Rate of Photochemical Isomerization of Endrin in Sunlight

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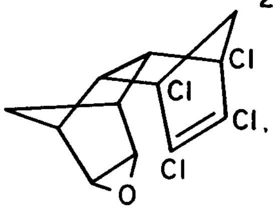
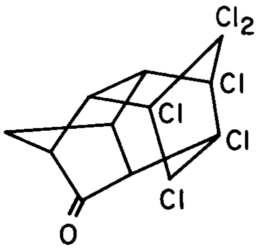
Previous studies by SOLOWAY *et al* (1960) have shown that endrin insecticide (I) isomerizes to the pentacyclic ketone, 1,8-*exo*-9,10,11,11-hexachloropentacyclo ($6.2.1.1^{3,6}.0^{2,7}.0^{4,10}$) dodecan-5-one (II) rather easily under both thermal and acid-catalyzed conditions. The behavior of endrin was reviewed in connection with its gas-liquid chromatographic analyses and it was found that in addition to II, an aldehyde, 4,5,6,7,8,8-hexachloro-4,7-methano-3,5,6-methenoindan-1-carboxaldehyde (III) was formed as the other principal product from the thermal treatment of endrin (PHILLIPS *et al*, 1962).

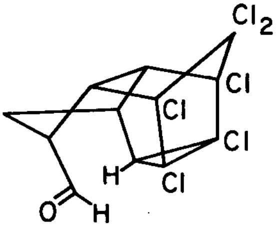
The structures of compounds discussed in this report are illustrated below:



I



II



III

ROBURN (1963) has reported the effect of sunlight and ultraviolet irradiation on chlorinated pesticides, including endrin. He reports endrin was partially converted to one main product and several minor ones, however identification of these products was not made. ROSEN$_{0}$(1966) has extended this work and by exposing endrin to a 2537 A germicidal lamp for forty-eight hours found 37% of the pentacyclic ketone (II) and 9% of the aldehyde (III). ZABIK (1971) reports that upon irradiation of endrin in solution it was converted to 1,8-*exo*-9,11,11-pentachloropentacyclo ($6.2.1.1^{3,6}.0^{2,7}.0^{4,10}$) dodecan-5-one.

This report describes the rate of photoconversion of endrin in the solid state to its isomerides on exposure to natural sunlight.

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Experimental

Individual glass planchets containing 10 mg of endrin as a thin layer, 24 µg per mm^2, were exposed to the sunlight. After the designated time, the samples were removed from the sunlight and the product weighed, isolated, and analyzed. The rate of disappearance of endrin and the appearance of products was followed by infrared spectroscopic methods. The samples were dissolved in 1 ml of reagent grade methylene chloride, a 1.0 mm sodium chloride cell was filled and the analyses carried out on a Beckman IR Spectrophotometer Model 4 using normal instrument settings. The scans were compared using the base line method with standards of the compounds, I, II, and III of comparable concentration in the same cell.

In order to verify the conclusion that the isomeric ketone was indeed II, the isomerization of endrin was carried out on a somewhat larger scale, 1 gram, and the products obtained further characterized. The photoproducts were chromatographed on Florisil eluting with a 1-to-1 hexane-methylene chloride solution. The elution solvent was removed from each fraction and an infrared spectrum taken. The peak fraction contained 85% of the total material. The melting point, elemental analysis, molecular weight, GLC retention time, insect toxicity index, and infrared spectrum were all in agreement with that required for II. Exposure of II to further sunlight caused no apparent change. Subsequent chromatographic fractions of the photoproducts yielded material which had an identical infrared spectrum to III.

Results and Discussion

The chemical isomerization of endrin reported by SOLOWAY et al (1960) yielded 50% of II, however, the balance of the reaction mixture was not resolved. The thermal isomerization reported by PHILLIPS et al (1962) produced a ratio of 12 parts of II, four parts of III, and one part of 2,2a,3,3,4,8-hexachlorodecahydro--1,5,2,4-ethanediylidenecyclopenta(cd)-pentalen-1-ol, plus other unidentified products. The photochemical isomerization of endrin in natural sunlight is more specific than either the chemical or thermal isomerization. It proceeds with the formation of primarily II plus minor amounts of other compounds, viz. III. A mechanism has been postulated by SOLOWAY (1967) for the formation of II from endrin via an intermediate formed by the shift of two bonds. As shown in Table 1, the disappearance of endrin and the conversion to the pentacyclic ketone (II) was more rapid in June than in October as would be expected in a brighter sun.

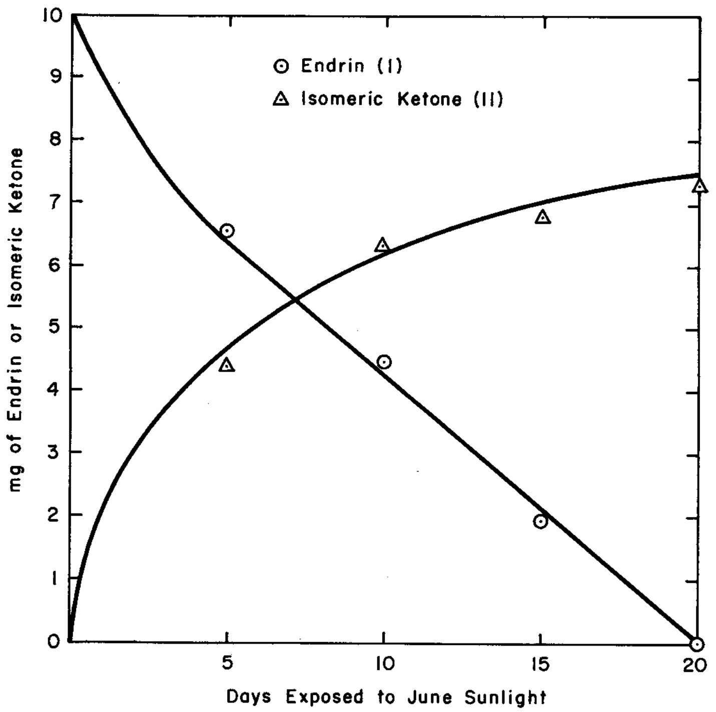

Figure I. PHOTOCHEMICAL ISOMERIZATION OF ENDRIN

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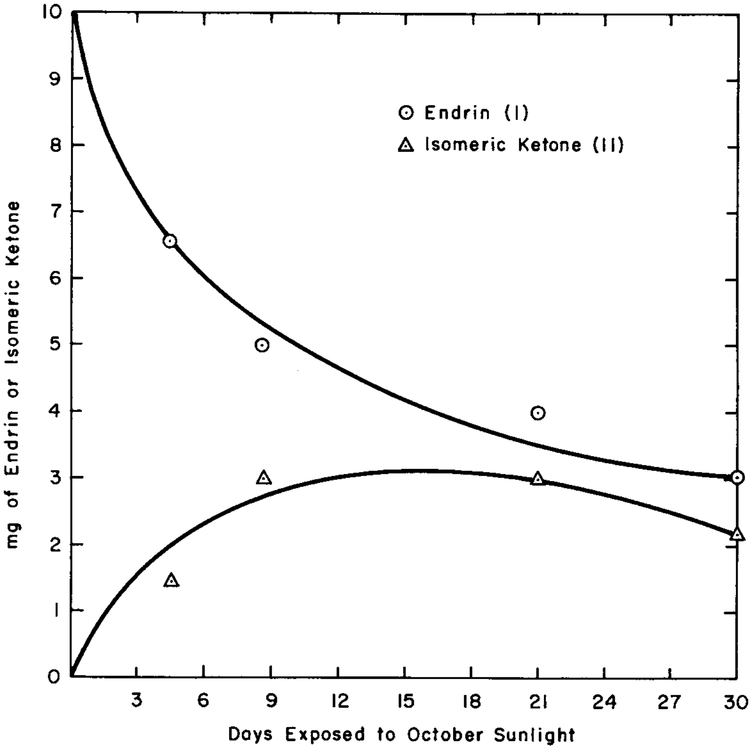

Figure 2. PHOTOCHEMICAL ISOMERIZATION OF ENDRIN

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TABLE 1

Endrin Photoproduct Formed vs. Sun's Intensity

Days Exposed	Month	% Isomeric Ketone (II) Formed
5	October	14
5	June	46
12	October	30
12	June	65

Figures 1 and 2 show the rates of isomerization of endrin under different light intensities of the sun.

As may be noted from Figure 2 the slope of the curves change rather sharply at about nine or ten days. Some change in the rate of isomerization could be attributed to the decreasing intensity of the sunlight, however, such a marked change in the shape of the curves make other possibilities more likely. As there was little or no color change in the materials any masking or quenching effect must necessarily arise from other sources. It has been observed that the thickness of the sample layer has an effect on the rate of isomerization; the thicker layer being isomerized more rapidly than a thinner layer. The reason that the total recovery of I and II is less in the October exposure (Figure 2) than the June exposure (Figure 1) is probably due to evaporation losses over an extended time span, and also the fact that II being formed is more volatile than I.

The results of numerous experiments showed that endrin was 50% isomerized to II in 7 ± 2 days in an intense summer sun with complete conversion of the endrin in 17 ± 2 days.

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