The Nature and Toxicity of the Photoconversion Products of Aldrin

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As part of the studies concerning the environmental fate of pesticides, the nature and toxicity of the products obtained when aldrin (I) is exposed to sunlight have been determined.

Previous work by Roburn (2) has shown that an aldrin film was converted to dieldrin (II) and a "smaller amount of an unknown substance" after exposure to ultraviolet light for 2 to 3 hours. Mitchell (3) found extensive photodecomposition after a one hour exposure on paper.

Our procedure consisted of dissolving aldrin in carbon tetrachloride in a Petri dish and evaporating the solvent. The dish was covered with a quartz plate (4) and exposed to sunlight for one month between mid-June and mid-July. A control sample, covered with taped glass was also "exposed". A three-day exposure was made earlier in June.

At the end of the one-month exposure period it was observed that 22% of the material had sublimed onto the underside of the quartz plate. This material consisted of 6.3% I, 2.4% II, 53% dieldrin photoconversion isomer (III)

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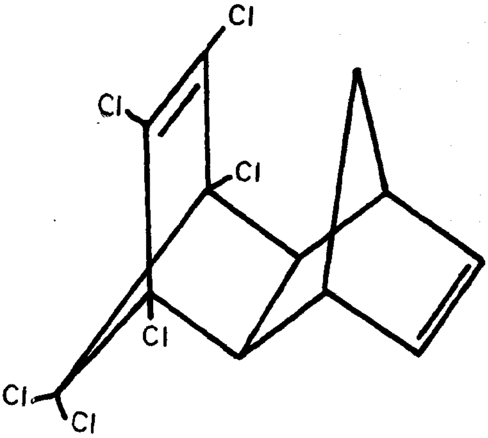
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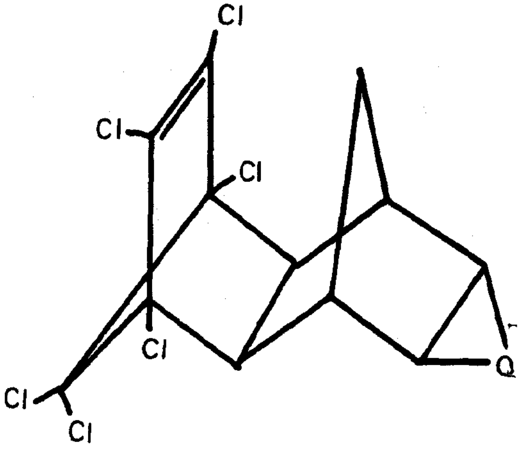
I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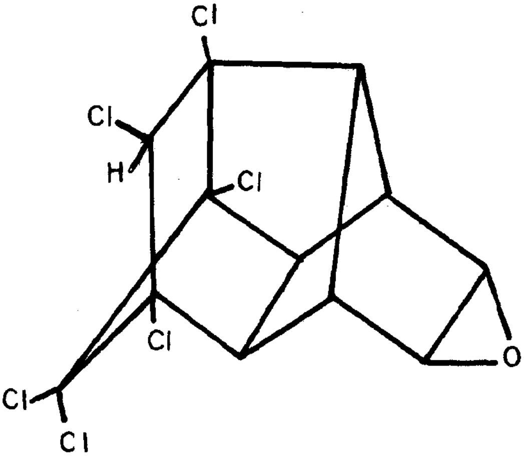
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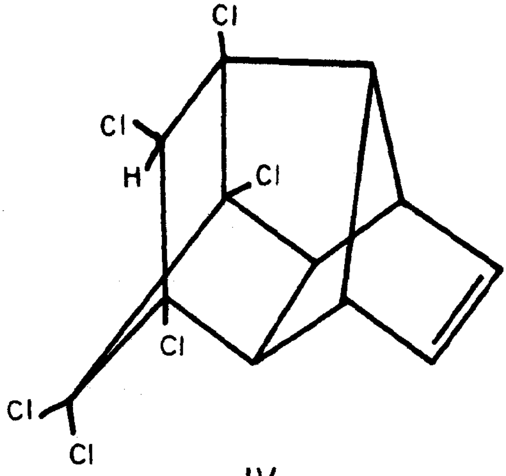
III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IV

37.8% aldrin photoconversion isomer (IV), and 0.5% polymeric material. The unsublimed material consisted of 1.5% I, 4.6% II, 16% III, 1.6% IV, and 76.3% polymer. The combined reaction mixture thus consisted of 2.6% I, 4.1% II, 24.1% III, 9.6% IV, and 59.7% polymeric material. The control sample contained only aldrin. The three-day exposure resulted in a product mixture consisting of approximately 13% I, 31% II, 7% III, 1% IV, and 46% polymeric material.

It is rather surprising that I is photolyzed so quickly by sunlight in view of the fact that its absorption maximum occurs at 2150 A^{o} while it is believed that essentially all sunlight below wavelength 2900 A^{o} is absorbed by the atmosphere (5). Crosby has also observed that some herbicides absorbing below 2900 A^{o} are photolyzed by sunlight (6).

The polymeric material was separated from the other products by taking advantage of its insolubility in hexane, while compounds I to IV were separated on a silica gel G column using hexane to elute I, IV, and II (in that order) and a mixture of hexane and ethyl acetate (7:3) to elute III. Quantitative analyses were performed by gas-liquid chromatography on a ¼-inch, 4-foot glass column containing 20% Dow Corning high vacuum grease on Chromasorb P, 60-80 mesh. At a temperature of 200^{o} and a flow rate of 90 ml/min, the retention times of II, III, and

IV relative to I on this column were 1.29, 2.74, and 1.47 respectively. The polymeric material remained on the column; the amount of this material being determined by its weight after filtration from hexane. The polymeric material also could not be eluted from columns containing liquid phases usually employed by residue chemists, i.e., DC 200, DC 11, and SE 30. If there has been any buildup of this material in our environment, it has easily been escaping detection by the most sensitive of residue analysis methods.

The polymeric material had an average molecular weight (7,8) of 482, exhibited carbonyl absorption in its infrared spectrum and contained (8) 38.36% carbon and 3.03% hydrogen. Polymeric material obtained by exposing I to a 2537 A^o ultraviolet lamp (9) for 47 hours at a distance of 6 cm, exhibited essentially the same infrared spectrum as the naturally irradiated polymeric material, had an average molecular weight of 540, and gave the following analysis: C, 37.24%; H, 2.52%, O, 8.60%; Cl, 50.77%. Compounds I to III were identified by comparison of their infrared spectra with those of authentic samples. The structure of III has recently been established (10, 11).

The aldrin photoconversion isomer (IV) was assigned the designated structure on the basis of instrumental analysis, epoxidation to III by m-chloroperbenzoic acid at room temperature (24 hours), and mechanistic similarity to the photoisomerizations of isodrin (12), dieldrin (10,11), and endrin (11). The formation of III by epoxidation of IV was confirmed by gas-liquid and thin-layer chromatography. The infrared spectrum of IV exhibited absence of chlorinated-olefin absorption at 1595 cm^{-1} as well as absence of methylene absorption at 1464 cm^{-1}. These peaks were found in an infrared spectrum of I. Olefin absorption at 3003 cm^{-1} and _cis_-olefin absorption at 722 cm^{-1} were shown by IV. The nuclear magnetic resonance spectrum (13) of IV in acetone-$\underline{d}_6$ exhibited a singlet at 5.12δ which was assigned to the migrated hydrogen on the basis of the reported chemical shift (4.98δ) for the protons of 1,2,3,4,5,6-hexachlorocyclohexane in acetone (14) and the chemical shift (5.33δ) for the migrated hydrogen of III in acetone-$\underline{d}_6$ (11). A multiplet centered at 5.90δ in the olefin region had twice the area of the singlet in accord with the proposed structure of IV. Other multiplets were found in the tertiary-hydrogen region between 3.53 and 2.55δ. Integration of this region showed it to have approximately five times the area of the singlet.

The melting point of IV was 185-6°, very nearly the same as that reported (10) for III, 188°. The latter value was confirmed in these laboratories. Because I and II are reported to melt at 104.5° and 176°, respectively (15), it was thought that IV had undergone thermal oxidation to III. However, analysis of the melted material by gas-liquid chromatography indicated that no such conversion had occurred.

Compounds I to IV and the polymeric materials obtained by both natural (one month) and artificial irradiation were examined for their toxicity to a susceptible laboratory strain (Wilson) of the adult housefly, Musca domestica. The compounds were applied in 1 ul acetone to 4-day old adult flies (16). The LD_{50} values taken from dosage-mortality regression lines based on at least 2 populations of the fly strain are given in Table 1. In this series the increased toxicity of III over II at 24 hours was not as great as observed previously (11), while IV was approximately 2 times as toxic at 24 hours as its parent compound I. The LD_{50} of III and IV at 6 hours is approximately 0.015 ug/fly, a level at which I and II under the same conditions produce little or no mortality. This fact coupled with the decreased toxicity differences of I, II, III and IV at 48 hours indicates that, rather than being more toxic than I and II, the isomers express their toxicity more rapidly, probably through more rapid penetration and distribution to the site of action. Studies on penetration and metabolism should clarify this aspect. The slight, possibly insignificant increased toxicity of IV over I at 48 hours may be due either to additional latent toxicity of I after 48 hours or possibly to a greater stability of IV to conversion to non-toxic products. The toxicities of the polymers, particularly that produced by natural means and containing less than 0.5% aldrin were

Table 1.

Toxicity of compounds to Musca domestica, LD_{50} ug/fly

Compound	LD_{50}, ug/fly	
	24 hours	48 hours
I Aldrin	0.0144	0.0085
II Dieldrin	0.0098	0.0078
III Dieldrin isomer	0.0083	0.0074
IV Aldrin isomer	0.0069	0.0065
Polymer (natural)*	0.04	
Polymer (artificial)†	0.179	

* Average molecular weight, 482
† Average molecular weight, 540

Table 2.

Acute toxicity of dieldrin and its photoconversion isomer (III) to male albino mice

Dose mg/kg	Mortality (died/tested)	
	Dieldrin	III
2.5	-	0/2,0/2
5.0	-	2/2,0/2
10.0	0/2	2/2,2/2
20.0	1/2	2/2
40.0	2/2	2/2
80.0	2/2	-

surprising, since it was expected that increased molecular weight would greatly reduce penetration and toxicity.

An indication of the mammalian toxicity of III has also been obtained. This compound was the only product found after the natural exposure of dieldrin to sunlight (11) and was apparently formed during aldrin-photolysis by isomerization of the light-produced dieldrin. It is also possible that some III was formed as a result of light-catalyzed oxidation of IV, in a manner analagous to the light-catalyzed oxidation of I to II. However, IV was not converted to III after a 48-hour exposure to ultraviolet light in the laboratory. The toxicity data of III to male albino mice, tabulated in Table 2, suggest that III is 2 to 4 times more toxic than dieldrin.

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7. Molecular weights were determined by osmometry in ethyl acetate.

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