The Photochemical Isomerization of Dieldrin and Endrin and Effects on Toxicity[1]

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The commonly-used insecticides dieldrin (I) and endrin (II) persist in our environment for extended periods (2). Because these insecticides are exposed to sunlight during this time, it is important to determine the identity and toxicity of materials being added to our environment by photochemical pathways. Previous studies have shown that both dieldrin and endrin are readily decomposed by ultraviolet light (3,4). In addition, it was found that one of the ultraviolet decomposition products of dieldrin was the same (by paper and gas chromatography) as the material that was obtained by exposing dieldrin-treated grass to sunlight under natural conditions for several months (4).

These studies extend Roburn's work. A single photo-conversion product was obtained in yields of 7% after three weeks and 25% after two months by exposing dieldrin to sunlight (5). The same compound was obtained in 66% yield by exposing dieldrin to a 2537 A^{o} germicidal lamp for 48 hours. This material was

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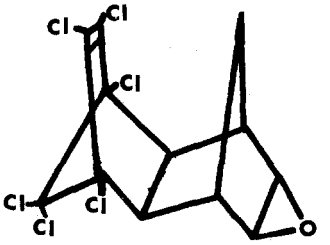
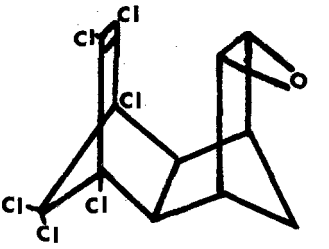


I



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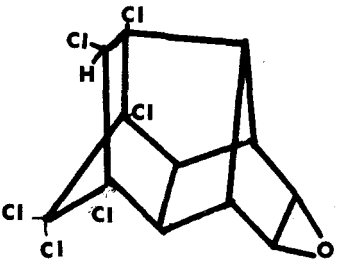

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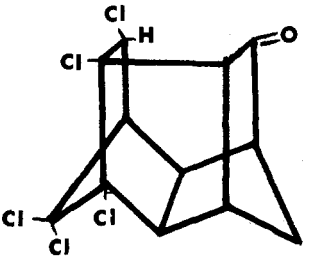

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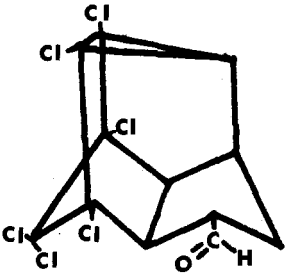

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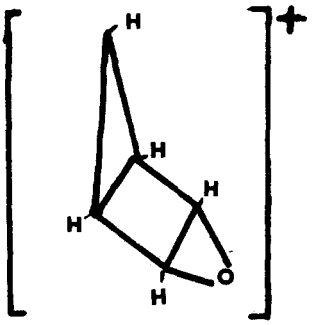
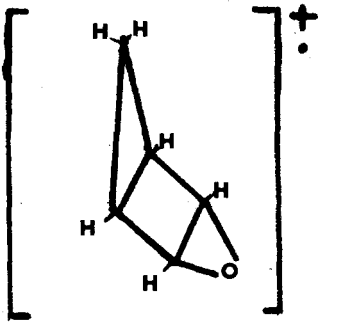


A



B

separated from starting material and other minor products by column chromatography on silica gel G, using hexane to elute dieldrin, and hexane-ethyl acetate (7:3) to elute the photo-conversion product. The laboratory and naturally-irradiated products were shown to be identical by comparison of their infrared spectra and by identical GLC and TLC behavior.

On the basis of instrumental analysis and mechanistic interpretation it appears that the photo-conversion product of dieldrin is its hexacyclo isomer, 10-oxa-3,6-exo- 4,5,13,13-hexachlorohexacyclo (6.3.1. $1^{3,6}.1^{9.11}.0^{2,7}.0^{5,12}$) tridecane (III). A comparison of the infrared spectrum of III with that of dieldrin showed the disappearance of the chlorinated-olefin peak at 1600 cm^{-1}, the disappearance of methylene absorption at 1470 cm^{-1}, and a small shift in epoxide absorption from 847 to 851 cm^{-1}. The mass spectrum (6) of III exhibited a parent ion at m/e 378 (indicating no change in molecular weight) and a base peak (non-chlorine containing) at m/e 81. This fragment most probably has structure A. In contrast, the mass spectrum of dieldrin exhibited a peak at m/e 82, probably fragment B. There was virtually no peak at m/e 82 in the degradation product. The n.m.r. spectrum (in acetone-d_6 with tetramethylsilane as reference) showed

ill-defined multiplets at 3.55, 3.44, 3.14, 2.89 and 2.45 δ as well as a singlet at 5.33 δ . We have assigned the latter peak to the migrated hydrogen on the basis of the reported chemical shift at 4.98 δ for the protons of 1,2,3,4,5,6-hexachlorocyclohexane in acetone (7). The ratio of the multiplets to the singlet at 5.33 was nearly 7:1, in accord with the proposed structure of III.

The ultraviolet irradiation of endrin, employing laboratory conditions identical to those used with dieldrin, yield 37% 1,8-exo-9,10,11,11-hexachloropentacyclo ($6.2.1.1^{3.6}$. $0^{2,7}$ $0^{4,10}$.) dodecan-5-one (IV) and 9% 4,5,6,7,8,8-hexachlorohexahydro-4,7-methano-3,5,6-methenoindan-1-carboxaldehyde (V). These compounds were isolated by thick layer chromatography on silica gel G by eluting with hexane-ethyl acetate (7:3), and exhibited identical infrared spectra to those of published spectra (8). Endrin was not converted to IV and V by the silica gel. The mechanism of formation of these two carbonyl compounds from endrin by thermal isomerization is thought to involve either a hydride shift or hydrogen abstraction of an epoxy-hydrogen (8). The geometry of the dieldrin molecule precludes involvement of an epoxy-hydrogen, and favors the participation of a methylene hydrogen. Present experiments on the exposure

of endrin to sunlight have not been completed but it is likely, on the basis of the preceding discussion, that the carbonyl compounds IV and V will be found.

Compounds I through V were examined for their toxicity to adult house fly, Musca Domestica, and larval mosquito, Aedes aegypti. The former species included a susceptible laboratory strain (Wilson) and a strain highly resistant to diazinon and less resistant to dieldrin. The laboratory strain of Aedes and its insecticide susceptibility have been reported recently (9). Compounds were applied topically in 1 ul. acetone to 4 day-old adult flies (10); 3 day-old mosquito larvae were exposed to the compounds suspended in water by means of 95% ethanol (9). The LD50 and LD90 in ug/fly and the LC50 and LC90 in p.p.m. for mosquitoes (Table 1) were taken from dosage-mortality regression lines. LD90 values for resistant house flies are not included since the strain is not homogeneous and regression lines are bi-phasic. Compounds IV and V were non-toxic to the house fly and mosquito at concentrations of 0.24 ug/fly and 0.096 p.p.m., respectively.

Based on the results obtained, III is approximately two times more toxic than dieldrin to the house-fly and mosquito. In addition, III was more rapid than

dieldrin in producing a toxic response in the house fly. These properties were also noted in the mixture of compounds (29% I, 66% III, obtained by ultraviolet irradiation of dieldrin in the laboratory). The relative toxicities of dieldrin, III and the mixture were approximately the same for both susceptible and resistant house flies, and possibly the site of action and mechanism for resistance for III and dieldrin are similar.

Although some chlorinated hydrocarbons may owe their activity to the formation of a charge-transfer complex (11), it seems that dieldrin would have less potential than DDT for such formation. Although III is more polar on the basis of solubility, by virtue of its proposed structure, it would seem to have less potential for forming charge-transfer complexes than dieldrin. Therefore, the increased toxicity and speed of action of III may be due not to a greater potential for complex formation, but to a more rapid and thorough penetration to the site of action and/or to a more precise fitting into hypothetical intermolecular lattices (12). Dieldrin has a topical:injection LC50 ratio (house fly) for 24 hours of 1.7 (13) indicative that dieldrin is relatively efficient in reaching the site of action. Studies are in progress to determine if III is actually more efficient than dieldrin.

Information on the mammalian toxicity of III and methods for its residual detection are forthcoming.

TABLE 1

$LD_{50}(LD_{90})$ ug/fly to Musca domestica and $LC_{50}(LC_{90})$ p.p.m. to Aedes aegypti of compounds.

	Hours	Dieldrin (I)	Dieldrin Isomer (III)	Mixture
Susceptible house fly	1	>.24	<.173	.09 (.2)
	2	>.24	.043 (.086)	.05 (.1)
	6	.035 (.07)	.01 (.019)	.018 (.06)
	26.5	.015 (.029)	.006 (.013)	.012 (.035)
Resistant house fly	6		.034	.058
	26.5	.032	.017	.025
Susceptible mosquito	24	.0058 (.0084)	.0029 (.0046)	

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