layer was separated, dried and the solvent distilled to leave 33.2 g. of material melting over the range 95–110°. This product was recrystallized from petroleum ether to yield 24.11 g. (76%) of triphenylchloromethylgermane, m.p. 116–118°. An analytical sample melted at 117.5–118.5°.

Anal. Calcd. for $C_{19}H_{17}GeCl$: Ge, 20.54. Found: Ge, 19.88, 19.67.

Although the germanium analysis is slightly low, it is believed the product is actually triphenylchloromethylgermane; reaction with magnesium followed by hydrolysis gave a 67% yield of triphenylmethylgermane. An attempt, however, to repeat this preparation of triphenylgermylmethylmagnesium chloride failed, as did subsequent attempts to react triphenylchloromethylgermane with lithium in ether and sodium iodide in acetone. The phenyl groups may have a deactivating influence on the carbon–chlorine bond, because Seyferth and Rochow[17] reported no difficulty in preparing trimethylgermylmethylmagnesium chloride.

Triphenylallylgermane.—To 100 ml. of an ether suspension of 51.9 g. (0.147 mole) of triphenylchlorogermane was added 0.212 mole of allylmagnesium bromide[18] in 200 ml. of ether over a period of 1.5 hr. The mixture was stirred

(17) D. Seyferth and E. G. Rochow, *J. Org. Chem.*, **20**, 250 (1955).
(18) Prepared according to the directions of H. Gilman and J. H. McGlumphy, *Bull. soc. chim.*, **43**, 1322 (1928).

overnight at room temperature, then the ether was removed by distillation and the residue heated at 100° for 48 hr. The ether was re-added and 100 ml. of 6 N hydrochloric acid was added dropwise while the flask was cooled in an ice-bath. After stirring 2 hr. the mixture was filtered to give 1.6 g. of material melting over the range 210–230°. This material was not further identified. The ether layer was separated, washed with water and dried over anhydrous sodium sulfate. The solvent was then removed by distillation and the residue distilled over the range 194–200° (2.0 mm.) to give 44.3 g. of impure product melting over the range 77–90°. This material was crystallized twice from ethanol to yield 30 g. (59%) of triphenylallylgermane, m.p. 90–91.5°. An analytical sample melted at 90–91°.

Anal. Calcd. for $C_{21}H_{20}Ge$: Ge, 21.05. Found: Ge, 21.24, 21.19.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF TEXAS]

Allylic Chlorides. XXIII. The 1-Chloro-2-methyl-2-butenes

BY LEWIS F. HATCH AND PAUL R. NOYES

cis- and *trans*-1-chloro-2-methyl-2-butene have been prepared and their infrared spectra and physical properties obtained. Their relative reactivities with sodium ethoxide in ethanol and potassium iodide in acetone were determined. The relative reactivity of these two isomers with iodide ion is compared with the similar activity of *o*- and *p*-methylbenzyl chloride. The similarity between the allyl chloride system and the benzyl chloride system is discussed.

A number of methyl substituted allyl chlorides have been reported previously from this Laboratory: allyl chloride, methallyl chloride,[1,2] *cis*- and *trans*-crotyl chloride,[3] 1-chloro-3-methyl-2-butene[4] and 1-chloro-2,3-dimethyl-2-butene.[5] Both isomers of 1-chloro-2-methyl-2-butene have now been synthesized and their relative reactivities have been determined with sodium ethoxide in ethanol and potassium iodide in acetone. These two isomers complete the series of allylic chlorides with methyl substitution around the carbon–carbon double bond.

1-Chloro-2-methyl-2-butene was first prepared in 1926 by Seyer and Chalmers[6] and since that time by several others using various methods of synthesis.[7-9] In all of these preparations no mention was made of geometrical configuration, but apparently the *cis* isomer was formed. Tamale and co-workers[10] prepared 1-chloro-2-methyl-2-butene

from the corresponding alcohol by use of phosphorus trichloride, but the configuration of the alcohol was not reported. The relative reactivity (9.18) of their material with iodide ion indicates that it contained about 10% of the *trans* isomer (Table I).

TABLE I

THE RELATIVE REACTIVITY OF VARIOUS METHYL SUBSTITUTED ALLYLIC CHLORIDES WITH POTASSIUM IODIDE AND WITH SODIUM ETHOXIDE,

$$\underset{R'}{\overset{R}{>}}C=C\underset{CH_2Cl}{\overset{R''}{<}}$$

R	Compound R'	R″	Iodide ion	Ethoxide ion
H	H	H	1.00^a	1.00^b
CH_3	H	H	1.56^c	4.43^c
H	H	CH_3	1.58^a	1.03^b
CH_3	H	CH_3	5.27^d	3.94^d
H	CH_3	H	8.35^c	5.14^c
CH_3	CH_3	H	28.1^e	
H	CH_3	CH_3	41.8^d	4.36^d
CH_3	CH_3	CH_3	150^f	

[a] L. F. Hatch, L. B. Gordon and J. J. Russ, THIS JOURNAL, **70**, 1093 (1948). [b] L. F. Hatch and H. E. Alexander, *ibid.*, **71**, 1037 (1949). [c] L. F. Hatch and S. S. Nesbitt, *ibid.*, **73**, 358 (1951). [d] M. Tamale, C. J. Ott, K. E. Marple and G. W. Hearne, *Ind. Eng. Chem.*, **33**, 115 (1941), report a value of 9.18 for 1-chloro-2-methyl-2-butene. [e] L. F. Hatch and L. S. Gerhardt, THIS JOURNAL, **71**, 1697 (1949). [f] L. F. Hatch and G. E. Journeay, *ibid.*, **75**, 3712 (1953).

(1) L. F. Hatch, L. B. Gordon and J. J. Russ, THIS JOURNAL, **70**, 1093 (1948).
(2) L. F. Hatch and H. E. Alexander, *ibid.*, **71**, 1037 (1949).
(3) L. F. Hatch and S. S. Nesbitt, *ibid.*, **73**, 358 (1951).
(4) L. F. Hatch and L. S. Gerhardt, *ibid.*, **71**, 1679 (1949).
(5) L. F. Hatch and G. E. Journeay, *ibid.*, **75**, 3712 (1953).
(6) W. F. Seyer and W. Chalmers, *Trans. Roy. Soc. Can.*, [3] **20**, III, 337 (1926).
(7) W. Chalmers, *ibid.*, [3] **22**, III, 69 (1928).
(8) D. V. Tishchenko, *J. Gen. Chem. (U.S.S.R.)*, **6**, 1116 (1936).
(9) J. Burgin, W. Engs, H. P. A. Groll and G. W. Hearne, *Ind. Eng. Chem.*, **31**, 1416 (1939).
(10) M. Tamale, C. J. Ott, K. E. Marple and G. W. Hearne, *ibid.*, **33**, 115 (1941).

cis-1-Chloro-2-methyl-2-butene now has been prepared by the reaction between *cis*-2-methyl-2-butene-1-ol and phosphorus trichloride in pyridine. The alcohol was obtained by lithium aluminum hydride reduction of tiglic acid (*cis*-2-methyl-2-butenoic acid). This acid was synthesized from methyl ethyl ketone and hydrogen cyanide by the method of Buckles and Mock.[11]

trans-1-Chloro-2-methyl-2-butene was prepared in a manner analogous to that used for the *cis* isomer. The angelic acid (*trans*-2-methyl-2-butenoic acid) was prepared from tiglic acid.[11] Bromination of tiglic acid gave α,β-dibromo-α-methylbutyric acid which on dehydrobromination with alcoholic potassium hydroxide formed β-bromoangelic acid (*trans*-2-bromo-2-methyl-2-butenoic acid). This bromo acid was converted to angelic acid by treatment with aqueous sodium amalgam.

The allylic chlorides were isolated and purified by low temperature distillation. Low temperatures also were used during handling and storage to minimize allylic rearrangement.[5,12] The chlorides were characterized by their method of preparation and by their infrared spectra. Both isomers showed an absorption at 7.94 μ which is characteristic of a β-substituted allylic chloride.[13] Infrared spectra were also obtained for all of the intermediates.

The relative reactivities of both *cis*- and *trans*-1-chloro-2-methyl-2-butene were determined in the reactions with potassium iodide in acetone at 20° and with sodium ethoxide in ethanol at 50° (Table I).

The results obtained with ethoxide ion were predictable from previous work. Both isomers were approximately four times as reactive as allyl chloride (and methallyl chloride). The introduction of a β-methyl group into the crotyl chlorides apparently decreases the reactivity slightly. Geometrical configuration has a definite but minor influence on the rate of reaction.

The β-methyl group and geometrical configuration both play an important role in determining the reactivity of the 1-chloro-2-methyl-2-butenes with iodide ion. The influence of a β-methyl group is appreciably greater when there is a γ-methyl group in the molecule, especially when the γ-group is *cis* to the chloro-methyl group (Table I). *cis*-1-Chloro-2-methyl-2-butene is approximately 3.4 times as reactive as the corresponding crotyl chloride (*trans*-crotyl chloride) while *trans*-1-chloro-2-methyl-2-butene is 5 times as reactive as *cis*-crotyl chloride. There is also a 5-fold increase in reactivity between 1-chloro-3-methyl-2-butene and 1-chloro-2,3-dimethyl-2-butene (Table I). Both of these pairs of compounds have a γ-methyl group *cis* to the chloromethyl group. Methallyl chloride is only 1.6 times as reactive as allyl chloride.

Interesting comparisons can be made between the 1-chloro-2-methyl-2-butenes and *o*- and *p*-substituted benzyl chlorides[14] with respect to the influence of the configuration of the molecule on its SN2 reactivity with iodide ion.

(11) R. E. Buckles and G. V. Mock, *J. Org. Chem.*, **15**, 680 (1950).
(12) W. G. Young and J. T. Lane, THIS JOURNAL, **59**, 2051 (1937).
(13) R. E. Kitson, *Anal. Chem.*, **25**, 1470 (1953).
(14) J. C. Charlton and E. D. Hughes, *J. Chem. Soc.*, 855 (1956).

Rel. react.   2.5   3.8   28

Rel. react.   1.00   5.3   42
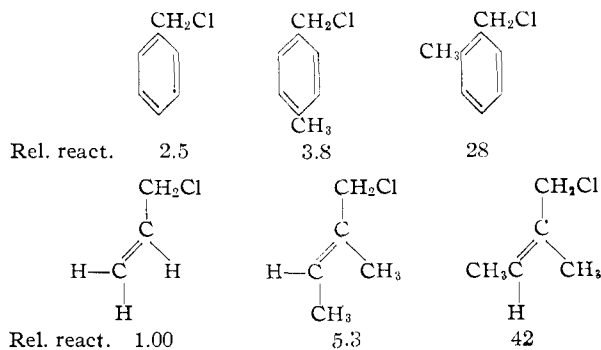
p-Methylbenzyl chloride and *cis*-1-chloro-2-methyl-2-butene have similar structures with respect to the methyl and chloromethyl groups and their reactivities are in the same order of magnitude. Of possibly more significance is the fact that *o*-methylbenzyl chloride is 7.4 times more reactive than the *para* isomer and *cis*-1-chloro-2-methyl-2-butene is 7.9 times more reactive than its *trans* isomer.

The resonance contribution should be the same in both pairs of isomers. The inductive effect will be different between *o*- and *p*-methylbenzyl chloride but probably not sufficiently different to account for the large difference in reactivity. There should be very little difference in inductive effects between the allylic isomers. The increased reactivity of the *ortho* and *cis* isomers, therefore, must be related to the geometry of the molecule. This has been considered by Charlton and Hughes[14] for *o*- and *p*-methylbenzyl chloride. They state that the kinetic effect of the *o*-methyl group could not possibly be steric. They assume the presence of some kind of direct polar effect of the *o*-methyl group, possibly derived from the electrostatic attraction between methyl hydrogen atoms and the semi-polar halogen atoms in the transition state. This same proposal should apply equally well to the effect of the *cis*-methyl group of γ-methyl allylic chlorides.

If the *ortho* effect and the *cis* effect are the result of methyl hydrogen atoms, then *o*- and *p*-chlorobenzyl chloride[15] and the 1,3-dichloro-2-methylpropane[1] should not show these effects.

Rel. reactivity   7.0   9.1

Rel. reactivity   8.6   33
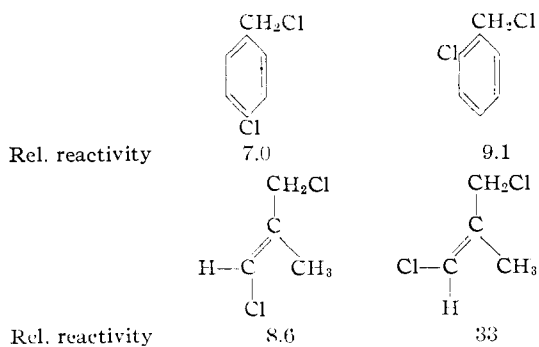
A chlorine atom in going from the *p*-position to the *o*-position of benzyl chloride causes a 1.4 increase in reactivity. A corresponding change of a methyl group causes a 7.4 increase. A simple interpretation of these data is to ascribe the small

(15) G. M. Bennett and B. Jones, *ibid.*, 1815 (1935).

ortho effect of the chlorine atom to the increased inductive effect of the *o*-position over the *p*-position and to assume that these observations substantiate the proposal[14] that the large *ortho* effect of the methyl group is not related to inductive factors and probably not to steric effects. This is an over simplification, however, for the methyl group is electron donating while the chlorine atom is electron attracting and the nature of the transition state for *o*-methyl- and *o*-chlorobenzyl chlorides may be different.

The corresponding chlorine atom shift from *trans*-1,3-dichloro-2-methylpropene to the *cis* isomer increases the reactivity by a factor of 3.6. It is not clear why a chlorine atom in the *cis* position should be relatively more activating than one in the *o*-position. A chlorine atom in the *p*-position of benzyl chloride increases the rate of reaction by a factor of 1.8 over *p*-methylbenzyl chloride while in the *trans*-allylic system the increase is 1.6. This is an illustration of the similarity between the effect of a *p*-substituent on benzyl chloride and a *trans*-γ-substituent on allyl chloride.

These relationships indicate that substituted benzyl chlorides and allylic chlorides are similar for steric, inductive and resonance effects, and generalizations obtained in one series may be related to the other series. They also indicate that any study made with *cis–trans*-allylic chlorides must take into account the configuration of the molecules. The radioactive chloride ion exchange reaction of England and Hughes noted by Vernon[16] is an example.

Acknowledgment.—The authors are grateful for the financial assistance given to this work by the Research Corporation. The authors also wish to thank the Monsanto Chemical Co. for the use of their infrared equipment and Dr. R. E. Kitson, Textile Fibers Department, E. I. du Pont de Nemours and Co., Inc., Kinston, N. C., for helpful suggestions to the interpretation of the infrared spectra.

Experimental

cis-1-Chloro-2-methyl-2-butene. *cis*-2-Methyl-2-buten-1-ol.—Tiglic acid[11] (m.p. 62.5–63.5°, 0.50 mole) was reduced with lithium aluminum hydride (0.63 mole) in diethyl ether at 0° to *cis*-2-methyl-2-buten-1-ol. Redistillation of the alcohol resulted in a 70% yield (0.35 mole) of the *cis* isomer. *cis*-2-Methyl-2-buten-1-ol was also prepared in a 71% yield by the lithium aluminum hydride reduction of tiglaldehyde (b.p. 117°); b.p. 137–138°, n^{20}D 1.4422, n^{25}D 1.4402, n^{30}D 1.4382, d^{20}_4 0.8639, d^{25}_4 0.8600, d^{30}_4 0.8557; lit.[17] b.p. 138°, n^{21}D 1.4421, d^{21}_4 0.8668.

cis-1-Chloro-2-methyl-2-butene.—*cis*-2-Methyl-2-buten-1-ol (0.55 mole) was converted to the corresponding chloride by treatment with phosphorus trichloride (0.22 mole) in the presence of pyridine. A 50% yield (0.24 mole) of *cis*-1-chloro-2-methyl-2-butene was isolated by flash distillation. The product was purified by redistillation at 3° under 6 mm. pressure; b.p. 108.0–108.5°, n^{20}D 1.4480, n^{25}D 1.4454, n^{30}D 1.4428, d^{20}_4 0.9328, d^{25}_4 0.9276, d^{30}_4 0.9223; lit.[10,18] b.p. 110°, n^{20}D 1.4481, d^{20}_4 0.9327.

trans-1-Chloro-2-methyl-2-butene. *trans*-2-Methyl-2-buten-1-ol.—Angelic acid (m.p. 44.0–44.5°) was prepared in an 86% yield by the treatment of β-bromoangelic acid[11] with 9% sodium amalgam. The angelic acid (0.50 mole)

in diethyl ether was reduced with lithium aluminum hydride (0.63 mole) in diethyl ether at 0°. The reaction mixture was worked up in the usual manner and *trans*-2-methyl-2-buten-1-ol was isolated by distillation in a yield of 67% (0.33 mole), b.p. 136.0–136.5°, n^{20}D 1.4427, n^{25}D 1.4407, n^{30}D 1.4387, d^{20}_4 0.8658, d^{25}_4 0.8620, d^{30}_4 0.8578.

Anal.[19] Calcd. for $C_5H_{10}O$: C, 69.72; H, 11.71. Found: C, 69.80; H, 11.57.

trans-1-Chloro-2-methyl-2-butene.—*trans*-2-Methyl-2-buten-1-ol (0.38 mole) was converted to *trans*-1-chloro-2-methyl-2-butene by reaction with phosphorus trichloride (0.12 mole) in the presence of quinoline (0.85 mole). Less than the amount of chlorinating agent recommended by Juvala[20] was used. This was done because the boiling point of the phosphorus trichloride was lower than the boiling point of the organic chloride produced. This minimized the possibility of phosphorus trichloride being a contaminant of the product during the distillation. Quinoline was used in place of pyridine because of its higher boiling point. *trans*-1-Chloro-2-methyl-2-butene (0.16 mole) was isolated by flash distillation at 0° and 2 mm. pressure. A 43% yield was obtained. The allylic chloride was purified by redistillation at 6.5 mm.; b.p. 105–106°, n^{20}D 1.4450, n^{25}D 1.4424, n^{30}D 1.4398, d^{20}_4 0.9284, d^{25}_4 0.9232, d^{30}_4 0.9178.

Anal.[21] Calcd. for C_5H_9Cl: Cl, 33.9. Found: Cl, 33.8, 33.7.

TABLE II

RELATIVE REACTIVITIES OF *cis*- AND *trans*-1-CHLORO-2-METHYL-2-BUTENE

Reaction with potassium iodide in acetone at 20°

cis-1-Chloro-2-methyl-2-butene

Time, hr.	1.00	1.50		2.00	2.50	3.00
Reacted, %	39.4	55.2		64.2	68.4	74.9
k, hr.$^{-1}$ mole^{-1}	2.60	2.84		2.77	2.50	2.53
Average k		2.65 ± 0.12				
Rel. react.[a]		5.27				

trans-1-Chloro-2-methyl-2-butene

Time, hr.	0.17	0.25		0.33	0.42	0.50
Reacted, %	49.3	63.7		75.5	80.6	85.2
k, hr.$^{-1}$ mole^{-1}	20.5	20.8		22.1	20.9	20.5
Average k		21.0 ± 0.5				
		41.8				

Reaction with sodium ethoxide in ethanol at 50°

cis-1-Chloro-2-methyl-2-butene

Time, hr.	2.00	4.00		6.00	8.00	10.00
Reacted, %	34.1	49.6		58.9	66.5	71.0
k, hr.$^{-1}$ mole^{-1}	4.68	4.68		4.58	4.68	4.62
Average[b]		4.65 ± 0.04				
Rel. react.[b]		3.94				

trans-1-Chloro-2-methyl-2-butene

Time, hr.	4.00	5.00		6.00	7.00	8.00
Reacted, %	59.3	65.00		69.9	73.1	76.3
k, hr.$^{-1}$ mole^{-1}	5.14	5.16		5.16	5.13	5.18
Average k		5.15 ± 0.02				
Rel. react.[b]		4.36				

[a] Allyl chloride as 1.00 with k = 0.502. [b] Allyl chloride as 1.00 with k = 1.18.

3,5-Dinitrobenzoates of *cis*- and *trans*-2-Methyl-2-buten-1-ol.—The 3,5-dinitrobenzoates were prepared by a standard procedure using approximately 0.5 g. of 3,5-dinitroben-

(16) C. A. Vernon, *J. Chem. Soc.*, 4462 (1954).

(17) A. Lauchenauer and A. Schinz, *Helv. Chim. Acta*, **34**, 1514 (1952).

(18) The physical constants were reported for 1-chloro-2-methyl-2-butene with no reference to the geometrical configuration.

(19) Analysis by Dr. C. G. Skinner, The Clayton Biochemical Institute, The University of Texas, Austin, Texas.

(20) A. Juvala, *Ber.*, **63B**, 1989 (1930).

(21) E. Chablay, *Ann. Chim.*, **1**, 510 (1914).

zoyl chloride and 0.2 ml. of the alcohol.[22] The products were recrystallized three times from hot ethyl alcohol.

3,5-Dinitrobenzoate of *cis*-2-Methyl-2-buten-1-ol: m.p. 99.0–99.2° (cor.). *Anal.*[23] Calcd. for $C_{12}H_{12}N_2O_6$: N, 10.00. Found: N, 9.81.

3,5-Dinitrobenzoate of *trans*-2-Methyl-2-buten-1-ol: m.p. 106.5–107.0 (cor.). *Anal.*[23] Calcd. for $C_{12}H_{12}N_2O_6$: N, 10.00. Found: N, 9.88.

Reaction of the 1-Chloro-2-methyl-2-butenes with Potassium Iodide in Acetone at 20°.—The procedure used was the same as that described previously.[1] With the usual modified second-order rate equation, the plot of $\log 5 - Z/(5)(1 - Z)$ vs. time where Z is the fraction of potassium iodide having reacted in time t, gave a straight line between 14 and 74% reacted for *cis*-1-chloro-2-methyl-2-butene and between 4

(22) N. D. Cheronis and J. B. Entrikin, "Semimicro Qualitative Analysis," Thomas Y. Crowell Co., New York, N. Y., 1947, p. 221.

(23) Clark Microanalytical Laboratory, Urbana, Ill.

and 85% for the *trans* isomer. The data are presented in Table II.

Reaction of 1-Chloro-2-methyl-2-butenes with Sodium Ethoxide in Ethanol at 50°.—The procedure used was similar to that described previously.[2] However, the method of analysis of the unreacted sodium ethoxide was modified. The amount of excess base was determined by titrating with a standardized dilute solution of dry hydrogen chloride in ethanol. Phenolphthalein was used to determine the end-point of the titration. The sodium ethoxide solution was 0.0525 M for the reaction of *cis*-1-chloro-2-methyl-2-butene (0.0524 M) and 0.0647 M for the reaction with the *trans* isomer (0.0562 M). The data were calculated using the rate expression for a second-order reaction. A plot of $\log b(a - x)/a(b - x)$ vs. time gave a straight line for the *cis* isomer between 34 and 71% reacted and between 26 and 78% for the *trans* isomer. The data are given in Table II.

AUSTIN, TEXAS

Stereochemistry of Allylic Rearrangements. VIII. The Acid-catalyzed Rearrangement of *cis*- and *trans*-5-Methyl-2-cyclohexenol in Aqueous Acetone[1]

BY HARLAN L. GOERING AND ERNEST F. SILVERSMITH[2]

The isomeric 5-methyl-2-cyclohexenols (I and II) rearrange in 35% aqueous acetone at 30° in the presence of acid but not in the absence of acid. The rate of the acid-catalyzed rearrangement is proportional to the acid concentration over the range of concentrations investigated (to 0.1 M). Rates of loss of optical activity and geometric isomerization have been determined for both geometric isomers. At the same acid concentration, the pseudo first-order rate constant for the loss of optical activity (k_α) is larger than the pseudo first-order constant for isomerization (k_i) by factors of 8 and 16 for I and II, respectively. The greater rate of racemization than of isomerization for both isomers cannot be accounted for by the carbonium-ion mechanism in its simplest form, i.e., the mechanism involving dissociation of the conjugate acid of the allylic alcohol to water and the allylic cation followed by recombination. It appears that the 5-methyl-2-cyclohexenyl carbonium ion is involved as an intermediate in the isomerization. The excess racemization may be due to an SN2'-type reaction in which a water molecule attacks the γ-carbon atom of the conjugate acid of the allylic alcohol.
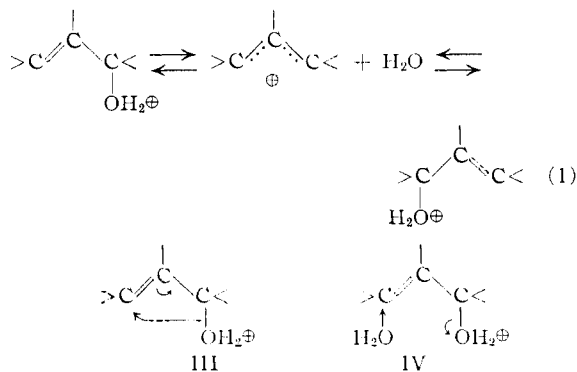
Introduction

The isomeric anionotropic rearrangement of the acid phthalates of *cis*-(I) and *trans*-5-methyl-2-cyclohexenol (II)[3] and the solvolysis of the acid phthalates,[4] *p*-nitrobenzoates[5] and corresponding chlorides[6] have been described in previous papers in this series. This paper describes a study of the acid-catalyzed isomeric rearrangement of I and II in aqueous acetone.

I   II
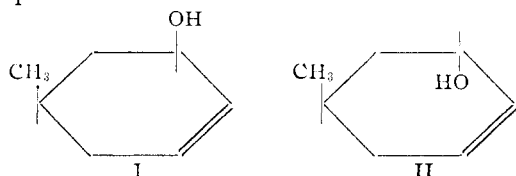
The kinetics of the acid-catalyzed rearrangement of allylic alcohols (the so-called oxotropic rearrangement)[7] have been investigated in several systems.[8] Braude and co-workers[8] have shown that the rate of rearrangement is proportional to the acid concentration—at high acid concentration

(1) This work was supported by the Office of Ordnance Research.

(2) National Science Foundation Fellow, 1954–1955.

(3) H. L. Goering, J. P. Blanchard and E. F. Silversmith, THIS JOURNAL, **76**, 5409 (1954).

(4) H. L. Goering and E. F. Silversmith, *ibid.*, **77**, 1129 (1955).

(5) H. L. Goering and E. F. Silversmith, *ibid.*, **77**, 6249 (1955).

(6) H. L. Goering, T. D. Nevitt and E. F. Silversmith, *ibid.*, **77**, 5026 (1955).

(7) E. A. Braude and E. R. H. Jones, *J. Chem. Soc.*, 436 (1944).

(8) (a) E. A. Braude, *Quart. Rev.*, **4**, 404 (1950); (b) *Ann. Rept. Chem. Soc.*, **47**, 114 (1949).

the rate is proportional to the acidity function (H_0)[9]—and have emphasized that the rearrangement involves a reversible protonation of the alcohol followed by rearrangement of the conjugate acid of the allylic alcohol. Several mechanisms have been suggested for the rearrangement including, (a) a dissociation–recombination carbonium-ion mechanism (eq. 1),[10] (b) an intramolecular process (summarized by III)[8,11] and (c) a SN2'-type process (summarized by IV).[8]

III   IV

(9) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 267.

(10) W. G. Young and J. F. Lane, THIS JOURNAL, **60**, 847 (1938); M. J. S. Dewar, "The Electronic Theory of Organic Chemistry," Oxford University Press, London, 1949, p. 88.

(11) W. G. Young, K. Nozaki and R. Warner, THIS JOURNAL, **61**, 2564 (1939).