Although the half-life of a 100 ppm solution of Sustar in dilute phosphate buffer at pH 7.2 was much longer (12 days) than at pH 3.6 (5 days), that of an environmentally more realistic concentration of 0.6 ppm in filtered creek water (pH 8.6) was only about 6 days. The decreased stability in natural water may be due to photosensitization by natural solutes (Lykken, 1972) or photochemically generated oxidants (Draper et al., 1976; Zepp et al., 1977).

The extractable organic photoproducts all had half-lives shorter than that of Sustar and would not be expected to accumulate. The observed terminal products consisted of unextractable, highly polar substances and carbon dioxide which probably formed via ring cleavage of quinones such as IV (Wong and Crosby, 1978). Both trifluoromethanesulfonic acid (XII) and its amide (V) were detected even after extended irradiation and appear to be photochemically stable.

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Photoreactions of Hydroxychlordene in Solution, as Solids, and on the Surface of Leaves

Harun Parlar,* Mohammed Mansour, and Rotraud Baumann

The photoreactions of the heptachlor transformation product 1-*exo*-hydroxychlordene (*exo*-4,5,6,7,-8,8-hexachloro-3a,4,7,7a-tetrahydro-4,7-methanoinden-1-ol) (2) dissolved in organic solvents, as a solid on glass, and dispersed on plant leaf surfaces have been investigated. In addition to the (2 + 2) cycloaddition typical for this substance class, an entirely novel intramolecular photoisomerization reaction was found. This reaction leads to cyclic ketone, 1,1a,2,2,3,*exo*-6-hexachloro-1a,2,3,3a,5a,5b-hexahydro-1,3-methano-1*H*-cyclobuta[*cd*]pentalen-4-one (8), whose structure was established by spectral data obtained by mass spectrometry, infrared spectrometry, and ¹H and ¹³C nuclear magnetic resonance measurements.

The degradation of pesticides under both biotic and abiotic conditions leads to residues which can accumulate in the biosphere. In this connection the reactions and

changes of pesticides caused by solar UV light are especially important (Crosby et al., 1965; Ivie et al., 1974; Gäb et al., 1975; Parlar and Korte, 1977; Liang and Lichtenstein, 1976). Intramolecular photoisomerizations, whose course is controlled exclusively by the excited state, are among the most important and likely pesticide transformation mechanisms. Neither proton-active compounds nor oxygen species [e.g., $^3\Sigma^-_g$ O_2, $^1\Delta_g$ O_2, $O(^3P)$, or $O(^1D)$] are required for these conversions. Consequently, reactions of this type represent the first possible step in many photochemical conversions if the structural requisites for
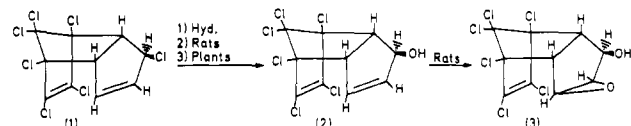
Institut für Ökologische Chemie der Gesellschaft für Strahlen- und Umweltforschung mbH München, D-8051 Attaching, Federal Republic of Germany (H.P., M.M., R.B.) and Institut für Chemie der Technischen Universität München, D-8050 Freising-Weihenstephan, Federal Republic of Germany (H.P.).

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Figure 1. Transformations of heptachlor (1) to 1-*exo*-hydroxychlordene (2) and 1-*exo*-hydroxy-2,3-epoxychlordene (3).

light absorption and a subsequent reaction are fulfilled. 1-*exo*-Hydroxychlordene (2) is known to be a transformation product of the cyclodiene insecticide heptachlor (1) in plants and soil (Weisgerber et al., 1972). There is no certainty either that this substance does not occur as the primary metabolite of heptachlor (1) in warm-blooded animals. Kaul et al. (1970) suggest that 1 is metabolized in rats to the end-product 1-*exo*-hydroxy-2,3-epoxychlordene (3) via 2 (Figure 1). Other groups of workers postulate that 2 is formed from 1 by a chemical and not an enzymatic route at least in plants (Weisgerber et al., 1972). The conversion is rapid because the chlorine atom in the allyl position can be attacked readily both by free radicals and ionically. 1-*exo*-Hydroxychlordene (2), in contrast to heptachlor (1), is relatively stable in biological systems and remains unchanged for long periods (Weisgerber et al., 1972). The present work describes the photochemical behavior of 2, and more particularly its photoisomerizations, with a view to determining possible derivative products of this chemical substance in the environment.

MATERIAL AND METHODS

Chemicals. The chloroform, dioxane, acetone, *n*-hexane, and petroleum ether used as solvents were 99.0% pure by gas chromatography (GC), while the triplet sensitizers acetophenone and benzophenone were of analytical reagent quality. Both the hexadeuterioacetone (acetone-d_6) and the lithium aluminum deuteride (LiAlD$_4$) were 99.5% deuterated. Heptachlor (1) was kindly supplied by Velsicol Chemical Corp. 1-*exo*-Hydroxychlordene (2) was prepared by hydrolysis of 1-*exo*-bromochlordene (5) with silver carbonate (Parlar et al., 1975); 5 itself is readily accessible from chlordene by allyl bromination with *N*-bromosuccinimide (Büchel, 1970). A small amount of the endo-product 6 was also formed (Figure 2). The crude product was subsequently purified by column chromatography (ϕ, 3 cm; length, 40 cm; grain size, 0.20–0.06 mm, E. Merck; eluent, 5:1 60–90 °C petroleum ether–methanol),

Table I. Melting Points and Chromatographic Characteristics of the Compounds 1–9

compd	mp, °C[a]	rel. retent. time[b]	R_f
1	95	1.00	0.55[c]
2	205	1.31	0.30[d]
3	nd[e]	2.92	0.16[d]
4	200	0.70	0.64[c]
5	63	1.40	0.55[c]
6	223	1.32	0.30[d]
7	224	nd	0.21[c]
8	180	1.7	0.70[d]
9	230	2.70	0.24[d]

[a] Uncorrected. [b] Relative to heptachlor (1). [c] *n*-Hexane. [d] Chloroform. [e] nd = not detected.

and a final recrystallization from *n*-hexane was carried out.

1-*endo*-Deuterio-1-*exo*-hydroxychlordene (2′) was synthesized by saponifying the 1-*exo*-deuterioheptachlor (1′) with silver carbonate in 2:1 methanol–water. Good yields of 1′ were obtained from the deuterated alcohol (6′) with thionyl chloride; 6′ was prepared by reduction of the α,-β-unsaturated ketone (7) with LiAlD$_4$ (Parlar, 1975) (Figure 3). Table I surveys the melting points and chromatographic characteristics of the compounds (1–9) and Table II the spectroscopical data of the compounds (5–9).

Chromatography and Spectroscopy. GC analyses were performed with a Packard Model 417 instrument (column length, 2 m; ϕ, 4 mm; 3% OV-1 on Chromosorb W-AW-DMCS, 80–100 mesh; injection port temperature, 250 °C; detection, FID or [63]Ni ECD at 300 °C; column, 140–200 °C; carrier gas, 40 mL/min nitrogen). A Hewlett Packard 3380 A integrator was used for the quantitative evaluation of the individual samples. Precoated 0.25 mm E. Merck silica gel 60F254 plates were used for the thin-layer chromatography. After the development, the plates were sprayed with 1% diphenylamine solution and irradiated for 5 min with a mercury high-pressure lamp to detect substances. All mass spectra were recorded with an LKB 9000 S instrument using an electron energy of 70 eV. An IBM 1130 digital computer was used to store the mass spectroscopic data via an interface (WDV & Co., Munich); plotting the data was performed with a Benson recorder. The ^{1}H NMR spectra were prepared with an R-32 90-MHz Perkin Elmer spectrometer and the ^{13}C NMR spectra with a Varian CFT-20 instrument. CDCl$_3$
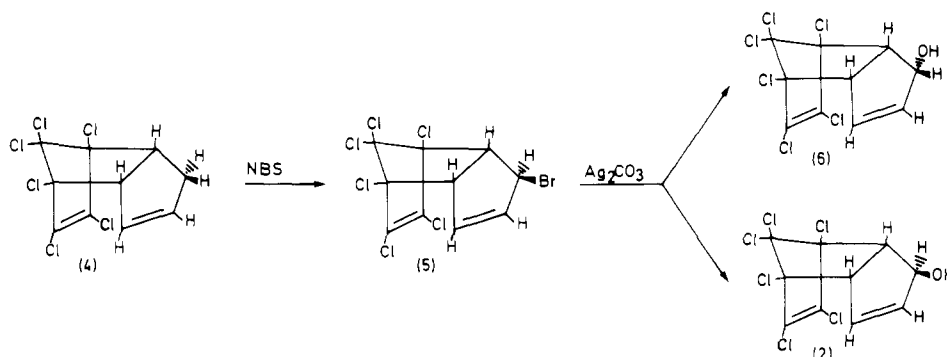

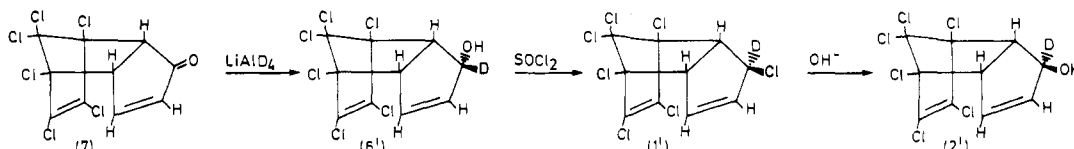**Figure 2.** Preparation of compounds 2 and 6 from chlordene (4).

Figure 3. Preparation of 1-*endo*-deuterio-1-*exo*-hydroxychlordene (2′) from compound 7.

Table II. Spectroscopic Characteristics of the Compounds 5-9

compd	MS data, m/e (rel intensity, %)^a	IR data (KBr), cm^{-1}	^{1}H NMR data, chemical shifts, δ	^{13}C NMR data, chemical shifts, δ
5	414 (12), 379 (5), 335 (13), 270 (100), 235 (70), 65 (79)	3010, 3015, 1600, 1370	1 H (6.10, m), 1 H (5.85, m), 1 H (4.90, m), 1 H (4.10, ddd), 1 H (3.80, dd)	138.52 (d), 132.23 (s), 130.26 (d), 128.66 (s), 103.5 (s), 82.23 (s), 80.48 (s), 60.74 (d), 60.59 (d), 48.64 (d)
6	352 (0), 317 (30), 316 (12), 270 (9), 216 (25), 183 (15), 81 (100)	3560, 3000, 2960, 1598, 1410	1 H (6.10, m), 2 H (6.80, m), 1 H (3.80, m), 1 H (4.60, dd), 1 H (2.70, s)	
7	350 (10), 315 (25), 280 (12), 270 (70), 235 (41), 80 (100)	3015, 3005, 2950, 1595, 1700, 1340	1 H (7.80, dd), 1 H (6.40, dd), 1 H (4.05, m), 1 H (3.40, d)	169.73 (s), 135.48 (d), 133.23 (d), 131.64 (s), 129.30 (s), 104.04 (s), 81.83 (s), 79.92 (s), 60.65 (d), 56.17 (d)
8	352 (7), 317 (35), 281 (45), 253 (40), 217 (100), 183 (27)	2995, 2900, 1740, 1395, 1340, 1330, 1255, 1245, 1205	1 H (4.55, s), 1 H (3.70, m), 2 H (3.20-3.65, m), 2 H (2.55, m)	163.18 (s), 96.53 (s), 79.42 (s), 74.61 (s), 71.20 (s), 64.64 (d), 60.33 (d), 46.72 (d), 46.26 (d), 39.95 (t)
9	352 (15), 317 (75), 282 (10), 246 (5), 211 (100)	2990, 2875, 1320, 1255, 1210	1 H (4.50, m), 1 H (5.20, s), 4 H (3.55, m)	

^{a} The relative intensity of the molecular ion and fragment ions refers to the first peak in each Cl cluster of the given peaks; the highest was considered as 100%.
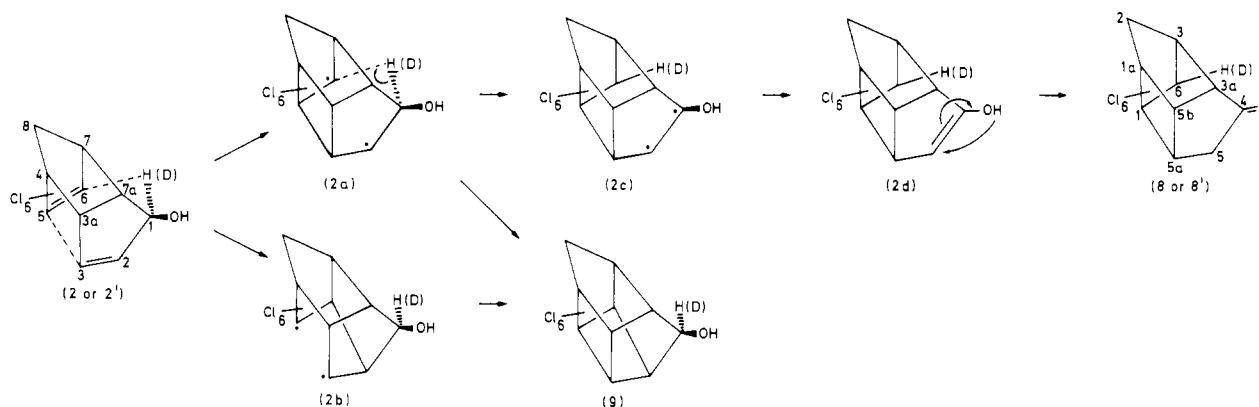

Figure 4. Photoreactions of 1-*exo*-hydroxychlordene (2).

served as solvent and tetramethylsilane as internal standard, and the KBr pellet infrared spectra were recorded with a Model 577 Perkin Elmer instrument.

Irradiation Procedure. An HPK 125 W Philips mercury high-pressure lamp was used for all the irradiation experiments. Irradiation of the invariably 5 × 10^{-2} M solutions was performed in acetone or dioxane. A water-cooled borosilicate glass filter served as light filter (λ > 290 nm). Oxygen-free solutions were used for the sensitized irradiations. The duration of irradiation was limited to 8 h for all the solvent-phase reactions. For the solid irradiations 0.5 g of 2 was dissolved in 25 mL of carbon tetrachloride, spread uniformly on glass plates, dried at 50 °C, and then irradiated through borosilicate glass (λ > 290 nm). For the irradiations on plant leaf surfaces (3-week-old white cabbage plants), 0.1 g of 2 was dissolved in 100 mL of diethyl ether-dioxane (10:1), sprayed uniformly onto 800 cm^2 of leaf surface, and then studied in a 7-day outdoor test (August 3-10, 1977; cloudless sky throughout; midday temperature = 25–28 °C). Leaf samples were taken at uniform 24-h intervals, extracted, purified by column chromatography, and analyzed by GC.

Extractions. To extract the white cabbage leaves (15 g in each case), they were initially comminuted mechanically and then Soxhlet-extracted with first 100 mL of hexane-acetone (10:1) and then 100 mL of acetone-

methanol (1:1). A control experiment confirmed that both 2 and photoproducts 7 and 8 were extracted nearly quantitatively (2 = 98%, 7 = 99.0%, 8 = 98.2%). After drying with sodium bicarbonate the extracts were concentrated to 10 mL under reduced pressure and cleaned up by passing through a small silica gel column (ϕ, 0.5 cm; length, 30 cm; grain size, 0.2–0.06 mm; solvent, 250 mL of 1:1 petroleum ether-acetone). Following evaporation to dryness the residue was dissolved in 5 mL of acetone and then examined by GC. The clean-up step was omitted after irradiation of the solid; here, the reaction products were dissolved in acetone directly and examined.

Preparation of 8 and 9 by Sensitized Irradiation of 2. Compound 2 (1.75 g) was dissolved in 100 mL of oxygen-free acetone and irradiated for 8 h through borosilicate glass. The solution was then concentrated to 5 mL. Pure photoproducts 8 (0.35 g) and 9 (0.40 g) were obtained by passing through a silica gel column (ϕ, 3 cm; length, 100 cm; grain size, 0.2-0.06 mm; eluent, chloroform).

RESULTS AND DISCUSSION

The UV irradiation (λ > 290 nm) of 4,5,6,7,8,8-hexachloro-3a,4,7,7a-tetrahydro-4,7-methanoinden-*exo*-1-ol (2) both in organic solvents (acetone and dioxane) and in the presence of the triplet sensitizers acetophenone and benzophenone showed that a strictly intramolecular ene reaction occurred in addition to the expected (2 + 2)
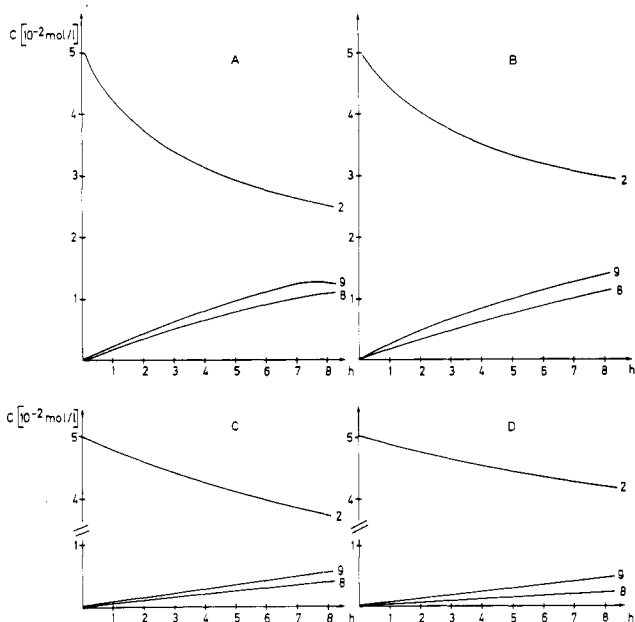
Figure 5. The course with time of the photoreaction of **2** in different solvents: (A) acetone, (B) 100:7 dioxane–acetophenone, (C) 100:7 dioxane–benzophenone, (D) dioxane.

Figure 6. The behavior of **2** out of doors as a function of time.

cycloaddition giving the full-cage isomer. This reaction has not been described hitherto for this substance class (Figure 4). Its first step is the formation of the new σ-bonds (**3** → **5** or **2** → **6**). Thus, the biradical intermediate stages **2a** and **2b**, which can recombine to compound **9**, are formed. Alternatively, however, the intermediate stage **2a** can react to the cyclic enol **2d** via the biradical **2c** by abstraction of the sterically favorably placed 1-endo hydrogen; **2d** rearranges to the new isomerization product **8** by keto–enol tautomerism. The irradiation experiments performed with the 1-endo deuterated compound **2** confirmed the course of the reaction and the intramolecular character of this reaction. Thus, deuterium was afterwards found in the expected 6-endo position of the compound **8'**. The intramolecularity of the reaction was also confirmed by irradiation of **2** in acetone-d_6. Spectroscopic examination of the once more isolated compound **8** showed clearly that no deuterium had been incorporated. The photoreaction occurred most rapidly in acetone but could also be sensitized with acetophenone and benzophenone. Direct, unsensitized irradiation led to the same photoproducts but in smaller yield. Figure 5 shows the concentration vs. time curves of the solvent-phase irradiations carried out.

The irradiation of solid 1-exo-hydroxychlordene **2** (0.59 g) clearly revealed the formation of **8** and the full-cage isomer **9**, but the main products were polymeric compounds. Oxidation and dechlorination products too were identified but were not characterized closely. After 8 h of irradiation the yield of **8** was 8.5%, while **9** was formed in 15.5% yield. The subsequently performed outdoor experiment confirmed the results in that the starting compound **2** could no longer be detected after 5 days (GC–EC). Figure 6 shows the course of this experiment
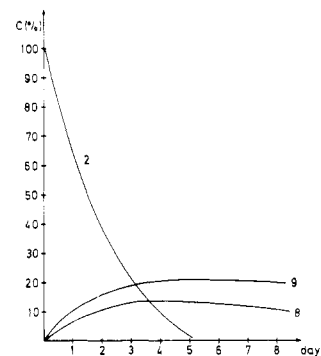
with time. After 4 days the concentration of the compounds **8** and **9** had altered little and in the case of **8** even revealed a slow decrease due, very probably, to the readier volatility of **8**. The concentration of **9** in the surface remained constant by virtue of its vapor pressure and its polarity. In this experiment, oxidation and dechlorination occurred, but the products were not isolated and characterized. The experiments show clearly that, after employing heptachlor (**1**), compound **8**, a cyclic ketone, can be found in the environment via the heptachlor transformation product 1-exo-hydroxychlordene (**2**). It is certain that the formation of the photoproduct **8** can be accelerated by triplet sensitizers. The triplet energy of benzophenone (69.2 kcal/mol) is still sufficient to speed up the photoreaction. Substances present on the surface of leaves, too, can catalyze the reaction. Compound **8** appears to be a stable, persistent product. On account of this both residue analysis and transformation of heptachlor (**1**) under biotic and abiotic conditions should lead to an anticipated appearance of compound **8**.

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