solution allows for a (Cl^{-I}/Pd^{IV}) ratio of only 5.1:1 whereas the dilute solutions contained presumably $PdCl_6^=$ ions.

A mixture of equal volumes of 1.47 *F* platinum (II) chloride (containing 0.058 *F* $PtCl_6^=$) in *ca.* 6 *F* hydrochloric acid and 2.0 *F* H_2PtCl_6 in 1.0 *F* hydrochloric acid had the same optical density as the sum of one-half of the optical densities of the two component solutions in the wave length region 430–560 mμ. Similarly, Beer's law applied to a 1:1 mixture of 0.234 *F* palladium(II) chloride and 2.0 *F* H_2PtCl_6, each in 1.0 *F* hydrochloric acid. The absorption spectra of the platinum solutions are illustrated in Fig. 2.

Discussion

The marked dichroism of the substance $Pd(NH_3)_2Cl_2{\cdot}M(NH_3)_2Cl_4$ (M = Pd or Pt) is consistent with the view that these have the same structure as that of $Pt(NH_3)_2Br_2{\cdot}Pt(NH_3)_2Br_4$ determined by Brosset, so that there is a chain $\cdots\cdots Pd^{II}\cdots\cdots Cl{—}M^{IV}{—}Cl\cdots\cdots Pd^{II}\cdots\cdots Cl{—}M^{IV}{—}$, along the needle axis of the crystal. Anomalous and strong light absorption due to the oscillation of electrons between the atoms in the +2 and +4 oxidation states under the influence of the electric vector of the light would occur only for light polarized with the electric vector along this axis. This should also be the axis of highest refractive index. It may be mentioned that crystal structure investigations of these substances in these laboratories to be published separately confirm this point of view. (For the larger crystals where the strong absorption was for light perpendicular to the needle axis, it is possible that the crystals have grown differently, and the *c* axis in this case is not the needle axis.) In view of the difference in the II–IV oxidation potentials for platinum and palladium (*ca.* −0.7 and −1.3 v.) one would expect, as observed, that the mixed platinum–palladium compound would be less colored than the palladium–palladium compound.

The magnetic studies, while not very precise, show that the palladium compound does not contain any unpaired electrons and hence no independent palladium(II) kernels. Syrkin and Belova[18] have reported that the substances $PtCl_3$, $Pt(H_2NCH_2CH_2NH_2)Cl_3$ and $Pt(NH_3)_2Cl_2(OH)$ are diamagnetic although they are formally compounds of tripositive platinum. The latter compound has been reported to be strongly dichroic.[19] Janes[20] reports that the compound of palladium(III), "$[Pd(NH_3)_2Cl_3]_2$" is diamagnetic, and we suppose that this refers to $Pd(NH_3)_2Cl_2{\cdot}Pd(NH_3)_2Cl_4$.

The non-occurrence of interaction absorption in solution shows that similar strongly colored polymers or dimers do not form, even in solutions which contain rather high concentrations of palladium-(II) and palladium(IV) or platinum(IV). It might be supposed that in solutions containing excess free chloride ion, the planar $PdCl_4^=$ ion would form two weaker bonds to chlorides in directions perpendicular to the plane, and that this effect would inhibit the formation of the chains illustrated above responsible for the strong coloration. However, this could not have been the case for the solutions studied which contained less chloride than that required for the formation of $PdCl_4^=$ and $PdCl_6^=$ ions.

Acknowledgment.—The authors wish to thank Professor Linus Pauling and Dr. E. S. Hughes for valuable discussions and Dr. Hans Zinsser for advice concerning the operation of the instrument used for the magnetic susceptibility measurements.

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(18) Ya. K. Syrkin and V. I. Belova, *Zhur. Fiz. Khim.*, **23**, 664 (1949); *C. A.*, **43**, 7277 (1949).

(19) G. B. Bokil and G. I. Distler, *Doklady Akad. Nauk S. S. S. R.*, **56**, 923 (1947); *C. A.*, **43**, 3683 (1949).

(20) R. B. Janes, THIS JOURNAL, **57**, 471 (1930).

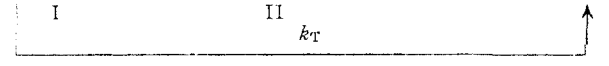
PASADENA, CALIF. RECEIVED SEPTEMBER 22, 1950

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

Allylic Rearrangements. XXXII. The Solvolysis and Intramolecular Rearrangement of α,α-Dimethylallyl Chloride[1]

BY W. G. YOUNG, S. WINSTEIN AND HARLAN L. GOERING[2]

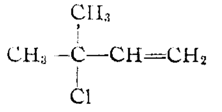
The acetolysis of α,α-dimethylallyl chloride (I) involves simultaneous solvolysis and intramolecular isomerization to primary chloride γ,γ-dimethylallyl chloride (II).



$$(CH_3)_2CHClCH{=}CH_2 \xrightarrow{k_i} (CH_3)_2C{=}CH{-}CH_2Cl \xrightarrow{k_p} \text{solvolysis products}$$

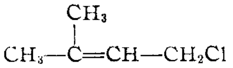
The kinetics have been treated so as to obtain the rate constants k_i, k_T and k_p. The possibility of a common intermediate for solvolysis and rearrangement of I is suggested and discussed.

In connection with a general investigation of the kinetics and products of replacement reactions of allylic compounds, we have scrutinized the acetolysis of α,α-dimethylallyl chloride (I) and γ,γ-dimethylallyl chloride (II). During this investigation it developed that a rearrangement of the tertiary chloride I to the primary isomer II proceeds concurrently with the solvolysis of the tertiary chloride and that it was possible to treat the kinetics of the simultaneous acetolysis and



$CH_3{-}C(CH_3)(Cl){-}CH{=}CH_2$

I



$CH_3{-}C(CH_3){=}CH{-}CH_2Cl$

II

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(1) Presented before the Organic Division of the American Chemical Society, Philadelphia, April, 1950.

(2) Postdoctoral research fellow 1948–1950. Department of Chemistry, University of Wisconsin, Madison, Wisconsin.

rearrangement of I so as to obtain accurate, reproducible kinetics for the rearrangement. As far as we are aware, this represents the first successful kinetic study of the isomerization of an allylic chloride. The results of this investigation and some of their implications are discussed in the present paper.

As the solvolysis of alkyl halides in glacial acetic acid is a reversible reaction,[3,4] the acetolyses were carried out in the presence of acetate ion to avoid back reaction.[5]

For acetolysis of the primary chloride at 24.96° a specific rate constant, showing no significant trends, is obtained from equation (1), the integrated expression for a first order reaction, where a is the original allylic halide concentration and x is the concentration of the reacted halide.

$$k = \frac{1}{t} \ln \frac{a}{a - x} \qquad (1)$$

TABLE I

SOLVOLYSIS OF 0.094 M γ,γ-DIMETHYLALLYL CHLORIDE AT 24.96 ± 0.01° IN AcOH, 0.094 N IN KOAc

Time, 10^{-2} sec.	10^2 M	10^6 k (sec.$^{-1}$)
882	7.609	2.35
1625	6.301	2.44
2424	5.191	2.43
2650	4.900	2.44
2858	4.634	2.46
3290	4.158	2.47
3731	3.738	2.46
4244	3.299	2.46
		Mean 2.44 ± 0.02 × 10^{-6}

Table I summarizes a typical run and Table II lists the results of all of the runs carried out with the primary halide together with the mean deviations in the reaction rate constants. The magnitude of these mean deviations constitutes a criterion of the accuracy attained in the experimental work for the acetolysis of I and II. As shown in the table, the rate is independent of acetate ion and chloride ion concentration at constant ionic strength. The effect of increasing ionic strength is smaller than the specific salt effects observed when potassium acetate is replaced by potassium toluenesulfonate at constant ionic strength, such a replacement increasing the rate. The rate is also slightly but consistently increased as allylic halide concentration is decreased.

TABLE II

RATE CONSTANTS FOR THE SOLVOLYSIS OF γ,γ-DIMETHYLALLYL CHLORIDE IN AcOH AT 25°

Run	(RX) 10^2 M	(KOAc) 10^2 M	(LiOAc) 10^2 M	(KOTs) 10^2 M	(LiCl) 10^2 M	μ 10^2 M	10^6k (sec.$^{-1}$)
1	3.77	4.806				4.806	2.21 ± 0.04
2	3.01	4.806				4.806	2.23 ± .03
3	9.474	9.429				9.429	2.44 ± .02
4	7.22	9.429				9.429	2.54 ± .02
5	5.10	4.737		4.692		9.429	2.83 ± .03
6	2.94	2.483		6.946		9.429	3.01 ± .04
7	8.988		9.569			9.569	2.27 ± .04
8	3.083		9.569			9.569	2.30 ± .06
9	4.458		4.715		4.872	9.587	2.30 ± .02
10	3.722		4.715		4.872	9.587	2.35 ± .01

When the tertiary isomer is acetolized, the rate constants, as obtained from the integrated expression for a first order reaction, show a considerable downward drift. The data may be handled as follows: A large scale plot of x against time may be prepared and the slope of the resulting curve can be determined at various points with the aid of a tangent meter. The slope (dx/dt) is then divided by the concentration of halide at the corresponding time to give the instantaneous first order rate constant k as defined by equation (2).

$$k = (dx/dt)/(a - x) \qquad (2)$$

The instantaneous rate constants decrease from *ca.* 15 × 10^{-6} sec.$^{-1}$ to about 2.2 × 10^{-6} by the time the reaction is 30% complete, thereafter remaining constant at 2.2 × 10^{-6}, the value for the primary isomer. A comparison of several plots of k against time, from different runs, shows them all to be identical within experimental error.

TABLE III

RATE OF REACTION OF α,α-DIMETHYLALLYL CHLORIDE AT 24.96° IN HOAc

Run 13, 0.04822 N KOAc, 0.0412 N (RX)

Time 10^{-4} sec.	(RX) 10^2 N	10^6 k (sec.$^{-1}$)	10^6 k (sec.$^{-1}$)[a]
0	4.117		
0.072	4.079		
.180	4.006		
.378	3.930	12.2	
.726	3.781	11.7	
1.032	3.680	10.9	
1.722	3.472	9.9	
2.454	3.312	8.9	
2.958	3.251	8.0	
4.338	3.024	7.1	
8.544	2.677	5.0	
11.130	2.530	4.4	
11.502	2.528	4.2	
17.346	2.221	3.6	2.21
18.186	2.190	3.5	2.14
19.212	2.144	3.4	2.30
26.442	1.835	3.1	2.14
34.326	1.521	2.9	2.23
42.996	1.285	2.7	2.15
		Mean	2.19

[a] Values obtained from integrated equation for a first order reaction, using a starting point after rearrangement is complete: $10^{-4}t = 11.502$; (RX) = 0.02528.

The instantaneous rate constant at zero time of *ca.* 15 × 10^{-6} represents the best obtainable value for the specific rate of solvolysis of the tertiary isomer. Table III shows a typical set of data obtained in the acetolysis of I, the rate constants calculated from equation (1) showing the large downward drift. By using the data obtained during the latter part of the run, after the rearrangement is complete (*i. e.*, after 30% reaction), equation (1) gives a constant that shows no trends and is identical with the value obtained for the primary isomer listed in Table II.

The data thus far discussed indicate that tertiary chloride I solvolyzes and isomerizes simultaneously in acetic acid, isomerization being essentially

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(3) Steigman and Hammett, THIS JOURNAL, **59**, 2536 (1937).

(4) Grunwald and Winstein, *ibid.*, **70**, 846 (1948).

(5) Roberts, Young and Winstein, *ibid.*, **64**, 2157 (1942).

complete by approximately 30% reaction, as verified by isolation of unreacted chloride. The kinetics are not consistent with a formulation which depends on reaction of a carbonium ion intermediate either with solvent to yield solvolysis product or external chloride ion to yield chiefly primary chloride. This can be seen, even before more data on the solvolysis of tertiary chloride I are presented, from the behavior of the primary chloride II, which yields the same carbonium ion as does its allylic isomer I. The fact that the rate constant for solvolysis of the primary chloride is constant throughout a run and deliberate increase in the initial concentration of chloride ion did not bring out a mass law[6] effect indicates that a carbonium ion is not returning to the primary isomer by reaction with external chloride ion

The data indicate that the isomerization of the tertiary chloride I to primary chloride II is intramolecular. The following over-all formulation is consistent with the facts. R_TCl is the tertiary chloride and k_T and k_i are the specific rates of solvolysis and isomerization, respectively. R_PCl is the primary isomer and k_p is the specific rate of solvolysis for this isomer. The value of k_T is obtained from the x, t plot by determining the instantaneous rate constant at $t = 0$, and the value of k_p is known from the solvolysis of the primary isomer. This latter value can also be obtained

$$\begin{tikzcd} R_TCl \arrow[r, "k_T"] \arrow[dr, "k_i"'] & \text{Products} \\ & R_PCl \arrow[u, "k_p"'] \end{tikzcd}$$

from the solvolysis of the tertiary isomer inasmuch as this is the constant value which the instantaneous rate constant reaches after isomerization is complete.

From the rate of decrease of the instantaneous rate of solvolysis for the tertiary isomer from equation (2), the specific rate of isomerization, k_i, can be determined by reference to equation (3). This equation expresses the total over-all rate of solvolysis of a mixture of the two isomeric chlorides, F representing the mole fraction of tertiary isomer in the total remaining halide at any time. Thus

$$dx/dt = k_T(a - x)F + k_p(a - x)(1 - F) \quad (3)$$

$(a - x)F$ is the concentration of the tertiary isomer at any instant and $(a - x)(1 - F)$ represents the concentration of the primary isomer at any time. From equation (2) and (3) the expression for F shown in equation (4) is obtained. The instantaneous

$$(k - k_p)/(k_T - k_p) = F \quad (4)$$

rate constants k at any time as well as k_p and k_T are available as previously described, and thus the value of F can also be obtained for any time, t.

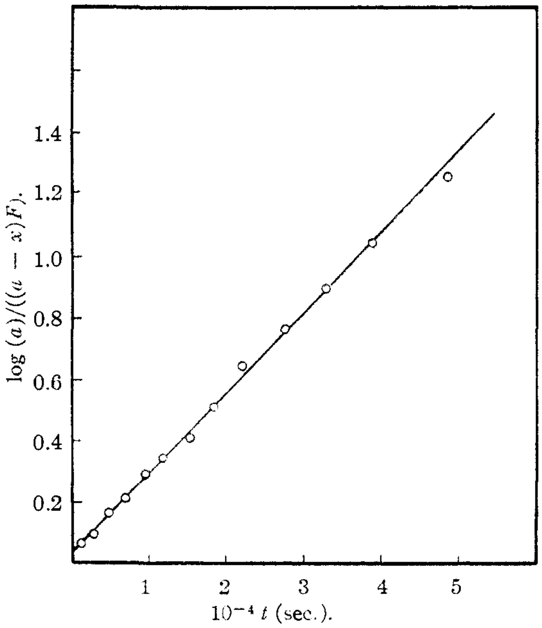

Fig. 1.

The concentration of tertiary chloride $(a - x)F$, should, according to the formulated scheme, fall off in a first order manner, with a rate constant equal to $(k_T + k_i)$ as expressed in equation (5).

$$-d[(a - x)F]/dt = (k_T + k_i)(a - x)F \quad (5)$$

Integration of equation (5), recalling that when $t = 0$, $(R_TCl) = a$, gives equation (6), which makes it possible to evaluate the sum $(k_T + k_i)$ as the slope of the plot of $\ln a/(a - x)F)$ against time. Thus, since k_T is known, k_i can be determined.

$$\ln a/(a - x)F = (k_T + k_i)t \quad (6)$$

The specific first order rate of isomerization, k_i, has been evaluated for several runs by use of the relationship shown in equation (6). Figure 1 is a typical graph obtained by the described procedure. An indication of how well the data were fitted by a straight line is obtainable from Table IV which summarizes the probable error r[7] of the dependent variable $\log (a)/((a - x)F)$ as well as the probable error p[8] of the slope. The probable error of the slope averages slightly less than 1% of the slope. The probable error for a single value of $\log (a)/((a - x)F)$ is of the order of ±0.019 which is less than 2% of the total range of 1.20. The magnitude of these errors indicates a satisfactory fit, especially considering that the data being plotted are already derived from a previous plot.

TABLE IV

PROBABLE ERRORS OF THE FITS OF EXPERIMENTAL DATA TO EQUATION (6)

Run	Slope	p	r^a
11	0.217	0.003	0.028
12	.226	.001	.022
13	.224	.004	.018
14	.214	.001	.021
15	.258	.001	.013
16	.247	.004	.012
	Mean	0.002	0.019

[a] The total range of the dependent variable $\log (a)/((a - x)F)$ was of the order of 1.20.

As Fig. 1 indicates, the least squares line does not intersect the origin as the equation predicts.

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[6] Hughes, *Trans. Faraday Soc.*, **37**, 601 (1941).

[7] Crumpler and Yoe, "Chemical Computation and Errors," John Wiley and Sons, Inc., New York, N. Y., 1940, p. 222.

[8] Margenau and Murphy, "Mathematics of Physics and Chemistry," D. Van Nostrand Co., Inc., New York, N. Y., 1943, p. 502.

The other plots were similar in this respect, all showing a positive intercept greater than the probable error of the intercept. This phenomenon may be due to unavoidable errors in the making and reading of the plots leading to this final fit. It is difficult to estimate the effect of original experimental errors in this treatment, and the procedure of measuring the slope of the x,t plot at 0 time to obtain k_T leaves much to be desired in the way of accuracy. An error in k_T would be reflected in the F value which could be responsible for the positive intercept.

Table V summarizes the various kinetic runs on the tertiary chloride and lists the derived specific rate constants for solvolysis and rearrangement. Here again only very small ionic strength effects were noticed for k_p. The values of k_T also appear to be quite unaffected by changes in ionic strength; however, these values are not accurate enough to detect small effects. The values of k_i appear to increase somewhat with ionic strength. By increasing chloride ion at constant ionic strength (Run 14) all of the constants are seen to be independent of initial chloride ion concentration.

TABLE V

THE SOLVOLYSIS AND REARRANGEMENT OF α,α-DIMETHYLALLYL CHLORIDE IN AcOH AT 24.96 ± 0.01°

Run	(RX) 10^2 M	(KOAc) 10^2 M	(LiOAc) 10^2 M	(KCl) 10^2 M	$10^6k_{T_1}$ (sec.$^{-1}$)	10^6k_i (sec.$^{-1}$)	10^6k_p[a] (sec.$^{-1}$)
11	2.05	4.822			16	35	2.07
12	1.60	4.822			15	37	2.01
13	4.12	4.822			16	36	2.19
14	3.13	3.599		1.202	16	34	2.20
15	9.65		9.569		14	45	2.18
16	4.65		9.569		15	42	2.15

[a] This value is the mean of the value obtained from the integrated equation for a first order reaction after the rearrangement is complete.

The effect of initially added chloride ion is scrutinized further in Table VI, which compares the rates of the solvolysis reaction without added chloride ion with the run containing 0.012 N initial chloride ion and a run containing 0.024 N initial chloride ion. The experimental analyses in the latter run were too inaccurate due to the chloride ion to permit good evaluation of rate constants; however, semi-quantitative comparison of per cent. reaction at certain time intervals is possible. It is quite clear that the results are quite insensitive to initially added chloride ion and, thus, there is no serious disturbance from either bimolecular isomerization of tertiary chloride or reaction of a carbonium ion with external chloride ion.

TABLE VI

COMPARISON OF RATE OF SOLVOLYSIS OF α,α-DIMETHYLALLYL CHLORIDE WITH AND WITHOUT ADDED CHLORIDE ION IN HOAc AT 25°; $\mu = 0.048$

Time 10^{-4} sec.	% reaction[a] KOAc = 0.048 M RX = 0.03 M	% reaction[b] KCl = 0.012 M KOAc = 0.036 M RX = 0.0313 M	% reaction[b] KCl = 0.0241 M KOAc = 0.024 M RX = 0.0226 M
0.40	5.0	5.0	5.0
0.90	10.0	10.0	10.0
1.60	15.0	15.0	14.0
2.55	20.0	20.0	19.0
3.90	25.0	25.0	24.0
9.00	35.0	35.0	34.0
16.20	45.0	45.0	45.0

[a] These % solvolysis values obtained from the best fit of the data from three independent runs. [b] These % solvolysis values obtained from a plot of % reaction *vs.* time for the indicated conditions.

From equations (3), (6) and equation (7), which represents the net change in the concentration of the primary chloride

$$\frac{\mathrm{d}[(a-x)(1-F)]}{\mathrm{d}t} = k_i(a-x)F - k_p(a-x)(1-F) \quad (7)$$

the relationship shown in equation (8) can be derived.[9] This equation expresses

$$(a-x) = \frac{a}{k_p - k_T - k_i}\left[(k_p - k_T)\mathrm{e}^{-(k_T + k_i)t} - k_i e^{-k_pt}\right] \quad (8)$$

the total halide concentration $(a - x)$ as a function of time throughout the entire solvolysis and rearrangement of the tertiary chloride. After evaluating the required constants by the method described, it is possible to substitute in equation (8) and to compare the derived values of $(a - x)$ with the experimental ones. In Table VII the values of $(a - x)$ as determined by experimental analysis are compared for a run with the value calculated by equation (8). The satisfactory comparison of these results over the entire range of 55% reaction, which is over five half-periods for the rearrangement, indicates again the satisfactory fit of the data by the scheme outlined.

TABLE VII

REACTION OF 0.096 N α,α-DIMETHYLALLYL CHLORIDE AT 25° IN HOAc, 0.096 N IN LITHIUM ACETATE. DATA FROM RUN 15 FITTED BY EQUATION (8)

Time 10^{-3} sec.	10^2 (RX) obsd.[a]	10^2 (RX) calcd.[b]
0	9.653	9.653
1.14	9.497	9.50
2.64	9.345	9.33
3.36	9.281	9.25
6.12	8.973	8.94
11.04	8.554	8.51
18.66	8.112	8.01
29.16	7.592	7.50
44.46[c]	7.195	7.03
86.10	6.361	6.27
97.26	6.221	6.12
114.00	5.956	5.88
170.76	5.255	5.16
189.42	5.056	4.95
201.30	4.875	4.83
261.18	4.306	4.21

[a] These values obtained by analysis during run 15. [b] This value obtained from equation (8) using the specific rate constants listed in Table V, run 15. [c] At this time rearrangement is *ca.* 90% complete.

It is clear that the isomerization of tertiary chloride I to primary chloride II in acetic acid under the conditions employed is intramolecular in the sense that external chloride ion is not involved. The isomerization is in an over-all sense an example of the intramolecular process visualized

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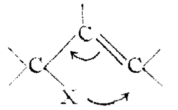
(9) **We are indebted to Dr. Ernest Grunwald for the derivation of this equation.**



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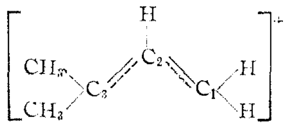

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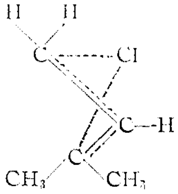
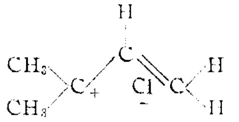
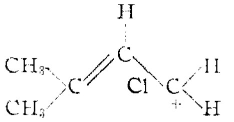


V

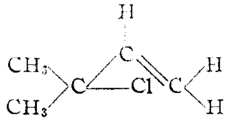
by Hughes[10] and illustrated by formula III. In considering the exact path followed by the migrating chloride ion in the isomerization, it is useful to consider the structure of a pentenyl carbonium ion and its interaction with a chloride ion in a position roughly at the half-way point in the isomerization. The planar pentenyl carbonium ion IV with sp^2 hybridization at carbon atoms C_1, C_2 and C_3 has a p orbital on each of the carbon atoms C_1, C_2 and C_3 with the axis perpendicular to the plane. Two electrons constitute the split double bond indicated by the dotted lines and the species is still electron-deficient, C_1 and C_3 sharing a positive charge. When a nucleophilic chloride ion is placed on IV in a central position, it seems best to place it above the plane of IV so as to produce V. In V an atomic orbital of chlorine overlaps the p orbitals on C_1 and C_3. Undoubtedly, some rehybridization of the orbitals on C_1 and C_3 will give further stabilization. On this basis V can be described by contributing structures VI, VII, VIII and IX. The structure V corresponds to a special type of 4-ring. The relative contributions of VIII and IX relative to those of VI and VII are difficult to assess. The smaller they are, the more nearly V represents an ion-pair.



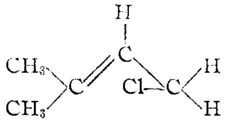
VI



VII

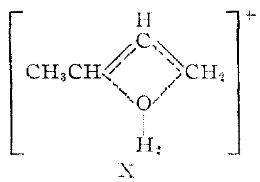


VIII



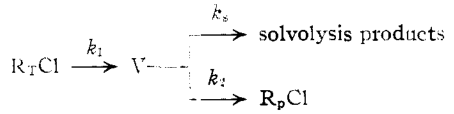
IX

Intramolecular allylic isomerizations have been sometimes considered in other connections such as acid-catalyzed alcohol isomerizations[11,12] (see X), and we have now added the case of chloride isomerization.



X

The species V which could serve as a transition state for the intramolecular isomerization may actually represent an intermediate of appreciable life. In fact, there is some indication, although much more work is required in this direction, that a common intermediate V occurs for both solvolysis and isomerization of the tertiary chloride. This type of formulation would be consistent with the observed kinetics, according to the scheme



$$R_TCl \xrightarrow{k_1} V \begin{cases} \xrightarrow{k_s} \text{solvolysis products} \\ \xrightarrow{k_2} R_PCl \end{cases}$$

k_T and k_i, previously evaluated, being given by equations (9) and (10).

$$k_T = k_1 \frac{k_s}{k_2 + k_s} \qquad (9)$$

$$k_i = k_1 \frac{k_2}{k_2 + k_s} \qquad (10)$$

The indication that the latter formulation applies here stems from the fact, reported elsewhere, that in alcoholysis the tertiary chloride gives no indication of concurrent isomerization. Also, the alcoholysis rate is nearly identical with the acetolysis rate instead of being somewhat smaller.[4] These facts could be understood on the basis that k_s is much larger than k_2 in the nucleophilic solvent ethanol, where k_T becomes equal to k_1, instead of a fraction of k_1 as would be supposed it represents in acetic acid.

The intermediate V recalls the intermediate X originally suggested by Young, Nozaki and Warner[11] in connection with acid-catalyzed isomerization of the butenyl alcohols, and we have gone further in the discussion of the structure of such possible intermediates than was possible earlier.

The implications of the possible occurrence of intermediate V in solvolysis–rearrangement are important and the phenomenon is being further investigated. Further, it suggests a kind of return (of which there may be many examples) of a more or less completely ionized intermediate back to a halide or similar species. We term this "internal return," distinct from the "mass law" effect[6] or "external return."

Experimental

Materials.—The pentenyl chlorides were prepared by the addition of hydrogen chloride to isoprene according to the method of Ultee.[13] The isomers were separated by fractionation through a five-foot glass helices packed column, at reduced pressure. The primary isomer, γ,γ-dimethylallyl chloride, had $n^{20}D$ 1.4495, b.p. 67.2° (165 mm.). The tertiary halide, α,α-dimethylallyl chloride had $n^{20}D$ 1.4188, b.p. 41° (200 mm.). These physical properties are in agreement with previously reported values.[13] The purity of the individual halides is further substantiated by rate measurements, reported elsewhere, which would detect the presence of the allylic isomer.

Anhydrous acetic acid was prepared by overnight refluxing of the calculated amount of Baker and Adamson reagent grade acetic anhydride and Baker and Adamson reagent grade 99.5% glacial acetic acid. The solvent was shown to be anhydrous by a Karl Fischer titration.

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[10] Hughes, *Trans. Faraday Soc.*, **34**, 185 (1938).

[11] Young, Nozaki and Warner, This Journal, **61**, 2564 (1939).

[12] Braude and Jones, *J. Chem. Soc.*, 436 (1944).

[13] (a) Ultee, *ibid.*, 531 (1948); (b) Young and Webb, unpublished work; (c) *C. A.*, **43**, 111*h* (1949); (d) *C. A.*, **43**, 114 (1949).

In order to prepare a solution of potassium acetate in glacial acetic acid, Baker and Adamson reagent grade potassium acetate was dried at 130° *in vacuo* to constant weight, and dissolved in the desired amount of anhydrous acetic acid. Solutions of other added salts, such as lithium chloride or potassium chloride, in glacial acetic acid were prepared in a similar manner.

Anhydrous solutions of *p*-toluenesulfonic acid in acetic acid were prepared by adding the calculated amount of acetic anhydride to a solution of Eastman Kodak Co. white label *p*-toluenesulfonic acid monohydrate in glacial acetic acid.

The solvent containing lithium acetate was prepared by dissolving Baker and Adamson reagent grade lithium carbonate in glacial acetic acid and refluxing the resulting solution with the calculated amount of acetic anhydride.

The solvent containing potassium acetate and potassium tosylate was prepared by mixing the proper amounts of toluenesulfonic acid in acetic acid and potassium acetate in acetic acid.

Titrations.—Analyses were performed by titrating the remaining acetate ion in an aliquot of reaction mixture, with standard *p*-toluenesulfonic acid in glacial acetic acid. A slight excess of toluenesulfonic acid was added and the excess was back titrated with a standard solution of sodium acetate in glacial acetic acid. All concentrations of acetic acid solutions were related to the sodium acetate in glacial acetic acid which was used as the primary standard.[14]

The concentration of the solution of toluenesulfonic acid in acetic acid was arranged so that the maximum amount of solution required throughout a kinetic run would not exceed the 5 ml. capacity of the microburet. Frequent comparison of standard solutions showed them to be quite stable over a period of three months.

Brom phenol blue was found to be a suitable indicator for the required titrations.[4] When the chloride ion concentration of the solution being titrated was greater than 0.025 *N*, the following procedure was followed due to the buffering effect of the chloride ion. For each titration solutions were prepared having the same ionic strength and chloride ion concentration as that of the sample being titrated at the equivalence point. Lithium perchlorate and lithium chloride were used to prepare these solutions. By matching the indicator color in the sample being titrated with the indicator color in the prepared "blank" solution, the equivalence point could be established quite accurately in solutions containing chloride ion up to 1 *N*. The precision decreased as chloride ion increased due to the increased buffer capacity of the solution.

This procedure was used for the dual purpose of eliminating ionic strength effects on the indicator color and correcting for the change in acetate ion concentration at the equivalence point with change in chloride ion concentration.

A measure of the accuracy of the titrations can be obtained from the results summarized in Table II. In ten independent kinetic runs, some of which contained as much as 0.05 *N* chloride ion at the start, the mean deviation averaged about 1.3%.

Rate Measurements.—The concentration of acetate ion in the solvent was determined just before starting a run by titration with standard toluenesulfonic acid in glacial acetic acid. The concentration of other added salts was determined from the weight of the salt (previously dried to constant weight) added. In the case of the hygroscopic lithium chloride the concentration was more conveniently obtained by Volhard titration for chloride ion. Concentrations are all given at 25°. All of the rate work reported is for 24.96 ± 0.01°. Reaction solutions were made up by adding the pure halides, from a pipet, to the thermostated solvent in a normax volumetric flask. The solution was rapidly made up to the mark with thermostated solvent and thoroughly mixed.

For runs involving α,α-dimethylallyl chloride, 5-ml. aliquots were withdrawn from the volumetric flask and analyzed. Time was counted from time of mixing till time of completion of the titration. The total titration required about 20 seconds. During the initial stages of the reaction analyses were made quite frequently (*ca.* every 30 minutes). As the reaction progressed the time interval between analyses was increased. Table III shows the time intervals used throughout a typical run. After four or five hours the reaction had slowed down to where it was advisable to seal the remaining reaction mixture in ampules of *ca.* 6-ml. capacity. This transfer was made as rapidly as possible so as not to disturb the rate. At appropriate time intervals ampules were opened and aliquots analyzed.

Throughout the course of a run about sixteen analyses were made. Due to the kinetic behavior and the data desired, the analyses were concentrated on the first part of the reaction, most points being taken before the rearrangement was complete (30% reaction). The reactions were followed to about 60% completion. Throughout the kinetic work the temperature of the room was held as constant as possible so as not to affect the concentrations of the standard solutions. The initial concentration was obtained from Volhard chloride ion determination and from the infinity titer, the Volhard method giving results of high precision. These independent methods agreed as well as could be expected considering the difficulties of obtaining the titer of the highly buffered solution resulting from complete reaction.

For runs on γ,γ-dimethylallyl chloride the reaction mixture was sealed in ampules. Time was counted from time of mixing in some runs and from a later point in other runs. The described techniques were used to follow the reaction.

Conversion of α,α-Dimethylallyl Chloride to γ,γ-Dimethylallyl Chloride in Glacial Acetic Acid.—The specific rate of isomerization of 4.5×10^{-5} sec.$^{-1}$ represents a half life of about 4.25 hr. Thus 25 hr. corresponds to 6^+ half-periods for rearrangement. During this time it is shown by the kinetic data (such as that appearing in Table III) that *ca.* 35% of the total halide will be solvolyzed.

A solution of 26.15 g. (0.25 mole) of α,α-dimethylallyl chloride in 220 ml. of glacial acetic acid containing 0.010 mole of lithium acetate was placed in a 25° thermostat. A small amount of brom phenol blue indicator was added so that it could be shown that excess acetate ion was always present throughout the run. As the reaction progressed, a solution of 0.090 mole of lithium acetate in 100 ml. of glacial acetic acid was added from a buret. From the kinetic data it was possible to determine the proper rate of addition of the lithium acetate solution so that acetate ion was always present; however, large concentrations of acetate ion were avoided. After a total time of 24 hr. the solution was poured into 150 ml. of chilled low boiling petroleum ether. The solution was shaken with one 150-ml. portion of ice-water. After separation of the layers the organic layer was washed with three 25-ml. portions of ice-cold 10% aqueous sodium carbonate. The organic layer was dried over potassium carbonate and fractionated. The fractionation yielded less than 0.25 g. of the starting α,α-dimethylallyl chloride and 8.5 g. of the primary isomer, γ,γ-dimethylallyl chloride.

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[14] Winstein, Hanson and Grunwald, THIS JOURNAL, **70**, 812 (1948).