

Experimental

Runs were carried out as in previous papers² in the series being duplicated at each of three temperatures for each compound.

Typical run: 2-chloro-5-nitrobenzophenone at 59.9°

Initial concn. ArCl = 0.00473, OMe⁻ = 0.00667 M

Titration reading: 11.00 11.51 11.93 12.29 12.94 13.23 13.73 14.13 14.61 14.90 15.18 16.73 19.26 (inf.)

Log term: 0.1661 1763 1833 1910 2066 2145 2295 2432 2619 2748 2886 4017

Time (min.): 0 30 60 90 150 180 240 300 360 420 460 900

Rate constant: $4.923 \pm 0.018 \times 10^{-4}$ l. moles⁻¹ secs.⁻¹

Rate constants for 2-chloro-5-nitrobenzamide

| | | | |
|--------|-------|-------|----------------------------|
| 45.35° | 2.436 | 2.444 | Av. 2.44 $\times 10^{-3}$ |
| 59.9° | 1.014 | 1.016 | Av. 1.015 $\times 10^{-2}$ |
| 75.3° | 4.050 | | 4.05 $\times 10^{-2}$ |
| 81.6° | 6.893 | 6.930 | Av. 6.91 $\times 10^{-2}$ |

Giving activation energy 20700 \pm 50

log₁₀ frequency factor 11.6 \pm 0.05

Products.—These were isolated direct from the surplus reaction mixture by cold aqueous acidification (HCl) and found to be the pure 2-methoxy-5-nitro compounds and in all cases infinity readings agreed with those expected.

Preparation of Materials. The 2-chloro-5-nitrobenzoic acid was prepared as in part IV.³ The 2-chloro-5-nitrobenzamide was obtained in 36% yield from the acid *via* the acid chloride; m.p. 179°, lit. 178°, 180°. ^{6,7} 2-Chloro-5-nitrobenzanilide was prepared in 61% yield from the acid *via* the acid chloride; m.p. 158°, lit. 158°. ⁸ The methyl

(6) P. J. Montagne, *Rec. trav. chim.*, **18**, 57 (1900).

(7) J. J. Blanksma, *ibid.*, **65**, 207 (1946).

(8) J. Meisenheimer, P. Zimmermann and U. Kummer, *Ann.*, **446**, 217 (1926).

2-chloro-5-nitrobenzoate was synthesized as in part IV.³

2-Chloro-5-nitroacetophenone (a).—A small amount was prepared in poor yield by condensing sodiummalonic ester in dry ether with the 2-chloro-5-nitrobenzoyl chloride, followed by hydrolysis and decarboxylation of the conden-

sation product. This is analogous to the preparation by Johnson and Offenbauer⁹ of 4-(*p*-hydroxyphenyl)-hexahydroacetophenone. The required product separated from the steam distillate; m.p. 58–61°, lit. 62°. The yield was 14%, and 18% of the original acid was recovered.

(b) **2-Chloroacetophenone** (b.p. 227–228° at 771 mm.) was prepared in 73% yield from 2-chlorobenzoyl chloride by the method of Walker and Hauser.¹⁰ It was then nitrated with pure nitric acid by the method of Thorpe and Brunskill¹¹ in 30% yield, giving a product m.p. 62°.

2-Chloro-5-nitrobenzophenone was obtained in 61% yield from the acid chloride by a Friedel-Crafts reaction¹²; m.p. 85–86°, lit. 86°.

All m.p.'s are corrected.

Assistance from the Research Grant to Australian Universities is gratefully acknowledged.

(9) W. S. Johnson and R. D. Offenbauer, *THIS JOURNAL*, **67**, 1049 (1945).

(10) H. G. Walker and C. R. Hauser, *ibid.*, **68**, 1386 (1946).

(11) L. Thorpe and E. R. Brunskill, *ibid.*, **37**, 1261 (1915).

(12) F. Ullmann and E. Mallet, *Ber.*, **31**, 1595 (1898).

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[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE ETHYL CORPORATION]

The Mechanism of Dehydrohalogenation of Benzene Tetrachloride and Related Compounds¹

BY HAROLD D. ORLOFF AND ALFRED J. KOLKA

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The mechanism of the base-catalyzed dehydrochlorination of polychlorocyclohexenes, such as benzene tetrachloride, pentachlorocyclohexene and hexachlorocyclohexene, has been elucidated by kinetic and product distribution studies. Of four modes of elimination which were found to take place, at least two occur simultaneously and competitively in a given isomer. In general, the rates of these processes decrease in the following sequence: *trans*-1,2; *trans*-1,4; *cis*-1,2; *cis*-1,4. The elimination reactions exhibit second-order kinetics and are consistent with bimolecular mechanisms which may be either concerted or involve the formation of a carbanion intermediate in a multiple-stage process. The initial attack by base appears to be favored at an axial rather than an equatorial allylic hydrogen substituent. The results of this investigation clarify the mechanism of dehydrohalogenation of benzene hexachloride and related polychlorocyclohexanes.

The base-catalyzed dehydrochlorination of benzene hexachloride (BHC) has been shown by Cristol² to proceed by two different mechanisms, depending on whether at least one pair of vicinal chlorine and hydrogen substituents is present in a *trans* relationship. The α -, γ -, δ - and ϵ -isomers, in which *trans* elimination of hydrogen and chlorine is sterically possible, undergo a normal bimolecular (E₂) reaction in which nucleophilic attack by the base removes a β -proton, with formation of olefin and elimination of halide ion in a single synchronous process. The β -isomer, in which all vicinal pairs of hydrogen and chlorine are *cis*, reacts at a

much slower rate by a multiple-stage process in which only the proton is removed in the rate-determining step and a carbanion intermediate is formed. In a subsequent step, the latter undergoes inversion and decomposes to olefin and chloride ion.

Hughes, Ingold and Pasternak,³ on the other hand, do not consider the carbanion intermediate mechanism probable. They have suggested that the greater energy of activation (32 kcal./mole) of β -BHC, compared with that (*ca.* 20 kcal./mole) of the other isomers is employed in part to force "the relevant portion of the molecule more nearly into the desirable *anti*-configuration, and partly to force the mechanism against the still imperfect orientation of the bonds involved." We consider that the

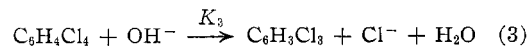
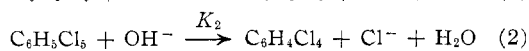
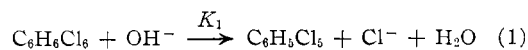
(1) Presented before the Organic Division of the American Chemical Society, Buffalo, N. Y., March 24, 1952, Abstracts, p. 6K.

(2) S. J. Cristol, *THIS JOURNAL*, **69**, 338 (1947); S. J. Cristol, N. L. Hause and J. S. Meck, *ibid.*, **73**, 674 (1951).

(3) E. D. Hughes, C. K. Ingold and R. Pasternak, *J. Chem. Soc.*, 3832 (1953).

data presented in this paper are consistent with a carbanion-intermediate mechanism as proposed by Cristol.²

The dehydrochlorination of BHC was considered² to proceed in three successive stages



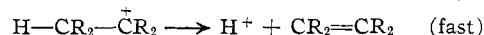
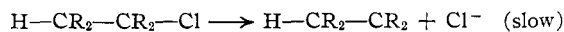
Second-order kinetics observed in studies with α -, β -, γ - and ϵ -BHC indicated that for these isomers 1 was slow and rate-determining, and was followed by two successive rapid stages 2 and 3. In the case of δ -BHC, however, the data indicated 2 to be slower than 1, which suggested the possibility of isolating pentachlorocyclohexene, the monodehydrochlorination product. Utilizing polarographic techniques, Nakazima, *et al.*,^{4a} established that 2 was indeed slower than 1 for γ - as well as for δ -BHC and succeeded in preparing γ -pentachlorocyclohexene (γ - $\text{C}_6\text{H}_5\text{Cl}_5$) from γ -BHC and δ - $\text{C}_6\text{H}_5\text{Cl}_5$ from δ -BHC. These syntheses have been adequately confirmed by Cristol² and others.^{3,5} Monodehydrohalogenation has been applied^{4b} to a number of heptachlorocyclohexane isomers as well; the reaction products were the corresponding hexachlorocyclohexenes ($\text{C}_6\text{H}_4\text{Cl}_6$).

The preparation of pentachlorocyclohexene and the related chlorocycloolefins, tetrachlorocyclohexene (benzene tetrachloride, BTC) and hexachlorocyclohexene, by additive chlorination in the presence of an iodine catalyst⁶ has made it possible to undertake a study of the mechanisms of steps 2 and 3 without interference from 1. Since the mechanism of the further dehydrochlorination of the $\text{C}_6\text{H}_5\text{Cl}_5$ products of step 1, whether isolatable or not, determines the ratio of trichlorobenzene isomers which are the final products of the reaction, a knowledge of the processes involved should contribute materially to the elucidation of the dehydrohalogenation of BHC and other chlorocyclohexane derivatives. One point in particular has not been clarified. Thus, alkaline dehydrochlorination of α -, β -, γ - and δ -BHC has been reported^{3,7} to yield mixtures of 1,2,4-, 1,3,5- and 1,2,3-trichlorobenzene. The formation of the latter isomer in yields as high as 20% cannot be accounted for solely on the basis of β -elimination.^{2,8}

The chlorocycloolefins under consideration are allylic chlorides and as such may be expected to be highly reactive by both uni- and bimolecular sub-

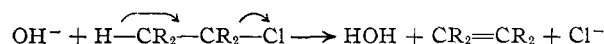
stitution and elimination reactions.⁹ α -BTC⁸ liberated free iodine when refluxed with potassium iodide in acetone while a solution in ethanolic silver nitrate failed to give a silver chloride precipitate after two weeks at 25°. On the other hand, dehydrochlorination took place immediately in 1% ethanolic sodium hydroxide at room temperature.

Three elimination mechanisms are recognized^{10,11}: (1) the two-stage **unimolecular mechanism** (E_1) in which a carbonium ion intermediate is formed in a rate-determining ionization and subsequently decomposes to yield the expected olefin



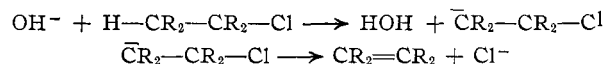
No evidence for this mechanism has been found at any stage of the alkaline dehydrochlorination of the chlorocycloolefins.

(2) The **bimolecular concerted mechanism** (E_2) in which a basic reagent extracts the protonic part of a combined hydrogen atom, while the electron-attracting group simultaneously separates, in a single concerted process, in possession of an extra electron



Eliminations proceeding by this mechanism, such as those of α -, γ -, δ - and ϵ -BHC, require that chlorine and hydrogen be present in a *trans* relationship on adjacent carbon atoms.

(3) The **bimolecular carbanion intermediate mechanism** proposed by Cristol² to account for



the slow bimolecular dehydrochlorination of β -BHC which, for stereochemical reasons, cannot proceed by a normal E_2 elimination. This process involves three steps: (i) base attack which gives rise to an unstable carbanion intermediate; (ii) inversion of the carbanion in order to meet the steric requirements for *trans* elimination; (iii) loss of halide ion and formation of the corresponding olefin. Although insufficient evidence is available to differentiate between the various alternatives, Miller and Noyes¹² considered i and ii as more probable than iii for the rate-determining step. With β -BHC, at least, the data support i.¹³

Hughes¹¹ has assigned the designation $\text{E}_{1\text{cB}}$ to the bimolecular carbanion-intermediate reaction which must thus be considered as a "unimolecular elimination of the conjugated base" of the halogenated compound. In view of recent evidence^{13,14} for the existence of the carbanion intermediate, the reaction might preferably be regarded as of an " $\text{E}_{2\text{c}}$ " type, that is, a bimolecular elimination with formation of a carbanion intermediate. Mechanisms 2 and 3 may be considered also as bimolecular *trans*-1,2 and *cis*-1,2 eliminations, respectively.

As pointed out by Hughes and Ingold,¹⁰ uni- and

(4) (a) M. Nakazima, T. Okubo and Y. Katumura, *Botyu-Kagaku*, **14**, 10 (1949); (b) **15**, 97 (1950).

(5) R. A. Pasternak, *Acta Cryst.*, **4**, 316 (1951); R. Riemschneider, N. Schuster and E. Böttcher, *Ans. Schädlingskunde*, **24**, 145 (1951); R. Riemschneider, *Z. Naturforsch.*, **7b**, 125 (1952).

(6) (a) G. Calingaert, M. E. Griffing, E. R. Kerr, A. J. Kolka and H. D. Orloff, *THIS JOURNAL*, **73**, 5224 (1951); (b) H. D. Orloff, A. J. Kolka, G. Calingaert, M. E. Griffing and E. R. Kerr, *ibid.*, **75**, 4243 (1953); (c) A. J. Kolka, H. D. Orloff and M. E. Griffing, *ibid.*, **76**, 1244 (1954).

(7) T. van der Linden, *Ber.*, **45**, 231 (1912).

(8) P. S. Skell and C. R. Hauser, *THIS JOURNAL*, **67**, 1661 (1945); G. W. Hearne and T. W. Evans, Symposium on Halogenation of Hydrocarbons, Division of Petroleum Chemistry, A.C.S. Meeting, Sept. 6-9, 1948, St. Louis, Mo., p. 46.

(9) E. D. Hughes, *Trans. Faraday Soc.*, **37**, 603 (1941).

(10) E. D. Hughes and C. K. Ingold, *ibid.*, **37**, 657 (1941).

(11) E. D. Hughes, *Quart. Reviews (London)*, **5**, 245 (1951).

(12) S. I. Miller and R. M. Noyes, *THIS JOURNAL*, **74**, 629 (1952).

(13) S. J. Cristol and D. D. Fix, *ibid.*, **75**, 2647 (1953).

(14) L. C. Leitch and H. J. Bernstein, *Can. J. Research*, **28B**, 35 (1950).

bimolecular mechanisms may be differentiated by ascertaining the effect of the basicity of the reagent on the rate of reaction. If elimination is accelerated by substituting a strong base (e.g., OH^-) for a weak base (e.g., OPh^- or R_3N), the result may be considered adequate evidence for an E_2 mechanism; if the rate is unaffected essentially from one reagent to the other, the mechanism is E_1 . Clearly, the rate of formation of a carbanion intermediate by nucleophilic attack on a proton (E_{2c}) also must be susceptible to the basicity of the reagent in the manner established for the *trans*-1,2 (E_2) elimination. Thus, it should be possible to establish whether the first step in the dehydrochlorination of a chlorocycloolefin involves the fission of a chloride ion or nucleophilic attack at a proton.

The alkaline dehydrochlorination of α -BTC and of γ -hexachlorocyclohexene, carried out with several bases in 80% (vol.) ethanol, showed that the rates of elimination increased substantially with the basicity of the reagent (Fig. 1). The dehydrohalogenation of the chlorocycloolefins, therefore, is bimolecular and, depending on the steric factors involved, E_2 or E_{2c} . In order to stabilize the atomic electrical shells in the molecule, the chloride ion is eliminated essentially simultaneously in the one-stage concerted process or subsequently in the multiple-stage carbanion-intermediate process. In a study of nine isomers, comprising tetra-, penta- and hexachlorocyclohexene, the established mechanism of β -elimination failed to explain the ratios of chlorobenzene isomers obtained in base-catalyzed

reactions. To account for these products, four mechanisms have been postulated and confirmed experimentally: *cis*-1,2, *trans*-1,2, *cis*-1,4 and *trans*-1,4. Depending on the steric relationship of the hydrogen and chlorine, each chlorocycloolefinic isomer reacts by at least two of these modes; some react by as many as three.

The results of this investigation also indicate that the allylic proton is the focus of the initial attack by the nucleophilic reagent. Consideration of reaction mechanisms involving base attack on a non-allylic proton require a combination of (1) normal β -elimination and formation of a conjugated diene intermediate followed by 1,2-elimination to yield the final chlorobenzene, and (2) 1,2-elimination and formation of a non-conjugated diene intermediate followed by 1,4-elimination. In either case molecular rearrangement would be necessary to explain all the reaction products obtained. While such mechanisms may explain the formation of 1,2,3-trichlorobenzene from BHC,³ they appear to be less probable from a thermodynamic consideration and, in the case of the BTC isomers, give no correlation between conformation, rates of elimination and product distribution. On the other hand, attack at the allylic proton allows a mechanism which is consistent with all of the experimental data and which is applicable to BTC, penta- and hexachlorocyclohexene.

Of the four processes involved in the allylic mechanism, only the *trans*-1,2 proceeds by the concerted bimolecular (E_2) mechanism reported for the majority of chlorine compounds. *cis*-1,2-Elimination involves the bimolecular multiple-stage carbanion-intermediate mechanism found by Cristol for β -BHC.² The 1,4-conjugate mechanism, which may proceed *cis* or *trans*, depending on the steric structure of the isomer, may be explained on the basis of the following sequence, illustrated in Fig. 2 for BTC and $\text{C}_6\text{H}_4\text{Cl}_6$: (1) nucleophilic attack on Ia or Ib by base to remove an allylic proton and form a carbanion IIa; (2) resonance shift to yield IIb, followed by (3) *trans*-1,2-elimination of the chloride ion from the δ -carbon. Depending on whether the 1,4-conjugate process is *cis* or *trans*, inversion, probably at the γ -carbon of IIb, may be necessary. Because of the requirement for inversion in *cis*-1,4-elimination, we can predict *a priori* that it should proceed at a measurably slower rate than the *trans*-1,4-process. As the result of the elimination of one molecule of hydrogen chloride from the allylic carbons of the chlorocyclohexene, tri- or pentachlorocyclohexadiene (IIIa and IIIb, respectively) are obtained. Aromatization of the resulting polychlorocyclohexadiene, by elimination of a second molecule of hydrogen chloride, results in the formation of two of three possible chlorobenzene isomers: *o*- and *m*-dichlorobenzene (IVa) in the case of BTC, and 1,2,3,4- and 1,2,3,5-tetrachlorobenzene (IVb) in the case of $\text{C}_6\text{H}_4\text{Cl}_6$. This mechanism has been confirmed by product distributions actually obtained: α -BTC yielded 47.8% *o*-, 50.4% *m*- and 1.8% *p*-dichlorobenzene, whereas γ - $\text{C}_6\text{H}_4\text{Cl}_6$ gave 74.2% 1,2,3,4-, 52.6% 1,2,3,5- and only 0.2% 1,2,4,5-tetrachlorobenzene. The formation of the isomer not explained by this scheme, that is, *p*-

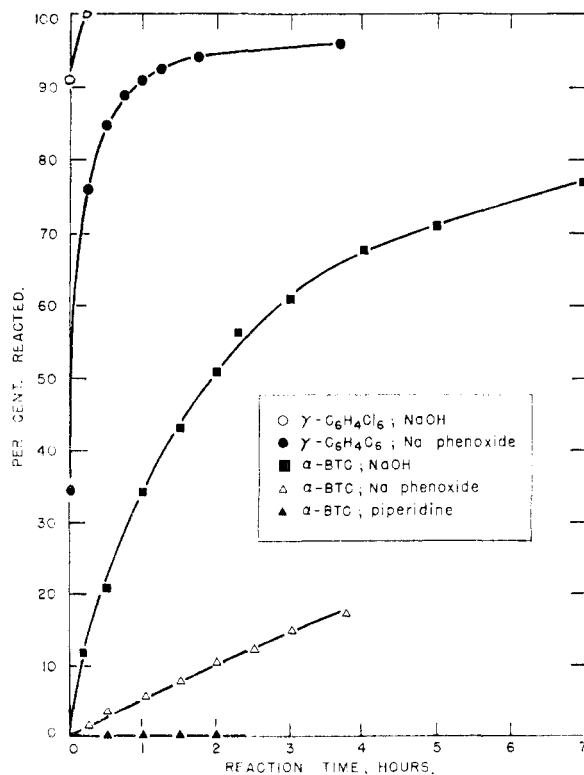
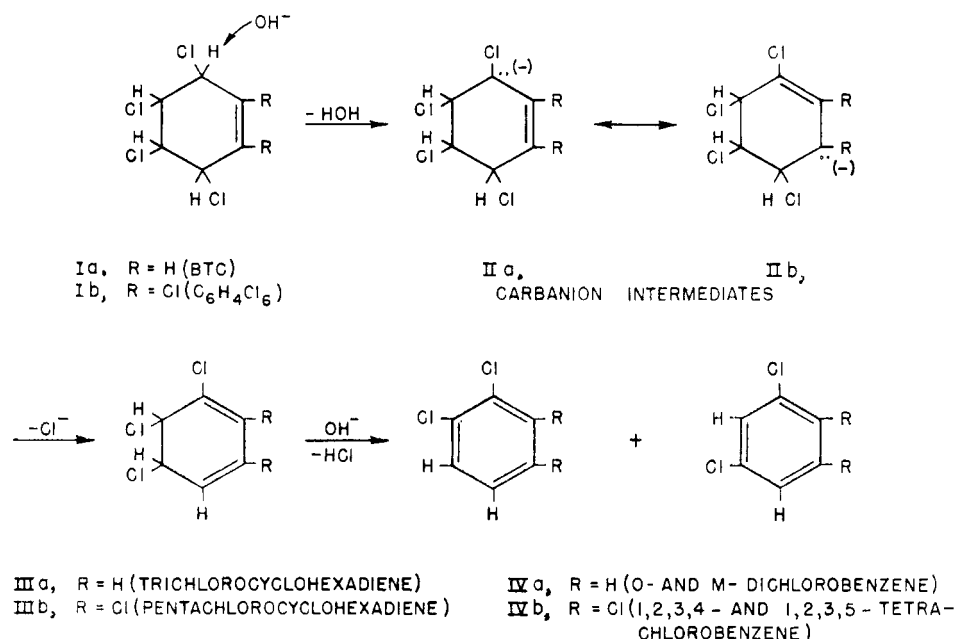
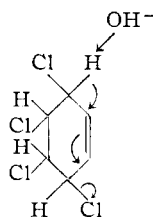


Fig. 1.—Effect of base strength on dehydrohalogenation of α -BTC and γ - $\text{C}_6\text{H}_4\text{Cl}_6$ in 80% (vol.) ethanolic solution at 28.9°; concentrations: chlorine compound, 0.01 *M*; base, 0.02 *M*.

Fig. 2.—Mechanism for 1,4-conjugate elimination in BTC and in $\text{C}_6\text{H}_4\text{Cl}_6$.

dichlorobenzene or 1,2,4,5-tetrachlorobenzene, results from 1,2-elimination which occurs simultaneously with the 1,4-process.

An alternate mechanism may be visualized. In *cis*-1,4-elimination, the base may attack the allylic proton and form a carbanion intermediate as before. The latter may be stabilized by inversion of the carbon atom and by a concerted series of electron displacements which result in ejection of the chloride ion from the δ -carbon. In *trans*-1,4-elimination, inversion may not be necessary for the series of displacements which terminate in the elimination of the chlorine and the entire process may actually be a synchronous one in which the carbanion has essentially no independent existence. This would require a smooth transfer of electrons over the system



As shown by the experimental data presented be-

low, the *trans*-1,4-process appears to be favored over the *cis*-1,4, whereas the latter proceeds more readily than the *cis*-1,2. These facts support the latter mechanism over that given in Fig. 2.

Pentachlorocyclohexene has a less symmetrical olefinic structure ($-\text{CH}=\text{CCl}-$) than BTC ($-\text{CH}=\text{CH}-$) or $\text{C}_6\text{H}_4\text{Cl}_6$ ($-\text{CCl}=\text{CCl}-$). Although initial base attack can take place at either allylic hydrogen, the preferred attack will be that determined by the spatial orientations of these hydrogen substituents and by the electrostatic (electron withdrawal) effect of the single chlorine substituent on the unsaturated carbon. In process A (Fig. 3), 1,4-elimination leads to 1,2,5,6-tetrachlorocyclohexadiene-1,3 (IIIa) which aromatizes to 1,2,3- and 1,2,4-trichlorobenzene by further reaction with base and liberation of hydrogen chloride; in B the monodehydrochlorination product, 1,3,5,6-tetrachlorocyclohexadiene-1,3 (IIIb), breaks down to yield 1,2,4- and 1,3,5-trichlorobenzene. Since 1,2,4-trichlorobenzene is common to both 1,4-processes as well as to 1,2-elimination which proceeds concurrently, it may be expected to predominate in the resultant isomeric mixture. This, in fact, is the case.

Table I gives the isomer distribution of the trichlorobenzenes obtained by alkaline dehydrochloro-

TABLE I
PRODUCTS OF DEHYDROCHLORINATION OF BHC ISOMERS

| BHC isomer Symbol Conformation | | Trichlorobenzene (%) ^a | | | | | | | | |
|-----------------------------------|--------|-----------------------------------|--------|-------------------|------------|--------|-------------------|------------|--------|------------------|
| | | 1,2,4- | | | 1,2,3- | | | 1,3,5- | | |
| | | This paper | Ref. 3 | Ref. 7 | This paper | Ref. 3 | Ref. 7 | This paper | Ref. 3 | Ref. 7 |
| β | eeeeee | 89.1 | 82.0 | 86.4 | 4.6 | 4.2 | 5.3 | 6.3 | 13.8 | 8.3 |
| δ | aeeeee | 85.7 | 85.4 | | 5.1 | 3.9 | | 9.2 | 10.7 | |
| α | aaeeee | 76.1 | 76.1 | 76.1 ^b | 20.1 | 14.9 | 17.0 ^b | 3.8 | 9.0 | 6.9 ^b |
| γ | aaaaee | 83.4 | 78.2 | 82.4 | 5.0 | 4.2 | 4.7 | 11.6 | 17.6 | 12.9 |
| ϵ | aeaeae | 95.0 | | | 5.2 | | | 0.0 | | |
| η | aeaaee | 93.2 | | | 6.8 | | | 0.0 | | |

^a Data reported by van der Linden⁷ were obtained by the use of ethanolic KOH, and thermal analysis of products. Our values and those cited in ref. 3 were obtained with ethanolic NaOH and analyses performed by infrared spectrophotometry.

^b With ethanolic NaOH and α -BHC, van der Linden⁷ obtained 75.9% 1,2,4-, 17.6% 1,2,3- and 6.5% 1,3,5-trichlorobenzene.

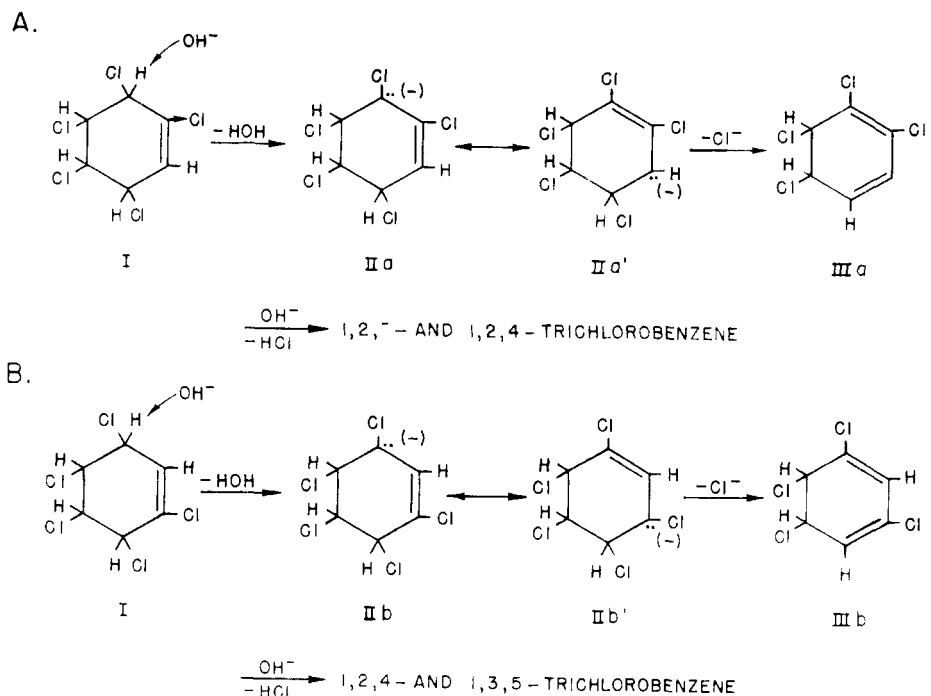


Fig. 3.—Mechanisms for 1,4-conjugate elimination in pentachlorocyclohexene.

mination of pure BHC isomers. Since elimination of hydrogen chloride from the latter proceeds *via* pentachlorocyclohexene, the values obtained must be identical with those of the $\text{C}_6\text{H}_5\text{Cl}_5$ intermediate. Whether the latter is a single isomer resulting from *trans*-1,2-elimination of polar hydrogen and chlorine substituents or a mixture¹⁵ of isomers, the appreciable quantities of 1,2,3-trichlorobenzene formed can be attributed only to 1,4-elimination.

The absence of 1,3,5-trichlorobenzene in the dehydrochlorination products of ϵ - and η -BHC suggests that the electron withdrawal effect of the chlorine on the unsaturated carbon atom may be important and favor base attack as shown by process A (Fig. 3). The carbanion IIa can undergo 1,4-elimination, as illustrated, to yield the 1,2,3- and 1,2,4-isomers or, in addition, can react by a 1,2-mechanism which only yields 1,2,4-trichlorobenzene.

Reaction rate studies have been carried out with all five of the known BTC isomers, three $\text{C}_6\text{H}_5\text{Cl}_5$ and one $\text{C}_6\text{H}_4\text{Cl}_6$ isomer. Second-order kinetics were observed in all cases, thus confirming the reaction to be bimolecular and the rate-determining step to involve nucleophilic attack by base on a proton, in a one-stage concerted or multiple-stage process, rather than ionization of a C-Cl bond by an E_1 mechanism. Dehydrohalogenation of BTC proceeds, therefore as

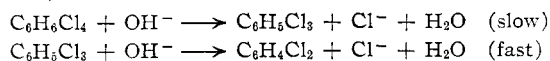


Figure 4 records the results of the kinetic studies with BTC, which were carried out with stoichiometric reagent concentrations (0.01 *M* BTC, 0.02 *M*

NaOH) in 80% (vol.) ethanol at 28.9°. Using the expression $k = (a/(a-x) - 1)/2at$ (where a = initial BTC concentration, moles/liter; x = BTC reacted in time t , moles/liter; t = reaction time, sec.; k = rate constant, liter/mole-sec.), a straight line relationship was obtained by plotting $a/(a-x)$ against t . The line, in each case, intersected the origin ($t = 0$, $a/(a-x) = 1$). Product distribution was obtained by performing the dehydrohalo-

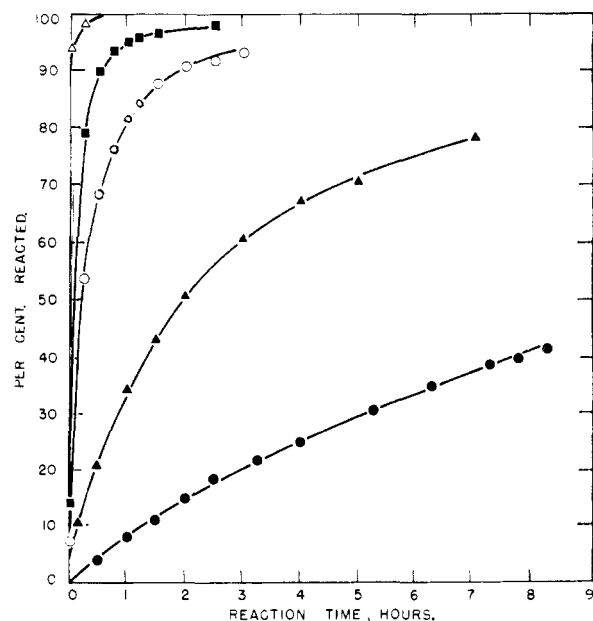


Fig. 4.—Dehydrochlorination of BTC isomers in 80% (vol.) ethanolic solution at 28.9°; concentrations: BTC, 0.01 *M*; NaOH, 0.02 *M*: Δ , ϵ -BTC (eeae); \blacksquare , γ -BTC (eeea); \circ , β -BTC (aeaa); \blacktriangle , α -BTC (eeaa); \bullet , δ -BTC (eeee).

(15) Theoretically, six of the BHC isomers, α , β , γ , δ , ϵ and η (aeaeae), can each yield only a single isolatable pentachlorocyclohexene; η (aeaeae) can form three while θ (aeaeae) can produce two separable steric isomers.

generations under reflux in 95% ethanol at slightly higher base concentration (10% NaOH). The results, arranged in order of increasing reaction rate, are given in Table II. The values for *o*- and *p*-dichlorobenzene represent minima for 1,4- and 1,2-elimination, respectively; those for the *m*-isomer may be attributed to either mechanism. Since it is not possible to determine the contributions of 1,2- and 1,4-elimination in the formation of *m*-dichlorobenzene, quantitative data pertaining to the over-all 1,2:1,4 ratios cannot be presented. Nevertheless, a qualitative interpretation of the importance of steric effects can be made from the data in Table II.

TABLE II
DEHYDROCHLORINATION OF BTC ISOMERS

| Iso- mer | Confor- mation | <i>k</i> (liter/ mole-sec.) 28.9° | <i>k</i> (rela- tive) | Dichlorobenzene, % | | |
|-------------|-------------------|---|--------------------------|-----------------------|----------------------|---------------------------------------|
| | | | | <i>Ortho</i> (1,4) | <i>Para</i> (1,2) | <i>Meta</i> (1,2 and/or 1,4) |
| δ | eeee | 1.20×10^{-3} | 1 | 15.8 | 60.5 | 23.7 |
| α | eeaa | 7.18×10^{-3} | 6 | 47.8 | 1.8 | 50.4 |
| β | aeaa | 6.67×10^{-2} | 56 | 2.9 | 66.0 | 31.1 |
| γ | eeea | 2.72×10^{-1} | 248 | 28.4 | 28.9 | 42.7 |
| ϵ | eeae | 8.33 | 6950 | 7.5 | 67.5 | 25.0 |

On the basis of nucleophilic attack on an allylic proton, the following interpretation is proposed:

1. The chlorine and hydrogen substituents in δ -BTC are all in a *cis* relationship to each other, since the chlorines are all *trans* (eeee). Hence, only *cis* elimination is sterically possible. This is consistent with the reaction rate, which is slower than for the other isomers in which *trans* elimination may occur. Both 1,2- and 1,4-eliminations take place, the former being preferred (60.5% *p*-, 15.8% *o*-dichlorobenzene).

2. α -BTC (eeaa) can react by *cis*-1,2- or *trans*-1,4-elimination. The formation of only 1.8% *p*-dichlorobenzene indicates that *cis*-1,2-elimination is not favored. The rate for α -BTC exceeds that for the δ -isomer by a sixfold factor and indicates that the *trans*-1,4 is favored over both *cis* processes.

3. β -BTC can lose hydrogen chloride by a *trans*-1,2-mechanism from either of the two equilibrium conformations $aeaa \rightleftharpoons aeaa$. The low yield (2.9%) of *o*-dichlorobenzene confirms the preference for *trans*-1,2- as compared with *cis*-1,4-elimination, the only other possibility. Comparison of the rate values for the α - and β -isomers indicates that the one-step concerted bimolecular (E_2) mechanism involved in the *trans*-1,2-elimination in β -BTC proceeds more readily than the *trans*-1,4-process involved in the dehydrochlorination of α -BTC. The *cis*-1,2-elimination observed by Cristol² in β -BHC, on the other hand, is slower by a factor of 7,000 to 24,000 than the *trans*-1,2 (E_2) elimination in α -, γ - and ϵ -BHC. The greater facility of the *trans*-1,4 as compared with the *cis*-1,2 mechanism suggests that the former process takes place by a concerted process involving a smooth transfer of electrons over the 1,4-system, rather than by a multiple-step process involving inversion. In the case of *cis*-1,2-elimination, inversion of the carbanion is necessary before the free electron pair on the β -carbon is in a position to enter the octet of the α -carbon on the side remote from the chlorine substituent.

4. In γ -BTC, the eeee conformation provides steric conditions which will allow three mechanisms: *cis*-1,2, *trans*-1,2 and *trans*-1,4. The almost equal yields of *o*- and *p*-dichlorobenzene show that the *trans*-1,4-process contributes as much as both of the 1,2-processes. One allylic hydrogen in the γ -isomer is axial while the other is equatorial. Neglecting the less preferred *cis*-1,2-elimination, it is noted that the axial hydrogen can participate in the *trans*-1,4-process, while the equatorial hydrogen must take part in the *trans*-1,2-elimination. If the energy and steric barriers to ring conversion¹⁶ are sufficiently low, the eeee conformation should yield the aaaa form in which an axial allylic hydrogen could participate in a planar four-centered transition state necessary for facile 1,2-elimination.¹⁷ The latter mechanism then should predominate over 1,4-elimination. Actually, *o*- and *p*-dichlorobenzene were formed in approximately equal amounts, thereby indicating that, presumably as a result of steric factors, ring conversion did not take place readily. Thus, in the case of the γ -isomer, the less-favored *trans*-1,4-process, involving axial hydrogen and chlorine substituents and proceeding without conversion, is competitive with the *trans*-1,2 mechanism which requires the conversion $eeaa \rightarrow aaaa$.

5. Finally, as indicated by the high ratio of *para:ortho* dichlorobenzene, ϵ -BTC (eeae) reacts primarily by a *trans*-1,2 orientation for hydrogen and chlorine which would permit the favored E_2 process; the only other possibilities are *cis*-1,2- and *cis*-1,4-elimination. The relatively high reaction rate of ϵ -BTC is associated with the presence of an allylic axial hydrogen in the thermodynamically predominant conformation (eeae), which can participate in *trans*-1,2 elimination.

The results of this investigation show that where more than one mode of elimination is possible, the order of preference is: *trans*-1,2 > *trans*-1,4 > *cis*-1,2 > *cis*-1,4. Quantitatively, the ratio of these processes appears to be dependent on the energy requirements of the elimination mechanism as compared to the energy involved in ring conversion.

The relative rates of dehydrohalogenation (Table II) of β - and ϵ -BTC indicates that the predominant conformation of the former isomer is aeaa rather than eaaa. From the percentages of dichlorobenzenes obtained, the ratios of 1,2:1,4-elimination in the two isomers appear to be of the same order of magnitude; 1,2-elimination is favored in both cases. Since the dehydrochlorination of ϵ -BTC (eeae) involves the initial elimination of an allylic axial hydrogen together with a vicinal axial chlorine, twice the rate would be expected from β -BTC if the configuration of the latter were eaaa because two allylic hydrogens here are axial and vicinal to axial chlorines. The fact that the rate constant for β -BTC is smaller than that for ϵ -BTC by a factor of 125 indicates that β -BTC exists predominantly in the aeaa conformation and that an appreciable energy barrier to ring conversion (to eaaa) is present. The predominance of the aeaa form for β -BTC has

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(17) D. H. R. Barton and E. Miller, *THIS JOURNAL*, **72**, 1066 (1950).

been confirmed by dipole moment and electron diffraction measurements.¹⁸

Theoretically, β -BTC may be dehydrochlorinated in two ways: (1) initial elimination of an equatorial hydrogen from the conformation *aeaa*, followed by a vicinal equatorial chlorine; (2) conversion to the form *eeaa*; base attack to remove an axial hydrogen, followed by a vicinal axial chlorine. An unequivocal distinction between both processes cannot be made on the basis of the end result because the products are identical. Process 2, however, is more probably a correct representation since the conditions for a planar four-centered transition state, necessary for facile *trans*-1,2-elimination, are present.

On the reasonable assumption that rearrangement does not occur, base attack on a *non-allylic* proton can lead only to *o*- and *m*-dichlorobenzene. The formation of the *para* isomer in good yield and a consideration of the kinetic data provide conclusive evidence that the initial base attack must take place on an allylic proton. The inadequacy of the "non-allylic" mechanism to elucidate the relative rates of dehydrochlorination obtained may be seen in the data tabulated below; δ -BTC (*eeee*) has been omitted because *trans*-elimination is not possible and consequently no steric predictions can be made.

| Isomer Symbol | Conformation | Type diene formed in non-allylic process (<i>trans</i> -1,2) | Non-allylic process, statistical possibilities <i>trans</i> -1,2- elimination |
|------------------|--------------|---|--|
| α | <i>eeaa</i> | Non-conjugated | 1 |
| β | <i>aeaa</i> | Conjugated | 2 |
| γ | <i>eeea</i> | Conjugated | 1 |
| ϵ | <i>eeae</i> | Non-conjugated | 1 |

The relative rates of elimination of the four isomers, on the basis of the "non-allylic mechanism" may be predicted as $\beta > \gamma > \alpha, \epsilon$. This is not in agreement with the observed sequence: $\epsilon > \gamma > \beta > \alpha$.

Penta- and Hexachlorocyclohexene.—Kinetic and product distribution studies with penta- and hexachlorocyclohexene, summarized in Table III, confirm the mechanisms proposed in the preceding section. Sufficient quantities of other isomers of these compounds were not available for inclusion in the investigation. Since γ -C₆H₅Cl₃ has not been obtained in crystalline form, the possibility of a

trace impurity exists and hence does not warrant reporting a rate constant for the isomer at this time. As in the case of the other cycloolefins, the rate data, however, indicated clear-cut second-order kinetics.

Hughes, Ingold and Pasternak³ have suggested that, inasmuch as β - and δ -BHC yield the identical intermediate δ -pentachlorocyclohexene, the ratio of trichlorobenzenes from all three materials should be very close. This conclusion is confirmed by our data (Tables II and III). The identity of composition of the trichlorobenzene isomers from γ -BHC and the corresponding cycloolefin, γ -C₆H₅Cl₃, is consistent with the probability that the latter is the sole intermediate of γ -BHC.

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Experimental Part

Materials Investigated.—The benzene tetrachloride isomers employed were prepared and purified as previously reported.^{6b} The recrystallized isomers melted as follows: α , 33.2–33.5°; β , 79.2–79.7°; γ , 88.2–88.6°; δ , 51.7–52.0°; ϵ , 98.8–99.4° (all values cor.). The melting points of the penta- and hexachlorocyclohexenes^{6a} are reported in Table III.

Measurement of Reaction Rates.—The kinetic studies on the BTC isomers were performed in thermostated 200-ml. three-neck round-bottom flasks, equipped with thermometer and glass agitator. A neutral absolute ethanolic solution (100.0 ml.) of the isomer (0.2748 g., 0.00125 mole) was diluted with 18.62 ml. of distilled water and allowed to come to equilibrium at $28.9 \pm 0.2^\circ$. The volume was brought to 125.0 ml. by the rapid introduction of 6.38 ml. of 0.3918 *N* carbon dioxide-free sodium hydroxide solution from a graduated pipet. The final reaction solution, therefore, was 0.01 *M* with respect to BTC and 0.02 *M* with respect to base. Aliquot samples (5.00 ml.) were removed at frequent intervals and quenched in 10.00 ml. of 0.02237 *N* hydrochloric acid solution. The extent of the reaction was determined by back titrating with 0.01115 *N* sodium hydroxide to a phenolphthalein end-point and correcting for a blank determination made without BTC. No error was introduced by preparing the alcohol solution several hours in advance of the run; titrations showed that the isomer did not undergo reaction with the solvent on standing at room temperature for 24 hours. The data from this series of experiments are plotted in Fig. 4. The reaction rate constant for ϵ -BTC was calculated from a second run in which the reagent concentrations were reduced by a factor of five.

Runs with the ϵ -BTC, C₆H₅Cl₅ and C₆H₄Cl₆ isomers were carried out in the same manner, but at lower concentrations, namely, 0.002 *N* chlorine compound and 0.004 *M* sodium hydroxide. A 45.0-ml. solution in absolute neutral ethanol, containing 0.001 mole of the compound (0.2199 g. of BTC, 0.2544 g. of C₆H₅Cl₅ or 0.2888 g. of C₆H₄Cl₆) was diluted to 400 ml. with additional alcohol. Distilled water (94.9 ml.) was added, the solution was brought to temperature and 5.10 ml. of 0.3918 *N* sodium hydroxide solution was introduced. Aliquot samples (25.0 ml.) were quenched in 10.00 ml. of 0.02237 *N* hydrochloric acid and back titrated with 0.01115 *N* sodium hydroxide to the phenolphthalein end-point.

Determination of Product Distribution from Dehydrochlorination.—Ten ml. of a 10% ethanolic sodium hydroxide solution was added dropwise to a refluxing solution of 0.10–0.20 g. of pure isomer in 95% ethanol. After refluxing for six hours, the solution was cooled, diluted with 200 ml. of water and extracted three times with 10-ml. quantities of carbon disulfide. The extract was water-washed, dried with anhydrous sodium sulfate and evaporated to 5–10 ml. An infrared curve for the solution was recorded with a Beckman IR-2 spectrophotometer. Using a curve obtained with a synthetic mixture of the components formed in the dehydrohalogenation, the product composition was calculated by a base-line method. The isomer ratios obtained in this manner are accurate to approximately $\pm 1\%$.

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TABLE III
DEHYDROCHLORINATION OF PENTA- AND HEXACHLOROCYCLOHEXENE ISOMERS

| Isomer | Pentachlorocyclohexene β | γ | δ | Hexachlorocyclohexene γ |
|---|-----------------------------------|--------------|-------------------------|-----------------------------------|
| M.p., °C. (cor.) | 70.5–71.3 | ^a | 68.2–68.6 | 101.0–101.6 |
| Steric structure ^b | Unknown | -eeaaa | -eeee | aueeee |
| <i>k</i> (liters/mole-sec.) | 5.72 | ... | 0.339 | 5.29 |
| Dehydrochlorination products: | | | | |
| 1,2,4-C ₆ H ₃ Cl ₃ | Not detd. | 84.9 | 86.6(85.3) ^c | ... |
| 1,2,3-C ₆ H ₃ Cl ₃ | Not detd. | 4.7 | 5.7(3.9) ^c | ... |
| 1,3,5-C ₆ H ₃ Cl ₃ | Not detd. | 10.4 | 7.7(10.8) ^c | ... |
| 1,2,3,4-C ₆ H ₂ Cl ₄ | ... | ... | ... | 47.2 |
| 1,2,3,5-C ₆ H ₂ Cl ₄ | ... | ... | ... | 52.6 |
| 1,2,4,5-C ₆ H ₂ Cl ₄ | ... | ... | ... | 0.2 |

^a B.p. 115–116° at 4.0 mm., ^b ²⁰D 1.5630. ^b See refs. 6 and 16 for discussion of stereochemistry and nomenclature of cyclohexane derivatives. ^c Data reported in ref. 3.

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