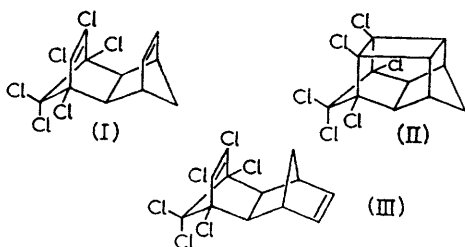


## The Photolysis of Aldrin\*

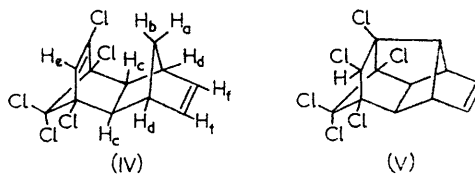
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ALTHOUGH isodrin (I) is converted<sup>1,2</sup> into 1,8,9,10,11,11-hexachlorohexacyclo[6,2,1,1<sup>3,6</sup>,0<sup>2,7</sup>,0<sup>4,10</sup>,0<sup>5,9</sup>]dodecane (II) by ultraviolet light in ethyl acetate under a carbon dioxide blanket for 7 days, its stereoisomer, aldrin (III), is not photolyzed



spectra suggest that it is 1,2,4,10,10-penta-chloro-1,4,4a,5,8,8a-hexahydro-1,4-*endo,exo*-5,8-dimethanonaphthalene (IV), m.p. 84–86°, and 1,8,9,10,11,11-hexachloropentacyclo[6,2,1,1<sup>3,6</sup>,0<sup>2,7</sup>,0<sup>9,12</sup>]dodec-4-ene (V), m.p. 185–186°, in yields of 24 and 13% (g.l.c. analysis), respectively. There was about 9% unchanged aldrin. Other



under identical conditions. As solid aldrin was easily converted into a number of products by sunlight in the presence of air,<sup>3</sup> aldrin was irradiated under previously described conditions.<sup>1</sup>

Within 7 days, at least two products were obtained: a material whose mass and n.m.r.

unidentified materials, with retention times greater than those of (III), (IV), and (V), were observed.

Materials were separated by preparative g.l.c. Re-injection of (IV) and (V) showed that no decomposition had occurred during separation.

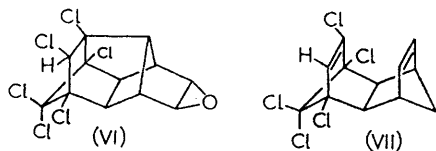
Structures of (IV) and (V) are based largely on spectral data.† In addition, (V) was converted

\* Paper of the Journal Series, New Jersey Agricultural Experiment Station, Rutgers—the State University.

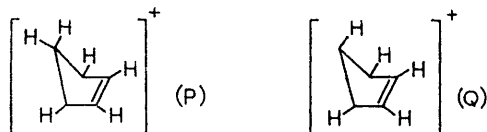
† Mass spectra were performed on a Hitachi RMU-6D mass spectrometer by Morgan-Schaffer Corp., Montreal; n.m.r. spectra on Varian A-60 spectrometers, and in the case of (V) with the aid of a C-1024 time averaging computer.

into its epoxide (VI)<sup>4,5</sup> by *m*-chloroperbenzoic acid.

The mass spectrum of (IV) exhibited a molecular ion at *m/e* 328 as well as a base peak at *m/e* 66



(fragment P), the same base peak found in an aldrin spectrum.<sup>6</sup> In contrast, the mass spectrum of (V) exhibited a molecular ion at *m/e* 362 and a peak at *m/e* 65 (fragment Q), suggesting that a hydrogen atom had migrated to the chlorinated portion of the molecule.



The n.m.r. spectrum of (IV) in CDCl<sub>3</sub> showed an AB-type quartet centred at  $\delta$  1.72 (H<sub>a</sub>, H<sub>b</sub>), multiplets centred at  $\delta$  2.88 (H<sub>d</sub>) and 6.28 (H<sub>f</sub>), and singlets at  $\delta$  2.71 (H<sub>c</sub>) and 5.94 (H<sub>e</sub>), and is similar to the n.m.r. spectrum of aldrin. The areas of the peaks centred at  $\delta$  2.71, 2.88, 5.94, and 6.28 were in the ratio 2:2:1:2. The area measurement of the AB-type quartet was complicated by a singlet at  $\delta$  1.28 (attributable to <sup>13</sup>C splitting of silicone grease protons).<sup>7</sup> One disturbing aspect is that H<sub>b</sub> absorption was centred at  $\delta$  2.16 in (IV) but at 1.60 in aldrin. The *J*<sub>ab</sub> values were 11 c./sec. in both compounds. At the present time we have no good explanation as to why H<sub>b</sub> but not H<sub>a</sub> absorption changed, but it is difficult to imagine any structure other than (IV) that would fit the spectral evidence.

Corroboration for the indicated structure of (IV) has now been given by Crosby and Henderson.<sup>8</sup>

The formation of (IV) and (V) is analogous to that of the products obtained from the photoisomerizations of isodrin<sup>1,2</sup> and its epoxide endrin,<sup>5</sup> and the photoisomerization of dieldrin to (VI).<sup>4,5</sup> The i.r. spectrum of (V) exhibited absence of both chlorinated-olefin absorption at 1595 cm.<sup>-1</sup> and methylene absorption at 1464 cm.<sup>-1</sup>. By comparison, these peaks were found in an aldrin spectrum. Olefin absorption at 3003 cm.<sup>-1</sup> and *cis*-olefin absorption at 722 cm.<sup>-1</sup> were also shown by (V). The n.m.r. spectrum of (V) in hexadeuteroacetone showed a singlet at  $\delta$  5.12, attributable to the migrated hydrogen on the basis of reported chemical shifts,  $\delta$  4.98 and 5.33, respectively, for the protons of 1,2,3,4,5,6-hexachlorocyclohexane<sup>9</sup> and the migrated proton in (VI),<sup>5</sup> both in hexadeuteroacetone. A multiplet centred at  $\delta$  5.90 in the olefin region had twice the area of the singlet in accord with the structure of (V). Other multiplets were found in the tertiary-hydrogen region between  $\delta$  2.55 and 3.53. Integration of this region showed it to have approximately 5 times the area of the singlet.

Compound (V) was one of the products obtained in the solid state irradiation, but (IV) was not. It had been separated in the earlier work by chromatography on silica gel, and therefore, did not contain any silicone grease impurity. The i.r. spectra of the materials isolated by the two different methods were identical.

It is quite apparent why (IV) and (V) were not observed in earlier investigations. To remove the starting material, the reaction mixtures were treated with permanganate, the subsequently formed di-acids being removed in basic solution. Oxidation of (II) could not occur, but oxidation of (IV) and (V) could. It is probable that the photolysis of isodrin gave in addition to (II), the pentachloro-compound (VII).

We thank Dr. R. A. Sauer for his help with the interpretation of the n.m.r. spectrum of (IV); Drs. D. Z. Denney and J. E. Godderz for obtaining the n.m.r. spectra of (IV) and (V), respectively; Shell Chemical Co. for gifts of aldrin, and the Bureau of State Services for a U.S.P.H.S. research grant.

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<sup>5</sup> J. D. Rosen, D. J. Sutherland, and G. R. Lipton, *Bull. Environ. Contamin. Toxicol.*, 1966, **1**, 133.

<sup>6</sup> R. O. Mumma and T. R. Kanter, *J. Econ. Entomol.*, 1966, **59**, 491.

<sup>7</sup> D. Z. Denney, private communication.

<sup>8</sup> D. G. Crosby and G. L. Henderson, Amer. Chem. Soc. 2nd Western Regional Meeting, San Francisco; as reported in *Chem. Eng. News*, Nov. 7, 1966, 84.

<sup>9</sup> R. K. Harris and N. Sheppard, *Mol. Phys.*, 1963-4, **7** (6), 595.