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In practice, the user either prepares a punch card containing the search parameters and initiates a batch processing program or enters his parameters through a typewriter keyboard as a time-sharing program. In the latter case, when processing on the IBM 1800, his program will directly enter the background processing queue for execution on a time-sharing basis with laboratory monitoring.

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## Identification of Photoaldrin Chlorohydrin as a Photoalteration Product of Dieldrin

A photoproduct produced by the thin film irradiation of dieldrin (I) with germicidal lamps has been isolated and identified. Based on glc, ir, nmr, ms, and melting point comparisons with independently

synthesized material, the product (IV) is considered to be a chlorohydrin derived from photodieldrin. The isolation and synthesis of the chlorohydrin is described.

Solid-state irradiation of thin films of dieldrin (I) produces photodieldrin (II) and several minor photoproducts (Benson, 1971; Harrison *et al.*, 1967; Rosen *et al.*, 1966). Benson reported that one minor product appeared to be a chlorohydrin (IV) derived from photodieldrin. We have investigated this chlorohydrin.

#### EXPERIMENTAL SECTION

**Photoaldrin Chlorohydrin (IV) (1,1,2,3,3a,5(or 6),7a-heptachloro-6(or 5)-hydroxydecahydro-2,4,7-metheno-1H-cyclopenta[*a*]pentalene).** Ten milliliters of concentrated HCl and 0.5 g of ZnCl<sub>2</sub> were added to a solution of 1.0 g (2.6 mmol) of 99+ % photodieldrin in 100 ml of absolute ethanol. (The samples of dieldrin and photodieldrin were prepared for use as reference standards in earlier work; their purities were determined by electron capture glc.) The solution was heated on a steam bath for 18 hr and then poured into 300 ml of water. The white precipitate was recrystallized once from acetone-hexane to give 0.8 g (1.9 mmol, 73%) of colorless crystalline product, mp 204.5–206.5°.

The mass spectrum showed a molecular ion at *m/e* 414 (calculated, 414) and an intense M – Cl peak at *m/e* 379. The chlorine isotopic ratio observed indicated that the compound contained 7 chlorine atoms. The ir (KBr) showed a nonbonded hydroxyl at 3600 cm<sup>-1</sup> and major bands at 1053 and 818 cm<sup>-1</sup>. The nmr spectrum (100 MHz in DMSO-*d*<sub>6</sub>) showed a singlet at  $\delta$  5.56, a doublet of doublets at  $\delta$  4.16 (*J* = 5.2 Hz), a doublet of doublets at  $\delta$  3.73 (*J* = 5.2 Hz), and the hydroxyl proton as a doublet at  $\delta$  5.76 (*J* = 5 Hz). Gas chromatographic retention times relative to aldrin on a 6-ft

10% DC-200 column and a mixed 10% DC-200 and 15% QF-1 column were 8.6 and 11.6, respectively. The operating parameters are described in the Pesticide Analytical Manual (1968).

*Anal.* C, calcd 34.54; found, 34.55, 34.56. H, calcd 2.28; found, 2.10, 2.11.

Aldrin chlorohydrin (III) was prepared in the same manner as IV in 84% yield, mp 150–152°. The mass spectrum showed a molecular ion at *m/e* 414 (calcd, 414) and a strong M – Cl peak at *m/e* 379. The observed chlorine isotopic ratio indicated a total of 7 chlorine atoms in the molecule. The ir (KBr) showed a hydrogen-bonded hydroxyl at 3240 cm<sup>-1</sup>, the double bond at 1595 cm<sup>-1</sup>, and major bands at 1054, 1037, 817, and 808 cm<sup>-1</sup>. Its glc retention times relative to aldrin on the DC-200 and mixed columns were 3.6 and 4.0, respectively.

**Photoaldrin Chlorohydrin (IV) from Irradiation of I.** Thin films of 99.7% dieldrin (see above) (200 mg each, 2 g total) in five 0.5-in. petri dishes were exposed to two G.E. G30T8 germicidal lamps at a distance of 4.5 cm for 24 hr. The tan solids were combined and crystallized from 5 ml of hot absolute ethanol. The solid (photodieldrin) was filtered off and the mother liquor was found to be much richer in photoaldrin chlorohydrin (glc). Additional crystallization of photodieldrin occurred on standing; the filtrate contained approximately 50% of the desired component (by measurement of glc peak area) in addition to photodieldrin and unreacted dieldrin.

Evaporation of solvent from the filtrate gave a dark oil which was chromatographed on a silica gel column with benzene as eluting solvent. Several fractions rich in the desired component (glc) were obtained. Concentration of the com-

bined fractions gave 30 mg of tan solid which was recrystallized once from acetone-hexane to give 22 mg of colorless crystalline solid, mp 202–204°, and the mixed melting point with authentic photoaldrin chlorohydrin was 204–206°. The isolated chlorohydrin was identical with the authentic compound by glc, nmr, ms, and ir.

#### RESULTS AND DISCUSSION

Aldrin chlorohydrin (III) and photoaldrin chlorohydrin (IV) were prepared by a procedure based on the method of Wiencke and Burke (1969). These chlorohydrins were converted back to their epoxide precursors by the alkali pre-column reaction gas chromatography procedure of Miller and Wells (1969). When III was treated with potassium tertiary butoxide in *tert*-butyl alcohol, authentic dieldrin was isolated. These reactions demonstrate that skeletal rearrangements do not occur in the formation of the chlorohydrins and that a *trans*-chlorohydrin configuration may be assumed. The reactions are summarized in Figure 1.

The irradiation experiments of Benson (1971) were repeated to confirm the presence of IV. Thin films of solid dieldrin (I) were placed in petri dishes and irradiated for 24 hr with germicidal lamps. Two of the four dishes were covered with quartz plates to determine whether HCl produced in a semi-closed system would provide an enhanced yield of IV. At the end of the irradiation period, the covered dishes contained 4.4 and 5.2%, and the uncovered dishes contained 4.7 and 6.0% IV (based on glc comparison with a standard). Thus, the quartz covered plates had no effect on the conversion of I to IV.

Dieldrin was irradiated in ten portions, and the product component corresponding to IV (by glc) was isolated from the combined irradiation mixture. The isolate was identical with authentic IV (see Experimental Section).

It will be noted that two *trans*-chlorohydrins, IVa and IVb, derived from the exo epoxy group of photodieldrin are possible, and that each of these may exist as a *dl* pair (Figure 2). We have made no attempt to establish whether the synthetic material and the isolated photoproduct are mixtures of these isomers or a single compound. The analytical techniques used did not indicate the presence of isomeric forms.

Aldrin chlorohydrin (III) and photodieldrin (II) appear to be the likely precursors of IV, which is formed in approximately 5% yield from I. In separate 24-hr irradiation experiments, III gave a 40% conversion to IV, while II gave only a 1.5% conversion. Inspection of high-loading glc chromatograms of the original revealed no detectable quantity of III. Thus, if III is an intermediate, its rate of conversion to IV must be much faster than the rate of its formation from I.

The formation of IV appears to involve the addition of the elements of HCl to I or II. Because of changes in our program, the work had to be terminated, and the source of this HCl was not investigated.

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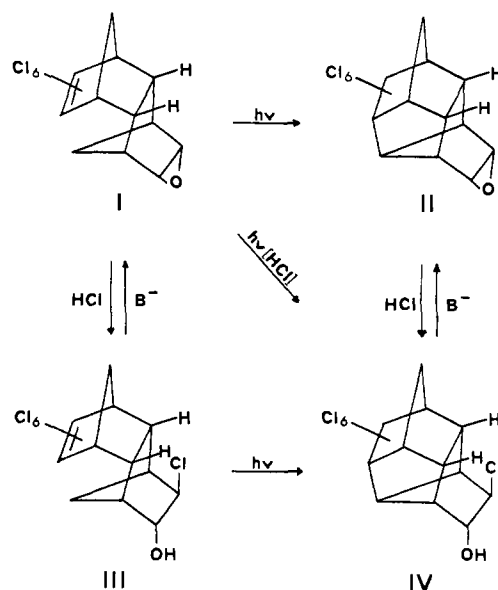


Figure 1. Summary of reactions

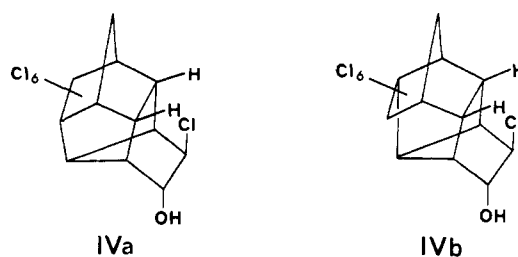


Figure 2. Possible geometric isomers of IV

Barron for the mass spectra, Elizabeth A. Hansen for the nmr spectra, Jo-Yun T. Chen for the ir spectra, and Charles Graichen and John W. Butler for the elemental analyses.

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