

On the Sensitized Photoisomerization Reaction of the Insecticide β -Dihydroheptachlor

Photoisomerization reactions of the cyclodiene insecticide β -dihydroheptachlor (1) were studied in the presence of different sensitizers. With the help of column chromatography two new isomerization products (3 and 4) were isolated and identified by spectroscopic methods (MS, IR, and ^1H NMR). It was found that β -dihydroheptachlor (1) is unstable toward UV light with wavelengths above 290 nm, which predominate in the troposphere.

β -Dihydroheptachlor (2-*exo*-4,5,6,7,8,8-heptachloro-4,7-methano-3a,4,7,7a-tetrahydroindan) (1) is a cyclodiene insecticide of very low toxicity to warm-blooded animals. It was developed by Büchel et al. (1964, 1966a). The compound is present as active ingredient in Holtan and in Bl 1948 (Büchel et al., 1966b). Preparation is by Lewis acid-catalyzed addition of chlorine to chlordane (Büchel et al., 1964; Falbe and Schulze-Steinen, 1967). Mainly three dihydroheptachlor isomers are formed in proportions varying with the reaction conditions. Of these isomers, β -dihydroheptachlor (1) is the most active compound comparable to DDT or chlordane (Büchel et al., 1964). As a cyclodiene insecticide this compound has a low toxicity. In many cases the lethal dose is not reached even when large amounts are given (Chamber et al., 1965). β -Dihydroheptachlor (1) is rapidly metabolized in warm-blooded animals (Ludwig, 1965) and soil microorganisms convert it to hydrophilic metabolites (Poonawalla and Korte, 1968). The consequence is that, at least in biological respects, β -dihydroheptachlor (1) is an environmentally compatible insecticide. The question whether this compound is also transformed under abiotic environmental conditions, especially by the action of the solar UV irradiation, is important when this substance is subjected to an ecotoxicologic assessment.

So far little has been reported about the photochemical reactions of β -dihydroheptachlor (1) (Vollner et al., 1971). Photo- β -dihydroheptachlor (2) was the only identified photoisomerization product. We have found that other intramolecular proceeding photoisomerization reactions of β -dihydroheptachlor are feasible as well. It was possible to show that the formation of these products is dependent on temperature. Moreover, with the help of the product analysis, which was carried out, we were able to detect dechlorination reactions, which normally do not occur with other cyclodiene insecticides under these conditions of irradiation ($\lambda > 290$ nm).

MATERIALS AND METHODS

A Philips HPK 125 mercury high-pressure lamp and Pyrex filters were used for irradiation. The concentration of the irradiated solution of β -dihydroheptachlor was at around 0.027 mol/L. Irradiation times were 16 h in all the experiments. The solvents (140 mL; dioxane/sensitizer, 30:1) were purged with nitrogen to remove dissolved oxygen. For the irradiation at room temperature at cylindrical Pyrex photoreactor was used. The low-temperature experiments were carried out in a double-walled irradiation vessel made of the same material.

A Carlo-Erba gas chromatograph Model Fractovap 2200 (2 m column length, 4 mm diameter; 3% OV-1 on Chromosorb W-AW-DMCS (80–100 mesh); injection port temperature, 250 °C; detector temperature, 300 °C; column temperature, 180 °C; nitrogen as carrier gas; flow rate, 40 mL/min) equipped with a FID detector and Hewlett Packard 3380 A integrator were employed for qualitative

and quantitative analysis. For thin-layer chromatography, silica gel plates with a layer thickness of 0.25 mm (Merck, Darmstadt) were used, with petroleum ether as solvent. After developing, the plates were sprayed with 1% diphenylamine solution and irradiated with UV light for about 5 min ($\lambda = 254$ nm) to detect substances. Separation of the photoproducts was performed by column chromatography (length, 1 m; ϕ , 4 cm). Silica gel from Merck Co. (grain size 0.20–0.06 mm) served as adsorbent and petroleum ether (bp 60–90 °C) was used for elution. The elution speed was 1 mL/min. Individual examination of the fractions (respectively, 50 mL) was carried out by gas chromatography and thin-layer chromatography. The starting compound β -dihydroheptachlor (1) was isolated in fractions 10–14, compounds 5 and 6 were isolated in fractions 17–18, compounds 3 and 4 in fractions 28–31 and compound 2 in fractions 33–40. Table I gives the respective TLC and GLC characteristics and melting points of compounds (1–6). The mass spectra of the gas chromatographically pure compounds were obtained by direct inlet and those of mixtures by GC/MS LKB 9000 S [column length, 2 m; ϕ , 4 mm; 3% OV-1, W-AW-DMCS (80–100 mesh)]. The electron energy was 70 eV. The MS data were processed by a digital computer IBM 1130 via an Interface (WDV Company, Munich, West Germany). The elementary composition of the molecule and fragment ions was based on the first peak in each Cl cluster. The ^1H NMR spectra (CDCl_3 , Me_4Si) were recorded by a 90 MHz R-32 apparatus from Perkin-Elmer. Infrared spectra were obtained with KBr disks of the sample using a Perkin-Elmer Model 577 instrument.

RESULTS

It is evident by our investigations that the photoisomerization of β -dihydroheptachlor (1) is dependent on temperature. Irradiation experiments below -70 °C show that the parent compound (1) is stable under these conditions. Photoproducts (2–6) could be detected from -70 °C onwards. The product analysis after irradiation under different temperature conditions (-70 to $+25$ °C) indicates that the reactions proceed uniformly. Important differences in the concentrations of the photoproducts could not be observed. Vollner et al. (1971) isolated only one photoproduct (compound 2) by UV irradiation, which could be separated by column chromatography and they identified it by spectroscopic methods. The mono- and didechloro products 5 and 6, however, were obtained by UV irradiation of β -dihydroheptachlor (1) with wavelengths above 230 nm in protonated solvents. In a different article, Scharf (1965) attributed the formation of photoisomer (2) to an intramolecular photoreaction, the so-called ($\pi\sigma \rightarrow 2\sigma$) reaction. In the first step of this process, the excited chlorinated double bond abstracts the 2-*endo* hydrogen atom, forming a radical intermediate (2a) which recombines subsequently to compound 2 (Figure 1). However, as we were able to show, the activated chlori-

Table I. Physical Data of the Compounds 1-6

Compound	R_f^a	t_R^b	Mp, °C
2- <i>exo</i> -4,5,6,7,8-Heptachloro-3a,4,7,7a-tetrahydro-4,7-methanoindan (1)	0.46	1.00	136
2,3,3,3a,4,5,8- <i>exo</i> -Heptachloro-1,2,3,3a,4,5,6,6a-octahydro-1,5:2,4-dimethanopentalene (2)	0.15	2.15	151
1,1,2,3- <i>exo</i> -3a,7a,5- <i>exo</i> -Heptachloro-3a,4,5,6,7,7a-hexahydroindan (3)	0.20	1.80	nd ^c
1,1a,2,2,3,5,6-Heptachloro-1a,2,3,3a,5a,5b-hexahydro-1 <i>H</i> -cyclobuta[<i>cd</i>]pentalene (4)	0.25	1.80	nd ^c
2- <i>exo</i> -4,6,7,8,8-Hexachloro-3a,4,7,7a-tetrahydro-4,7-methanoindan (5)	0.37	0.75	122
2- <i>exo</i> -4,7,8,8-Pentachloro-3a,4,7,7a-tetrahydro-4,7-methanoindan (6)	0.32	0.80	117

^a Solvent system: *n*-hexane. ^b 3% OV-1 on Chromosorb W-AW-DMCS; 180 °C; flow rate, 40 mL/min. ^c Not detected.

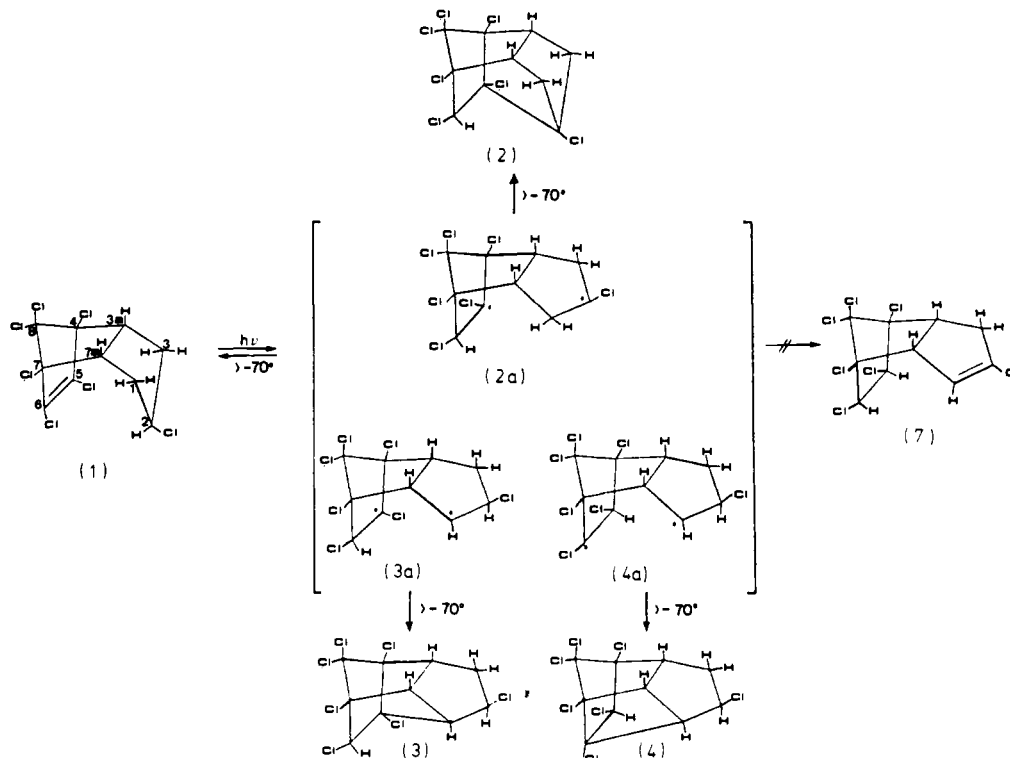


Figure 1. Photoisomerization reactions of β -dihydroheptachlor (1) with wavelengths above 290 nm.

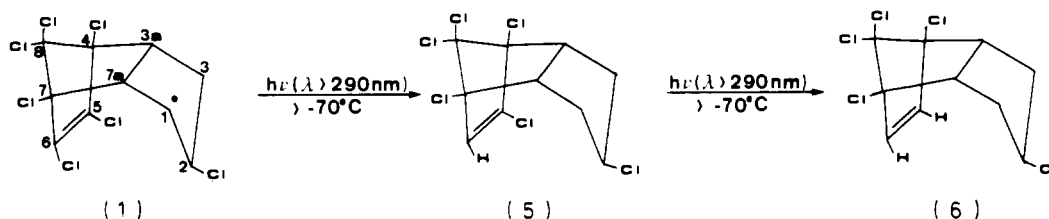


Figure 2. Photodechlorination reactions of β -dihydroheptachlor (2).

nated double bond abstracts both the endo hydrogen atoms on the C_2 and the endo hydrogen atoms on the C_1 and C_3 , respectively. (The two positions are stereochemically identical because of the symmetry of the molecule). Thus, not just one radical intermediate (2a) but two additional ones (3a and 4a) are formed, and their further reaction leads to the hitherto unknown photoisomerization products 3 and 4. Formation of the hydrogen transfer product (7) (Parlar et al., 1975), which may be described as an abstraction of the second hydrogen atom by the chlorinated double bond, was not observed. In contrast, dechlorination of 1 was found to take place under these conditions ($\lambda > 290$ nm) (Figure 2). Unlike the photoisomerization these steps proceed intermolecularly. By using acetone- d_6 as solvent it could be demonstrated that in both compounds 6 and 7 deuterium is incorporated instead of hydrogen. Mass spectroscopic studies of the photoisomerization products 2, 3, and 4, which were isolated in the same experiment, show that no deuterium

was incorporated in these compounds (intramolecular formation).

Acetone, acetophenone, and benzophenone all sensitize the photoisomerization reaction. In contrast, excited triphenylene ($E_T = 66.6$ kcal/mol) is unable to effect the triplet energy transfer. Therefore, the triplet state of lowest energy of β -dihydroheptachlor is between 66.6 and 68.5 (Figure 3).

Spectroscopical methods were applied for the structure elucidation of photoproducts 2-6. In addition, authentic reference substances were available in the case of compounds 2, 5 and 6. A comparison of the 1H NMR spectra of the starting compound (1) with those of 5 and 6 shows that 5 and 6, unlike β -dihydroheptachlor (1) have two olefinic protons which are recorded as singlets at δ 6.10 and 6.05. The signals of the other protons had the same multiplicity and chemical shift as those of compound 1. Only the signals of the 2-endo hydrogen atoms of compounds 5 and 6 undergo a small downfield shift. IR spectra

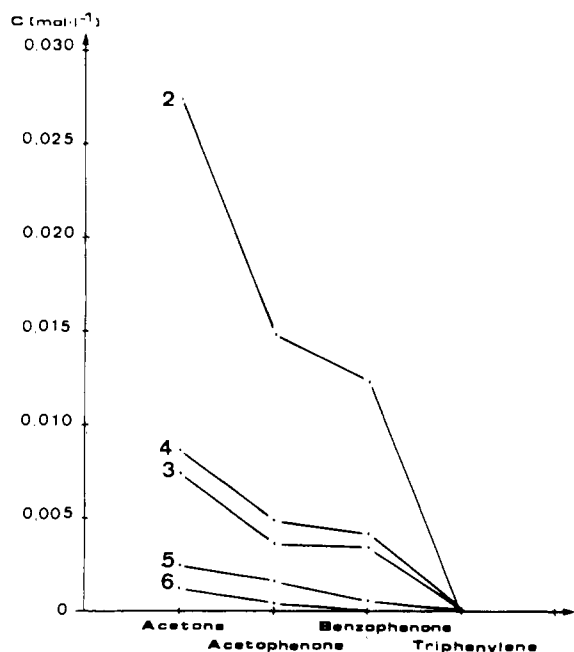


Figure 3. The effects of sensitizers on the concentration of photoproducts (after 16 h of irradiation).

of 5 and 6 show C=C-H vibrating of low intensity above 3000 cm^{-1} . A very intense band at 1595 cm^{-1} is due to the monodechlorinated double bond of compound 5. In contrast, the absorption of the double bond of compound 6 is not observed.

M^+ peaks of compounds 5 and 6 (338 with five and 304 with four chlorine atoms) indicate dechlorination. The retro-Diels-Alder fragments of 236 with five chlorine atoms (compound 5) and the 202 with four chlorine atoms (compound 6) confirm the proposed structures.

The ^1H NMR, IR, and MS data for compound 2 agree with the values obtained by Vollner et al. (1971). Structure elucidation of compounds 3 and 4 is based on the same methods. The data obtained in ^1H NMR spectroscopy, more especially the coupling constants, agree with the values of compounds with the same carbon skeleton, which were described by Lahaniatis (1976) and by Parlar et al. (1975). The proposed structures are also confirmed by the mass spectroscopic behavior of these compounds. Both compounds (3 and 4) have a molecular peak at m/e 372 with low intensity. The further fragmentations are induced by loss of Cl atoms (e.g., 337 with six chlorine atoms, 302 with five chlorine atoms, 267 with four chlorine atoms). IR spectra of these compounds point to the saturated character of these substances because the typical absorption band ($\nu = 1590\text{--}1610\text{ cm}^{-1}$) is absent.

It is evident from these results that β -dihydroheptachlor (1) is relatively unstable toward UV light with wavelengths $\lambda > 290\text{ nm}$ which predominate in the troposphere. Rapid dechlorination of this compound leads to the didechlorinated compound 6, which has a nonchlorinated double bond and can therefore very easily be attacked by biotical and abiotical processes. The isolation of photoisomerization products 2, 3, and 4 demonstrates that all structurally possible free-radical intermediates (2a, 3a, and 4a) are formed exclusively from β -dihydroheptachlor (1) and not indirectly from compound 7. [During UV irradiation of the aldrin-dieldrin metabolite dihydrochlordenedicarboxylic acid, it was found that the hydrogen transfer product (analogously to compound 7) participates in the formation of these free-radical intermediates (Parlar et al., 1975).]

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