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THE SOLVOLYSIS OF 1,1-DIBROMO(3.1.0)BICYCLOHEXANE[1,2]

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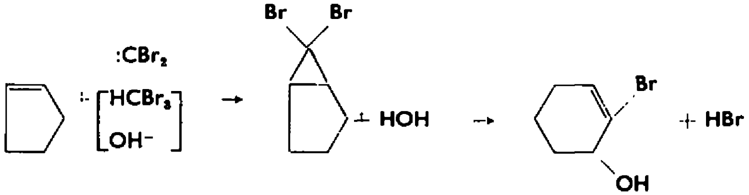
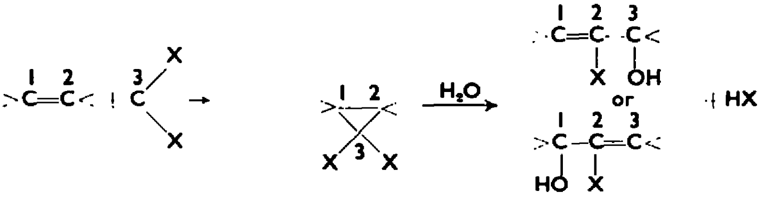
Abstract—The solvolysis of 1,1-dibromo(3.1.0)bicyclohexane has been kinetically detailed and found to proceed by simultaneous first order and series first order processes. The intermediate in the series first order process has been identified and its rate measured independently. Thermodynamic activation parameters were measured and were found to be consistent with the proposed reaction scheme.

INTRODUCTION

THE synthesis and reactions of compounds formed upon the addition of dihalomethylenes to olefins have received much recent attention.[4] One of the interesting sequences is the addition of dibromomethylene to cyclopentene, yielding 1,1-dibromo(3.1.0)bicyclohexane (I), which upon hydrolysis affords 2-bromocyclohexen-3-ol (II).[5] By this sequence, therefore, a third carbon atom is inserted between two olefinic carbons



I



In order to gain information on the details of this mechanism, we undertook a kinetic study of the solvolysis of I. We wish to report the results of a portion of this study.

EXPERIMENTAL

Compounds. 1,1-dibromo(3.1.0)bicyclohexane and 2,3-dibromocyclohexene were prepared as previously reported.[5] They were purified by distillation through a Nester Pt spinning band column.

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[2] Abstracted from a portion of the M.S. thesis of Lila Gatlin, The Pennsylvania State University (1959).

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[4] J. Hine, *Divalent Carbon*. Ronald Press, New York, N.Y. (1964).

[5] P. S. Skell and S. S. Sandler, *J. Amer Chem. Soc.* **80**, 2024 (1958).

Rate runs. The standard sealed ampoule technique was used for all kinetic studies. Since the reaction liberates HBr, the rate was followed in most cases by titration at 0° with standard NaOMe in absolute MeOH using brom cresol green as indicator. The concentration of reactant was about 0·015 M. Baths were regulated to ±0·02° and were calibrated against National Bureau of Standards thermometers.

Solvent. The solvent was prepared by diluting doubly distilled 95% EtOH–water azeotrope with distilled water to the density of 80% EtOH. This solvent, density 0·8542 at 19°, was used for all rate studies.

Errors. The standard sealed ampoule technique described above is considered to have approximately 2% error. Some of the sources of error were those typical of any volumetric analysis—errors in sample transfer, burette reading, endpoint observation, etc. Rate runs were corrected for the time necessary for the ampoules to reach thermal equilibrium.

TABLE 1. HYDROLYSIS OF 0·0147 M(I), AT 75°

Time min	Vol. (ml) of 0·0153 N base per 5 ml aliquot	$C\infty - Ct$	$k \times 10^4$ sec^{-1}
3	0·693	4·080	4·02
6	1·128	3·645	5·14
9	1·627	3·146	6·15
13	2·264	2·509	7·16
17	2·682	2·091	7·27
22	3·189	1·584	7·72
30	3·788	0·985	8·30
37	4·099	0·674	8·44
47	4·419	0·354	8·93
∞	4·773		

TABLE 2. SUMMARY OF SALT, ACID, BASE RUNS

k sec^{-1}[a]	Temp	Added salt	% Increase over average of runs without added salt
$5{\cdot}18 \times 10^{-5}$	50°C	—	
$5{\cdot}15 \times 10^{-5}$	50°C	—	
$6{\cdot}68 \times 10^{-5}$	50°C	0·05 N NaCl	29·2
$5{\cdot}55 \times 10^{-5}$	50°C	0·05 N NaBr	7·3
$5{\cdot}93 \times 10^{-5}$	50°C	0·018 N NaOMe	14·7
$7{\cdot}92 \times 10^{-4}$	75°C	—	
$8{\cdot}40 \times 10^{-4}$	75°C	—	
$8{\cdot}42 \times 10^{-4}$	75°C	0·05 N NaBr	3·2
$8{\cdot}47 \times 10^{-4}$	75°C	0·01 N HCl	3·8
$9{\cdot}27 \times 10^{-4}$	75°C	0·01 N NaOMe	13·6

[a] For purposes of comparison, k has been calculated from initial rate points by the time ratio method.[6] In all cases individual runs varied in the same way as that found in Table 1.

[6] For general Ref. see A. A. Frost and R. G. Pearson, *Kinetics and Mechanism* (2nd Edition) Chaps. 3, 8. J. Wiley, New York (1961).

RESULTS AND DISCUSSION

Typical rate data for the hydrolysis of I, including a standard point by point computation of pseudo first order rate constants, are presented in Table 1. These results typify those obtained in over thirty rate runs. In every case, although the experimental conditions were varied by changes in reactant concentration as well as by the addition of salts, acid and base (Table 2), Guggenheim plots using reliable initial data afforded rate constants one third less than those evaluated from reliable terminal data. Further, plots of acid formed versus time did not exhibit the smooth transcendental behaviour expected for first order processes, but rather resulted in S-shaped curves, Fig. 1.

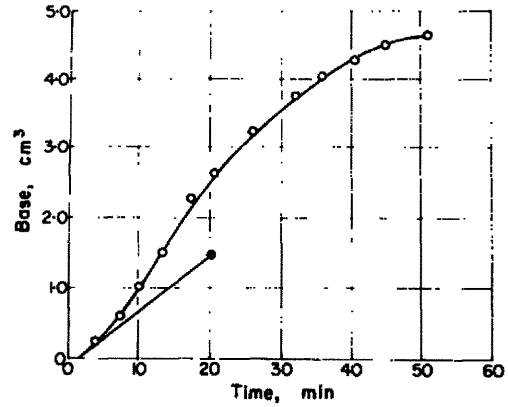
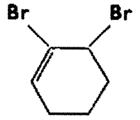


FIG. 1. A plot of base consumed versus time for the solvolysis of 1,1-dibromo(3.1.0)bicyclohexane(0). Closed circle; Initial slope.

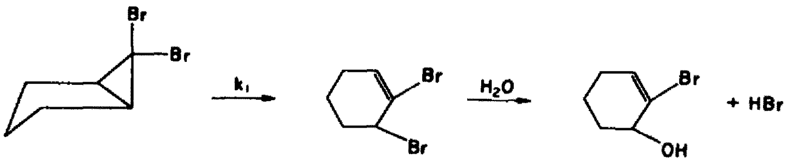
The starting material was known to contain a small amount of the allylic dibromide (III).



III

If I and III had reacted by parallel first order processes, a decreasing rather than increasing rate constant should have been observed. The presence of this impurity, therefore, could not have complicated the rate data in the manner indicated.

A similarity between the S-shaped curve of product formed versus time for a series first order process and that obtained in this investigation was noted. Since it was known that I thermally rearranged to III, the possibility that the hydrolysis might be occurring via the allylic dibromide, a series first order process, was explored.



Rate constants were evaluated for this mechanism using a time ratio method[6] based on Eq. (1) where γ is III/I_0, κ is k_2/k_1 and $k_1t = \tau$.

$$\gamma = e^{-\tau} + \frac{1}{1-\kappa}(\kappa e^{-\tau} - e^{-\kappa\tau}) \qquad (1)$$

The values of κ obtained for τ_{70}/τ_{35} and τ_{70}/τ_{50} were 1·7 and 2·0 respectively. These values differed by 15 to 18% whereas the experimental method is considered to have only 2% error. For $\tau = 1{\cdot}7$, k_1 is $1{\cdot}00 \times 10^{-4}$ sec^{-1} and k_2 is $1{\cdot}7 \times 10^{-4}$ sec^{-1}.

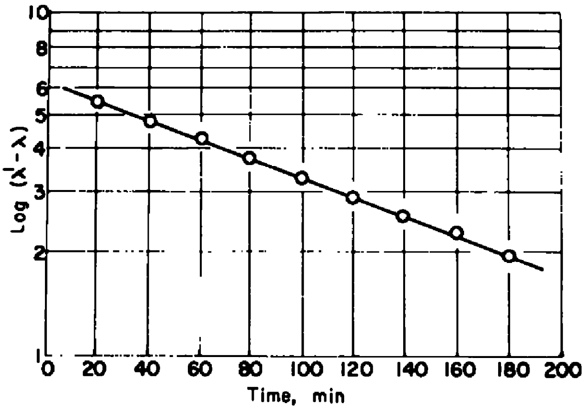


FIG. 2. Guggenheim plot for solvolysis of 2,3-dibromocyclohexane (see Ref. 6).

In order to further examine this mechanism, the pure allylic dibromide (III) was solvolyzed. This hydrolysis represented the path, $III \xrightarrow{k_2} II$ and provided an independent means of measuring k_2. Hydrolysis rates for III at 50° under conditions identical to that used for I gave excellent first order kinetics. A typical run is shown in Fig. 2. The first order rate constants calculated by the method of Guggenheim[6] showed no drift from 10 to 90% reaction. The slope of the Guggenheim plot exhibited a least squares average deviation of ±0·5%. Duplicate runs gave an average rate constant of $(1{\cdot}06 \pm 0{\cdot}01) \times 10^{-4}$ sec^{-1}. The average k_2 for these runs was 39% less than that calculated from Eq. (1); consequently, the reaction does not fit a series first order mechanism.

A comparison of the concentration versus time curves of Fig. 1 and that for typical series order reaction differed in one very important way. The experimental concentration versus time curve did not approach the origin asymptotically, but instead had an initial slope which was definitely non-zero. For a series first order mechanism, some minimum concentration of the intermediate must be formed before any observable amount of the product would appear. Since the experimental method follows only the concentration of the product, the initial slope should be zero. For this additional reason the series first order mechanism could not be considered as a reasonable explanation of the rate data.

Simultaneous first order and series first order processes were then considered,

$$\begin{tikzcd} I \arrow[r, "k_1"] \arrow[rr, bend right, dashed, "k_3"'] & III \arrow[r, "k_2"] & II \end{tikzcd} \qquad \text{(Mechanism III)}$$

For this mechanism, k_2 was known from the hydrolysis of III and k_3 could be estimated from the initial slope of the plot of product formed versus time. Using this k_2 and k_3, k_1 was calculated[6] from Eq. (2). Table 3 shows this calculation.

$$\phi = \frac{1}{(k_2 - (k_1 + k_3)} [(k_3 - k_2)e^{-(k_1+k_3)t} + k_1 e^{-k_2 t}] \tag{2}$$

Rate constants so obtained fit this function from 15 to 80% reaction with an average deviation of 1·24% as shown in Table 4.

Time ratios were calculated for $\kappa_1 = k_1/k_2$ and $\kappa_2 = k_3/k_2$ for the above rate constants. Eq. (3) is the parametric form of Eq. (2).

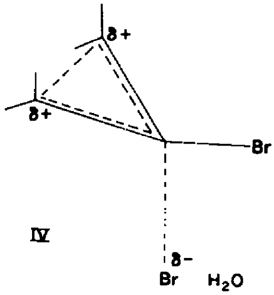
$$\phi = \frac{1}{1 - (\kappa_1 + \kappa_2)} [(\kappa_2 - 1)e^{-(\kappa_1+\kappa_2)} + \kappa_1 e^{-\tau}] \tag{3}$$

Again the rate constants obtained for this mechanism (and Eq. 2) gave values of k_1 and k_2 which were consistent with the observed time ratios.

Reevaluation of the rate data on the basis of this mechanism appeared to be the correct approach. The data fit the integrated expression with a deviation well within the limits of experimental error.[7] As further evidence for this mechanism, the intermediate (III) was isolated at a time corresponding to maximum concentration and identified from its IR spectrum. Thus III was a stable, stored intermediate.

The precision of the rate data appeared to depend on the storage time of the starting material. Table 5 shows that the order of decreasing accuracy in fit of Eq. (2) is 50° > 75° > 25°. This is precisely the order in which the runs were made after final purification of I. The runs at 25° were made with material stored for about two weeks. IR analyses indicated that about 3% of allylic material was present. Since Eqs. 2 and 3 were integrated with the initial conditions such that at $t = 0$, III_0 and $II_0 = 0$, they do not contain terms in III_0 and II_0 which would normally appear.

Activation parameters were obtained and are summarized in Table 5. The ΔS‡ values are all negative. A transition state of the type;



IV

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[7] The time ratio calculations are equation fit calculations. They do confirm, however, that all time ratios give the same values of k_1 and k_2. The agreement of k_2 from the allylic runs with the k_2 which fits Mechanism III is extra evidence in disguise. Even though k_2 from the allylic runs as such was used to find k_1, the same value would have been obtained even if k_2 had been completely unknown originally. Then a computer solution, easily obtained, would have to have found a k_2 in agreement with an experimental k_2 to obtain the equation fit.

TABLE 3. TIME RATIO CALCULATIONS

$k_2 = 0·165$

$k_1 = 1·10$ $\quad {}^{*}\phi_{70} = 0·300 \quad \phi_{50} = 0·50 \quad \phi_{35} = 0·65 \quad \phi_{20} = 0·80$

$\tau_{70} = 2·03 \quad \tau_{50} = 1·36 \quad \tau_{35} = 0·970 \quad \tau_{20} = 0·615$

	$\frac{\tau_{50}}{\tau_{35}}$	$\frac{\tau_{70}}{\tau_{35}}$	$\frac{\tau_{70}}{\tau_{50}}$	$\frac{\tau_{35}}{\tau_{20}}$
Calculated time ratios	1·40	2·09	1·49	1·57
†Time ratios, run 35	1·38	2·04	1·47	1·55
% Deviation	1·42	2·38	1·33	1·26
Avg. % dev. = 1·59%				

* $\phi_{70} = \phi$ at 70% reaction.

† A correction of −2 min was used for each time to adjust for time to reach thermal equilibrium.

TABLE 4

$t = 50°$

Equation fit calculations.

$k_1 = 1·17 \times 10^{-4}$ sec^{-1} $\quad k_2 = 1·06 \times 10^{-4}$ sec^{-1} $\quad k_3 = 1·75 \times 10^{-5}$ sec^{-1}

Time min	ϕ Observed	ϕ Calculated	% Deviation
82·5	0·850	0·834	1·88
101·0	0·800	0·785	0·6
156·5	0·650	0·639	1·69
216·5	0·500	0·495	1·00
398·0	0·200	0·202	1·00
		average % deviation =	1·24%

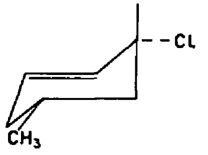
TABLE 5. SUMMARY OF RATE CONSTANTS AND ACTIVATION PARAMETERS*

	k_1	k_2	k_3	Average % deviation in equation fit
75°	$1·67 \times 10^{-3} \pm 0·02$	$1·06 \times 10^{-3} \pm 0·02$	$2·40 \times 10^{-4} \pm 0·04$	2·60
50°	$1·17 \times 10^{-4} \pm 0·02$	$1·06 \times 10^{-4} \pm 0·01$	$1·75 \times 10^{-5} \pm 0·05$	1·24
25°	$2·97 \times 10^{-6} \pm 0·30$	$6·04 \times 10^{-6} \pm 0·30$	$1·71 \times 10^{-6} \pm 0·10$	5·80
Δ Ea, Kcal	$23·80 \pm 0·69$	$20·61 \pm 0·60$	$23·44 \pm 0·69$	
Δ H‡, Kcal	$23·16 \pm 0·69$	$19·97 \pm 0·57$	$22·80 \pm 0·66$	
ΔS‡, eu at 50°	$-5·03 \pm 0·15$	$-15·09 \pm 0·45$	$-9·91 \pm 0·27$	

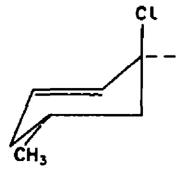
* All activation parameters were calculated from the data at 50° and 75°, the 25° data being used as a confirmatory point.

with vibrational freedom restricted about the carbon-halogen bond, would be consistent with such negative values. The halogen may either collapse to the allylic compound or be removed by the solvent.[8] This could explain a negative $\Delta S_{\neq}$ for k_1 and k_3.

Goering *et al.*[9] obtained negative entropies of activation of similar magnitudes



$\Delta S^* = -7{\cdot}07 \pm 0{\cdot}6$



$\Delta S^* = -10{\cdot}3 \pm 1{\cdot}7$

in the hydrolysis of 3-chloro-5-methyl cyclohexene. This reaction path is analogous to the path, III $\xrightarrow{k_2}$ II. The entropies of activation are consistent with that for k_2.

This study exhibits, again, the need for companion kinetic and synthetic studies to verify a reaction mechanism that might have appeared from one point of view to be rather straightforward and from the other exceedingly complex.

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[8] It was mentioned by one of the referees that IV could be an intermediate that could "internally return" to starting material along the lines indicated by Winstein (S. Winstein *et al.*, *J. Amer. Chem. Soc.* **76**, 2597 (1954); also see R. E. Glick, Ph.D. thesis, UCLA, 1954, for special cases). The solvent, salt, acid and base effects minimize such possibilities, although the internal rearrangement of I → III could be obviously couched in terms of the rearrangement of an "intimate ion-pair."

[9] H. L. Goering, T. D. Nevitt and E. F. Silversmith, *J. Amer. Chem. Soc.* **77**, 5026 (1955).