784. *Mechanism of Elimination Reactions. Part XVIII.* Kinetics and Steric Course of Elimination from Isomeric Benzene Hexachlorides.*

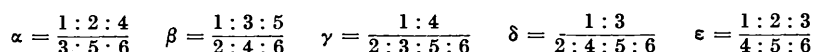By E. D. HUGHES, C. K. INGOLD, and R. PASTERNAK.

The kinetics and products of alkaline dehydrochlorination in alcoholic solvents, of four stereoisomers of benzene hexachloride have been studied. For some isomers one, and for others two rate-controlling steps can be distinguished, all of second order. Where there were two, the intervening product was isolated. Dr. H. W. Thompson analysed all the final products. The overall picture suggests interplay in $E2$ processes of facilitation by the electromeric effect and by an initial *anti*-relation between the parts of the 1 : 2-eliminant.

THAT stereochemical situations, as well as polar structural conditions, have a kinetic effect on heterolytic olefin elimination has long been obvious; but it was Hückel, Tappe, and Legutke (*Annalen*, 1940, **543**, 191) who first clearly expressed the view that such steric

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* Part XVII, preceding paper.

effects, like polar effects, must depend on mechanism. Actually, mechanism had not then been demonstrated in any of the stereochemically critical cases; but it was intrinsically likely that the rules previously established as governing the stereochemical course of substitution at saturated carbon (Cowdrey, Hughes, Ingold, Masterman, and Scott, *J.*, 1937, 1252) would find a close parallel in elimination from saturated systems. Later, when mechanism had been kinetically determined by us in several useful cases, including some of those now described in detail, definite stereochemical rules on the lines foreshadowed were suggested (Dhar, Hughes, Ingold, Mandour, Maw, and Woolf, *J.*, 1948, 2117). We shall be concerned here only with the rule of bimolecular anti-elimination, *viz.*, that in $E2$ reactions of $H-C_\beta-C_\alpha-X$, the HC_β-electrons enter C_α on the side remote from X. This "$E2$ rule" was applied to interpret the course of eliminations in alicyclic compounds, particularly in the *cyclo*hexane series.

One group of kinetic investigations of elimination from *cyclo*hexane stereoisomers has been concerned with the benzene hexachlorides, which, on treatment with alkali, undergo triple dehydrochlorination to give mixtures of trichlorobenzenes. The known isomers of the benzene hexachlorides have the following chlorine positions :

$$\alpha = \frac{1:2:4}{3:5:6} \quad \beta = \frac{1:3:5}{2:4:6} \quad \gamma = \frac{1:4}{2:3:5:6} \quad \delta = \frac{1:3}{2:4:5:6} \quad \varepsilon = \frac{1:2:3}{4:5:6}$$

Cristol first reported that the α-, γ-, and δ-isomers are readily dehydrochlorinated by alkali in aqueous alcohol, α and γ in simple second-order reactions, and δ by a kinetically more complex process, while the β-compound was hardly affected under the conditions employed (*J. Amer. Chem. Soc.*, 1947, **69**, 338). It was concluded that, for the α- and the γ-compound the first step, and for the δ-isomer the second step, of dehydrochlorination was rate-controlling. It was noted that in the β-compound all 1 : 2-HCl atom-pairs are *cis*-pairs, and that the inactivity of this isomer pointed to a restriction on *cis*-elimination. Nearly at the same time, it was found by one of us, first, that both the α- and the β-isomer suffer simple second-order dehydrochlorination in aqueous alcohol, the first step being rate-controlling in each case, though it is slower and more highly activated in the reaction of the β-compound (Pasternak, Ramsay Fellowship Reports, London, 1948). Secondly, it was found that the reactions of both the γ- and the δ-isomer, although occurring readily, are kinetically complex : detailed analysis showed that in each case the first and the second step of dehydrochlorination share control of the rate. Cristol, Hause, and Meek subsequently reported activation energies of the rate-controlling first steps of dehydrochlorination of the α-, β-, and ε-isomers; and they gave a figure for the γ-isomer, though without recognising that here the measured reaction is not simple (*J. Amer. Chem. Soc.*, 1951, **73**, 674). Their useful values of activation energy are added to Table 1, which summarises our results for the rates and Arrhenius parameters both of the first steps of dehydrochlorination of the α- and the β-isomer, and of the dissected first and second steps of the reactions of the γ- and the δ-compound.

TABLE 1. *Parameters of the equation $k_2 = Ae^{E_A/RT}$ for the dehydrochlorination of benzene hexachlorides by alkali in aqueous ethyl alcohol.*

| | E_A (in kcal./mole) | | | | $\log_{10} A$ (with A in sec.$^{-1}$ mole^{-1} l.) | | | |
| | 1st step | | | 2nd step | 1st step | | | 2nd step |
Solvent †	80%	90%	100%	90%	80%	90%	100%	90%
α	18·5 *	19·0	—	—	—	13·5	—	—
β	31·0,* 32·3	32·3	33·2	—	18·5	18·6	19·1	—
γ	—	20·4	—	20·1	—	14·4	—	13·9
δ	—	21·6	—	21·1	—	16·4	—	15·0
ε	21·4 *	—	—	—	—	—	—	—

* Values of activation energy by Cristol, Hause, and Meek (*loc. cit.*). Entropies of activation were computed with Eyring's rate equation.
† Aqueous ethyl alcohol specified by the percentage of ethyl alcohol by volume taken.

Contemporaneously with these kinetic studies, Nakajimo, Okubo, and Katamura discovered, by a polarographic method, the two rate-controlling steps in the reactions of the γ- and the δ-isomer; and, guided by these indications, they proceded to isolate the monode-

hydrochlorinated intermediates (*Botyu-Nakagu*, 1949, **14**, 10). Before we knew of this work, to which Dr. Cristol kindly drew our attention, we also had isolated them, and had measured their rates of dehydrochlorination, as a check upon the rate constants obtained by the somewhat difficult analysis of overlapping second-order reactions. The monode-hydrochlorination product from the γ-hexachloride was obtained as a liquid, but that from the δ-isomer is crystalline, and its crystal-structure was determined (Pasternak, *Acta Cryst.*, 1951, **4**, 316).

In all this work there has been no evidence of any measurable dehydrochlorination step which is not of second order. The fact that, for the β-compound, the Arrhenius energy of activation is 32 kcal./mole, instead of about 20 kcal./mole, as for the other isomers, is clearly to do with the *cis*-relation of all 1 : 2-HCl atom-pairs. Cristol, Hause, and Meek assume that in this case the bimolecular mechanism, that is, the one-stage process *E*2, is replaced by unimolecular elimination in the conjugate-basic carbanion, that is, by the mechanism we label *E*1*cB*, which would require the same kinetics, a rate-controlling proton-extraction by the alkali yielding a carbanion, which then quickly loses a chloride ion. However, a more conservative view seems equally tenable, namely, that the mechanism remains *E*2, and that the extra 12 kcal./mole of activation energy is employed partly 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. This interpretation would help us to understand why, for the β-isomer, the frequency factor is abnormally great : for the transition state of reaction could be attained only with much deformed bonds, which will presumably begin to break at a smaller degree of charge transfer, so that there is less solvation, and a higher statistical probability, in this transition state than in the transition states formed with the same bonds when less distorted.*

The striking fact about the four easily dehydrochlorinated benzene hexachlorides is that they fall into two classes with respect to the relation between the rates of the stages : in the reactions of the α- and the ε-compound, only the first step is rate-controlling, whereas in those of the γ- and the δ-isomer the first two steps share control of the rate. This can be understood on the hypothesis that the first elimination is of *trans*-HCl, and that, only when the second elimination can be of *trans*-HCl to give a second double-bond conjugated with the first, does the electromeric effect of the developing conjugation make the second reaction step much faster than the first. The third step, which directly gives the aromatic ring, can be assumed always to be much more rapid than either of the first two steps.

In order to simplify the detailed explanation, we will assume 1 : 2-elimination always, neglecting 1 : 4-elimination, though it doubtless occurs to some extent in the later steps of these dehydrochlorinations, as will be noted below. Using the numbering given on p. 3833, one observes that the α-compound can develop double bonds by *trans*-5 : 6- followed by *trans*-1 : 2-elimination, and that, since the formed 5 : 6 : 1 : 2-diene is conjugated, the second step of elimination will, according to our hypothesis, take place much more rapidly than the first, which will thus be wholly rate-controlling. The ε-isomer can undergo *trans*-2 : 3- followed by *trans*-4 : 5-elimination, to give a conjugated 2 : 3 : 4 : 5-diene, and hence the same kinetic situation will arise.

The δ-compound, after a *trans*-5 : 6-elimination, the initial occurrence of which is definitely established by Pasternak's crystal analysis of the isolated monochlorodehydro-chlorination product, can continue reaction only by undergoing a *cis*-elimination. Presumably it will do this with least difficulty when a conjugated diene is being produced, as by 1 : 2-*cis*-elimination to give a 5 : 6 : 1 : 2-diene. We can infer that the unfavourable stereochemistry will make the second step of this dehydrochlorination much slower than the second steps of those of the α- and the ε-isomer, and that it might make the second reaction step of the δ-compound slower than the first step. As can be seen from the rates in Table 2, the second reaction step of the δ-compound has about one-twelfth of the rate of the first : both steps are significantly rate-controlling, but the second is more strongly

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* In a paper which has just appeared (*J. Amer. Chem. Soc.*, 1953, **75**, 2647), Cristol and Fix describe a test for mechanism *E*1*cB* by Skell and Hauser's deuterium method. The test failed to show that **this** mechanism has any importance.

so. We conclude that the accelerative influence of the electromeric effect, which arises during the production of a conjugated diene, is more than counterbalanced by the retarding influence of the *cis*-relation between the parts of the eliminant.

The γ-compound, after an initial *trans*-2 : 3-elimination, has two possibilities of continued reaction : either it can undergo a *trans*-5 : 6-elimination without producing a conjugated system; or it can produce such a system in the stereochemically difficult way, as by a *cis*-4 : 5-elimination. Supposing that the 2 : 3-double bond would not much influence the formation of a 5 : 6-double bond, the first alternative gives us a second reaction-step which should have about one-half of the rate of the first, this statistical factor arising from the complete equivalence of the 2 : 3- and the 5 : 6-position in the original γ-hexachloride. The second alternative provides a second reaction step, which, according to our experience with the δ-hexachloride, should have a rate about one order of magnitude smaller than that of the first step. We can further foresee that, of these two conceivable alternatives, the effective one will be that which furnishes the faster second step; and hence the conclusion which our hypothesis offers for comparison with experiment is that the first two steps of dehydrochlorination of the γ-compound are comparably rate-controlling, and that the rate of the second is of the order of one-half of that of the first. As can be seen from Table 2, this is true to an approximation.

As Table 2 shows, rates of alkaline dehydrochlorination of benzene hexachlorides are not much changed by increasing the water content of the medium. This general result accords with the primary conclusion to be drawn from the theory of kinetic solvent effects (Hughes and Ingold, *J.*, 1935, 252; cf. *J.*, 1948, 2043), *viz.*, that no large effects are expected to arise from even a considerable change in solvent polarity, since the one unit of electric charge in the reactants is carried unaltered into the transition state of reaction. More precisely, the observed rates are, on the whole, slightly decreased on increasing the water

TABLE 2. *Rate-constants (k_2 in sec.$^{-1}$ mole^{-1} l.) of the rate-controlling steps of dehydrochlorination of the benzene hexachlorides by alkali in aqueous ethyl alcohol.*

T (° K)	Solvent : % EtOH 80%	90%	100%	T (° K)	Solvent : % EtOH 80%	90%	100%
	α (1st Step)				β (1st Step)		
258·3	—	0·00230	—	328·4	—	0·00137	—
264·2	—	0·00705	—	334·2	—	0·00319	—
273·2	0·0150	0·0200	0·0312	341·2	—	0·00870	—
287·2	—	0·109	—	350·2	0·0238	0·0301	0·0273
293·2	—	0·228	—	363·0	0·121	0·149	0·136

T (° K)	Solvent : % EtOH 80%	90%	100%	Solvent : % EtOH 80%	90%	100%
	γ (1st Step)			γ (2nd Step)		
264·7	—	0·00312	—	—	—	—
273·2	—	0·0112	—	—	0·00592	—
280·0	—	0·0274	—	—	0·0158	—
287·2	0·0527	0·0685	0·0967	0·0278	0·0400	0·0518
293·4	—	0·146	—	—	0·0770	—
301·2	—	—	—	—	0·192	—
	δ (1st Step)			δ (2nd Step)		
246·0	—	0·00186	—	—	—	—
251·8	—	0·00508	—	—	—	—
258·3	0·0110	0·0148	0·0120	—	—	—
265·2	—	0·0451	—	—	0·00356	—
273·2	—	—	—	0·00958	0·0113	0·0138
287·2	—	—	—	—	0·0778	—
293·4	—	—	—	—	0·163	—

content, as, indeed, is usual in the corresponding reactions of simple alkyl halides; but, in the case of the β-isomer only, the first 10% of water anomalously produces a very small increase of rate. The general small retardation by water can be made consistent with the theory of solvent effects, as extended for the discussion of secondary kinetic phenomena, if

we assume an identical reagent, with equal degrees of hydrogen bonding in the initial and the transition state, so that we can suppose that there is a greater spread of charge in the latter, a circumstance which should cause increased solvent polarity to produce small reductions of rate. Cristol and Barasch (*J. Amer. Chem. Soc.*, 1952, **74**, 1658), having already noted the slightly anomalous kinetic behaviour of the reaction of the β-compound with changes of solvent, have made it the basis of a criticism of the theory. But the example is a poor one, because, in a highly distorted transition state, such as may arise here, the close compensations, for instance, of hydrogen bonding, which often lead to secondary kinetic effects of simple character, could not reasonably be expected.

Cristol and Barasch saw further theoretical difficulties in the results of their analysis of the solvent effect on the temperature coefficient of the rate, having failed to appreciate that no rate equation, in applying which functions of temperature are treated as constants, can be expected to give useful results when applied to changes of temperature coefficient associated with such small rate changes as are here involved.*

The compositions of the mixtures of trichlorobenzenes finally produced by dehydrochlorination of α-, β-, and γ-benzene hexachloride were first determined by van der Linden by the freezing-point method (*Ber.*, 1912, **45**, 231). Dr. H. W. Thompson very kindly analysed our final products from the α-, β-, γ-, and δ-hexachloride, and from the crystalline pentachloro-intermediate derived from the δ-isomer, by the infra-red spectral method, bands between 9·5 and 13·5 μ being used for the intensity measurements. His results are in Table 3, to which we have added van der Linden's figures for comparison.

The identity of composition of the product from the δ-hexachloride with that of the product given by the pentachloro*cyclo*hexene obtained from the δ-hexachloride, indicates fairly definitely that the isolated crystalline pentachloro-compound is the only pentachloro-intermediate formed from the δ-hexachloride.

We know from Pasternak's crystal analysis that this pentachloro-intermediate is formed from the δ-hexachloride by *trans*-elimination, and has the structure (I). We should expect a single pentachloro-intermediate to be formed from the β-hexachloride, and, though it must in this case be formed by *cis*-elimination, it should have the same structure (I). In view of the considerably higher temperatures at which the intermediate must be formed and decomposed in the dehydrochlorination of the β- than in that of the δ-hexachloride, the compositions of the final trichlorobenzene mixtures, as given in Table 3, are not inconsistent with the assumption that the reactions of these two hexachlorides pass through a common intermediate.

In accordance with our hypothesis of preferential *trans*-elimination, we expect other pentachloro-intermediates from the γ- and the α-hexachloride : the γ-compound should give (II), and the α- isomer either (III) or (IV) or both. The intermediate as isolated from the γ-hexachloride is a liquid and is certainly different from (I). On comparing the com-

TABLE 3. *Compositions (measured by Dr. H. W. Thompson) of the trichlorobenzene mixtures obtained from benzene hexachlorides and from an isolated pentachloro-intermediate.*

(Van der Linden's values in parentheses.)

| Trichlorobenzene | Benzene hexachlorides | | | | Pentachloro-intermediate from δ |
	α	β	γ	δ	
1 : 2 : 4-	76·1 (76)	82·0 (87)	78·2 (82)	85·4	85·3
1 : 3 : 5-	9·0 (7)	13·8 (8)	17·6 (13)	10·7	10·8
1 : 2 : 3-	14·9 (17)	4·2 (5)	4·2 (5)	3·9	3·9

positions, as given in Table 3, of the trichlorobenzene mixtures finally formed from the γ- and the α-hexachloride, and from the δ-hexachloride, the temperatures throughout being comparable, we find some evidence that the reactions of the γ- and the α-isomer go

* Cristol and Begoon (*J. Amer. Chem. Soc.*, 1952, **74**, 5025) have complained of the behaviour of the theory of kinetic solvent effects in another case, that of the bimolecular dehydrohalogenation of halogeno-ethylenedicarboxylic acids; but an error must have crept into their application of the theory. They claim an anomaly, inasmuch as the reactions go more slowly in more aqueous alkaline media, though actually this is consistent with the theory in its elementary form.

through intermediates which are different both from each other and from the intermediate of constitution (I), which arises certainly from the δ- and, as we think, from the β-isomer.

(I)   (II)   (III)   (IV)
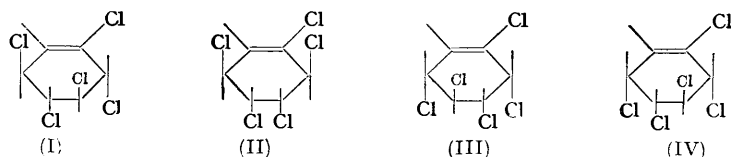
It is probable that the dehydrochlorinations of all the hexachlorides examined pursue parallel paths in the second and the third steps. The details are obscure; but we can conclude that these paths do not consist exclusively of 1 : 2-eliminations, since, if they did, 1 : 2 : 3-trichlorobenzene would not appear in the product. The formation of this substance can be understood if we may assume either that at least one of the later steps of dehydrochlorination involves 1 : 4-elimination in at least one of its parallel paths, or that, before at least one of the later steps in at least one of its parallel paths, anionotropic rearrangement intervenes. Either assumption is entirely reasonable, and often they are equivalent.
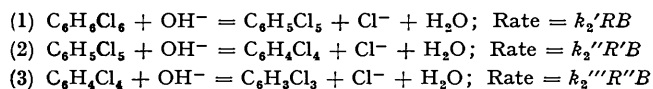
EXPERIMENTAL

Materials.—The four benzene hexachlorides were kindly given by Dr. L. J. Burrage of Imperial Chemical Industries Limited. They were substantially pure as received, but were recrystallised three times, the β-compound from acetone, and the other isomers from chloroform. Their uncorrected m. p.s were α 158°, β 207°, γ 113°, and δ 138°. The solvents we call " 80% " and " 90% " aqueous alcohol were made by mixing 8 and 9 volumes of dry ethyl alcohol with 2 and 1 volumes of water, respectively.

Measurements.—The runs were followed by potentiometric titration of chloride ion with 0.00500M-silver nitrate, and with 0.0100M-hydrochloric acid. In some cases, as a check, alkali disappearance was followed by titration with acid, lacmoid being used as indicator. In all the runs on which the rate figures already quoted are based the initial concentration of the hexachloride was about 0.002M and that of the alkali about 0.01M; but some runs have been done with higher alkali concentrations, up to 0.2M, and these disclose a small negative salt effect. Initial concentrations were determined, or checked, by completing the reaction and titrating both the chloride ion and the residual alkali : the sum of these measurements gives the initial alkali, while one-third of the chloride ion is equal to the initial benzene hexachloride. Reaction was stopped in samples withdrawn for analysis by adding them to excess of ethyl alcohol acidified with nitric acid.

For the α-, γ-, and δ-hexachlorides the aliquot method was used. The alkali, in the form of carbonate-free *ca.* 0.5M-sodium hydroxide or -sodium ethoxide, was added only after the solution of the benzene hexachloride in the ethyl alcoholic solvent had reached the temperature of the thermostat. Owing to the higher temperature required for the reaction of the β-isomer, the sealed-tube method was in this case more convenient. The reaction solution was made up at 0° and measured samples were enclosed under nitrogen in sealed tubes, which were together immersed in the thermostat, and successively withdrawn to be broken under acidified ethyl alcohol. Allowance was made for thermal expansion, when calculating the second-order rate constants.

Calculations.—No sign was detected of first-order elimination from any of the benzene hexachlorides, not even from the β-isomer, for which such a process might have been expected, since second-order elimination proceeds relatively slowly. Therefore, analysis of the rate data has been approached on the assumption that the total reaction consists of three consecutive steps each of second order, although the assumed kinetics of the third step are immaterial. The stoicheiometry, and rate constants, of the steps are taken to be as follows :

(1) $C_6H_6Cl_6 + OH^- = C_6H_5Cl_5 + Cl^- + H_2O$; Rate $= k_2'RB$

(2) $C_6H_5Cl_5 + OH^- = C_6H_4Cl_4 + Cl^- + H_2O$; Rate $= k_2''R'B$

(3) $C_6H_4Cl_4 + OH^- = C_6H_3Cl_3 + Cl^- + H_2O$; Rate $= k_2'''R''B$

where R, R', R'', and B are the concentrations at time t of $C_6H_6Cl_6$, $C_6H_5Cl_5$, $C_6H_4Cl_4$, and alkali, respectively. The measured quantity, the concentration of chloride ion, being x at time t, we have, $3R_0 = x_\infty$.

The overall reactions of the α- and the β-hexachloride accurately obey that second-order law which would result from the assumption that k_2' is measurable, and k_2'' and k_2''' are incomparably great. The overall reactions of the γ- and the δ-isomer deviate from any simple second-order form, and the deviations are interpreted on the basis that k_2' and k_2'' are comparable and measurable, while k_2''' is incomparably great.

When step (1) alone is rate-controlling the rate equation is :

$$k_2' = \frac{2 \cdot 303}{t(B_0 - x_\infty)} \log_{10} \left\{ \frac{x_\infty}{B_0} \cdot \frac{B_0 - x}{x_\infty - x} \right\}$$

Writing $C = 2 \cdot 303/(B_0 - x_\infty)$, $D' = \log_{10}(B_0/x_\infty)$, and $Y = \log_{10}\{(B_0 - x)/(x_\infty - x)\}$, we see that the plot of Y against t gives a straight line with a Y-axial intercept of D', and a slope of k_2'/C. This determines k_2'.

If step (2) alone were rate-controlling, the rate equation would be :

$$k_2'' = \frac{2 \cdot 303}{t(B_0 - x_\infty)} \log_{10} \left\{ \frac{2x_\infty}{3B_0 - x_\infty} \cdot \frac{B_0 - x}{x_\infty - x} \right\}$$

Writing $D'' = \log_{10}\{(3B_0 - x_\infty)/2x_\infty\}$, we see that the plot of Y against t gives a straight line making an intercept of D'', and having a slope of k_2''/C. This would determine k_2''.

When steps (1) and (2) share control of the rate, step (3) being still excluded from control, the plot of Y against t is not in general a single straight line ; but it becomes asymptotic to one straight line towards the beginning, and to another straight line towards the end of the reaction. The Y-axial intercept of the plot, or of the initial limiting line, is D', while that of the final limiting line is D''. These relations serve to test the assumption that the two rate-controlling steps are indeed steps (1) and (2). The initial limiting slope of the plot is $k_2'/3C$, and the final limiting slope is k_2''/C. These relations give k_2' and k_2''. In case $k_2' = 3k_2''$, the plot of Y against t degenerates into a single straight line, so that, when k_2' is close to $3k_2''$, it becomes difficult to distinguish joint rate-control by the two steps from rate-control by one step only. Otherwise expressed, the two steps cannot be distinguished because the kinetic overlap is uniform and continuous. Supposing that joint·rate-control is established, the steps being distinguishable, then an alternative way of deducing k_2' is to apply to readings of the initial rate that rate-equation which ignores steps (2) and (3) of the reaction :

$$k_2' = \frac{2 \cdot 303}{t(B_0 - x_\infty)} \log_{10} \left\{ \frac{\frac{1}{3}x_\infty}{B_0} \cdot \frac{B_0 - x}{\frac{1}{3}x_\infty - x} \right\}$$

The following equations, due essentially to Skrabal (*Monatsh.*, 1916, **37**, 137 ; 1919, **40**, 363), are of value for the purpose of guiding experiments on the isolation of the immediate product of step (1) in cases of joint control by steps (1) and (2). The maximum concentration $i_{max.}$ in which the intermediate can be built up is given by the equation, $i_{max.} = aK^{1/(1-K)}$, where $K = k_2'/k_2''$, and a is the initial concentration of the benzene hexachloride. The initial concentration b of alkali needed in order to produce this quantity of intermediate, is given by

$$b = a(4 - 3K^{1/(1-K)} - 2K^{K/(1-K)})$$

Errors.—All the rate data recorded above are results from duplicate or triplicate runs, mostly consistent to within 2%. The Arrhenius plots, with one exception mentioned below, were linear to within 2% in the rate constants. A considerable systematic error, *e.g.*, 10%, may well be present in those rate constants which are extracted by analysis of the overlapping reaction steps of the γ- and the δ-hexachloride. But these errors seem likely to be much the same at the different temperatures, so that they should have no serious effect on the determinations of Arrhenius parameters. The kinetic overlap is greatest for the γ-hexachloride, and our worst Arrhenius plot was that of the second reaction step of this isomer : the deviations here amounted to 4% in the rates, but even this error does not affect the figures for E_A, or for $\log_{10} A$, to the accuracy to which they are given in Table 1.

Isolation of Intermediates.—The δ-hexachloride was allowed to react with 1·1 mols. of sodium ethoxide in ethyl alcohol. After the solution had become neutral, the organic solutes were precipitated with water, collected, dried, and fractionally crystallised from light petroleum. Some unchanged hexachloride was recovered, and the more soluble δ-pentachloro*cyclo*hexene, m. p. 67—68°, was isolated [Found : C, 28·8 ; H, 2·0 ; Cl, 69·6 ; hydrolysable Cl, 27·9% ; M (Rast), 201. Calc. for $C_6H_3Cl_5$: C, 28·3 ; H, 2·0 ; Cl, 69·7 ; hydrolysable Cl, 27·9% ; M, 254].

This underwent dehydrochlorination in alkaline " 90% " aqueous alcohol, according to the second-order rate law, the rate constant at 273·2° K being 0·0122 sec.$^{-1}$ mole^{-1} l.

The γ-hexachloride was caused to react with 1·5 mols. of sodium ethoxide in ethyl alcohol. By partial evaporation of the solvent, about half of the original quantity of the hexachloride was crystallised and recovered. The mother-liquor was diluted with water and extracted with ether, and the material thus obtained was distilled. The first fraction contained trichlorobenzenes, whilst a second fraction consisted essentially of the γ-pentachloro*cyclo*hexene, and a residue of the γ-hexachloride remained. This pentachloro-compound was obtained as a viscous liquid, b. p. 130°/9—10 mm. [Found : C, 28·7; H, 2·2; Cl, 69·2; hydrolysable Cl, 27·7, 27·9%; M (Rast), 236]. It underwent dehydrochlorination in dry alcoholic sodium ethoxide according to a second-order law, the rate constant at 287·2° K being 0·0605 sec.$^{-1}$ mole^{-1} l.

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