# Synthesis of Known and Suspected Environmental Products of Heptachlor and Chlordene

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The photoisomerizations of the insecticides dieldrin (1,2,3,4) aldrin (5), endrin (1), heptachlor (6,7,8,9), heptachlor epoxide (7,9), chlordene (7,9) and $\alpha$-chlordane (9) have been extensively studied. On the basis of our present knowledge, it can be reasonably assumed that all these photoisomerizations do occur in sunlight, especially after volatilization from soil. It is conceivable that such a photo-reaction is involved in the environmental chemistry of metabolites of both heptachlor and chlordene. These materials are respectively hydrolyzed (10) and metabolized (11) to 1-hydroxychlordene (I). The latter may, in turn, be metabolically or chemically oxidized to 1-ketochlordene (II)(12)(13) a material which may undergo photoisomerization to photoheptachlor-ketone (III) in sunlight. The major aim of the present study was to make a quantity of III available for identification of possible residues as well as for toxicological and metabolic studies. It was postulated that III was a possible insect metabolite of photoheptachlor (IV)(6). The foregoing discussion is presented schematically in Fig. 1.

## Experimental

### Reagents

(a) All analytical grade solvents were used without further treatment except for benzene and hexane, which were redistilled. Pesticidequality acetone was used for the photolysis.

(b) Technical heptachlor (City Chemical Corp.) was purified by elution with a solution of hexane and benzene (95.5) through a Florisil (Fisher Scientific Co., 60-100 mesh) column, using 30 g Florisil for 1 g heptachlor. The eluate was evaporated, its residue recrystallized three times from hexane-ether (8:2). The resulting material was chromatographically pure (GLC and TLC).

(c) Reference standards of chlordene, heptachlor, and 1-hydroxychlordene were the generous gifts of Velsicol Chemical Corp., Chicago, Illinois.

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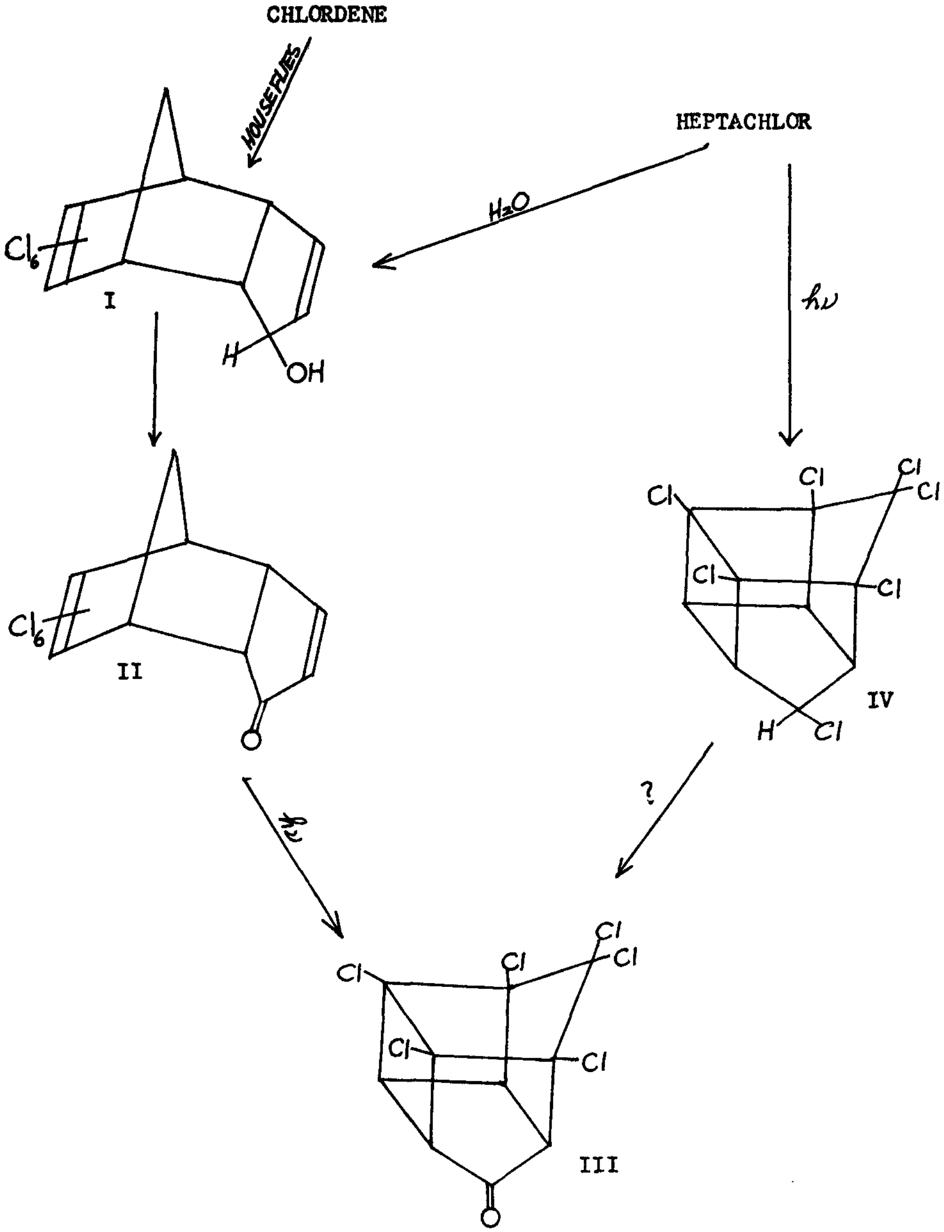

Fig. 1. Possible environmental pathways for heptachlor and chlordene.

## 1-Hydroxychlordene (I)

Ten g purified heptachlor were dissolved in 250 ml boiling 95% ethyl alcohol. Distilled water was added dropwise until the solution became cloudy. Ethyl alcohol was then added to make the solution clear again. Fifteen g of silver carbonate were added and the mixture was vigorously refluxed overnight. The reaction mixture was then concentrated to one-third its volume, and while hot, filtered with suction. The residue was washed with hot acetone (2x100 ml), the filtrate again concentrated, and transferred to a 1 liter separatory funnel containing 400 ml distilled water. Extraction with benzene followed by evaporation of the dried (anhydrous sodium sulfate) extract under reduced pressure gave 9 g of a clear gum. The latter crystallized immediately upon trituration with a solution of hexane-ether (8:2). An attempt to dissolve the crystals in ether gave 0.2 g insoluble material, which upon recrystallization from chloroform had m.p. 305-306° C. and an infrared spectrum identical to that of the "heptachlor dimer" obtained from chromous chloride reduction of heptachlor (14). The ether-soluble material was recrystallized from a solution of hexane-ether (9:1) to obtain 8.1 g of material, m.p. 201-202°C. (lit.(15) m.p. 199-201°C). Another 0.5 g was obtained from the mother liquor for a total yield of 93%. The infrared spectrum of the synthesized material was identical with that of authentic I.

## 1-Ketochlordene (II)

Modified (16) Jones' (17) reagent (217 g sodium dichromate, 170 ml acetic acid and 550 ml water) was added dropwise to a solution of 10 g I in 150 ml acetone until the reaction mixture no longer changed color, i.e., from red to green. An excess 1-2 ml. were added and the mixture was vigorously stirred for 1 hr, after which time unreacted Jones' reagent was decomposed by the addition of methyl alcohol. Evaporation under reduced pressure gave a green residue to which 300 ml water was added before extracting with ether. The organic layer was washed with 10% potassium bicarbonate solution, dried over anydrous sodium sulfate, and evaporated to give 8.6 g white solid m.p. 180-195°C. The material was purified by elution with a hexane-ether (7:3) solution through a charcoal column followed by three recrystallizations from the same solvent and a final recrystallization from methyl alcohol. The purified material (75% yield) melted at 225-227°C. (lit.(18) m.p. 200°C.). The infrared and nuclear magnetic resonance spectra of the material, however, were identical to those observed by Cochrane (18).

### Photoheptachlor-ketone (III)

A solution of 3.5 g II in 1 liter acetone was irradiated for 7 hrs with a 450-watt Hanovia lamp through a Pyrex filter. Nitrogen gas was bubbled through the reaction solution during the course of the reaction. The irradiated solution was evaporated under reduced pressure to give a light-yellow oil. The oil was chromatographed on a 25 g silica gel (J.T. Baker 80-200 mesh) column using 300 ml of a solution of hexane-benzene (1:1) as eluent. Evaporation of the eluate under reduced pressure resulted in a white oil which crystallized upon addition of a few drops of hexane. Recrystallization from hexane afforded 2.4 g (69% yield) of the photoproduct, III. The melting point of the material was difficult to determine because sublimation started at ca $253^{o}$C. On Eastman silica gel sheets with benzene as eluent, III had Rf = 0.39 and II had Rf = 0.74 (12 cm. solvent front). The spots were visualized with Mitchell's reagent (19) and U.V. light.

## Results and Discussion

The present methods for preparation of 1-hydroxychlordene all employ chlordene as starting material (20). Our alternate route takes advantage of the active allyl chloride in heptachlor. Thus, refluxing with silver carbonate in aqueous ethanol afforded 1-hydroxychlordene in high yield (21). Oxidation of the latter to 1-ketochlordene had been carried out previously (18) by the use of activated manganese dioxide as the oxidant. Unfortunately, commercially available manganese dioxide varies in activity and the manufacture of manganese dioxide in the laboratory is quite tedious, especially the step where the very fine manganese dioxide has to be filtered. In contrast, Jones' reagent is simple to prepare and gives good yields. The photoisomerization of 1-ketochlordene to photoheptachlor-ketone is formally analagous to the acetone sensitized photoisomerization of endo-tricyclo $(5.2.1.0^{2,6})$-deca-4,8-diene-3-one to pentacyclo $(5.3.0.0^{2,5}.0^{3,9}.0^{4,8})$decan-10-one (22) as well as the acetone-sensitized (7,8,9) and benzophenone-sensitized (6,23) photoisomerization of heptachlor to photoheptachlor. Further support for the assignment of structure III to the photoproduct is based on its mass spectrum parent ion at m/e 350 and infrared spectrum which exhibited a carbonyl absorption at 1818 $cm^{-1}$ (instead of 1720 $cm^{-1}$ in II) consistent with a strained carbonyl. In addition, absorptions due to Cl-C=C-Cl and H-C=C-H in the 1600 $cm^{-1}$ region were absent.

For simplicity, we have used trivial names throughout the text. The chemical names for the compounds discussed are as follows: I is 1,7,8,9,10, 10-hexachloro-*endo*-tricyclo $(5.2.1.0^{2,6})$ deca-4,8-dien-3-ol; II is 1,7,8,9,10,10-hexachloro-*endo*-tricyclo $(5.2.1.0^{2,6})$deca-4,8-dien-3-one; III is 4,5,6,6,7,8-hexachlorpentacyclo$(5.3.0.0^{2,5}.0^{3,9}.0^{4,8})$decan-10-one; IV is 4,5,6,6,7,8,10-heptachloropentacyclo$(5.3.0.0^{2,5}.0^{3,9}.0^{4.8})$decane. The published name for IV is incorrect (8).

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