

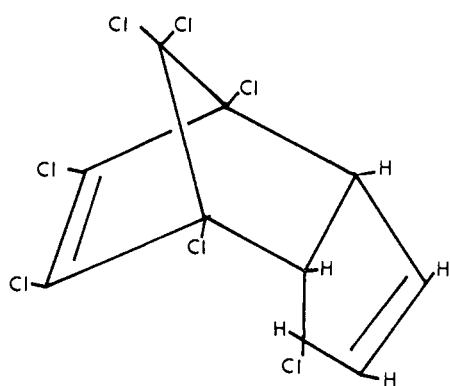
COMMUNICATIONS

Sensitized Photolysis of Heptachlor

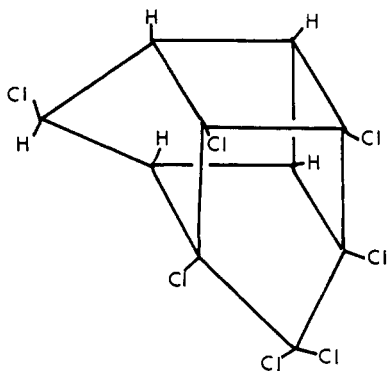
The conversion of heptachlor to its cage isomer photoheptachlor in the presence of benzophenone has been studied again because of a published report questioning the action of benzophenone as a sensi-

tizer for this reaction. The results of the present investigation clearly indicate that benzophenone is indeed acting as a photosensitizer.

Since publication of a report on the benzophenone-sensitized photoconversion of heptachlor (I) to photoheptachlor (II) in benzene (Rosen *et al.*, 1969), several



I



II

reports dealing with this reaction have appeared. Benson *et al.* (1969) observed formation of II upon exposure of I to sunlight in the absence of any solvent and also observed that the reaction was readily sensitized by acetone. Ivie and Casida (1970) were able to effect the conversion in sunlight within 1 hr on bean leaves by using rotenone as a sensitizer. McGuire *et al.* (1970) also found the formation of II to be sensitized by acetone. The latter authors also attempted to use benzophenone as a sensitizer in a cyclohexane solvent, but were unable to obtain II in this system. They concluded, therefore, that benzophenone was not a sensitizer for the photoconversion of I to II and that the sensitizer in Rosen *et al.*'s system was in fact the solvent benzene. Such a conclusion seems unwarranted, as it is well known that photolysis of benzophenone in solvents with easily abstractable hydrogen atoms (such as cyclohexane) leads to the rapid destruction of benzophenone (Calvert and Pitts, 1966).

EXPERIMENTAL

Materials. Heptachlor, 99.8% pure, was generously supplied by Dr. Percy B. Polen, Velsicol Chemical Corp., Chicago, Ill. The solvents, benzene and cyclohexane, were both Mathieson, Coleman, and Bell Pesticide quality.

Irradiation Conditions. Heptachlor (0.01 mole) in 1-l. benzene was exposed to a 450-watt Hanovia lamp both in the presence and absence of 0.01 mole benzophenone through a 1.8 mm borosilicate glass filter. Such a filter effectively stops most of the light transmission below 297 nm. The solutions were irradiated for periods of 3 and 6 hr at 20° C. Nitrogen was bubbled through the solution from ½ hr before irradiation and continued throughout the period of irradiation. In an identical way, 0.01 mole benzophenone was irradiated for 3 hr in 1-l. cyclohexane.

Assay. Formation of photoheptachlor and loss of benzophenone were monitored by gas-liquid chromatography using previously described conditions (Rosen *et al.*, 1969).

RESULTS AND DISCUSSION

The results of these simple experiments are quite clear. In benzene solution, in the presence of benzophenone, photoheptachlor was formed within 3 hr; in the absence of benzophenone, no photoheptachlor was detected even after 6 hr. In fact, no loss of heptachlor was observed. Furthermore, irradiation of benzophenone in cyclohexane under identical conditions led to the complete disappearance of benzophenone within 3 hr. It is obvious that benzophenone, and not benzene, is the sensitizer for this reaction. In cyclohexane, benzophenone cannot act as a sensitizer because triplet benzophenone preferentially abstracts a hydrogen atom from the solvent instead of transferring its energy to heptachlor.

LITERATURE CITED

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