E. Ultraviolet Co., Middletown, Conn.). Three lamp-types were used interchangeably, emitting radiation of 253.7, 300, and 360 nm (Cat. No. N.P.R.-2537, N.P.R.-3000, and N.P.R.-3600, respectively).

Water-cooled, quartz immersion wells were used to maintain a constant solution temperature during photolysis. Reactions were carried out at 21° C using a magnetically stirred system.

Analytical Equipment. All melting points were uncorrected and determined on a Hoover capillary melting point apparatus. Infrared spectra were recorded with a Perkin-Elmer Model 337 grating spectrophotometer. Visible and uv spectra were obtained in spectrophotometric grade solvents and recorded with a Beckman Model DB and Model DU instrument, respectively. Nuclear magnetic resonance spectra were recorded using a Varian A-60 and a Jelco C 60-H high resolution spectrometer. Tetramethylsilane was used as an internal standard. Samples were dissolved in spectrophotometric grade carbon tetrachloride, deuterated methylene chloride-d_2, chloroform-d_1, or in dimethylformamide-d_7.

Gas-liquid chromatographic analyses were accomplished with a Beckman Model GC-4 instrument, and equipped with electron-capture and flame-ionization detectors. Gas chromatography columns were of borosilicate glass, 6 ft × 1/8 in. i.d. Prepurified helium (99.997% purity) and nitrogen were used as the carrier gases in electron-capture and flame-ionization detection, respectively. Carrier gas flow was 40 ml per min. The following temperature parameters were employed: column temperature 220° C, inlet temperature 260° C, and detector temperature 280° C. A 5% Dow 11, 1% NGS, and a 2$^1/_2$% SE-30 liquid phase on 60/80 mesh Chromosorb W, and a 11% OV-17/QF-1 liquid phase on Gas Chrom Q (1:3) were used as the column packings (Applied Science Laboratories, Inc., State College, Pa.). The columns were conditioned until Endrin and *p,p'*-DDT standards each gave only one peak. Quantitations were based on peak area.

Thin-layer chromatography was accomplished on Kieselgel H with *n*-hexane-benzene (4:1). Column chromatography was done on various aluminas with different eluting solvents.

Elemental analyses were performed by Spang Microanalytical Laboratory, Ann Arbor, Mich. Vapor pressure osmometry determinations were performed by ArRo Laboratories, Inc.

Mass spectral data were obtained using an LKB-9000 gas chromatograph-mass spectrometer. Samples were introduced *via* a direct probe into the ionization source. Spectra were run at an ionization voltage of 12, 30, and 70 electron volts (eV).

Experimental Photochemical Procedures. Irradiation of Endrin was carried out under varying conditions of both concentration of Endrin in appropriate solvents and output energy of the uv sources (253.7 to 300 nm). In varying the concentration of Endrin in solution from 0.3 to 8.9% by weight, the rate of disappearance of Endrin showed at least 60% conversion in 8 hr. The extent of the reaction was followed by both gas chromatography and ir spectrometry.

At concentrations greater than 1%, precipitation occurred during the photoreaction due to the insolubility of the photolytic product. After an initial lag of 1 hr, precipitation commenced and continued until, at the end of the second hour of photolysis, the reaction had to be stopped because of the density of the photoproduct. A coloration change

in the reaction medium from a clear solution to a dark, orange-brown, along with the evolution of a pungent odor, accompanied the reaction. The photoproduct was removed by filtration. The reaction was then continued until precipitation was no longer apparent. The recovered product was washed with cyclohexane or hexane and dried. Up to an 80% yield of a pure white crystalline material was recovered from such photolysis reactions.

Irradiation in hexane solution gave essentially the same results as those obtained with cyclohexane. Photolysis of Endrin in solution at 300 nm and in sunlight proceeded with formation of the same major photoproduct.

Nitrogen gas was bubbled through the reaction system on various trials, collecting any volatile acids in a standardized sodium hydroxide solution. No change in results was noticeable when nitrogen gas was bubbled through the reaction solutions. It was determined that 0.70 mole of acid per mole of Endrin was evolved during the reaction.

Preparation of Compounds. 1,8,9,11,11-pentachlorohexacyclo[6.2.1.1^{3,6}.0^{2,7}.0^{4,10}.0^{5,9}]dodecan-5-ol (XII) was prepared under the conditions generally used for the Haller-Bauer oxidation. A mixture of 4.00 g of the photoproduct XI and 1.28 g of sodamide in 150 ml of nanograde benzene was heated under reflux. After 7 hr the reaction mixture was cooled by immersion in an ice bath and 250 ml of ice water was slowly added to the rapidly stirred mixture. The organic layer was separated. The aqueous layer was extracted three times with 100-ml portions of methylene chloride containing a little chloroform, dried over magnesium sulfate, and the solvents were removed under reduced pressure to obtain a white crystalline product. This was dissolved in hot carbon tetrachloride, filtered hot, and cooled in an ice bath to yield 2.60 g of white crystals. On removal of the remaining solvent, an additional 0.90 g was recovered to bring the total yield to 80%. Final purification of the product was afforded by chromatography using neutral alumina and eluting with methanol-carbon tetrachloride (1:9).

Compound XII was also prepared under dehydrohalogenation conditions (Grummitt *et al.*, 1945). A mixture of 2.00 g of photoproduct XI and 1.25 g of potassium hydroxide was refluxed in 60 ml of absolute ethanol for 17 hr. The reaction solution underwent coloration changes, from colorless to yellow to cherry red. The solution was then poured into 200 ml of ice water, filtered, and extracted three times with 100 ml portions of ethyl ether. The combined ether extracts were saturated with sodium chloride solution, separated, and dried over magnesium sulfate. It was then filtered and the ether removed by distillation under reduced pressure at room temperature to yield 2.0 g of crude product. This was recrystallized from absolute ethanol to obtain 1.60 g of product in two crystalline forms: the major portion in the form of needles, and the other in the form of clusters. These were purified by chromatography using 55 g of Fisher alumina (activity I) eluting with carbon tetrachloride-methanol (1:1), and followed by final recrystallization from absolute ethanol-water (1:1) to obtain 1.55 g of the pure product (70% yield). Product melted from 204–207° C with decomposition. The ir and nmr spectra and the elemental analysis were consistent with XII.

1,5,8,9,11,11-Hexachlorohexacyclo[6.2.1.1^{3,6}.0^{2,7}.0^{4,10}.0^{5,9}]-dodecane (XVI). A 0.50 g quantity of compound XII plus 0.70 ml thionyl chloride were refluxed in 20 ml of spectrograde carbon tetrachloride for 100 hr. The solvent was removed by distillation under reduced pressure to obtain a yellow oily product which, on being set aside for 2 weeks, crystallized.

Gas chromatographic analysis indicated a product yield of 93%. The ir and nmr spectra were consistent with a chlorine substitution at carbon-5.

Hexacyclo[6.2.1.1^{3,6}.0^{2,7}.0^{4,10}.0^{5,9}]dodecanol (XIV). To 2.00 g of the photoproduct XI was added 2.0 g of finely cut lithium metal under a nitrogen atmosphere in 30 ml of anhydrous tetrahydrofuran. On the addition of 10 ml of *tert*-butyl alcohol to the mixture, a smooth exothermic reaction was initiated which was controlled by immersion in an ice bath. After 24 hr the unreacted lithium was removed and the reaction mixture was poured into water, extracted with four 60 ml portions of methylene chloride, dried over magnesium sulfate, and filtered. The solvent was removed by distillation under reduced pressure to obtain 0.750 g of product. Purification involved two chromatographic elutions through Woelm alumina (Activity I) and sublimation at water aspirator pressure to obtain a white crystalline product. The product had a melting point of 184–186° C (sub). The ir and nmr spectra and the elemental analysis were consistent with the structure.

Residue Analysis Procedures. A 100 g sample from the composite soil cores (1 kg) was used to determine residue levels in the soil samples. Enough water was added to bring the moisture content to approximately 25%. To this slurry was added 200 ml of hexane-acetone (1:1) mixture. This was shaken for 10 min and then allowed to stand for 12 to 14 hr. The mixture was next shaken for 10 min more and the hexane layer was decanted off. The mixture was then successively extracted with two additional 100 ml portions of hexane. The combined hexane extract was then washed with two 100 ml portions of distilled water, dried over anhydrous sodium sulfate, and reduced to 10 ml. This 10 ml was placed on a 30 × 2 cm column of activated Florisil-Celite (5:1) and eluted with 300 ml of hexane. The collected 300 ml was reduced to 5 ml prior to gas chromatographic analysis. Quantitation was based on dry weight of the soil sample. Chemical identification of the residue was confirmed by gas chromatography-mass spectrometry.

RESULTS AND DISCUSSION

The major photoproduct of Endrin became of immediate interest for two reasons. (1) The gas chromatographic retention time of the photoproduct, using a 2$^1/_2$% SE-30 column at different temperatures, was nearly identical to that of Endrin. Either material, or a mixture of the two, gave only a single peak with a proportional increase of area as one increased the concentration. Endrin and its photoproduct were successfully separated on an 11% OV-17/QF-1 column. (2) The ir spectrum of the product was nearly superimposable on that of compound VII above 1350 cm^{-1}.

Physical-Chemical Data. The melting point of the photoproduct was not sharp, but rather indefinite, melting from 215–218° C with some prior softening. On close examination the compound was found to undergo three crystalline phase changes prior to melting. The elemental analysis of the product established that the equivalent of a photodechlorination reaction (elimination of chlorine with the addition of one hydrogen) had occurred with the photodecomposition of Endrin. Calculated for C$_{12}$H$_9$Cl$_5$O: C, 41.4; H, 2.6; Cl, 51.2%; and found: C, 42.09, 41.93; H, 2.79, 2.88; Cl, 49.64, 49.55%. Mass spectra and vapor phase osmometry placed the molecular weight at 346.5 g/mole.

Mass Spectral Analysis. The fragmentation pattern indicated the presence of five chlorines, consistent with the

elemental analysis. The molecular ion was present at m/e 344 (Cl = 35.0). Isotopic abundances at P + 2, P + 4, P + 6, and P + 8 were in good agreement with those expected for a compound containing five chlorines (Silverstein and Bassler, 1967). The mass spectrum of the photoproduct is graphically presented in Figure 1.

Visible, Infrared, and Ultraviolet Spectroscopy. The ir spectrum of the photoproduct (Figure 2) showed strong absorption at 1745 cm^{-1}, which could be attributed to a carbonyl in a five-membered ring with no α methylene groups. A medium intensity absorption at 1465 cm^{-1} can be ascribed to a methylene group. The weak lines at 2960 and 2890 cm^{-1} can be ascribed to the carbon-hydrogen stretching frequency of a five-membered ring and the tertiary carbon-hydrogen stretching, respectively (Rosen et al., 1966). Multiple bonding frequencies were absent from the spectrum, which was also confirmed by lack of absorption in the visible and uv regions. Finally, absorption frequencies below 1400 cm^{-1} were too numerous and strong to be of much value in assigning the presence of functional groups.

Nuclear Magnetic Resonance Spectrometry. The nmr spectrum of the product (Figure 3) revealed at least five chemically distinct types of protons, based on observed chemical shifts. The first type was attributed to the protons of a methylene group at 8.2 τ. This group showed a solvent effect with increasing dielectric constant (D_e) of the solvent. In carbon tetrachloride (D_e = 2.2) the methylene group appeared as a singlet. In methylene chloride (D_e = 9.1) there appeared an AB type quartet, with area integration of 1:5:5:1, J = 7.2 cps, and ΔJ = 7.4 cps. In dimethyl formamide (D = 36.7) the AB type quartet had an area integration of 1:1.6:1.6:1 with ΔJ = 16.6 cps.

The second type of proton was attributed to a tertiary hydrogen, which appeared as a broad symmetrical multiplet at 7.2 τ.

The third type of proton was also attributed to a tertiary hydrogen. Total integration assigned four protons to this region of 6.7 to 6.9 τ. The coupling in this region did not allow satisfactory resolution to assign J and τ values from the spectrum.

The fourth type of proton appeared as a multiplet at 6.65 τ, and was obscured by the four tertiary hydrogens in the 6.7 to 6.9 region. This one hydrogen multiplet was assigned as a tertiary hydrogen adjacent to two vicinal dichloride systems.

The fifth type of proton was attributed to a hydrogen bonded to a vicinal dichloride system. It appeared as a sharp singlet at 5.4 τ. Spin decoupling techniques failed to alter the spectrum. This proton will not be split since it is 90° to the adjacent proton and therefore coupling should be very small.

Chromatography. Thin-layer chromatography of Endrin and it's photoproduct on Kieselgel H with n-hexane-benzene (4:1) gave R_f's of 0.425 and 0.200, respectively.

Gas chromatography of Endrin (VII) and photoproduct on a 1.83 m (1.59 mm i.d.) glass column packed with 11% OV-17/QF-1 on Gas Chrom Q (1:3) at operating parameters previously given gave relative retention times of 1.00, 7.23, and 3.68, respectively.

Consideration of Molecular Structures. The hydrocarbon portion of Endrin (IX) was assumed to be left intact, as supported by nmr and ir data and the three known thermal derivatives of Endrin. The opening of the epoxide to form the carbonyl with the equivalent of photodechlorination required the formation of a new carbon-carbon bond to be consistent
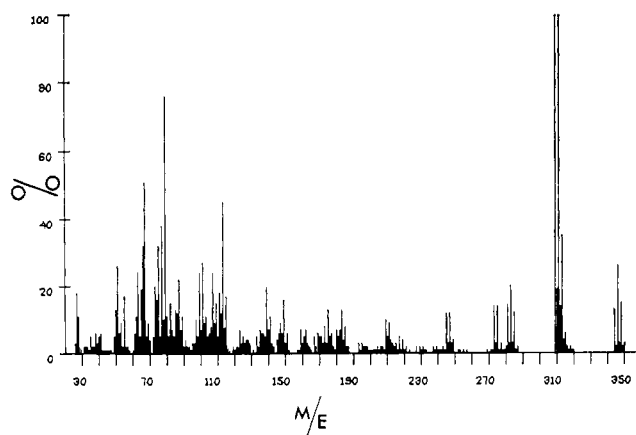

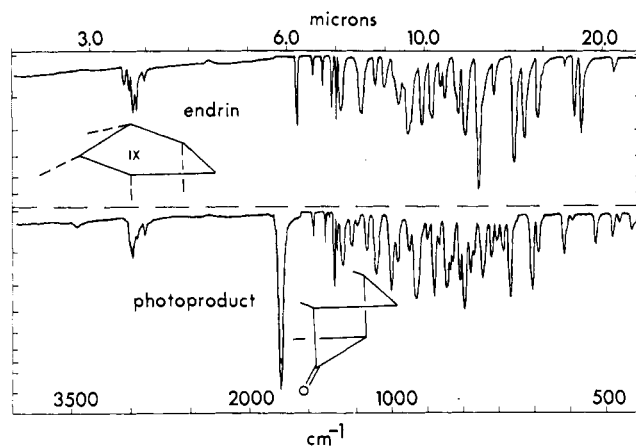Figure 1. Mass spectrum of Endrin photoproduct

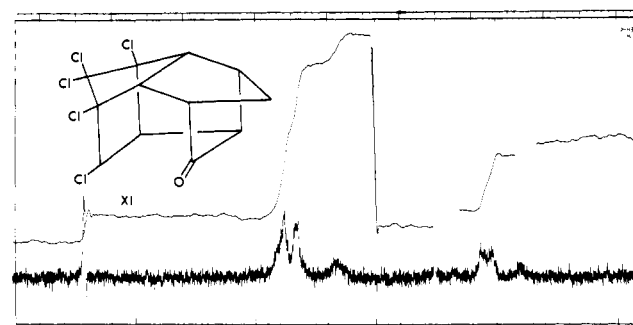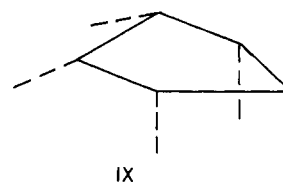Figure 2. Infrared spectra of Endrin and Endrin photoproduct

Figure 3. Nuclear magnetic resonance spectrum of Endrin photoproduct

with the mass spectral data. The absence of a methylene group α to the carbonyl (ir spectra) shows that the new carbon-carbon bond is formed α to the carbonyl.

IX

Considering the spectral data and the well documented chemistry of Endrin, and that five-membered ring closures are preferred as photolytic products of analogous *endo*-

dicyclopentadiene derivatives (Dilling, 1966), two models were immediately suggested (X and XI).

X

XI
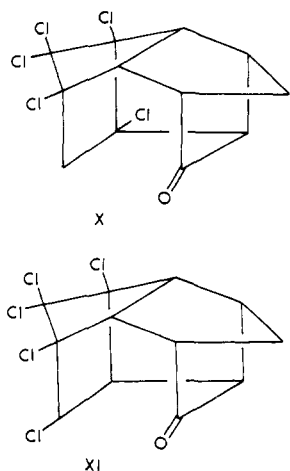
The nmr data are consistent with the chemical shifts expected of XI. Model X is incompatible with the nmr spectrum—not showing the second methylene absorbance of carbon-9, expected somewhat downfield of that *exo*-methylene of the hydrocarbon portion of Endrin.

Data supporting the proposed half-cage ketone system of XI were evident from the chemistry of the photoproduct. Structural considerations of these models led to the conclusion that XI should not be capable of olefin formation. Such olefin formation could be easily detected by a very sharp, characteristic band at 1600 cm^{-1} for mono- and dihaloethylene in the infrared. Application of Attenburrow's (1961) dehalogenation procedures to the product resulted in only starting material being recovered. Dehydrohalogenation using alcoholic potassium hydroxide also failed to produce any olefin; however, reaction did occur and a new product was formed which exhibited a hydroxyl band in the ir spectrum.

During an investigation of the chemistry of XI it was converted into other known ring systems. Initial efforts were directed at the carbonyl group. However, it was quickly discovered that the product was unreactive. Attempts to prepare the tosyl hydrazone and the hydrazone derivatives were fruitless. Likewise, the photoproduct was unreactive to normal oxidation and reduction procedures. Carbonyl reducing procedures involving the Huang-Minlon modification of the Wolff-Kischner, the Clemmensen, and the thioketal reductions were unsuccessful. Even drastic conditions, utilizing phosphorus pentachloride at high temperatures in a sealed tube, failed. The Baeyer-Villiger and Haller-Bauer oxidations did not give any expected products. The photoproduct reacted under the Haller-Bauer conditions to give a clean reaction to compound XII.


XII
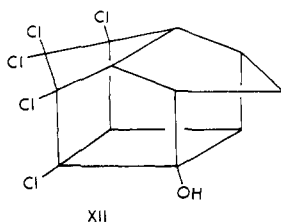
Elemental analysis showed XII to be an isomer of the photoproduct. The ir spectrum compared favorably with the spectrum of the product obtained from the photoproduct

following its reaction with alcoholic potassium hydroxide. The carbonyl band had been replaced by a hydroxyl band in the infrared. The nmr of XII in methylene chloride-d_2 showed the loss of the singlet at 5.4 τ but no absorption characteristic of a secondary alcohol. This observation led to the conclusion that ring closure had occurred by base-catalyzed homoenolization. Ring closures of this type are not unknown (Soloway, 1960). For example, one of the more familiar cases is the direct formation of the hexachloro birdcage alcohol (XIII), as reported by Winstein (Carter *et al.*, 1965). Compound XI could easily undergo such homoenolization. Therefore, XII could be assigned the structure 1,8,9,11,11 - pentachlorohexacyclo[6.2.1.1^{3,6}.0^{2,7}.-0^{4,10}.0^{5,9}]dodecan-5-ol.
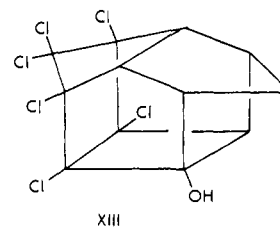
XIII

If structures XII and XIII were dechlorinated, the resulting products would be identical and have the relationship of the hydroxyl group to the methylenes, as shown below (XIV).

XIV
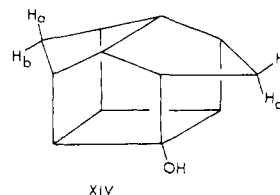
Compound XIV has been prepared by Winstein (Carter *et al.*, 1965). The far methylene protons from the hydroxyl showed an AB type quartet with chemical shift values of 8.52 and 8.22 τ, with J_{AB} = 10.5 cps. The near methylene H$_a$H$_b$ signal appeared as a singlet at 8.28 τ, superimposed on one member of the H$_a$H$_b$ quartet, indicating that H$_d$ was probably deshielded by the hydroxyl.

Compound XIV was not originally prepared by the dechlorination of XI. However, it did arise from the lithium, *tert*-butyl alcohol reduction of the photoproduct. Reduction was originally carried out to obtain its hydrocarbon skeleton. However, in the isolated reaction product only two methylene groups appeared in the nmr instead of the expected four. Elemental analysis confirmed this suspicion by reporting two less hydrogens in the product than expected (expected C$_{12}$H$_{16}$ and found C$_{12}$H$_{14}$). Subsequent work led to the realization of the possibility of homoenolization since lithium metal is a Lewis base. The nmr of XIV in chloroform-d_1 was identical to Winstein's (XIV).

These chemical data support the proposed half-cage ketone system postulated for the photodecomposition product of Endrin. Further, the nmr data of the photoproduct are capable of differentiating between X and XI and are definitive evidence for XI.

The photochemistry of VII, 1,8-*exo*-9,10,11,11-hexachloropentacyclo[6.2.1.1^{3,6}.0^{2,7}.0^{4,10}]dodecan-5-one, was also investigated. Compound VII was readily prepared (Soloway, 1960) and photolyzed to determine whether VII might be a possible route in the formation of XI from VI. A 1.45 g quantity of VII was ground to a fine powder and dissolved in 1250 ml of cyclohexane. After 26 hr of irradiation at

253.7 nm, gas chromatographic analysis did not show the presence of XI.

Isolation of XI from Field Samples. The photoproduct of Endrin, XI, has been detected under field conditions. A muck soil, treated with Endrin for 5 years at the rate of 2 lb per acre, was extracted and analyzed for the presence of Endrin and/or its photoproduct. Gas chromatography-mass spectrometry, thin-layer chromatography indicated that photoproduct XI was present, and constituted up to 5% of the total Endrin residue (determined to be 20 ppm).

CONCLUSIONS

Endrin underwent a photolysis reaction in hexane and in cyclohexane at 253.7 and at 300 nm to yield as the major product a half-cage ketone, 1,8-exo-9,11,11-pentachloropentacyclo[6.2.1.1^{3,6}.0^{2,7}.0^{4,10}]dodecan-5-one (XI) in 80% yields. This photolytic product of Endrin has been detected in the field. Its similarity to Endrin when analyzed on several gas chromatographic columns and resistance to chemical degradation indicate the potential that this photodecomposition might play in the buildup of an unidentified toxic residue in the environment.

Stimulated by the work of the Rutgers group on the metabolism of photoaldrin and photodieldrin (Khan *et al.*, 1969), we have initiated a study of the comparative metabolism and toxicology of this new photoproduct of Endrin.

ACKNOWLEDGMENT

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