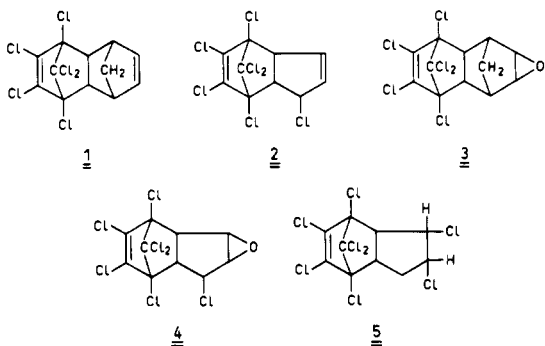


## Degradation of Cyclodiene Insecticide-Like Vinylic Chloro Compounds by Ozone

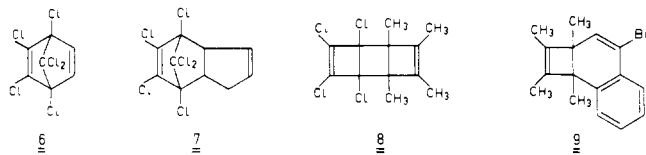
Gopalpur Nagendrappa<sup>1</sup> and Karl Griesbaum\*

The vinyl dichloro compounds 2,3-dichlorobicyclo[2.2.1]hept-2-ene and 4,5-dichlorotetracyclo[6.2.1.1<sup>3,6</sup>.0<sup>2,7</sup>]dodec-4-ene, which bear structural similarity to cyclodiene insecticides, were treated with ozone in the participating solvent methanol. This resulted in the quantitative cleavage of the two substrates at the chlorinated double bonds, yielding the corresponding esters dimethyl *cis*-1,3-cyclopentanedicarboxylate and dimethyl *cis*-3,5-tricyclo[5.2.1.0<sup>2,6</sup>]decanedicarboxylate, respectively. The relevance of this ozone cleavage to environmental pollution by similarly structured organic chloro compounds and the course of the cleavage reaction are discussed.

The insecticides aldrin (1), heptachlor (2), dieldrin (3), heptachlor epoxide (4) or chlordane (5), belonging to the so-called cyclodiene group, have been and are in part still playing a role in insect control. But they are persistent types of insecticides, and pose problems of environmental contamination and therefore have caused considerable concern (White-Stevens, 1971). Though their slow degradation in the environment takes place under various circumstances, the chlorinated double bond usually does not undergo rapid cleavage by oxidation (O'Brien, 1967; Tahori, 1972) not even in the presence of the active oxidant ozone. Thus, it was reported by Hoffmann and Eichelsdörfer (1971) that upon ozone treatment of the aforementioned cyclodiene insecticides 1–5 in water or hexane, only aldrin (1) and heptachlor (2) underwent quick reaction, while the remaining compounds 3–5 underwent slow or no reaction. This can be readily explained by rapid attack of ozone at the nonchlorinated double bonds in 1 and 2 as opposed to sluggish attack at the chlorinated double bonds in 3–5. Similar observations had been



reported for the ozonolysis of other compounds containing halogenated double bonds. Thus, ozonolysis of 6 (Slagel, 1966), 7 (Franz, 1965), 8 and 9 (Criegee, 1969 and 1970, respectively) resulted almost exclusively in the ozone cleavage of the corresponding nonhalogenated double bonds.



Notwithstanding these reports, questions concerning the interaction of ozone with substrates containing vinyl halide

structural units have received increasing attention in recent years. As a result of these activities, it has been conclusively demonstrated that halogenated double bonds indeed are attacked by ozone, albeit at considerably lower rates than nonhalogenated double bonds. Substrates that have been examined comprise compounds containing fluorinated (Gozzo and Camaggi, 1968; Gillies, 1975), chlorinated (Griesbaum and Keul, 1975; Gäb et al., 1976; Griesbaum and Hofmann, 1976), and brominated double bonds (Griesbaum and Brüggemann, 1972).

It is, however, a common feature and, from an ecological viewpoint, a considerable drawback of most of the above cited results that the major part of the halogen content remained in the various ozonolysis products. If this were not so, the interaction of ozone with cyclodiene insecticides and many other industrially important vinyl chloro compounds could be ecologically beneficial, as it would aid in the degradation of these compounds in the environment. This is particularly so if such pollutants occur in water or in the off-gases of industrial operations, where deliberate ozone treatment can be performed. Although the concentration of ozone in the atmosphere near the surface of the earth is small, its effect on chemical compounds cannot be ignored either, as its depletion in the atmosphere with higher pollution level, as in industrial cities, has been reported by Wayne and Pitts (1969).

Based on the informations which we accrued on the course of the ozonolysis of chlorinated and brominated olefins, we anticipated that the vinyl halide substituents could be effectively removed by performing the ozonolysis in a proton-donating solvent such as, e.g., methanol. Therefore, in the present investigation, we have synthesized 2,3-dichlorobicyclo[2.2.1]hept-2-ene (12) and 4,5-dichlorotetracyclo[6.2.1.1<sup>3,6</sup>.0<sup>2,7</sup>]dodec-4-ene (13) as model compounds of cyclodiene insecticides and studied their ozone degradation.

## EXPERIMENTAL SECTION

**Preparation of the Starting Materials 12 and 13.** A mixture of 33.0 g (0.5 mol) of cyclopentadiene and 130 g (1 mol) of trichloroethylene was heated in a sealed ampule in an autoclave at 180–190 °C for 10–12 h. Distillation of the reaction product through a 10-cm column afforded crude 10 and crude 11 in the following fractions 1 and 2, respectively: fraction 1, bp 50–65 °C, 0.1–0.05 Torr, 24.0 g (24.4%); fraction 2; bp 65–85 °C, 0.05 Torr, 21.0 g (15.6%).

**2,3-Dichlorobicyclo[2.2.1]hept-2-ene (12).** A mixture of 22.0 g of fraction 1 from above and 0.10 g of 5% palladium on charcoal in 100 mL of ethyl acetate was hydrogenated at ambient temperature for 45 min. The catalyst was filtered off and the product was distilled over a 10-cm column to yield 20.0 g (91%) of the crude hydrogenation product of 10, bp 46–52 °C, 0.09 Torr. Of this, 18.0 g (0.09 mol) was dehydrochlorinated by refluxing it

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overnight in a solution of 14.0 g (0.13 mol) of potassium *tert*-butoxide in 150 mL of *tert*-butyl alcohol. The cooled reaction mixture was combined with 300 mL of water and extracted with pentane; the pentane extract was washed with water, dried over sodium sulfate, and distilled to yield 11.6 g (79%) of **12**: bp 63–66 °C, 12 Torr; purity by GLC approximately 96%;  $n_D^{20}$  1.5091;  $^1\text{H NMR}$  ( $\text{CCl}_4$ ,  $\text{Me}_4\text{Si}$  as internal standard), multiplet centered at 2.93 ppm for the bridgehead protons; multiplet between 2.00 and 1.07 ppm for the remaining six protons; IR (neat), C=C stretching band at 1605  $\text{cm}^{-1}$ ; MS  $m/e$  162, 164, 166, relative ratios 9:6:1 ( $\text{M}^+$ ). Anal. Calcd for  $\text{C}_7\text{H}_8\text{Cl}_2$ : C, 51.53; H, 4.91; Cl, 43.55. Found: C, 53.10; H, 5.17; Cl, 41.71.

#### 4,5-Dichlorotetracyclo[6.2.1.1.<sup>3,6,0</sup>2,7]dodec-4-ene (**13**).

A portion consisting of 21.0 g of fraction 2 from above was hydrogenated and subsequently dehydrochlorinated as described for the preparation of **12**. After removal of pentane, 12.3 g (67.6%) of the solid **13** was obtained, which was recrystallized from ethanol and sublimated at vacuum: mp 81–82 °C; IR ( $\text{CCl}_4$ ), C=C stretching band at 1603  $\text{cm}^{-1}$ ; MS  $m/e$  228, 230, 232, relative ratios 9:6:1 ( $\text{M}^+$ ). Anal. Calcd for  $\text{C}_{12}\text{H}_{14}\text{Cl}_2$ : C, 63.15; H, 6.14; Cl, 30.70. Found: C, 64.02; H, 6.29; Cl, 29.27.

**Ozonolysis of 2,3-Dichlorobicyclo[2.2.1]hept-2-ene (**12**)**. A solution of 3.26 g (0.02 mol) of **12** in 100 mL of dry methanol was treated with 0.025 mol of ozone at ambient temperature, and the reaction product was left in the closed reaction vessel overnight. Then the solution was purged with nitrogen and the solvent was removed by distillation at 12 Torr. The remaining liquid residue of 3.50 g (94%) consisted mainly of the diester **14a**: bp 75 °C, 12 Torr; NMR ( $\text{CCl}_4$ )  $\delta$  1.5–2.3 (m, 6 H), 2.3–3.1 (m, 2 H) 3.66 (s, 6 H).

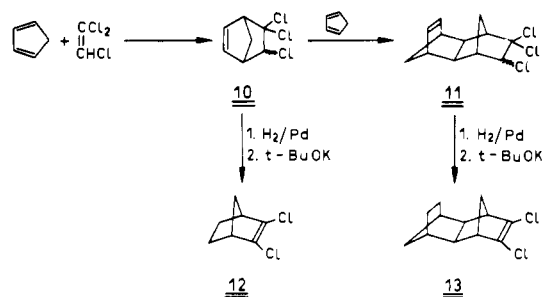
Hydrolysis of the crude ester **14a** was performed by refluxing 3.50 g of **14a** in a solution of 2.8 g (0.05 mol) of potassium hydroxide and 25 mL of 70% ethanol for 4 h. After cooling, the reaction mixture was neutralized with dilute hydrochloric acid and extracted four times with 25 mL of ether each. The combined ether extracts were washed with water and dried over sodium sulfate, and the ether was distilled to give 2.43 g (81%) of the diacid **14b**: mp (recrystallized from water) 121–122 °C (Perry, 1965; mp 120.5–121 °C). Anal. Calcd for  $\text{C}_7\text{H}_{10}\text{O}_4$ : C, 53.16; H, 6.32. Found: C, 53.31; H, 6.18.

**Ozonolysis of 4,5-Dichlorotetracyclo[6.2.1.<sup>3,6,0</sup>2,7]-dec-4-ene (**13**)**. A solution of 3.0 g (0.013 mol) of **13** in 150 mL of methanol was treated with 1.25 equiv of ozone at ambient temperature and worked up as described above for the ozonolysis of **12**. After removal of the ether, 3.2 g (97%) of the diester **15a** was obtained: mp (recrystallized from pentane) 70–71 °C;  $^1\text{H NMR}$  ( $\text{CCl}_4$ ,  $\text{Me}_4\text{Si}$  as internal standard)  $\delta$  3.63 (s, 6 H); IR ( $\text{CCl}_4$ ) carbonyl band at 1735  $\text{cm}^{-1}$ .

Hydrolysis of the ester **15a** was performed by refluxing 3.0 g (0.012 mol) of **15a** in a solution of 1.68 g (0.03 mol) of potassium hydroxide and 20 mL of 70% ethanol for 8 h. From the reaction mixture, ethanol was removed by vacuum distillation, the remaining residue was dissolved in water and neutralized with concentrated hydrochloric acid, and the precipitated solid was filtered off and recrystallized from a mixture of pentane and benzene to yield 2.66 g (86%) of **15b**: mp 220–222 °C (Soloway, 1952, mp 216–217 °C).

The diacid **15b** was converted into the corresponding anhydride by refluxing it in an excess of acetic anhydride for 5 h, removing acetic anhydride under vacuum, and recrystallization of the residue from a mixture of benzene

Scheme I



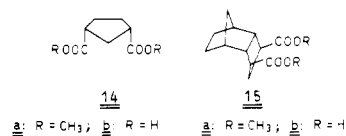
and ethyl acetate: yield, 2.3 g (94%); mp 153–155 °C (Soloway, 1952 mp 152–153 °C). Anal. Calcd for  $\text{C}_{12}\text{H}_{14}\text{O}_3$ : C, 69.90; H, 6.79; O, 23.30. Found: C, 69.61; H, 6.90; O, 23.50.

## RESULTS AND DISCUSSION

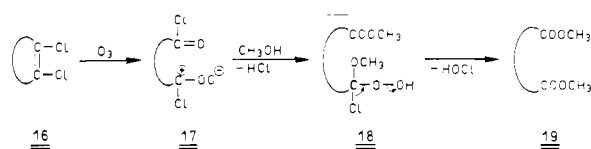
The dichloroolefin substrates **12** and **13** used in this investigation were synthesized via the sequence of reactions shown in Scheme I.

Diels-Alder reaction of trichloroethylene with cyclopentadiene afforded a mixture of compounds, from which isomeric **10** and isomeric **11** could be individually isolated by fractional distillation. Conversion of **10** into **12** and of **11** into **13** was achieved by catalytic hydrogenation of the individual substrates over palladium-charcoal and subsequent dehydrohalogenation with potassium *tert*-butoxide.

Ozonolysis of the substrates **12** and **13** was performed in methanol solution at ambient temperature and resulted in virtually quantitative conversion to the corresponding diester cleavage products **14a** and **15a**, respectively. The structures and the stereochemical identities of these diesters was established by hydrolysis which resulted in the formation of the known diacids **14b** (Perry, 1965) and **15b** (Soloway, 1952), respectively. The stereochemistry of the cleavage product **15** is indicative of an exoendo fusion of the two rings during the addition of the Diels-Alder adduct **10** to cyclopentadiene in the reaction step  $10 \rightarrow 11$ .



On the basis of other evidence obtained by Gáb (1976) and Griesbaum et al. (1972, 1975, 1976) during the study of the ozonolysis of substrates containing halogenated double bonds, it is reasonable to assume a Criegee-type reaction course (Criegee, 1968) for the ozone cleavage step. Accordingly, ozonolysis of a cyclic dichloroolefin of structure **16** would result in the formation of the intermediate **17**, containing an acyl chloride type "carbonyl" fragment and a  $\alpha$ -chloroperoxide-type "zwitterion" fragment. Subsequent reaction of this intermediate with methanol could proceed to the diester **19** in the manner depicted in the sequence  $17 \rightarrow 18 \rightarrow 19$ .



It is obvious that ozone cleavage of **12** and **13** or of other substrates containing dichloroolefin structures could be also performed in the presence of water as participating solvent. In such cases, carboxylic acids would be directly formed as cleavage products. This could be of interest as

an initial step for the removal of chloroolefin materials from water by ozone treatment, since the organically bound chlorine is completely removed as HCl with concomitant introduction of functional groups which render the molecules amenable to biological degradation. Recent unpublished work in our laboratory had demonstrated, that the ozonolysis of vinyl chloride type olefins in water indeed produces the corresponding carboxylic acid fragments: ozonolysis of 1-chlorocyclopentene and of 1-chlorocyclohexene in water-acetone afforded the corresponding diacids in approximately 85% yield.

#### ACKNOWLEDGMENT

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#### LITERATURE CITED

- Criegee, R., *Chimia* **22**, 392 (1968).  
Criegee, R., Huber, H., *Angew. Chem.* **81**, 749 (1969).  
Criegee, R., Schweikhardt, C., Knoche, H., *Chem. Ber.* **103**, 960 (1970).

- Franz, J. E., Knowles, W. S., Osuch, C. J., *J. Org. Chem.* **30**, 4328 (1965).  
Gäb, S., Nitz, S., Parlar, H., Korte, F., *Angew. Chem.* **88**, 479 (1976).  
Gillies, G. W., *J. Am. Chem. Soc.* **97**, 1276 (1975).  
Gozzo, F., Camaggi, G., *Chim. Ind. (Milan)* **50**, 197 (1968).  
Griesbaum, K., Brüggemann, J., *Chem. Ber.* **105**, 3638 (1972).  
Griesbaum, K., Keul, H., *Angew. Chem.* **87**, 748 (1975).  
Griesbaum, K., Hofmann, P., *J. Am. Chem. Soc.* **98**, 2877 (1976).  
Hoffmann, J., Eichelsdörfer, D., *Vom Wasser* **38**, 197 (1971).  
O'Brien, R. D., "Insecticides: Action and Metabolism", Academic Press, New York, N.Y., 1967, pp 136-144.  
Perry, R. H., *J. Org. Chem.* **30**, 2593 (1965).  
Slagel, R. C., *J. Org. Chem.* **31**, 593 (1966).  
Soloway, S. B., *J. Am. Chem. Soc.* **74**, 1027 (1952).  
Tahori, A. S., Ed., "Pesticide Chemistry", Vol. VI, Gordon Breach Publishers, London, 1972.  
Wayne, R. P., Pitts, J. N., *J. Chem. Phys.* **50**, 3644 (1969).  
White-Stevens, R., Ed., "Pesticides in the Environment", Vol. 1, Part 1, Marcel Dekker, New York, N.Y., 1971, pp 91-92.

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## Reductive Dechlorination of the Toxaphene Component 2,2,5-*endo*,6-*exo*,8,9,10-Heptachlorobornane in Various Chemical, Photochemical, and Metabolic Systems

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2,2,5-*endo*,6-*exo*,8,9,10-Heptachlorobornane, one of the most toxic components of toxaphene insecticide, undergoes reductive dechlorination at the geminal dichloro group to yield 2-*endo*,5-*endo*,6-*exo*,8,9,10-hexachlorobornane and 2-*exo*,5-*endo*,6-*exo*,8,9,10-hexachlorobornane in the following systems: photolysis in hexane solution with UV light; triphenyltin hydride in hexane containing 2,2'-azobis(2-methylpropionitrile); reduced hematin in glacial acetic acid-*N*-methyl-2-pyrrolidone; bovine rumen fluid; sewage primary effluent; rat liver microsomes under anaerobic conditions with NADPH as the critical cofactor; rats and houseflies in vivo. This heptachlorobornane is also dehydrochlorinated to give 2,5-*endo*,6-*exo*,8,9,10-hexachloroborn-2,3-ene in the triphenyltin hydride and reduced hematin systems and in rats and houseflies in vivo. Reduced hematin and the tin hydride system also convert the heptachlorobornane to 2,5-*endo*,8,9,10-pentachlorotricyclene. Fat from rats treated orally with toxaphene contains products similar in GLC characteristics to toxaphene itself whereas liver and feces contain toxaphene-derived products of greatly altered GLC properties.

Essential knowledge of the metabolic and environmental fate of toxaphene, the major chlorinated hydrocarbon insecticide used in the United States, has developed slowly in recent years with associated advances in identification of components and improvement of analytical procedures. Toxaphene undergoes rapid dechlorination in mammals (Casida et al., 1974; Crowder and Dindal, 1974; Ohsawa et al., 1975) and is metabolized in houseflies (Hoffman and Lindquist, 1952) and in a cotton leafworm enzyme preparation (Abd El-Aziz et al., 1965, 1966). No toxaphene metabolite other than chloride ion was identified in these studies, in large part because of difficulties in examining

such a complex mixture of polychlorobornanes and other materials (Holmstead et al., 1974).

One toxaphene component, 2,2,5-*endo*,6-*exo*,8,9,10-heptachlorobornane (I), constitutes up to 8% of the technical grade insecticide (Palmer et al., 1975; Saleh and Casida, 1977) and four octachlorobornanes, each derivable by addition of one chlorine atom to I, make up an additional ~15% of toxaphene (Matsumura et al., 1975; Saleh and Casida, 1977; Turner et al., 1975, 1977). Heptachlorobornane I has relatively high biological activity and is one of the most easily isolated components of toxaphene. It is therefore a suitable model compound for use in studies to gain an understanding of reactions involved in detoxication of several polychlorobornane components of toxaphene. An aqueous reduced hematin system degrades this heptachlorobornane to unidentified products by reductive dechlorination and dehydrochlorination, and it also dechlorinates many other toxaphene components (Khalifa et al., 1976). The present study and a preliminary report

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