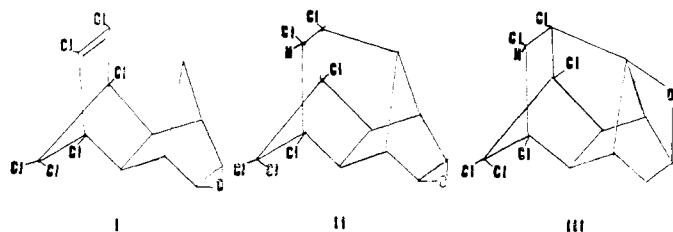


Preparation of the Photoisomers of Aldrin and Dieldrin

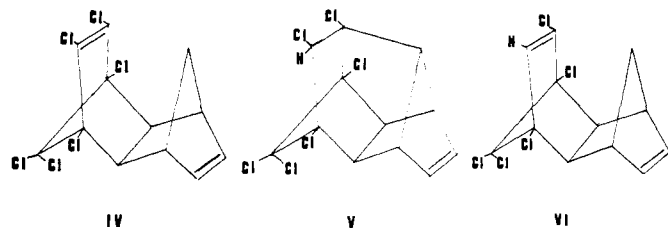
The photoisomers of aldrin and dieldrin have been prepared in 77 and 75% yield, respectively, by

benzophenone-sensitized photolysis.

The photoisomerization of dieldrin (I) to 1,1,2,3,3*a*,7*a*-hexachloro-5,6-epoxydecahydro-2,4,7-metheno-1*H*-cyclopenta[*a*]pentalene (II) was reported by Parsons and Moore (1966), Robinson *et al.* (1966), and Rosen *et al.* (1966). The structure (III) proposed by Harrison *et al.* (1967) is inconsistent with the material's nuclear magnetic resonance spectrum.



The photoisomer of aldrin (IV), 1,1,2,3,3*a*,7*a*-hexachloro-2,3,3*a*,3*b*,4,6*a*,7,7*a*-octahydro-2,4,7-metheno-1*H*-cyclopenta[*a*]pentalene (V) was obtained in low yield by exposure of solid aldrin to sunlight (Rosen and Sutherland, 1967) and to a low-pressure ultraviolet lamp in ethyl acetate (Rosen, 1967). The latter reaction yielded 1,2,4,10,10-pentachloro-1,4,4*a*,5,8,8*a*-hexahydro-1,4-*endo,exo*-5,8-dimethanonaphthalene (VI) as the major product.



Recently, V was observed to be approximately 10 times more toxic to mosquito larvae than aldrin (Sutherland and Rosen, 1968). A material with such toxic properties might have considerable potential as an insecticide. The authors, therefore, decided to devise an improved synthesis of V for the purpose of determining toxicity to other insects, for use in metabolic studies, and to provide a starting point for an economical, commercial process.

EXPERIMENTAL

Chemicals

Aldrin (1,2,3,4,10,10-hexachloro-1,4,4*a*,5,8,8*a*-hexahydro-1,4-*endo,exo*-5,8-dimethanonaphthalene) and dieldrin (1,2,3,4,10,10-hexachloro-6,7-epoxy-1,4,4*a*,5,6,7,8,8*a*-octahydro-1,4-*endo,exo*-5,8-dimethanonaphthalene), 99+ % pure, were generously supplied by the Shell Chemical Co.

Irradiation Lamps

Two types of photochemical immersion lamps (Ultra-Violet Products, San Gabriel, Calif.) were used: the PCQ-9G-1, a low pressure lamp with principal wavelength at 2537 Å and an output of 2.5 watts; the LAQ-054, a medium pressure lamp emitting between 2680 and 3560 Å, with a peak at 3075 Å. No output data on the LAQ-054 are presented because of the unavailability of an applicable standard in this region.

Preparation of Photoisomers

Aldrin (1.46 grams, 0.004 mole) or dieldrin (1.52 grams, 0.004 mole) was dissolved in 20 ml. of benzene which contained benzophenone (0.73 gram, 0.004 mole). The solution was purged with carbon dioxide for 15 minutes before turning on the LAQ-054 lamp. Exposures were conducted for 21 hours, during which time the carbon dioxide purge continued. At the end of the exposure period, benzene was evaporated in a stream of air. By treating the resulting semisolid with approximately 10 ml. of petroleum ether (30° to 60° C.), crystals of V were obtained. Recrystallization from hexane provided material whose melting point, 186.5–87.5° C. (corr.), and infrared spectrum were identical to those of material previously identified as V (Rosen and Sutherland, 1967).

The oil obtained by evaporation of the irradiated solution of dieldrin was crystallized by addition of approximately 10 ml. of hexane. Recrystallization from ethanol afforded material whose infrared spectrum was identical with that of material previously identified as II (Rosen *et al.*, 1966), melting point 192° C. (corr.). Parsons and Moore (1966) had reported m.p. 200–01° C. (uncorr.) for II. However, redetermination has given m.p. 192–93° C. (corr.) (Parsons, 1968).

Quantitative Analysis

Quantitative determination of reaction products was performed on a Research Specialties Model 600 gas chromatograph equipped with a flame ionization detector and a 1/4-inch, 2-foot glass column containing 5% DC-200 on Gas Chrom Q, 80- to 100-mesh. At a temperature of 195° C. and a flow rate of 80 ml. per minute the retention times of benzophenone, I, II, IV, V, and VI were 0.75, 4.48, 12.05, 2.75, 7.26, and 2.2 minutes, respectively.

RESULTS AND DISCUSSION

The benzophenone-sensitized photolyses of aldrin and dieldrin resulted in the formation of only one product in each case—the corresponding photoisomer—in yields of 77 and 75%, respectively. The synthesis was further facili-

tated by the ease of separation of the photoproducts from benzophenone and their corresponding starting materials. The economic aspects of the situation are also interesting. Benzophenone, which is not consumed in the reaction, as well as unused aldrin or dieldrin can be used in subsequent reactions, as can recovered solvent and carbon dioxide. Furthermore, if the toxicity ratio of V to aldrin observed with mosquito larvae is similar in other insects, formulations containing lesser amounts of pesticide could be used.

Exposure of aldrin to the PCQ-9G1 low pressure lamp in benzene in the absence of benzophenone resulted in less than 1% yield of V and no conversion to VI. Apparently, benzene absorbed most of the light energy, but no energy transfer to aldrin occurred.

The photolysis of aldrin in hexane exhibited an interesting concentration effect. Using a low pressure lamp at a concentration of 2 mg. per ml., Henderson and Crosby (1967) obtained VI but no V. The present authors have duplicated these results at 7 mg. per ml. However, at a concentration of 1 mg. per ml., a mixture of products containing 4.4 times as much V as VI was obtained.

Compounds II and V have been misnamed in several previous publications (Parsons and Moore, 1966; Rosen *et al.*, 1966; Rosen, 1967). The nomenclature used in this communication has been supplied by Loening (1968) who has also given von Baeyer names to II and V, respectively: 3,4,5,6,6,7 - hexachloro - 12 - oxahexacyclo-(6.5.0.0.^{2,10}.0^{3,7}.0^{5,9}.0^{11,13}) tridecane and 3,4,5,6,6,7-hexachloropentacyclo(6.4.0.0.^{2,10}.0^{3,7}.0^{5,9})dodec-11-ene.

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