Tetrahedron Vol. 41, No. 21, pp. 4905 to 4908, 1985
Printed in Great Britain.

0040-4020/85 $3.00 + .00

NEW PHOTOMETABOLITES OF ALDRIN

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(*Received in UK* 17 *May* 1985)

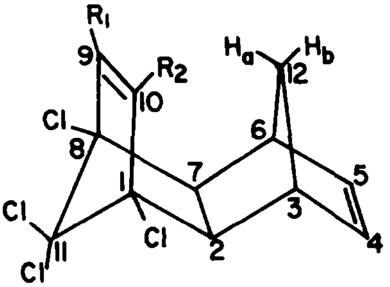
Abstract: A reinvestigation of the photochemical transformation of the cyclodiene insecticide aldrin has yielded four new metabolites. Their structures, based on spectroscopic grounds, is now reported.

Photochemical transformations of the cyclodiene insecticide aldrin (1) has been investigated extensively in the past[1] because of their importance as environmental pollutants and their ecotoxic significance. The well known photometabolites are photoaldrin[2](2), pentachloroaldrin[3](3), dieldrin[4] and photodieldrin[4]. The minor products, amounting in some cases by as much as 40%, had remained uninvestigated. In the hope of isolating some of these minor ones the photochemistry of 1 has been reinvestigated. In this paper we report the isolation and structures of four new photometabolites of aldrin formed under different conditions.

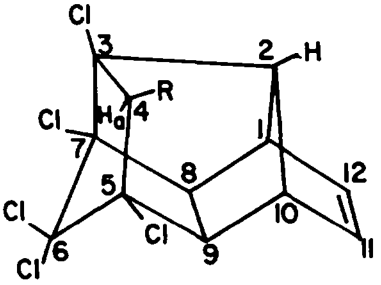
Irradiation of an hexane solution of 1 in quartz with light from a high pressure Hg lamp at room temperature yielded besides the known major products 2 and 3, two new minor photoproducts, The first one, a crystalline solid (m.p.58-60°), is formed from 1 by loss of two chlorine atoms as evidenced from its mass spectrum. The presence of a base peak at m/z 66 in this spectrum formed by retro Diels-Alder fragmentation, showed that this new metabolite has the same skeleton as the original molecule. In PMR spectrum this compound showed the presence of a new 2-proton peak at δ 6.30 in addition to three sets of 2-proton peaks present originally in the PMR spectrum of 1. These data agree with structure 4 for the new compound obviously formed by further loss of one vinylic chlorine atom from 3.

The second metabolite was obtained as a viscous liquid. Its mass spectrum showed it to be isomeric with 3 and the presence of a strong peak at m/z 65 in this spectrum indicated that it has the skeleton of photoaldrin. Its PMR spectrum was also similar to photoaldrin excepting that in place of the 1-proton peak at δ 4.89, two new 1-proton peaks appeared as doublets (J=12.5 Hz) in the high field regions of δ 1.0 and δ 1.8. Structure 5 is consistent with this data. The doublet at the lower field of δ 1.8 could be assigned to the syn proton H_{4a} of 5 as it would be more deshielded than the anti proton H_{4b} being away from the chlorinated face. The formation of this metabolite from pentachloroaldrin is analogous to the formation of photoaldrin from aldrin.

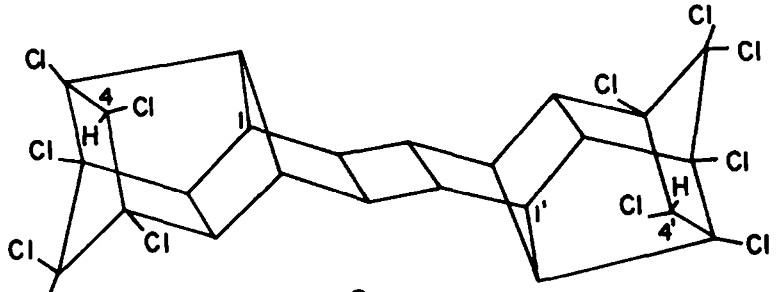
There are reports[5] of formation of unidentified minor products related to photoaldrin (**2**) from sensitised photoirradiations of **1**. A reinvestigation of this reaction using acetone as sensitiser and irradiation for a longer time, has now yielded two more new metabolites. The first one, also formed from photoaldrin, is the major product when the sensitiser acetone is used in smaller proportions ($< 10\%$). Its dimeric structure **6** is based upon its mass spectrum which not only shows molecular weight of 724, twice that of **2**, but a most intense peak at m/z 362 showing monomer formation under electron impact and no peak at m/z 66 indicating absence of aldrin like structure. Its PMR spectrum did not show any vinylic protons (as present in **2** at δ 6.30) but a new group of protons in the high field region in conformity with structure **6**. Moreover, a signal at δ 4.89 indicated the presence of $Cl-\overset{|}{\underset{|}{C}}-H$ group showing that only the double bond of **2** is involved in this dimerisation. It is possible to write four isomeric structures for this dimer from the above data but is difficult to distinguish between them. Structure **6**, having a staggard cis-anti-cis arrangement, is probably the most preferable one.



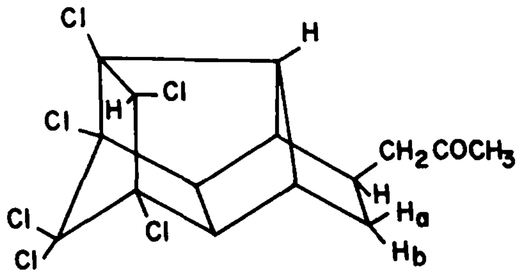
1, $R_1 = R_2 = Cl$
3, $R_1 = Cl, R_2 = H$
4, $R_1 = R_2 = H$



2, R = Cl
5, R = H_b



6



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Use of larger quantities of acetone or neat acetone in this irradiation process led to the formation of another new photometabolite from both 1 and 2. Structure 7 was given to this product on spectroscopic grounds. The compound gave a positive 2,4-DNP test and showed carbonyl absorption at ν 1720cm^{-1} in the infra red. In the mass spectrum a molecular ion peak at m/z 420 and the absence of a retro-Diels-Alder fragment at m/z 66 as well as the presence of a fragment formed by loss of $-COCH_3$ group agreed with structure 7. The absence of vinylic protons in its PMR spectrum and the presence of a 2-proton doublet at δ 3.19 confirms that the acetone residue has added on the double bond of photoaldrin (2) giving 7. On the basis of reported exo-orientation of similar acetone adduct of norbornene[6], this adduct is also assigned the exo-structure.

It is known[7] that the photoisomers of cyclodiene insecticides are more toxic than their precursors, however, the formation of these further dechlorinated and modified products may reduce their environmental hazards.

EXPERIMENTAL

PMR spectra were recorded at 60 MHz with a Varian KM360L spectrometer with TMS as internal reference. Mass spectra were recorded on Jeol JMS-D300 spectrometer in the EI mode.

Photolysis in hexane

A solution of aldrin (500 mg) in purified hexane (250 ml) was irradiated in a quartz cell with light from Hg lamp for 12 hrs. The solvent was removed under reduced pressure and the mixture was chromatographed on silica gel (50 g). The comumn was eluted with hexane and ten fractions of 20 ml each were collected.

Fractions (i) and (ii) gave the new metabolite 4 (29 mg), which crystallised from methanol as colourless cubes, m.p.58-60° (Found: C,48.20; H,3.6. $C_{12}H_{10}Cl_4$ requires C,48.64; H,3.4%). MS: 294 (M^+), 259 (M^+-Cl), 228 (M^+-66), 66 (M^+-$C_7Cl_4H_4$). PMR ($CDCl_3$) δ: 6.30 (2H,s,H_4 &H_5), 5.98 (2H,s,H_9& H_{10}), 2.85 (2H,brs,H_3& H_6), 2.68 (2H,s,H_2& H_7), 1.75 (1H,d, J=10Hz, H_{12a}), 1.25 (1H,d, J=10Hz, H_{12b}).

Fractions (iv), (v) and (vi) combined together gave unchanged 1 (90 mg).

Fractions (vii) and (viii) gave the known metabolite 3 (240 mg) m.p.82-85°.

Fractions (ix) and (x) gave a mixture (90 mg). It was rechromatographed on silica gel (10 g) and the column was eluted with hexane, when it gave (i) a further quantity of 3 (40 mg) and (ii) a new metabolite 5 (30 mg) as viscous colourless liquid (Found: C,43.42; H,3.0. $C_{12}H_9Cl_5$ requires C,43.57;H,2.7%). MS: 328 (M^+), 65 ($C_5H_5^+$). PMR ($CDCl_3$) δ :6.1 (2H,brm,H_{11}& H_{12}), 3.35 (1H,s,H_1), 3.20 (1H,s,H_{10}), 2.92 (1H,s,H_8), 2.46 (1H,s,H_9), 2.66 (1H,s,H_{2b}), 2.20 (1H,d, J=12Hz, H_{4a}), 1.90 (1H,d, J=12Hz, H_{4b}). Further elution of the original column with hexane containing 10% benzene gave only 2 (10 mg), m.p.186-88°.

Photolysis in hexane sensitised with acetone

A solution of aldrin (200 mg) in hexane (100 ml) containing acetone (20 ml) was irradiated as above. The mixture of photoproducts obtained on removal of solvent, was chromatographed on silica gel (25 g). The column was eluted with (i) hexane (20 ml) (ii) hexane-benzene (4:1, 20 ml) (iii) hexane-benzene (1:1, 40 ml) and (iv) benzene (20 ml).

Fraction (i) on removal of solvent gave a semisolid (50 mg) consisting (TLC) of 3 (major) & 5 (minor) and was not examined further.

Fraction (ii) gave largely 2 (80 mg) identical with authentic sample.

Fraction (iii) on removal of solvent gave the dimer (6) which crystallised from acetone as colourless rhombs (40 mg), m.p.242-45° (Found: C,39.80; H,2.60. $C_{24}H_{16}Cl_{12}$ requires C,39.45; H,2.19%). MS: m/z 724 (M^+), 362 ($M^+/2$). PMR ($CDCl_3$)

δ :4.82 (2H,brs,H_4& H_4'), 2.78 (2H,s,H_1& H_1'), 2.52-0.87 (12H,m).

Fraction (iv) gave a mixture (10 mg) (TLC) of photodieldrin and other polar compounds and was not examined further.

Photolysis in acetone

1 (500 mg) in acetone (200 ml) was irradiated as above until it disappeared. The solvent was removed and the intricate mixture of photoproducts were chromatographed on silica gel (50 g). The column was eluted with (i) hexane (50 ml), (ii) hexane-benzene (3:1, 50 ml) (iii) hexane-benzene (1:1, 75 ml) (iv) benzene (100 ml) and (v) benzene-ethylacetate (9:1, 50 ml).

Hexane eluate (i) gave a mixture (10 mg) of 3 and 5 (TLC).

Fraction (ii) and (iii) gave 2 (120 mg) and the dimer 6 (150 mg) respectively as major photoproducts.

Fraction (iv) yielded a mixture (145 mg) containing (TLC) of photodieldrin and a new metabolite. This mixture was rechromatographed on silica gel (20 g) which was eluted with benzene and 12 fractions of 10 ml each were collected. The first five fractions (50 ml) gave photodieldrin (50 mg), m.p. alone or when mixed with an authentic sample[4], 194-98°. The next three fractions (30 ml) gave unresolved mixture (30 mg). The last four fractions (40 ml) gave the metabolite 7 which crystallised from MeOH as colourless plates, m.p.62-65° (Found: C,42.10; H,3.5. $C_{15}H_{14}Cl_6$ requires C,42.55; H,3.3%). MS: m/z 420 (M^+), 405 (M^+-CH_3), 385 (M^+-Cl), 377 (M^+-$COCH_3$). PMR ($CDCl_3$) δ :4.85 (1H,s,H_4), 3.30 (1H,s,H_1), 3.21 (1H,s,H_{10}), 3.19 (2H,m,$\underline{CH_2}$-CO-CH_3), 2.95 (1H,s,H_8), 2.70 (1H,s,H_{2b}), 2.50 (3H,s,-CO-$\underline{CH_3}$), 2.36 (1H,s,H_9), 2.20 (1H,m,H_{12}), 1.90 (1H,m,H_{11a}), 1.80 (1H,m,H_{11b})

Fraction (v), the benzene-ethylacetate eluate (50 ml) of the main column, gave small amounts of a mixture of polar compounds which could not be separated further.

ACKNOWLEDGEMENT- Thanks are due to Indian Council of Agricultural Research, New Delhi, India, for financial support.

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Contribution No.274 from the Division of Agril. Chemicals.