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 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

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[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.

[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

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

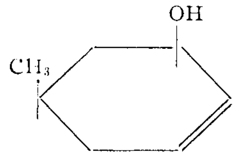
BY HARLAN L. GOERING AND ERNEST F. SILVERSMITH[2]

RECEIVED JULY 30, 1956

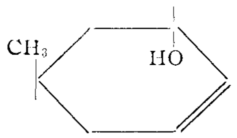
The isomeric 5-methyl-2-cyclohexenols (I and II) rearrange in 35% aqueous acetone at 30° in the presence of acid but not in the absence of acid. The rate of the acid-catalyzed rearrangement is proportional to the acid concentration over the range of concentrations investigated (to 0.1 M). Rates of loss 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 S_N2′-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.

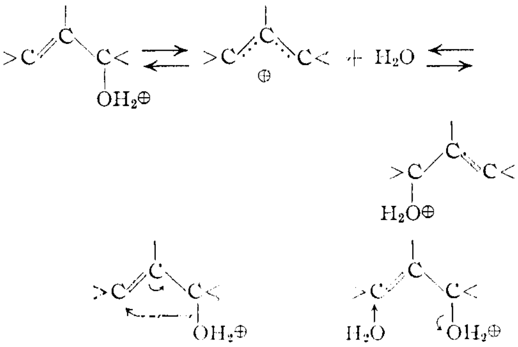


I



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 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 S_N2′-type process (summarized by IV).[8]



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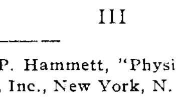
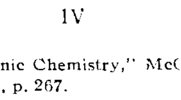


III



IV

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[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).

[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).

It is clear from earlier work, *viz.*, the kinetic studies of Braude,[8] that the conjugate acid of the allylic alcohol is the reactive species which rearranges. It appears that details of the mechanism(s) remain obscure. Braude[12] has claimed that the intramolecular (III) and intermolecular (IV) process have both been observed experimentally and has repeatedly emphasized[8,12,13] that the carbonium-ion mechanism (eq. 1) is unlikely. However, it appears that the arguments and evidence on which these inferences were based have not always been convincing. Evidently the report that the rearrangement in 80% aqueous ethanol does not give any of the ethyl ether of the rearranged carbinol[7] (which would probably rule out the carbonium-ion mechanism and point to the intramolecular process, III) is inconsistent with later observations[12,13a] that ethyl ethers are indeed formed in aqueous ethanol and in amounts that parallel the mole fraction of ethanol in the solvent. The observation that the apparent activation energies are relatively insensitive toward changes in the ionizing power of the solvent has also been taken as an indication that the rate-determining step does not involve dissociation of the conjugate acid of the alcohol to give the carbonium ion.[8b] However, it has been established[14] that reactions of the charge type involved in the carbonium-ion process (*i.e.*, $RX^{\oplus} \rightarrow R^{\oplus} + X$) are not very sensitive to changes in the ionizing power of the solvent.

It is noteworthy that it has been reported[13b] that *cis*- and *trans*-1,4-hexadien-3-ol rearrange in aqueous dioxane in the presence of acid to give *cis*- and *trans*-3,5-hexadien-2-ol, respectively. It appears that this observation is not readily accommodated by any of the suggested mechanisms for the rearrangement.

All things considered, it appears that the carbonium-ion process (eq. 1) and the S$_N$2′-type process (IV) are likely mechanisms for the rearrangement in aqueous solvents. Of these two the carbonium-ion mechanism appears to be the more likely (or more general) because of the numerous related reactions of allylic compounds which can be correlated by assuming that carbonium-ion intermediates are involved.[15] Or to put it another way, S$_N$1 reactions of allylic compounds are more general than S$_N$2′ reactions. It is of interest to note that the effect of structural changes on the rate of rearrangement of allylic alcohols[5] is that which would be predicted on the basis of a carbonium-ion mechanism. The observation[8] that the rate of rearrangement at high acid concentrations is apparently proportional to the acidity function rather than the acid concentration apparently favors the carbonium-ion mechanism rather than the S$_N$2′-type mechanism. Hammett[16] has pointed out that if a water molecule of the solvent is involved in the transition state of an acid-catalyzed solvolytic reaction (as is the case in IV but not in the carbonium-ion process) the rate should be proportional to the acid concentration: if a water molecule is not involved in the transition state, the rate should be proportional to the acidity function.

In the present work we have compared the rates of geometric isomerization and racemization of optically active I and II in order to obtain information concerning the mechanism of the isomeric rearrangement of the conjugate acid of allylic alcohols.

Results

The isomeric 5-methyl-2-cyclohexenols, I and II, rearrange in 35% aqueous acetone[17] at 30° in the presence of perchloric acid but not in the absence of acid. Rearrangement of optically active isomers results in the loss of optical activity and in geometric isomerization. The rate constants for loss of optical activity (k_α) at acid concentrations of 0.01 to 0.1 M and for isomerization (k_i) at an acid concentration of 0.1 M were determined. Both isomerization and loss of optical activity are first-order in acid and in alcohol. Since the acid concentration does not change during the reaction, isomerization is a reversible first-order process and loss of optical activity is an irreversible first-order process. The results of the pertinent kinetic experiments are shown in Tables I and II.

TABLE I

FIRST-ORDER RATE CONSTANTS FOR LOSS OF OPTICAL ACTIVITY OF 0.5 M I AND II IN 35% AQUEOUS ACETONE AT 30.12 ± 0.02°

Isomer	(HClO$_4$] 10^2M	[LiClO$_4$] 10^2M	Rotation Initial	Rotation Final	k_α, hr.$^{-1}$	k_α/[HClO$_4$]
I	9.64		0.76°	+0.09°	0.148 ± 0.004	1.5
II	9.64		−13.77		.370 ± .002	3.8
II	4.46	5.00	−14.07	−0.04	.170 ± .001	3.8
II	0.88	9.00	−14.10		.0350 ± .0001	4.0

TABLE II

FIRST-ORDER RATE CONSTANTS FOR ISOMERIZATION OF 0.5 M I AND II IN 35% AQUEOUS ACETONE AT 30.05 ± 0.02°

Isomer	$k_{i\ cis}$[a] hr.$^{-1}$	$k_{i\ trans}$,[a] hr.$^{-1}$	($k_{i\ cis} + k_{i\ trans}$) hr.$^{-1}$
		[HClO$_4$] = 0.0964 M	
I	0.024	(0.019)	0.043
I	.022	(.019)	.041
I	.019	(.025)	.044
I	.021	(.020)	.041
II	(.013)	.027	.040
II	(.016)	.024	.040
II	(.015)	.024	.039
II	(.015)	.024	.039
Av.	0.018 ± 0.004	0.023 ± 0.002	0.041 ± 0.001
		[HClO$_4$] = 0.2102	
II	(0.047)	0.063	0.110

[a] The values of $k_{i\ cis}$ or $k_{i\ trans}$ not enclosed in parentheses were obtained by extrapolation to zero-time. These values were subtracted from ($k_{i\ cis} + k_{i\ trans}$) to give the values shown in parentheses.

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(12) E. A. Braude, *J. Chem. Soc.*, 794 (1948).

(13) (a) E. A. Braude, E. R. H. Jones and E. S. Stern, *ibid.*, 396 (1946); (b) E. A. Braude and J. A. Coles, *ibid.*, 2085 (1951).

(14) See E. D. Hughes, *Trans. Faraday Soc.*, **37**, 601 (1941), for references.

(15) W. G. Young and R. H. DeWolfe, *Chem. Revs.*, **56**, 753 (1956).

(16) Reference 9, p. 273; see also C. A. Bunton, T. Hadwick, D. R. Llewellyn and Y. Pocker, *Chemistry and Industry*, 547 (1956), and references therein.

(17) The composition of the solvent is based on the volumes of the pure components (measured at 25°) before mixing.

The rate constants for the loss of optical activity, k_α, were determined from the rate of loss of optical activity of solutions of active I and II by use of the appropriate equation for a first-order reaction. These reactions were carried out in a thermostated all-glass polarimeter tube[6] and each value of k_α in Table I is the average (and mean deviation) of a large number of determinations during the reaction. In all cases the first-order constants (k_α) were steady throughout the reaction and the loss of optical activity was essentially complete. The last three experiments recorded in Table I show that at constant ionic strength k_α is proportional to the acid concentration. In the absence of acid $k_\alpha < 8 \times 10^{-5}$ hr.$^{-1}$ for II at 30° and thus it is clear that the acid-catalyzed process is cleanly isolated from an uncatalyzed process. Since the rearrangement involves the reversible formation of the conjugate acid of the alcohol followed by rearrangement,[8,11] the process responsible for the loss of optical activity can be summarized by equations 2 and 3 ($SH^\oplus$ represents lyonium ion). Thus k_α is a composite as illustrated by equation 4 in which k_α' is the first-order constant for the conversion of the conjugate acid of the alcohol to inactive products.

$$ROH + SH^\oplus \overset{K}{\rightleftharpoons} ROH_2^\oplus + S \qquad (2)$$

$$ROH_2^\oplus \xrightarrow{k_\alpha'} \text{inactive products} \qquad (3)$$

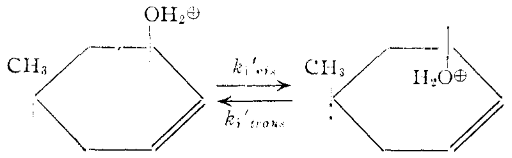
$$k_\alpha = Kk_\alpha' [SH^\oplus] \qquad (4)$$

As shown in Table I, small residual optical activities were observed. Evidently this is due to contamination of the samples of alcohol with 5-methyl-2-cyclohexenone. It previously has been shown that I and II are slowly oxidized to the unsaturated ketone on standing.[18] The residual activity and the absorption of reaction mixtures at 225 mμ[19] can be accounted for by 0.5% of the ketone in the alcohol. The signs of the residual activities are those that would be expected for the unsaturated ketone.[20]

The residual activity also could be due possibly to hydration of the double bond. It seems unlikely, however, that this would occur under the conditions of the kinetic experiments. In this connection it is noteworthy that the allylic alcohol was isolated in over 95% yield after about 10 half-periods for the loss of optical activity and the infrared spectra of the samples isolated in the isomerization experiments (in some cases after 150 half-lives) were composites of those for the pure isomers.

The rates of isomerization were measured by determining the configurational composition of the alcohol (infrared analysis) at appropriate intervals during the reaction. This reaction was found to be reversible as illustrated by equation 5.

Equations 6 and 7 relate the configurational composition of the alcohol, f (mole fraction of *cis* isomer), with the constants given in Table II.



(5)

$$-df/dt = k_{i\,cis}(f) - k_{i\,trans}(1 - f) \qquad (6)$$

$$-d(1 - f)/dt = k_{i\,trans}(1 - f) - k_{i\,cis}(f) \qquad (7)$$

During the early stages of the rearrangement of I and II the last terms in equations 6 and 7 are relatively unimportant. If these last terms are omitted integration gives equations 8 and 9, the equations that were used to determine $k_{i\,cis}$ and $k_{i\,trans}$.

$$k_{i\,cis} = (1/t) \ln f_0/f \qquad (8)$$

$$k_{i\,trans} = (1/t) \ln(1 - f)_0/(1 - f) \qquad (9)$$

The constants determined in this manner showed downward trends because of the reversible nature of the reactions. The values given in Table II were obtained by extrapolation to zero-time. Because of lack of precision in determining the configurational compositions, values of k_i for duplicate experiments showed some scatter as shown in Table II. However, there is convincing evidence that the values of k_i are fairly accurate. This is indicated by the fact that the equilibrium composition calculated from $k_{i\,cis}$ and $k_{i\,trans}$ agrees well with the experimentally observed value: 56% II as compared to 55% II (this value was determined by approaching equilibrium from both sides). There is additional evidence indicating that the values for k_i are quite accurate. The sum of the constants ($k_{i\,cis} + k_{i\,trans}$) can be determined from the equilibrium composition and the rate at which the isomers approach equilibrium. Starting with I the sum of the constants can be determined by use of equation 10 and starting with II the sum can be determined by use of a similar equation. In each kinetic experiment the sum of the constants as

$$\ln (1 - f_e)/(f - f_e) = (k_{i\,cis} + k_{i\,trans})t \qquad (10)$$

well as the initial rate of isomerization were determined and values of $k_{i\,cis}$ and $k_{i\,trans}$ were calculated from these. A typical kinetic experiment is summarized in Table III. It is significant that the sum of the initial rates of isomerization of I and II agrees well with the value determined from the first-order rate at which equilibrium is established.

TABLE III

RATE OF ISOMERIZATION OF 0.5 M I IN 35% AQUEOUS ACETONE AT 30.05 ± 0.02°; [$HClO_4$] = 0.0964 M

Time, hr.		$k_{i\,cis}$[a] hr.$^{-1}$	($k_{i\,cis} + k_{i\,trans}$)[b] hr.$^{-1}$
0.0	1.00	0.019[c]	
7.1	0.88	.018	0.043
11.7	.82	.017	.046
24.2	.71	.014	.043
30.8	.67	.013	.043
			0.044 ± 0.001

[a] Calculated by use of equation 8. [b] Calculated by use of equation 10. [c] Determined by extrapolation.

Since isomerization is summarized by equations 2 and 5, k_i is a composite as shown by equation 11.

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(18) H. L. Goering and J. P. Blanchard, THIS JOURNAL, **76**, 5405 (1954).

(19) J. P. Blanchard and H. L. Goering, *ibid.*, **73**, 5863 (1951).

(20) It has been shown previously, H. L. Goering and E. F. Silversmith, *ibid.*, **77**, 5172 (1955), that (−)-I is related to (−)-ketone and (−)-II (which has a positive rotation in 35% aqueous acetone) is related to (+)-ketone.

Comparison of equations 4 and 11 shows that providing k_α and k_i are determined for the same acid concentration, the ratio (k_i/k_α) will correspond to the ratio at which the conjugate acid of I or II isomerizes and loses optical activity, *i.e.*, k'_i/k'_α.

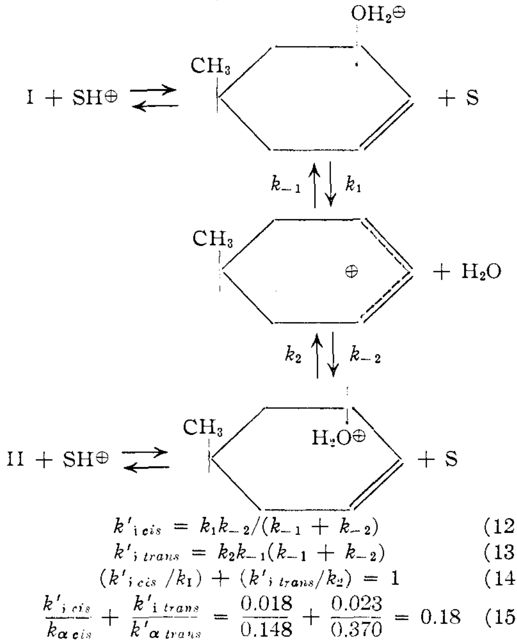
$$k_i = Kk_i'[\mathrm{SH}^\oplus] \qquad (11)$$

Values of k_i and k_α for 0.5 M I and II at 30° at an acid concentration of 0.0964 M are presented in Tables I and II. These data show that the conjugate acid of I loses optical activity 8 times faster than it isomerizes and the conjugate acid of II loses optical activity 16 times faster than it isomerizes.

Discussion

The present data demonstrate unequivocally that rearrangement of the conjugate acids of I and II does not proceed entirely by the carbonium-ion mechanism in its simplest form. According to this mechanism (illustrated for the present system in Chart 1) the rate constants for the loss of optical activity of the conjugate acids of I and II, k'_α (eq. 3), would be k_1 and k_2, respectively. The rate constants for isomerization of the conjugate acids of I and II (k_i, eq. 5) would be related to the constants shown in Chart 1 as shown by equations 12 and 13. From these equations the relationship shown in equation 14 becomes apparent. The latter equation shows that if indeed $k'_{\alpha\,cis} = k_1$ and $k'_{\alpha\,trans} = k_2$, the sum of the ratios of k'_i/k'_α (which equal the experimentally determined values of k_i/k_α providing both constants correspond to the same acid concentration) for the two isomers is unity. However, the data presented in Tables I and II show that the sum is 0.18 as illustrated by equation 15. Thus it is seen that the magnitude of k_α relative to that of k_i is too large to be consistent with the carbonium-ion mechanism.

CHART 1



$$k'_{i\,cis} = k_1k_{-2}/(k_{-1} + k_{-2}) \qquad (12)$$

$$k'_{i\,trans} = k_2k_{-1}(k_{-1} + k_{-2}) \qquad (13)$$

$$(k'_{i\,cis}/k_1) + (k'_{i\,trans}/k_2) = 1 \qquad (14)$$

$$\frac{k'_{i\,cis}}{k_{\alpha\,cis}} + \frac{k'_{i\,trans}}{k'_{\alpha\,trans}} = \frac{0.018}{0.148} + \frac{0.023}{0.370} = 0.18 \qquad (15)$$

It appears that the most likely mechanism for the reversible first-order isomerization (eq. 5) is the carbonium-ion mechanism shown in Chart 1. As pointed out in the Introduction, available information concerning acid-catalyzed rearrangements and reactions of allylic alcohols (and derivatives) indicates that carbonium-ion intermediates are involved, especially in reactive systems such as the present one. In this connection it appears to be especially significant that there is good evidence that the conjugate acids of the p-nitrobenzoates of I and II dissociate to give the 5-methyl-2-cyclohexenylcarbonium ion in 80% aqueous acetone.[5]

Assuming that isomerization proceeds by the carbonium-ion process, it is clear from the relative magnitudes of k'_α and k'_i that the conjugate acids of I and II lose activity faster than they are converted to the allylic carbonium ion, *i.e.*, k'_α (eq. 3) $> k_1$ or k_2 (Chart 1). Thus the carbonium-ion process is accompanied by a somewhat more rapid stereospecific rearrangement which results in racemization with retention of geometric configuration.

Either the intramolecular process (III) or the intermolecular S$_N$2′-type process (IV) could account for the excess racemization, providing that the latter process is stereospecific, *i.e.*, the entering group comes in *cis* to the departing group so that the geometric configuration is retained in the present system.[21] Of these two possibilities the latter is perhaps the more attractive because closely related reactions have been observed, *e.g.* S$_N$2′ reactions involving neutral nucleophilic reagents.[15,21] On the other hand, there do not appear to be any known examples of intramolecular allylic rearrangements in which the migrating group is positively charged.[5]

Experimental

Materials.—The preparation of racemic and optically active I and II has been described previously.[18] The solvent was prepared by mixing 65 volumes of conductivity water and 35 volumes of purified acetone[22] at 25°. Perchloric acid (reagent grade) was added to the water before measuring the volumes. Anhydrous lithium perchlorate was added after the water and acetone were mixed. It was found that a mixture of 35 ml. of acetone and 65 ml. of water occupies a volume of 98.0 ± 0.2 ml. The concentrations of lithium perchlorate given in Table I have been corrected for this volume shrinkage.

Preparation of Solutions.—The reaction mixtures were prepared by delivering exactly 1.5 ml. of the desired alcohol into a 25-ml. volumetric flask and diluting to the mark with thermostated solvent (30°). The concentrations of perchloric acid in these solutions were determined by titrating 4.965 ml. aliquots with 0.04979 M sodium hydroxide solution to the phenolphthalein end-point.

Polarimetric Rates.—The rates of loss of optical activity were determined by the method previously described[6] for the solvolysis of the 5-methyl-2-cyclohexenyl chlorides.

Rates of Isomerization.—The rates of isomerization were determined by periodically measuring the isomeric composition of the alcohol mixtures. Zero time was taken as the time that the solutions were mixed. One-milliliter samples were withdrawn at appropriate time intervals and delivered into 4 ml. of 0.05 N aqueous sodium hydroxide to stop the reaction. The resulting alkaline solutions were extracted 3 times with 1.5-ml. portions of carbon disulfide. The combined extracts were concentrated to 1 ml. under a stream of

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[21] G. Stork and W. N. White, THIS JOURNAL, **75**, 4119 (1953), have described an S$_N$2′ reaction in which the entering group becomes attached to the side of the allylic system originally occupied by the departing group. However, this reaction is of a different charge type than that involved in the present work, and it is possible that this could effect the stereochemistry of the reaction; see W. G. Young, I. D. Webb and H. L. Goering, *ibid.*, **73**, 1076 (1951).

[22] J. K. Kochi and G. S. Hammond, *ibid.*, **75**, 3445 (1953).

filtered dry air. The configurational composition of the alcohol mixture was determined from the infrared spectrum by the previously described method.[18,23] Except for slight carbonyl absorption (presumably due to traces of acetone), the spectra were composites of those for I and II.

To determine whether or not the isolation procedure results in fractionation, three synthetic mixtures of I and II containing 86, 55 and 31% I were dissolved in 35% aqueous acetone and isolated by the above procedure. The infrared spectra of the final solution corresponded to 86, 53 and 31% I, respectively. These experiments demonstrate that the isolation procedure is reproducible and does not result in fractionation. Moreover, the traces of acetone in the final solutions do not interfere with the analysis.

For one run on each of the isomeric alcohols (the third and seventh experiments in Table II) the compositions of the alcohol mixtures were determined from the infrared spectra of the pure liquid alcohols (no solvent). In these runs, all of the carbon disulfide was removed from the extracts at reduced pressure (*ca.* 25 mm.). While the carbon disulfide was being removed, the temperature of the residue did not exceed 28°. Bands at 11.86 μ (present only in the spectrum of I) and 12.38 μ (present only in the spectrum of II) were used for the analyses. A plot of composition against the ratio of the absorption at these two wave lengths for a series of synthetic mixtures of I and II was used to determine the compositions of the unknown mixtures. The infrared spectra of the isolated mixtures were composites of those of I and II.

MADISON, WISCONSIN

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(23) H. L. Goering, T. D. Nevitt and E. F. Silversmith, THIS JOURNAL, **77**, 4042 (1955).

[CONTRIBUTION FROM HICKRILL CHEMICAL RESEARCH FOUNDATION]

Reactions of the Cycloheptatrienylium (Tropylium) Ion

BY W. VON E. DOERING[1] AND L. H. KNOX

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The tropylium ion, whose preparation has been made more convenient, reacts as an electrophilic reagent with the bases water, hydrogen sulfide and ammonia to give ditropyl ether, sulfide and amine, respectively, with the bases acetamide, benzamide and succinimide to form the N-tropyl derivatives and with cyanide ion to give tropyl cyanide which can be hydrolyzed to an amide identical with Buchner's norcaradiene carboxamide and which reacts with phenylmagnesium bromide to give desoxybenzoin. The tropylium ion is converted both by chromic acid and silver oxide to benzaldehyde. In a reaction of some theoretical significance because it probably proceeds by way of the cycloheptatrienyl (tropyl) free radical, tropylium ion is reduced by zinc dust to ditropyl.

Cycloheptatrienylium or tropylium ion, the parent of the heptagonal aromatic system, was discovered two years ago among the products of the decomposition of dibromotropilidene.[2] Shortly thereafter a derivative, carboxycycloheptatrienylium ion, was synthesized in England by the same type of reaction.[3] Last year saw an original synthesis of the tropylium ion by the Curtius rearrangement of norcaradiene carboxazide[4] and the preparation of the benzotropylium ion.[5] The D_{7h} structure of the tropylium ion has now been put on an essentially "absolute" basis by the definitive infrared–Raman investigation of Lippincott and Fateley.[6] The present work reports additional characterization of the chemical behavior of the tropylium ion.

The previously described method of preparation[2] of tropylium bromide has been improved and standardized so that isolation of the intermediate dibromotropilidene is now avoided and the yield has been raised to 60% of theory. Tropylium bromide is well crystallized from absolute ethanol but contains solvent of crystallization. Unless this ethanol is removed by thorough drying *in vacuo* before the tropylium bromide is used in reaction with bases, tropyl ethyl ether is always formed as a disturbing by-product. An attempt to convert tropilidene dibromide directly to tropyl methyl ether by refluxing with sodium methoxide failed in its intended purpose but did lead, in an unexpected oxidative rearrangement, to a small amount of benzaldehyde. Tropylium iodide can be prepared easily by passing hydrogen iodide into an ethanolic solution of the bromide. Although the aqueous solution of the iodide is colorless or slightly yellow depending on the concentration, the crystals are dark red. This sequence of color in the crystals of the halide salts, chloride essentially colorless, bromide yellow and iodide red suggests a charge transfer spectrum.

In the reaction of tropylium ion with water, hydronium ion can be titrated and, assuming the other product to be tropyl alcohol, an equilibrium constant can be calculated.[2] Very intensive efforts to isolate tropyl alcohol from tropylium ion and hydroxide ion under a variety of conditions have led uniformly to ditropyl ether[2] alone. With dilute alkali some time is required for ditropyl ether to precipitate from relatively concentrated solutions. In the very dilute solutions used for titration, the reaction is completely reversible so that, with no apparent drift in *p*H, tropylium ion can first be titrated with 0.1 *N* hydroxide ion and then be brought back to its original state by titration with 0.1 *N* hydrochloric acid, the second titration curve being the mirror image of the first within experimental error. Presumably tropyl alcohol is formed initially and, being in equilibrium with tropylium ion, reacts further to give the less soluble ether.

Similarly with hydrogen sulfide and ammonia it

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(1) Sterling Chemistry Laboratory, Yale University, New Haven, Conn.

(2) (a) G. Merling, *Ber.*, **24**, 3108 (1891); (b) W. von E. Doering and L. H. Knox, THIS JOURNAL, **76**, 3203 (1954); (c) compare also H. J. Dauben, Abstracts of Papers, 126th Meeting of the American Chemical Society, New York City, September 12, 1954, p. 18-O: "Cycloheptatrienylium ('tropenium') salts (II) have been derived (D. L. Pearson) from 1,3,5-cycloheptatriene and its 1,6-dibromo and 7-(N-succinimidyl) derivatives."

(3) A. W. Johnson and M. Tisler, *Chemistry and Industry*, 1427 (1954).

(4) M. J. S. Dewar and R. Pettit, *ibid.*, 199 (1955).

(5) H. H. Rennhard, E. Heilbronner and A. Eschenmoser, *ibid.*, 415 (1955).

(6) W. G. Fateley and E. P. Lippincott, THIS JOURNAL, **77**, 249 (1955).