the equivalent product isolated in the previous experiment.

(4) **3β,17β-Diacetoxy-18-nor-5α,17α-pregnan-20-one (23b)**: 144 mg (16.4%); mp 155–157 °C. This product was identified with the equivalent product isolated in the previous experiment in the usual fashion.

(5) **3β-Acetoxy-17β-hydroxy-18-nor-5α,17α-pregnan-20-one (23a)**: 52 mg (7.5%); mp 145–151 °C. This product was identified in the usual fashion by comparison with the product isolated in the previous experiment.

The results of this experiment were confirmed by repetition with 401 mg of analytically pure bromo ketone **20** and with KOCH$_3$ prepared from 80 mg of potassium and 9.4 mL of absolute CH$_3$OH.

Quantitative Analysis by Gas Chromatography. The gas chromatographic determination (cf. above) of the proportion of the isolated products in the acetylated reaction mixture gave the following results: 14.8% of methyl 3β-acetoxy-17α-methyl-18-nor-5α-etianate (**21a**), 15.2% of methyl 3β-acetoxy-17β-methyl-18-nor-5α,17α-etianate (**22a**), 18.8% of 3β,17β-diacetoxy-18-nor-5α,17α-pregnan-20-one (**23b**), 39.6% of 3β-acetoxy-17β-hydroxy-5α,17α-pregnan-20-one (**23a**). The reaction mixture contained approximately 3% of the *D*-homo-18-norandrostane derivative to which we assign either structure **24a** or **24c**, as determined by weight since its retention time is similar to that of the diacetoxy ketone **23b**.

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Registry No. 1, 26708-88-3; **2**, 26708-89-4; **3**, 25352-81-2; **4**, 15991-93-2; **4a**, 64595-21-7; *trans*-**5**, 67010-79-1; *cis*-**5**, 67010-80-4; **6**, 1239-31-2; **7**, 571-20-0; **7a**, 3090-70-8; **7b**, 5424-40-8; **7c**, 17291-39-3; **8**, 85479-46-5; **8a**, 85479-47-6; **9**, 85479-48-7; **10**, 31427-29-9; **10a**, 85479-49-8; **11**, 85479-50-1; **12**, 85479-51-2; **12a**, 85479-52-3; **12b**, 85479-53-4; **12c**, 85479-54-5; **12e**, 85479-55-6; **13**, 85479-56-7; **13a**, 85479-57-8; **14**, 85479-58-9; **14a**, 85479-59-0; **15**, 85549-98-0; **16**, 85479-60-3; **17**, 85479-61-4; **17a**, 85506-83-8; **17b**, 85479-62-5; **17c**, 85479-63-6; **18**, 85479-64-7; *cis*-**19**, 85479-65-8; *trans*-**19**, 85479-66-9; **20**, 85479-67-0; **21a**, 73822-90-9; **22a**, 85479-68-1; **23a**, 85479-69-2; **23b**, 85479-70-5; **24a** (**24c**), 85479-45-4; 3β,17α-diacetoxy-18-nor-*D*-homo-5α,13β-androstane, 85479-71-6.

Ultraviolet Light Induced Dechlorination of Vicinal Polychlorocyclohexanes with Triethylamine[1]

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Photochemical dechlorination of *trans*- and *cis*-1,2-dichlorocyclohexanes (*t*- and *c*-DCC) in the presence of triethylamine (TEA) results in predominant dechlorination to form cyclohexene, where higher reactivity of the trans isomer over that of the cis ($\Phi_{t\text{-DCC}}/\Phi_{c\text{-DCC}} = 4.8$) is observed. Four stereoisomers of 1,2,3,4,5,6-hexachlorocyclohexanes, i.e., benzene hexachlorides (BHCs), were similarly dechlorinated to give their stereoselective benzene tetrachlorides (BTC), which mainly lose two adjacent chlorine atoms with a trans configuration to each other among the six chlorines available in BHC. Quantum efficiencies for the dechlorination of the four isomers α-, β-, γ-, and δ-BHC are 0.072, 0.060, 0.19, and 0.11, respectively, which correlate with their reduction potentials, implying that the reaction may be initiated by an electron transfer from TEA to BHC.

Organochlorine insecticides such as DDT [1,1,1-trichloro-2,2-bis(*p*-chlorophenyl)ethane], DTE [1,1,1,2-tetrachloro-2,2-bis(*p*-chlorophenyl)ethane], and BHC (1,2,3,4,5,6-hexachlorocyclohexane) are generally considered to be persistent environmental pollutants. However, several workers reported that under anaerobic conditions (such as in sewage sludge, the sediment of lake bottoms, and the soil of flooded fields) some of the organochlorine compounds, e.g., γ-BHC, were decomposed in a rather short period.[2] Similarly, electrochemical reduction[3] and radiolysis[4] of γ-BHC were found to give 3,4,5,6-tetrachlorocyclohex-1-enes (BTC) followed by subsequent dechlorination to benzene.

Photochemical instability of amine–halomethane systems was noticed by several workers.[5,6] Thus, the irradiation of CCl$_4$ solutions of aliphatic amines rapidly develops crystalline precipitates, the amine hydrochloride along with simultaneous formation of chloroform.[7]

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(1) Contribution No. 297.

(2) (a) Tsukano, Y.; Kobayashi, A. *Agric. Biol. Chem.* **1972**, *36*, 166. (b) Hill, D. W.; McCarty, P. L. *J.—Water Pollut. Control Fed.* **1967**, *39*, 1259. (c) Mathur, S. P.,; Saba, J. G. *Soil Sci.* **1975**, *120*, 301. (d) Tu, C. M. *Arch. Microbiol.* **1976**, *108*, 259. (e) Matsumura, F.; Benezet, H. J.; Patil, K. C. *Nippon Noyaku Gakkaishi* **1976**, *1*, 3. (f) Jagnow, G.; Haider, K.; Ellwardt, P. C. *Arch. Microbiol.* **1977**, *115*, 285. (g) Ohisa, N.; Yamaguchi, M. *Agric. Biol. Chem.* **1978**, *42*, 1819.

(3) (a) Beland, F. A.; Farwell, S. O.; Robocker, A. E.; Geer, R. D. *J. Agric. Food Chem.* **1976**, *24*, 753. (b) Fukami, H.; Kimura, H.; Nakajima, M. *Bochu Kagaku* **1953**, *18*, 51. (c) Schwabe, K.; Frind, H. *Z. Phys. Chem.* (*Leipzig*) **1951**, *196*, 342.

(4) Hamada, M., Kawano, E.; Kawamura, S. *Tetrahedron Lett.* **1977**, 2409.

(5) (a) Collins, R. F. *Chem. Ind.* (*London*) **1957**, 704. (b) Cromwell, N. H.; Foster, P. W.; Wheeler, M. M. *Ibid.* **1959**, 220.

(6) (a) Beichl, G. J.; Colwell, J. E.; Miller, J. G. *Chem. Ind.* (*London*) **1960**, 203. (b) Williams, H. *Ibid.* **1960**, 900. (c) Bunce, N. J. *J. Org. Chem.* **1982**, *47*, 1948. (d) Siegman, J. R.; Hansen, J. J. *Ibid.* **1982**, *47*, 2773.

Table I. Quantum Efficiency Φ_{disapp} and Reduction Potential ($-E_{1/2}$) of Chlorine Compounds

compd	Φ_{disapp}	$-E_{1/2}$,[a] V vs. SCE
α-BHC	0.072	−1.61
β-BHC	0.060	−1.95
γ-BHC	0.19	−1.47
δ-BHC	0.11	−1.60
t-DCC	0.025	[b] (−1.00)[c]
c-DCC	0.0052	[b] (−1.85)[c]

[a] In DMF containing 0.1 M TEAP. [b] Reduction potentials of DCC are lower than −2.30 V (vs. SCE) and are unable to be measured accurately. [c] The figures in parentheses show the reduction potentials of the corresponding dibromides.[17]

This photochemical instability of the amine–halomethane systems is understood in terms of a charge-transfer character of the absorption bands of the systems.[7b,8] That is, if the light-absorption process involves an electron transfer from the amine, the photoinstability may reasonably be understood as shown in the following equation.

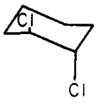
$$e^- + CCl_4 \rightarrow Cl^- + \cdot CCl_3$$

There are several papers on the photochemical dechlorination of geminal polychlorides such as CCl_4, but papers which treat the photodechlorination of vicinal chlorides are thus far unavailable.

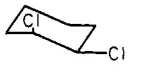
In our preliminary study, no complexation between γ-BHC and triethylamine (TEA) could be observed in acetonitrile. Nevertheless, γ-BHC was reduced to BTC with TEA on UV irradiation. This article deals with the photochemical dechlorination of vicinal dichlorocyclohexanes in the presence of TEA and with stereoselective formation of BTC from stereoisomeric BHC.

Results and Discussion

Photodechlorination of *trans*- and *cis*-1,2-Dichlorocyclohexanes with TEA. UV irradiation of a 15.2 mM solution of *trans*-1,2-dichlorocyclohexane (*t*-DCC) in acetonitrile with TEA through a quartz filter gradually gave cyclohexene in a yield of 88%. Formation of 1,3-cyclohexadiene, an alternative product expected from the loss of hydrogen chloride, was not observed by means of GC/MS analysis of the reaction mixture. Similarly, *cis*-1,2-dichlorocyclohexane (*c*-DCC) also yielded cyclohexene as the sole olefin, but the reactivity of *c*-DCC is much lower (ca. 1/5 in quantum efficiency) than that of *t*-DCC (see Table I).



t-DCC



c-DCC

Photodechlorination of γ-BHC with TEA in Benzene. Irradiation of 17.1 mM γ-BHC with varying amounts of TEA in 500 mL of benzene by UV light results in the decomposition of γ-BHC with an efficiency depending on the amounts of TEA and on the irradiation time. Time–conversion curves showed that 1 mol of γ-BHC was completely consumed with over 6 mol of TEA within 120 min and that the reaction ceased at a conversion of 35% when 1 mol of TEA was used. The conversion reaches 60% when 2 equiv of TEA was used.

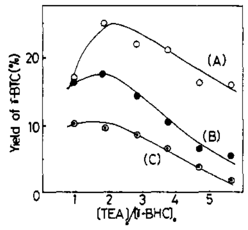
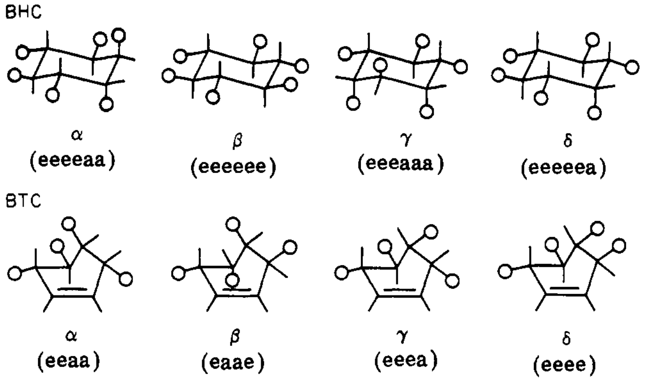


Figure 1. Effect of the ratio (α) of $[TEA]_0/[\gamma\text{-BHC}]_0$ on the yield of γ-BTC from γ-BHC in benzene at 20–25 °C: (A) irradiation for 40 min, (B) for 80 min, (C) for 150 min.

Chart I



GLC analyses of the reaction solution showed the formation of isomeric BTC (predominantly γ-BTC) along with further dechlorinated products such as dichlorobenzenes, chlorobenzene, and benzene. Figure 1 reveals that the optimum condition for the BTC is attained at an initial molar ratio of $[TEA]_0/[\gamma\text{-BHC}]_0 = 2$ irrespective of irradiation time.

Isomeric Distribution of BTC from Photolysis of Isomeric BHC. UV irradiation of a solution of γ-BHC (8.6 mmol) and TEA (17.8 mmol) in benzene (500 mL) for 70 min gave BTC (33%) as well as the recovery of γ-BHC (50%) (eq 1). GLC analysis showed that the reaction

$$\text{BHC} \xrightarrow[\text{PhH}]{h\nu/\text{TEA}} \text{BTC} + \text{TEA}\cdot\text{HCl} \qquad (1)$$

solution consisted of a mixture of 5% α, 85% γ, and 10% δ isomers; the γ- and δ-BTC among them were isolated by chromatography and characterized by spectral comparisons.[9,10] The structure of the α isomer was established by a GLC comparison with the authentic sample.[10] Photochemical stereoisomerization between the isomeric BTC may be trivial in view of the fact that the distribution of the isomeric BTC remains almost constant independent of the reaction time.

A series of isomeric BHCs with adjacent chlorine atoms fixed stereochemically at all six carbons, i.e., α-(eeeeaa), β-(eeeeee), γ-(eeeaaa), and δ-(eeeeea) BHC (Chart I), was selected in order to investigate the stereochemistry in the photodechlorination (e and a in parentheses indicate equatorial and axial chlorine atoms, respectively, in the order of C-1 to C-6).

Thus far five stereoisomers of BTC are known, i.e., α-(eeaa), β-(eaae), γ-(eeea), δ-(eeee), and ε-(eeae)BTC, where e and a similarly indicate the configuration of chlorine atoms in the order of C-3 to C-6.[11] GLC analysis

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[7] (a) Foster, R. W. *Chem. Ind. (London)* **1960**, 1354. (b) Stevenson, D. P.; Coppinger, G. M. *J. Am. Chem. Soc.* **1962**, *84*, 149.

[8] (a) Mulliken, R. S. *J. Phys. Chem.* **1952**, *56*, 801. (b) Mulliken, R. S. *J. Am. Chem. Soc.* **1952**, *74*, 811.

[9] Kurihara, N.; Sanemitsu, Y.; Nakajima, M.; McCasland, G. E.; Johnson, L. F. *Agric. Biol. Chem.* **1971**, *35*, 71.

[10] Calingaert, G.; Griffing, M. E.; Kerr, E. R.; Kolka, A. J.; Orloff, H. D. *J. Am. Chem. Soc.* **1951**, *73*, 5224.

Table II. Product Yields in the UV Irradiation of Isomeric BHC in Benzene at 20–25 °C

isomer of BHC	product yields, %			% trans elimination
	α-BTC (eeaa)	γ-BTC (eeea)	δ-BTC (eeee)	
α-(aaeeee)	14	25	61	75
β-(eeeeee)	5	28	67	67
γ-(aaaeee)	5	85	10	85
δ-(aeeeee)	9	61	30	61

[a] Small letters e and a indicate equatorial and axial chlorine atoms, respectively, in the order of C-1 to C-6 for BHC and C-3 to C-6 for BTC.

Table III. Epimerization between BHC Isomers during the Photochemical Dechlorination with TEA[a]

starting BHC	% conversion	% epimerization			
		α-BHC	β-BHC	γ-BHC	δ-BHC
α-BHC	50.0	93.9	1.3	3.5	1.3
β-BHC	41.7	1.2	96.8	2.0	*b*
γ-BHC	75.3	5.6	*b*	94.4	*b*
δ-BHC	64.7	8.9	1.8	0.8	88.5

[a] Irradiation was continued for 80 min. [b] Not detected.

shows the formation of the three most common BTC isomers among them, i.e., α-, γ-, and δ-BTC. Formation of the other two BTC (β and/or ϵ isomers) expected may be trivial, if they are even formed. The results are summarized in Table II. It is reasonable to assume that the isomeric distribution reflects the position of the most reactive chlorine substituent among the six chlorines in the cyclohexane rings, judging from the independence of the distribution on the irradiation time.

As is apparent from Table II, the reaction is considerably stereoselective. The selectivity is not very high. This may, in part, be attributable to interconversion between BHC isomers during the reaction, but the epimerization is much slower than the dechlorination, although the epimerization is observed in our cases. The epimerization between isomeric BHC was measured under identical conditions with those for the photochemical dechlorination with TEA, and the data are summarized in Table III. The most appreciable epimerization is observed in the case of δ-BHC which mainly gave α-BHC (8.9%) along the small amounts of β (1.8%) and γ isomers (0.8%). But the epimerization of the other BHC is much less efficient. Therefore, the isomeric distribution of BTC from BHC may not be seriously marred by the epimerization.

Table II shows that δ-BTC was mainly formed from α- and β-BHC, whereas γ-BTC was predominantly formed from γ- and δ-BHC. The results indicate that the dechlorination of BHC may preferably occur by trans elimination, which is in good accordance with the tendency observed with *t*- and *c*-DCC as stated above.

In spite of the favorable trans elimination, some minor isomeric BTC must invoke cis elimination, provided that the stereochemistry of the other four chlorine atoms remaining in BTC is unchanged during the reaction. The ratio of trans vs. cis elimination for the dechlorination of the isomeric BHC (2–17) is comparable to that for the intermolecular reactivity of *t*- and *c*-DCC (ca. 5) as seen in Table I.

The elimination (either trans or cis), however, cannot account for the formation of α- and γ-BTC from β-BHC. Such unexpected isomers can be at least in part due to the epimerization of BHC prior to the competitive dechlorination, especially in the case of δ isomer (vide supra). Moreover, the stereoselectivity may be intimately related with the reactivity of the dechlorination of BHC itself. Thus, β-BHC is the least reactive isomer and hence has time enough to epimerize into its isomers, which might cause the formation of the unexpected BTC isomers (e.g., α and γ isomers).

Quantum efficiencies for the disappearance of isomeric BHC are compiled in Table I. The most reactive isomer, γ-BHC, results in the most selective elimination, giving predominantly γ-BTC; β-BHC is the least reactive, giving a mixture marred by other BTC isomers. This fact suggests that the epimerization of BHC competes with the dechlorination and lowers the stereoselectivity, though it is not serious. Table I also shows that the efficiency for the dechlorination of BHC including DCC correlates with their reduction potentials.

Role of TEA. The basicity of TEA ($pK_a = 10.7$ in H_2O) is too weak to deprotonate BHC, in contrast to strong bases such as sodium methoxide (NaOMe). Photochemical dechlorination of β-BHC with NaOMe may go by way of a carbanion of BHC in the dark, giving trichlorobenzenes followed by their photochemical dechlorination.[12] Hence, no intermediates involving more than four chlorine atoms were detected in case of NaOMe.[13]

However, no reaction of BHC with TEA was observed in the dark. Moreover, photochemical dechlorination of BHC did not occur in the absence of TEA, which implies an alternative role of TEA, i.e., an electron donation to BHC. In fact, dechlorination of BHC to BTC was reported to occur under anaerobic conditions[2] or by electrochemical reduction at a reduction potential of −1.52 V (vs. SCE).[3] These reductive dechlorinations may proceed by two-electron transfer to BHC followed by releasing of two chloride ions (eq 2).

$$\underset{\text{BHC}}{C_6H_6Cl_6} \xrightarrow{+2e^-} \underset{1}{C_6H_6Cl_6^{2-}} \xrightarrow{-2Cl^-} \underset{\text{BTC}}{C_6H_6Cl_4} \tag{2}$$

TEA has its end absorption at the onset of around 250 nm (ϵ 243), and BHC is transparent at wavelengths longer than 230 nm in methanol. In contrast to the polyhalomethane–amine systems which form charge-transfer complexes in their ground states,[7b] the addition of BHC to TEA in hexane induces no bathochromic shift, implying no existence of definite charge-transfer complexes. TEA is nonfluorescent in polar solvents such as acetonitrile and alcohols but emits its fluorescence at 287 nm in deaerated pentane.[14] The Stern–Volmer plot for the quenching of the fluorescence by BHC in hexane shows that the excited singlet TEA is quenched by BHC with $k_q\tau = 125\ M^{-1}$. The quenching may probably be assumed to proceed through charge-transfer interaction between an excited TEA and BHC because of the low ionization potential of the former ($I_p = 8.06\ eV^{14b}$).

Benzene was usually used as the reaction solvent in our system, and hence the incident UV light would be almost completely absorbed by the solvent. The energy of excited benzene would be transferred exclusively to TEA rather than to BHC, since no quenching of the fluorescence occurred on addition of BHC instead of TEA. The fluorescence was quenched by TEA with $k_q\tau = 265\ M^{-1}$

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(11) Orloff, H. D.; Kolka, A. J.; Calingaert, G.; Griffing, M. E.; Kerr, E. R. *J. Am. Chem. Soc.* **1953**, *75*, 4243.

(12) Hine, J.; Weimer, R. D., Jr.; Longford, P. B.; Ramsey, O. B. *J. Am. Chem. Soc.* **1966**, *88*, 5522.

(13) Ogata, Y.; Takagi, K.; Sasoh, Y. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 884.

(14) (a) Muto, Y.; Nakato, Y.; Tsubomura, H. *Chem. Phys. Lett.* **1971**, *9*, 159. (b) Halpern, A. M.; Gartman, T. *J. Am. Chem. Soc.* **1974**, *96*, 1394.

in acetonitrile. Hence, the energy of an excited benzene would be transferred to TEA, which in turn transfers it energy to BHC.

An excited TEA would interact with BHC via a one-electron transfer to BHC (eq 3) in view of the correlation on the reactivity of the dechlorination with reduction potentials as revealed in Table I.[15]

$$\mathrm{BHC} + \mathrm{TEA}^{*} \rightarrow \underset{\mathbf{2}}{\mathrm{C_6H_6Cl_6}^{-}\cdot} + \underset{\mathbf{3}}{\mathrm{TEA}^{+}\cdot} \qquad (3)$$

Radical 4 from the cation radical 3 (eq 4), which is known as a powerful reducing agent,[16] may reduce 2 or 5 (eq 5), i.e., a neutral radical formed by elimination of

$$\mathrm{TEA} + \mathbf{3} \rightarrow \underset{\mathbf{4}}{\mathrm{CH_3\dot{C}HNEt_2}} + \mathrm{Et_3NH^{+}} \qquad (4)$$

$$\mathbf{4} + \underset{\mathbf{5}}{\mathrm{C_6H_6Cl_5}\cdot} \rightarrow \underset{\mathbf{6}}{\mathrm{CH_3CH{=}NEt_2}^{+}} + \underset{\mathbf{7}}{\mathrm{C_6H_6Cl_5}^{-}} \qquad (5)$$

chloride ion from 2. The anion 7 would give rise to BTC on release of chloride ion. In fact, TEA·HCl was obtained in a yield of 83% based on BHC consumed (eq 6). Accordingly, formation of immonium ion 6 was evidenced by detection of acetaldehyde in a photolysate of the BHC–TEA system in aqueous acetonitrile.

$$\mathbf{7} + \mathrm{Et_3NH^{+}} \rightarrow \mathrm{BTC} + \mathrm{TEA{\cdot}HCl} \qquad (6)$$

The optimum yield of BTC was obtained at $[\mathrm{TEA}]_0/[\mathrm{BHC}]_0$ = ca. 2 as shown in Figure 1, which correlates with eq 3–6. They indicate a stoichiometry which needs 2 mol of TEA/mol of BHC.

Finally, it is intriguing to note the stereochemical relationship between BHC used and BTC formed. Dianion 8 in the electrolysis of BHC was reported to be dechlorinated more easily when the dihedral angle of the vicinal chlorines is closer to either 180° or 0°. It was also observed that the reduction potential of cyclic chlorine compounds became the lowest at an angle close to 90°, i.e., *cis*-1,2-dichlorides.[17] These findings suggest that electrochemical dechlorination may occur in *trans*-dichlorides much easier than the cis isomers. The present photochemical dechlorination also indicates the preference of the trans elimination to the cis elimination, supporting the idea that the electron-transfer reduction may occur by way of TEA. The situation is clearer with simple cyclic dihalogen compounds. *trans*-1,2-Dichlorocyclohexane was dechlorinated to cyclohexene about 5 times as efficiently as the cis isomer. Therefore, the stereoselectivity can be reasonably explained in terms of the dihedral angles of the adjacent two chlorine atoms of BHC.

$$\underset{\mathbf{8}}{\mathrm{C_6H_6Cl_6}^{2-}}$$

Experimental Section

GC/MS spectra were recorded on a JEOL double-focussed mass spectrometer, Model JMS D-300, with a column packed with silicon OV-1 (1 m length) of Porapak QS (1 m length) at a column temperature of 100–230 °C. NMR measurements were done on a Hitachi NMR spectrometer, Model R-24B, with $\mathrm{Me_4Si}$ as an internal standard. General GLC analyses were done on a Yanagimoto gas chromatograph, Model G-180, operated with a column packed with PEG 20M (4 mm i.d. × 2 m) or Porapak QS (4 mm i.d. × 2 m) with $\mathrm{N_2}$ as the carrier. Fluorescence spectra were recorded on a Hitachi fluorescence spectrometer, Model 650-10S.

Materials. α-1,2,3,4,5,6-Hexachlorocyclohexane (α-BHC) was prepared by a procedure reported previously;[18] mp 156–158 °C (lit.[18] mp 157–158 °C). β-, γ-, and δ-BHC were of extra pure grade and used without further purification. Triethylamine of extra pure grade was distilled (bp 89–90 °C) before use. α-3,4,5,6-Tetrachlorocyclohexane (α-BTC) was synthesized according to the known procedure;[10] bp 81–89 °C (3 mmHg) [lit.[10] bp 80–85 °C (1.5 mmHg)]. *cis*-1,2-Dichlorocyclohexane was prepared according to the known procedure.[19]

General Procedures. A Halos high-pressure 300-W Hg lamp was used as a light source and was immersed in a reactor (1000 mL) equipped with a thermometer and a condenser. The reaction mixture was adjusted so as to contain BHC (2.5 g, 1.8 mM) and TEA (1.8 g, 3.6 mM) in benzene (500 mL). Acetonitrile was also used as a solvent to detect low-boiling materials such as benzene. The reaction mixture was deaerated by bubbling $\mathrm{N_2}$ through it and was irradiated through a quartz filter, making it necessary to scrape off TEA-HCl deposited on the wall of the lamp. Aliquots were taken out at appropriate time intervals and analyzed by means of GLC with bibenzyl or toluene as internal standards.

γ-BTC. A solution of 8.6 mmol of γ-BHC (2.5 g) and 17.8 mmol of TEA (1.8 g) in benzene (500 mL) was irradiated for 70 min under an $\mathrm{N_2}$ atmosphere by the UV lamp. The viscous brown oil was condensed in vacuo, separated from the precipitate including TEA-HCl (2.0 g, 83%), and chromatographed on a column packed with Florisil (100–200 mesh) with hexane as an eluant, yielding following two components: γ-BHC (1.0 g, 40%), identified by comparison with an authentic sample, and γ-BTC: 495 mg (33%); mass spectrum (20 eV), *m/e* (relative intensity) 222 ($\mathrm{M^+}$ + 4, 0.6), 220 ($\mathrm{M^+}$ + 2, 1.3), 218 ($\mathrm{M^+}$, 1), 187 (5), 185 (15), 183 (15), 151 (10), 149 (66), 147 (100), 129 (18), 122 (28), 103 (17), 102 (22), 101 (32), 78 (17), 77 (13). Their NMR and IR data were identical with those of the literature.[9,10]

δ-BTC. A solution of 8.6 mmol of β-BHC (2.5 g) and 17.8 mmol of TEA (1.8 g) in benzene was irradiated similarly for 3 h. In contrast to γ-BHC, the conversion was low (~10%), and the yield of δ-BTC was ~3% as estimated from the GLC peak area. The irradiation was stopped at this stage in spite of the low conversion in order to prevent contamination with other products. Florisil chromatography of the condensed oil afforded δ-BTC (oil, 50 mg) which was identified by its NMR and IR data in comparison with those of authentic samples.[9,10]

Dechlorination of *trans*- and *cis*-1,2-Dichlorocyclohexanes. A solution of 2.0 mmol of *trans*- or *cis*-1,2-dichlorocyclohexane (0.3 g) and 3.9 mmol of TEA (0.39 g) in acetonitrile (130 mL) was irradiated for 6 h under $\mathrm{N_2}$ by the UV lamp. The reaction was followed by means of GLC analysis of aliquots at appropriate time intervals. The production solution contained only cyclohexene, identified by GLC with a column of Porapak QS. The GC/MS at 20 eV was *m/e* (relative intensity) 82 ($\mathrm{M^+}$, 68), 67 (100), and 54 (49), in accordance with that of cyclohexene.[20]

Quantum Yields. The quantum yields were measured at a wavelength of 254 nm which was obtained from a 60-W low-pressure Hg lamp (Halos HIL 60) emitting exclusively 254-nm light and with the use of a merry-go-round apparatus. The amount of light quanta absorbed by sample solutions was obtained by a potassium ferrioxalate actinometer and was estimated to be 1.86×10^{18} quanta/min.[21] A solution of γ-BHC (0.208 mmol, 60.5 mg) and TEA (0.414 mmol, 41.8 mg) in 30 mL of benzene was irradiated for 30 min with the conversion of 9.0% of γ-BHC. Hence, the quantum yield for γ-BHC was calculated to be 0.19.

Quantum yields for the other BHC isomers (α, β, and δ isomers) were measured by following competitive dechlorination reactions. An equimolar mixture of one of α-, β-, or δ-BHC (100–110 mg, ~0.35 mmol) and the standard γ-BHC (100–110 mg, ~0.35 mmol) in the presence of TEA (150 mg, 1.5 mmol) in benzene (100 mL)

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(15) (a) Cohen, S. G.; Parola, A.; Parsons, G. H., Jr. *Chem. Rev.* **1973**, *73*, 141. (b) Whitten, D. G. *Acc. Chem. Res.* **1980**, *13*, 83.

(16) Griller, D.; Lossing, F. P. *J. Am. Chem. Soc.* **1981**, *103*, 1586.

(17) Zavada, J.; Krupicka, J.; Sicher, J. *Collect. Czech. Chem. Commun.* **1963**, *28*, 1664.

(18) Ogata, Y. "Theories of Organic Reactions"; Japanese ed.; Maruzen: Tokyo, 1962; p 415.

(19) Carroll, B.; Kubler, D. G.; Davis, H. W.; Whaley, A. M. *J. Am. Chem. Soc.* **1951**, *73*, 5382.

(20) Stenhagen, E.; Abrahamson, S.; McLafferty, F. W. "Registry of Mass Spectral Data; Wiley: New York, 1974; Vol. 1, pp 35, 38.

(21) Hatchard, C. H.; Parker, C. A. *Proc. R. Soc. London, Ser. A* **1956**, *294*, 518.

was irradiated for 5 h. The ratios of the slopes extrapolated to zero conversions of each pair (i.e., α-, β-, or δ-BHC to γ-BHC) gave their initial relative rates for the dechlorination, from which the corresponding quantum yields were obtained and summarized in Table I. Similarly, initial relative rates of *t*- and *c*-DCC to the standard γ-BHC were measured (*t*-DCC/*c*-DCC/γ-BHC ratio of 4.8:1:37), from which quantum yields for *t*- and *c*-DCC were obtained.

Polarography. Polarographic analysis was carried out on a Yanagimoto polarograph, Model P8. A solution of ca. 10^{-4} M samples in dimethylformamide (DMF) with 0.1 M tetraethylammonium perchlorate (TEAP) as a supporting electrolyte was bubbled with N_2 prior to the measurement. Typical polarograms for *t*- and *c*-DCC were not obtainable, which shows that they possess reduction potentials at least lower than −2.30 V, as control experiments without the sample enable one to sweep to potentials of −2.30 V in DMF. The results are compiled in Table I.

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Registry No. *c*-DCC, 10498-35-8; *t*-DCC, 822-86-6; α-BHC, 319-84-6; β-BHC, 319-85-7; γ-BHC, 58-89-9; δ-BHC, 319-86-8; TEA, 121-44-8.

Computer-Assisted Mechanistic Evaluation of Organic Reactions. 4. Organosilicon Chemistry

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CAMEO, an interactive computer program which predicts the products of organic reactions using mechanistic reasoning, has been enhanced to encompass nucleophilic and electrophilic processes involving organosilicon compounds. The existing modules for such reactions were modified to accommodate the special reactivity of silanes. This includes considerations such as the high affinity of silicon for oxy and halide anions, directing effects for electrophilic additions to allyl and vinyl silanes, stabilization of carbanions and of S_N2 transition states by adjacent silicon, stereochemistry of β-elimination reactions, and steric effects in the formation and removal of silyl protecting groups. Consequently, changes were required in several parts of the program, particularly in the perception of acidity levels and of the reactivity of nucleophiles and electrophiles. General procedures for handling the stereochemistry of β-elimination reactions have also been implemented and are described. The paper begins with a short summary highlighting examples of the novel nature of organosilicon chemistry. The modifications to CAMEO are then presented followed by analyses of sample reaction sequences predicted by the program.

A computer program, CAMEO, which predicts the products of organic reactions given starting materials and conditions, is under continued development.[1-3] Two important features of the program are that it is highly interactive, with structures being input and output on a computer graphics terminal, and that the program arrives at its predictions by mimicking traditional mechanistic reasoning.[1,3] In 1978, the first class of reactions to be implemented was base-catalyzed and nucleophilic processes that could include proton transfer, S_N2, E2, E1cB, and addition steps.[1] This followed extensive work on the parts of the program controlling structure entry and display (graphics) and the recognition of structural features such as functional groups, rings,[2] and stereochemistry (perception).[1] The mechanistic capabilities were subsequently enhanced to cover ylide chemistry and reactions of organolithium, magnesium, and lithium cuprate reagents.[3] This involved the implementation of halogen–metal exchange and detailed consideration of the competitions between exchange, proton transfer, and organometallic addition.[3]

During the last 2 years, the scope and sophistication of the program have increased substantially. Modules have now been added for acid-catalyzed and electrophilic reactions[4] including electrophilic aromatic substitution[5] and for six-electron cycloadditions including reactions with 1,3-dipoles.[6] The nucleophilic and electrophilic routines have also been enhanced to treat the special reactivity associated with organosilicon compounds. This addition, which is the topic of the present report, is clearly important since transformations involving organosilicon intermediates are now commonplace in syntheses of natural products. Silyl protecting groups and the directing ability of silicon have become powerful tools of synthetic organic chemists.[7]

Besides enhancing the capabilities of the program, the implementation of a new area of chemistry in CAMEO is intrinsically valuable since it requires the analysis and organization of literature data on reactivity. In the present case, the similarities and differences in behavior of carbon and silicon compounds must be clearly delineated so that the organosilicon chemistry can be efficiently merged into the existing routines for nucleophilic and electrophilic reactions. Thus, a short review of the special properties and reactivity of organosilanes is presented first. The incorporation of these characteristics into the CAMEO program is then described. The paper concludes with the presentation and analyses of sample synthetic sequences predicted by the program.

Key Aspects of Organosilicon Chemistry

The many facets of organosilicon chemistry and its applications in organic synthesis have been covered thoroughly in recent reviews.[7-10] The brief summary presented here focuses on the novel reactivity of organosilanes that is distinct from the behavior of corresponding carbon

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(1) T. D. Salatin and W. L. Jorgensen, *J. Org. Chem.*, **45**, 2043 (1980).

(2) B. L. Roos-Kozel and W. L. Jorgensen, *J. Chem. Inf. Comp. Sci.*, 21, 101 (1981).

(3) T. D. Salatin, D. McLaughlin, and W. L. Jorgensen, *J. Org. Chem.*, 46, 5284 (1981).

(4) D. McLaughlin and W. L. Jorgensen, to be submitted for publication in *J. Org. Chem.*

(5) B. L. Roos-Kozel, Ph.D. Thesis, Purdue University, 1981.

(6) J. A. Schmidt and W. L. Jorgensen, submitted for publication in *J. Org. Chem.*

(7) E. Colvin, "Silicon in Organic Synthesis", Butterworths, London, 1981.

0022-3263/83/1948-1970$01.50/0