

estrogenic activity. No further work with band 2 is contemplated.

ACKNOWLEDGMENT

We thank Francis Diaz, Walnut Grove Products, Atlantic, Iowa, for providing adequate amounts of sample for chemical analysis and bioassay tests. We thank Beth Schauerhammer for technical assistance.

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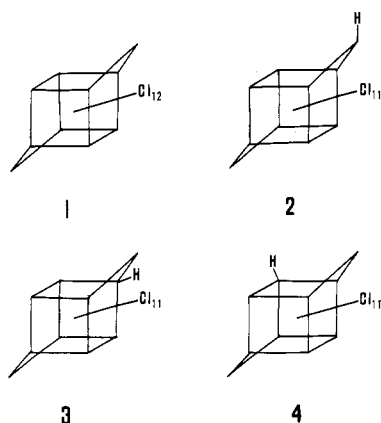
Received for review May 26, 1972. Accepted November 1, 1972.
 This research was supported in part by USPHS Research Grant No. 5RO1-FD-00035-06. Paper No. 7960, Scientific Journal Series, Minnesota Agricultural Experiment Station.

Photochemistry of Mirex

The photolysis of dodecachloropentacyclo[5.3.0.0^{2,6}.0^{3,9}.0^{4,8}]decane (Mirex) in hydrocarbon solvents yielded two major products. These photoproducts have been identified as a monohy-

dro derivative and a dihydro derivative. Possible structures for the derivatives (based on nmr, ir, and mass spectra) are discussed.

The insecticide Mirex (dodecachloropentacyclo[5.3.0.0^{2,6}.0^{3,9}.0^{4,8}]decane), structure 1, has been used extensively in the southern United States to control the imported fire ant. This persistent chlorocarbon has been implicated as a possible environmental problem in several recent papers (Lowe *et al.*, 1971; Ludke *et al.*, 1971; Van Valin *et al.*, 1968). In this report, evidence of Mirex degradation by photolysis in hydrocarbon solvents is presented. In all cases, the elemental analyses, mass spectra, and nmr spectra indicated that chlorine atoms were replaced with hydrogen atoms.



In an investigation of some chemical reactions of Mirex and related compounds, Dilling *et al.* (1967) synthesized several hydrogen derivatives of Mirex. Each product was characterized by elemental analyses, infrared, and nmr spectra. One monohydro derivative was assigned structure 2 (1,2,3,4,5,5,6,7,8,9,10 - undecachloropentacyclo[5.3.0.0^{2,6}.0^{3,9}.0^{4,8}]decane), and another monohydro derivative was assigned either structure 3 (1,2,3,4,5,5,6,7,8,10,10-undecachloropentacyclo[5.3.0.0^{2,6}.0^{3,9}.0^{4,8}]decane) or 4 (1,2,3,4,5,5,6,7,9,10,10 - undecachloropentacyclo[5.3.0.0^{2,6}.

0^{3,9}.0^{4,8}]decane). The mass spectra of these compounds (Dilling and Dilling, 1967) indicated that the predominant modes of fragmentation are dechlorination and cleavage of the pentacyclic decane skeleton in half.

EXPERIMENTAL SECTION

Technical Mirex, donated by the Allied Chemical Corp., was recrystallized three times from benzene and vacuum dried for 6 hr at 200°. Eastman technical isooctane was distilled twice through a five-ball Snyder column. After being washed with concentrated sulfuric acid, Eastman technical cyclohexane was passed through a silicic acid column, fractionally frozen, and then distilled. Gas chromatography and ultraviolet spectroscopy were used to establish the purity of all compounds used in the study. Spectral studies were performed with a Perkin-Elmer Model 270 mass spectrometer, a Perkin-Elmer Model 521 infrared spectrophotometer, and a JEOL Model MH-60II nuclear magnetic resonance spectrometer. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn.

Mirex in cyclohexane or isooctane (350 ml, 0.04 M) was placed in an Ace photochemical reactor and irradiated with a Hanovia 450 W, medium pressure, mercury lamp. No differences in the course of the reaction in these two solvents were observed. The Pyrex photochemical reactor and the quartz immersion well were water cooled in order to keep the reaction temperature below 32°. The solutions were stirred with a magnetic stirring bar and continuously aerated. The reactions were monitored with a Varian Aerograph Model 1400 gas chromatograph equipped with a flame ionization detector (column: 4 ft × 1 mm i.d.; 0.35% SE-30 on 100/120 mesh textured glass beads; 220°). Two major products were detected (retention times relative to Mirex were 0.70 and 0.55).

When 95% of the Mirex had disappeared (48 hr), the photoproducts (40% yield) were separated from the solution. Preliminary purification procedures involved evapor-

ating the solvent, vacuum drying the residue on Florisil at 130° and 360 mm pressure, and eluting the photoproducts with hexane. The final separation and purification was accomplished with preparative gas chromatography (column: 8 ft × 8 mm i.d. glass; 35% Dow Corning Hi Vac Grease (ethyl acetate soluble fraction) on Kromat FP; 290°). Other columns used to verify the purity of the photoproducts were: 4 ft × 1 mm i.d.; 0.35% diethylene glycol succinate (DEGS) on 100/120 mesh textured glass beads (230°); 4 ft × 3 mm i.d. 5% OV-210 on Anakrom ABS (230°); and 50 ft × 0.02 in i.d.; OV-1 support coated open tubular (SCOT) column (180°).

Monohydro Derivative of Mirex. The first product produced from the irradiation had a retention time relative to Mirex of 0.70 (SE-30 column). The purified product (decomposed above 350° without melting) gave the following spectra: ir (CCl₄) 3030 (w), 1230 (s), 1200 (m), 1185 (s), 1152 (w), 1135 (w), 1125 (s), 1110 (s), 1082 (w), 1065 (s), 1030 (m), 1008 (s), 980 (s), 890 (m), 645 (s), 615 (w), 575 (s), 545 (m), and 500 (s) cm⁻¹; nmr (CCl₄, TMS) δ 3.7 singlet (half-height, 2 Hz).

Anal. Calcd for C₁₀Cl₁₁H: C, 23.50; Cl, 76.30; H, 0.197; average mol wt 511. Found: C, 23.68; Cl, 76.34; H, 0.22; mol wt (mass spectroscopy) 510 (largest peak in parent ion cluster).

Dihydro Derivative of Mirex. The second major product from the irradiation had a retention time relative to Mirex of 0.55 (SE-30 column). The purified product (mp 252–254°) gave the following spectra: ir (CCl₄) 3030 (w), 1230 (s), 1200 (m), 1137 (s), 1070 (m), 1000 (s), 880 (w), 835 (m), 675 (m), 605 (m), 535 (m), and 490 (m) cm⁻¹; nmr (CCl₄, TMS) δ 3.7 singlet (half-height, 2 Hz).

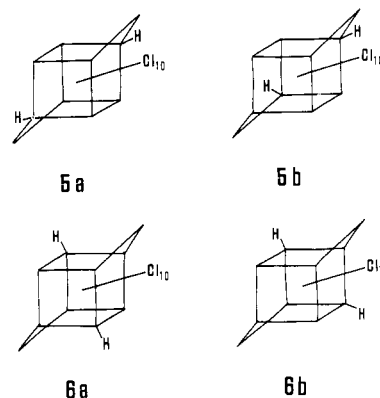
Anal. Calcd for C₁₀Cl₁₀H₂: C, 25.19; Cl, 74.37; H, 0.42; average mol wt 477. Found: C, 24.94; Cl, 74.24; H, 0.50; mol wt (mass spectroscopy) 476 (largest peak in parent ion cluster).

RESULTS AND DISCUSSIONS

There are only three possible monohydro derivatives of Mirex (structures 2, 3, and 4). The infrared spectrum of the monohydro photolysis product was not identical with either of the two monohydro isomers reported by Dilling *et al.* (1967). The compound with structure 2 was assigned unambiguously by Dilling; therefore, it can be eliminated as a photoproduct. Dilling *et al.* (1967) were unable to choose between 3 and 4 for the structure of their monohydro isomer. The gas chromatograms of the purified monohydro photoproduct consisted of one symmetrical peak on four different columns of widely differing polarity [DEGS, OV-1 (SCOT), OV-210, and SE-30]. The isomer 2 (Dilling *et al.*, 1967) is not a component of this material because the retention time of 2 relative to Mirex is 0.75, compared to 0.70 for the photoproduct (SE-30, 210°), and could therefore be easily detected. There was no band at 1600 cm⁻¹ (C=C), and intense bands at 1185 and 1200 cm⁻¹ were present in the infrared spectrum (KBr) of the photoproduct. These bands were not observed (Dilling *et al.*, 1967) in the spectrum of the other isomer (3 or 4), and strong bands were reported at 1257 and 1267 cm⁻¹ in the spectrum of this compound. There were very weak absorptions at these wavelengths in the spectrum of the photoproduct. Therefore, the photoproduct appears to be the remaining isomer, at worst contaminated with a small amount of the monohydro derivative 3 or 4 that was prepared by Dilling and coworkers.

Photolysis of the purified monohydro photoproduct revealed that it was a precursor of the dihydro photoproduct. The gas chromatogram of the dihydro compound also consisted of a single symmetrical peak on four differ-

ent columns [DEGS, OV-1 (SCOT), OV-210, and SE-30]. The mass spectrum of the dihydro product gave major peaks for the C₅Cl₅H⁻ ions, but none for the C₅Cl₄H₂⁺ or C₅Cl₆⁻ ions. The observed magnitudes of the peaks within the isotope clusters agreed well with those calculated from the number of chlorine atoms and the natural abundance of ³⁵Cl and ³⁷Cl. Any structure with nonequivalent hydrogens is inconsistent with these data. Furthermore, nmr spectra for both monohydro and dihydro derivatives gave one sharp peak at δ 3.7, and only 13 peaks were observed in the infrared spectrum of the dihydro photoproduct compared to 19 in the monohydro photoproduct. This suggests that the dihydro derivative has more symmetry than the monohydro derivative. Additionally, three of the adsorptions (3030, 1230, and 1200 cm⁻¹) which are characteristic of C-H stretching and bending modes in similar compounds (de Vries and Winstein, 1960) were identical for the monohydro and dihydro derivatives. Therefore, the possible structures for the monohydro photoproduct are 3 and 4 and for the dihydro compound are 5a, 5b, 6a, and 6b. Structures 5a or 6a were tentatively



chosen for the dihydro photoproduct because the nmr spectra of the mono- and dihydro photoproducts were identical.

ACKNOWLEDGMENT

The authors are indebted to the Entomology Research Division of the United States Department of Agriculture for financial support of part of this research.

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Received for review June 12, 1972. Accepted October 5, 1972.