tography and showed $n^{21}D$ 1.4885, λ_{max} 233 mμ (ε 11,300); γ_{max} (strong) 3.45, 3.50, 6.14, 6.94, 11.30 and 11.82 μ; (weak) 3.24, 5.60, 6.10, 6.26, 7.32, 7.48, 7.68, 7.90, 8.0, 8.2, 8.9, 9.12, 10.07, 10.39, 10.73 and 12.90 μ. The n.m.r. spectrum of X displayed signals at −92.2 (—CH_2—), −105.7 (CH_3—C═C), −123.7 and −137.2 (—CH_2C═C), −280.5 and −295.5 (CH_2═C) and −330.7 c.p.s. (CH═C).

Anal. Calcd. for $C_{10}H_{16}$: C, 88.16; H, 11.84. Found: C, 88.44; H, 11.69.

trans-**2,5-Dimethyl-1,3-hexadiene** (**XIIIa**).—This diene was obtained from isobutyraldehyde by the use of the procedure described above. Pure *trans*-2,5-dimethyl-1,3-hexadiene showed $n^{20}D$ 1.4432, λ_{max} 228 mμ (ε 22,100); λ_{max} 3.29, 3.40, 3.50, 6.10, 6.24, 6.88, 7.26, 7.33, 7.52, 7.68, 8.22, 8.38, 9.10, 10.33, 11.24 and 11.80 μ. The n.m.r. spectrum showed signals at −55.8 and −61.9 $(CH_3)_2$(C—H), −100.5 (CH_3—C═C), a sextet centered at *ca.* −123 (C—H), −263.4 (CH_2═C) and a complex set of six peaks from −298.8 to −349 c.p.s. (CH═CH).

Methylpentadienes.—A mixture comprised of 22% 4-methyl-1,3-pentadiene (XI) and 78% *trans*-2-methyl-1,3-pentadiene (XIIIa) was obtained by the dehydration of 2-methyl-2,4-pentane diol.[24] These dienes were readily separated using an adiponitrile column; XI displayed a longer retention time than XIIIa. The infrared spectra of these pure dienes were identical with those recorded in the API catalogue.[25]

cis-2-Methyl-1,3-pentadiene (XII) was obtained by thermal isomerization of 4-methyl-1,3-pentadiene (XI) and showed λ_{max} 222 mμ (5,000); γ_{max} 3.25, 3.42, 5.61, 6.13, 6.25, 6.95, 7.35, 8.05, 9.70, 9.95, 10.35(w), 10.85, 11.25, 13.20 and 14.85 μ. The n.m.r. spectrum was also consistent with the assigned structure, −103.4 (2 CH_3—C═C), −270.8, 279.8 and −322.5 c.p.s. (4 olefinic hydrogens).

Acknowledgment.—This work was supported in part by a grant from the Purdue Research Foundation. The authors are indebted to Mr. William E. Baitinger for determining the nuclear magnetic resonance spectra.

[24] According to M. G. Dupont and M. Darmon, *Bull. soc. chim. France*, **6**, 1208 (1939), the 2-methyl-1,3-pentadiene so produced is a mixture of *cis* and *trans* isomers. We, however, find that there is less than 0.2% of the *cis* isomer present.

[25] "Catalogue of Selected Infrared Absorption Spectograms," American Petroleum Institute Research, Project 44, National Bureau of Standards, Washington, D. C.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF WISCONSIN, MADISON 6, WIS.]

Stereochemistry of Allylic Rearrangements. XII. Oxygen Exchange Associated with the Acid-catalyzed Rearrangement of *cis*- and *trans*-5-Methyl-2-cyclohexenol[1,2]

BY HARLAN L. GOERING AND ROY R. JOSEPHSON

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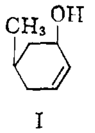
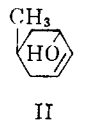
The acid-catalyzed isomeric rearrangement of *cis*- (I) and *trans*-5-methyl-2-cyclohexenol (II) in aqueous acetone results in interconversion of enantiomers (racemization) and geometric isomers (isomerization). With each isomer the rate of racemization (k_{rac}) is several times that of isomerization (k_i). Experiments with ^{18}O-labeled alcohols show that in the *cis* system most of the racemization is intramolecular, *i.e.*, little exchange is associated with the interconversion of enantiomers. On the other hand, in the *trans* system interconversion of enantiomers results in almost complete exchange. The stereochemical and exchange results are interpreted in terms of conformational considerations. The symmetrical 5-methyl-2-cyclohexenyl carbonium ion can exist in two conformations. Presumably the isomeric alcohols react *via* the quasi-axial conformers and give rise to carbonium ions which differ conformationally and in the way they are solvated.

Introduction

The acid-catalyzed ($HClO_4$) isomeric rearrangement of optically active *cis*-(I) and *trans*-5-methyl-2-cyclohexenol (II) in aqueous media results in formation of two products, racemic I and II—in this symmetrical system rearrangement without geometric isomerization results in interconversion of enantiomers (racemization). In an earlier investigation[3] it was found that in 35% aqueous acetone, both loss of optical activity (eq. 1) and isomerization (eq. 2) are pseudo first order, and for each isomer $k\alpha$ is several times larger than k_i. This means that there is "excess" racemization, or in other words there is a tendency for preservation of geometric configuration during the rearrangement.



I



II

Since loss of activity and isomerization are cleanly pseudo first order, the difference between $k\alpha$ and k_i for each isomer is the pseudo-first-order constant for racemization (eq. 3), *i.e.*, $k_{rac} = k\alpha - k_i$. Thus the total rate of rearrangement (disappearance of substrate) is measured by $k\alpha$ and rates of formation of the two products (isomerization and racemization) are measured by k_i and k_{rac}.

$$\textit{active}\ \text{I (or II)} \xrightarrow{k\alpha} \text{inactive products} \qquad (1)$$

$$\text{I} \underset{k_{i\text{II}}}{\overset{k_{i\text{I}}}{\rightleftharpoons}} \text{II} \qquad (2)$$

$$\textit{active}\ \text{I (or II)} \xrightarrow{k_{rac}} dl\text{-I (or II)} \qquad (3)$$

From the kinetic behavior—the rate of rearrangement ($k\alpha$) is proportional to the acid concentration[3]—it is clear that rearrangement involves reversible protonation of the substrate (eq. 4; $SH^{\oplus}$ is lyonium ion) followed by first-order rearrangement of the alcohol conjugate acid (eq. 5). The latter is the sum of the first-order rates of isomerization (eq. 6) and racemization (eq. 7).

$$\text{ROH} + \text{SH}^{\oplus} \overset{K_4}{\rightleftharpoons} \text{ROH}_2^{\oplus} + \text{S} \qquad (4)$$

$$\text{ROH}_2^{\oplus} \xrightarrow{k\alpha'} \text{inactive products} \qquad (5)$$

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[1] This work was supported by a grant (G-6285) from the National Science Foundation.

[2] First reported as a Communication, H. L. Goering and R. R. Josephson, *J. Am. Chem. Soc.*, **83**, 2585 (1961).

[3] H. L. Goering and E. F. Silversmith, *ibid.*, **79**, 348 (1957).

$$ROH_2^{\oplus} \xrightarrow{k_i'} \text{geometric isomer} \qquad (6)$$

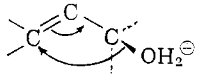
$$ROH_2^{\oplus} \xrightarrow{k_{rac}'} \text{racemic product} \qquad (7)$$

The pseudo first-order constants (k, eq. 1–3), which can be readily determined are related to the corresponding true first-order constants (k', eq. 5–7) as shown by eq. 8. Since k is proportional to the corresponding k', it is apparent that for each isomer the relative pseudo-first-order rates will correspond to the relative first-order rates at which the conjugate acid of the alcohol undergoes the various transformations.

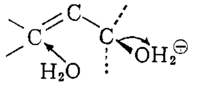
$$k = K_4[SH^{\oplus}]k' \qquad (8)$$

The observation that both conjugate acids racemize several times faster than they isomerize cannot be accommodated by a carbonium ion mechanism in its simplest form.[3] The 5-methyl-2-cyclohexenyl carbonium ion is related to both isomers and if only one intermediate, common to both isomers, were involved there could be no excess racemization (preservation of geometric configuration).

In the present work we have re-examined the relative rates of isomerization and loss of optical activity associated with this rearrangement. We have also measured the pseudo first-order rates of oxygen exchange of ^{18}O-labeled I and II (eq. 9) to determine if the "excess" racemization corresponds to an intra-(III)[3] or intermolecular process (IV)[3] or a combination of the two.



III



IV

$$R^{18}OH \xrightarrow{k_{exc}} ROH \qquad (9)$$

Results

Pseudo-first-order rate constants for loss of optical activity ($k\alpha$), equilibration of geometric isomers (k_{eq}, eq. 10), isomerization (k_i), racemization without geometric isomerization (k_{rac}) and oxygen exchange (k_{exc}) associated with the rearrangement in 35% aqueous acetone at 30° are given in Table I.[4]

$$\text{I (or II)} \xrightarrow{k_{eq}} \text{equilibrium mixture} \qquad (10)$$

The rate constant ($k\alpha$) for loss of optical activity of II was determined from its rate of loss of optical activity and found to be identical with that calculated for the present acid concentration (0.095 M) from data in reference 3. The value for I was computed from the earlier data.[3]

Rate constants for isomerization (k_i) were calculated from the pseudo-first-order constants for irreversible equilibration of the isomers (k_{eq}, eq. 10) and the equilibrium constant (K_{eq} = II/I = k_{iI}/k_{iII} = 1.22). These reactions were followed by isolation of the alcohol fractions from aliquots quenched with base and determination of the configurational compositions by capillary gas chromatography, a more convenient and precise method than the infrared analysis as used in the earlier work.[3] Equilibration reactions were followed to about 75% completion and were clearly first order. The equilibrium constant for isomerization (eq. 2) was determined from the isomeric composition (approached from both sides) after eight half-periods for isomerization.

TABLE I

PSEUDO-FIRST-ORDER RATE CONSTANTS FOR LOSS OF OPTICAL ACTIVITY ($k\alpha$), EQUILIBRATION OF GEOMETRIC ISOMERS (k_{eq}), ISOMERIZATION (k_i), RACEMIZATION (k_{rac}) AND OXYGEN EXCHANGE (k_{exc}) FOR I AND II IN 35% AQUEOUS ACETONE AT 30.2°; [$HClO_4$] = 0.095

Isomer[a]	I	II
$10k\alpha$, hr.$^{-1}$	1.46[b]	3.63[c]
$10\,k_{eq}$, hr.$^{-1}$	0.36 ± 0.04[d]	0.32 ± 0.03[e]
$10\,k_i$, hr.$^{-1}$	0.19 ± 0.02[f]	0.15 ± 0.02[f]
$10\,k_{rac}$, hr.$^{-1}$	1.27[g]	3.48[g]
$10\,k_{exc}$, hr.$^{-1}$	0.23 ± 0.03	1.5 ± 0.3

[a] Substrate concentration = 0.5 M. [b] Taken from ref. 3 and corrected for present acid concentration. [c] Measured in this work; the same value is obtained by calculation for present acid concentration from data reported in ref. 3. [d] Average (and mean deviation) for three independent experiments. [e] Average (and mean deviation) for four independent experiments. [f] Calculated from k_{eq} = 0.034 hr.$^{-1}$ and K_{eq} = II/I = 1.22. [g] Calculated from constants for racemization and isomerization, *i.e.*, $k_{rac} = k\alpha - k_i$.

Since $k_{eq} = k_{iI} + k_{iII}$ the same value should be obtained for the two isomers. As shown in Table I the constants for the isomers differ by less than the combined experimental uncertainties. The values given in the table are average values of three independent experiments for I and four independent experiments for II. The average of all seven experiments ($3.4 \pm 0.3 \times 10^{-2}$ hr.$^{-1}$) was used to calculate the isomerization rate constants.

Rates of oxygen exchange associated with the rearrangement of ^{18}O-labeled I (2.06 atom % ^{18}O-excess) and II (1.57 atom % ^{18}O excess) were found to be pseudo first order. These reactions were followed by isolation of the alcohol from quenched aliquots by gas chromatography and determination of the ^{18}O contents (in triplicate) of the alcohol fractions. Control experiments showed that isolation did not result in fractionation of isomers or change in ^{18}O content, *i.e.*, the samples analyzed were representative of the alcohol in the reaction mixture at the time of quenching.

Under the present conditions the ratio of exchangeable oxygen in the solvent to that in the alcohol fraction is large (>77). Thus reaction 9 can be treated as an irreversible process; the kinetic disturbance resulting from reincorporation of ^{18}O is negligible. The exchange reactions were followed to about 70% completion and trends were not detected. The value of k_{excI} in Table I is the average (and average deviation) of ten values obtained in three separate experiments. That of k_{excII} is the average of five values from two independent experiments. In connection with the interpretation of the results it is noteworthy that the first-order behavior of the exchange reactions establishes that isomerization results in complete exchange. The isomers undergo exchange at rates

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(4) The solvent composition is based on volumes of the pure components (25°) before mixing. Solvent, containing perchloric acid, was taken from the same batch for all experiments.

which differ by a factor of six and isomerization without exchange would result in drifts in the exchange constants (k_{excI} in particular would show a large upward drift because in this case rates of exchange and isomerization are comparable).

Comparison of exchange constants with the other constants provides a measure of exchange associated with rearrangement. In this connection the question of a possible isotope effect arises because in the exchange experiments the behavior of only that fraction of the alcohol that is isotopically labeled is observed. A small isotope effect would be expected for each of the two steps involved in the rearrangement (eq. 4 and 5). However, these effects would work in opposite directions and because of this cancellation the over-all effect should be very small—a negative isotope effect would be expected for the reversible protonation (*i.e.*, for eq. 4 $K_{^{16}\mathrm{O}}/K_{^{18}\mathrm{O}} = <1$) and a positive effect would be expected for the first-order rearrangement of the conjugate acid (*i.e.*, $k_{^{16}\mathrm{O}}'/k_{^{18}\mathrm{O}}' = >1$).[5] Thus presumably unlabeled alcohol reacts at essentially the same rate as ^{18}O-labeled alcohol and the exchange constants may be compared directly with the other constants.

The rate constants in Table I show the relative rates at which the conjugate acid of each isomer undergoes the various transformations and the amount of oxygen exchange associated with the rearrangement.[6] The conjugate acids are simultaneously converted to two isomers, the enantiomer and the geometric isomer. The rate of conversion of an optical isomer to its enantiomer ($k_{\mathrm{d}\rightarrow l}'$) is proportional to $k_{\mathrm{rac}}/2$ and the rate of conversion to the geometric isomer (k_{i}') is proportional to k_{i}. The sum of these rates represents the total rate at which an optical isomer changes its identity. The rate of oxygen exchange associated with these transformations (k_{exc}') is proportional to k_{exc}.

The relative magnitudes of $k_{\mathrm{d}\rightarrow l}'$, k_{i}' and k_{exc}' for each isomer are presented in Table II. In each case the data have been normalized for one hundred structural changes, *i.e.*, $k_{\mathrm{d}\rightarrow l}' + k_{\mathrm{i}}' = 100$. Thus the last number in the columns represents the number of transformations, out of one hundred, that involve exchange of oxygen.

TABLE II

RELATIVE RATES OF INTERCONVERSION OF ENANTIOMERS ($k_{\mathrm{d}} \rightarrow l'$), ISOMERIZATION ($k_{\mathrm{i}}'$) AND OXYGEN EXCHANGE ($k_{\mathrm{exc}}'$) FOR THE CONJUGATE ACIDS OF I AND II[a]

Conjugate acid of	I	II
$k_{\mathrm{d}} \rightarrow l'$[b]	77	92
k_{i}'	23	8
k_{exc}'	28	79

[a] Normalized so that $k_{\mathrm{d}} \rightarrow l' + k_{\mathrm{i}}' = 100$ for each isomer. Relative values are significant only when comparisons are made within a column.[6] [b] $k_{\mathrm{d}} \rightarrow l' = \frac{1}{2} k_{\mathrm{rac}}'$.

The data clearly show a striking difference in the oxygen exchange associated with the rearrangement of the two isomers. In the *cis* isomer I there is only a little exchange in excess of that resulting from isomerization—the data show that isomerization results in complete exchange (*vide supra*). Thus in this case, interconversion of enantiomers is primarily (93%) intramolecular (III). On the other hand, in the *trans* isomer II 79% of the structural transformations result in exchange. In this case interconversion of enantiomers is largely (77%) intermolecular (IV).

Discussion

From the earlier work[7] it is clear that the 5-methyl-2-cyclohexenyl system is a typical α,γ-dialkyl allylic system and undergoes carbonium ion reactions (ionization) with great facility. Ionization rates are rapid under a variety of solvolyzing conditions[7] and solvolysis of carboxylic esters of I and II involve alkyl–oxygen cleavage exclusively.[9] Moreover, the isomeric liquid chlorides ionize rapidly at low temperatures in non-polar solvents and in the absence of solvent as detected by racemization.[10] Because of the propensity for ionization, SN2 displacement has been realized only under the most favorable circumstance (reaction of the chlorides with tetramethylammonium acetate in dry acetone)[10] and even then ionization competed with displacement. For these reasons there is little doubt but that the rearrangement of the conjugate acids of I and II in aqueous media involves a carbonium ion process.

There are two additional points which support this conclusion. The only SN2 displacement reaction that has been observed in this system results in inversion of configuration,[10] *i.e.*, SN2 reactions are evidently much faster than SN2′ reactions as indeed would be expected.[11] Thus a process involving nucleophilic displacement by solvent would be expected to result in excess isomerization (inversion), not in excess racemization. Finally, it is significant that the conjugate acids of the *p*-nitrobenzoates of I and II dissociate to give the 5-methyl-2-cyclohexenyl carbonium ion 80% aqueous acetone.[9a]

In the present rearrangement both of the isomeric conjugate acids are related to the 5-methyl-2-cyclohexenyl carbonium ion (VIII). However, from the different behavior of the isomers it is obvious that they give rise to intermediates which differ. As has been pointed out,[2] this difference may be in the conformation of the symmetrical 5-methyl-2-cyclohexenyl carbonium ion and in the way that the ion is solvated. Indeed, the simple carbonium ion mechanism[3] can be refined and expanded along these lines so as to provide a logical rationalization of the present results.

Since allylic carbonium ions are planar[7]—this arrangement allows for maximum π-electron de-

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(5) In other work it has been observed by Dr. K. D. McMichael of these laboratories that $k_{^{16}\mathrm{O}}/k_{^{18}\mathrm{O}} \approx 1.1$ for the first-order alkyl–oxygen cleavage of allylic *p*-nitrobenzoates (alkyl oxygen labeled).

(6) Significance should not be attached to the magnitude of a rate constant for one isomer relative to that for the other. The relative reactivities of the conjugate acids of I and II cannot be determined because K_4 (eq. 4 and 8) probably is not identical for the two isomers. Thus the ratio of the pseudo-first-order constants for I and II will not necessarily correspond to the ratio of the first-order constants for the conjugate acids.

(7) For leading references see ref. 8.

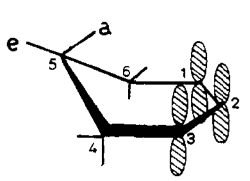
(8) H. L. Goering, *Record Chem. Progr.*, **21**, 109 (1960).

(9) (a) H. L. Goering and E. F. Silversmith, *J. Am. Chem. Soc.*, **77**, 6249 (1955); (b) **77**, 1129 (1955); (c) H. L. Goering and J. T. Doi, *ibid.*, **82**, 5850 (1960).

(10) H. L. Goering, T. D. Nevitt and E. F. Silversmith, *ibid.*, **77**, 4042 (1955).

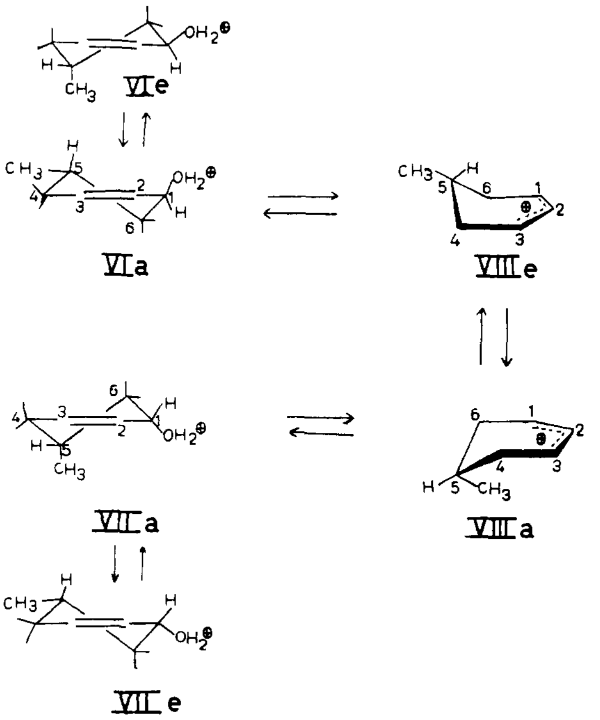
(11) R. H. De Wolfe and W. G. Young, *Chem. Revs.*, **56**, 753 (1956).

localization—it is apparent that the most favorable geometry for a cyclohexenyl carbonium ion will be one in which five ring members are in a plane and one, C_5, is out of plane as illustrated by V (C_1, C_2 and C_3 carbon–hydrogen σ-bonds have been omitted for clarity). If, as in the present case, there is a substituent at C_5, axial (a) and equatorial (e) type conformations are possible. It seems reasonable that because of different steric requirements these two conformers will be solvated differently.



V

Presumably the isomeric alcohol conjugate acids VI and VII exist as equilibrium mixtures of the two half-chair conformers[12] as illustrated in the accompanying scheme. If in each case the same type of conformer is stereoelectronically[13] better suited for heterolysis than its partner, the initially formed 5-methyl-2-cyclohexenyl carbonium ion derived from one isomer will differ conformationally from that produced by the other. For example, the quasi-axial[12b] conformers VIa and VIIa would form the equatorial (VIIIe) and axial (VIIIa) carbonium ions, respectively, (heterolysis of the C_1-oxygen bonds in VIa and VIIa with simultaneous rehybridization of C_1 and minimum movement of the nuclei in the cyclohexene moieties relates VIa to VIIIe and VIIa to VIIIa).



At first glance the assumption that the isomers react *via* their quasi-axial conformers, as implied in the scheme, may appear tenuous. Geometrically, quasi-axial and quasi-equatorial bonds in cyclohexenyl systems differ less than axial and equatorial bonds in cyclohexyl systems[12b] and in the latter case the axial derivatives ionize only about three times faster than their equatorial conformers.[14] However, inspection of Dreiding models reveals a subtle but important factor involved in 2-cyclohexen-1-yl systems but not in cyclohexyl systems and this concerns stereoelectronic requirements for facile rupture of allylic bonds. As has been repeatedly emphasized,[7,8,15] the preferred geometry for rupture of allylic bonds is that in which the bond is in a plane perpendicular to that of the double bond. This arrangement allows for maximum overlap of the developing p-orbital with the π-orbital (maximum delocalization in the transition state) and smooth conversion to the planar allylic cation, radical or anion. Now, models show that a quasi-axial cyclohexene bond can assume this stereoelectronically favorable orientation with respect to the double bond with little distortion or departure from the unstrained half-chair conformation. On the other hand, a quasi-equatorial bond can attain this orientation only with considerable distortion of the ring and in fact in this case the ring is probably forced into the energetically less favored[12] half-boat conformation. This suggests that the transition state related to the quasi-axial conformer may be favored by as much as 2 to 3 kcal./mole—the energy difference for the two cyclohexene conformers is about 2.7 kcal./mole[12a]—in which case reaction *via* the quasi-axial conformers VIa and VIIa may be one or two orders of magnitude faster than reaction *via* their quasi-equatorial partners. In other work, rigid systems are being investigated to establish if in fact cyclohexene quasi-axial derivatives are more reactive than their quasi-equatorial isomers.

An obvious corollary of the picture developed thus far is that the 5-methyl-2-cyclohexenyl carbonium ion conformers will react preferentially so as to form quasi-axial bonds (microscopic reversibility). This means that bonding will be stereoelectronically favored on the side of the ring occupied by the out-of-plane C_5 carbon atom. Bonding on the other side would result in formation of a quasi-equatorial bond. Thus VIIIe and VIIIa will give rise to the *trans*- and *cis*-5-methyl-2-cyclohexenyl isomers, respectively. Although in the present discussion we are concerned with a particular carbonium ion reaction, it is apparent that these same factors apply in general for allylic anionic, cationic and radical reactions in cyclohexene systems.

If it is assumed that the energy barrier for conversion of the solvated carbonium ion to conjugate acid (VIIIe to VI and VIIIa to VII) is lower than that for conformational interconversion of the carbonium ion (VIIIe$\rightleftarrows$VIIIa) the scheme accommodates the excess racemization. Accord-

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[12] (a) C. W. Beckett, N. K. Freeman and K. S. Pitzer, *J. Am. Chem. Soc.*, **70**, 4227 (1948); (b) D. H. R. Barton, R. C. Cookson, W. Klyne and C. W. Shoppee, *Chemistry & Industry*, 21 (1954).

[13] E. J. Corey and R. A. Sneen, *J. Am. Chem. Soc.*, **78**, 6269 (1956).

[14] S. Winstein and N. J. Holness, *ibid.*, **77**, 5562 (1955).

[15] H. L. Goering and R. R. Jacobson, *ibid.*, **80**, 3277 (1958).

ing to this view heterolysis results in formation of the symmetrical 5-methyl-2-cyclohexenyl carbonium ion and consequently optical activity is lost. Geometric configuration, however, is preserved until conformational interconversion of the solvated carbonium ion occurs. To correspond to the relative rates of racemization and isomerization (Table I) requires that the ratio of return to conjugate acid to conformational interconversion be about 23 for VIIIe and 7 for VIIIa.

In connection with the assumption concerning energy barriers it would seem that the barrier for transformation of the solvated carbonium ion to conjugate acid may be very small, *e.g.*, <5 kcal./mole. The water molecule involved in the reaction is in the solvation shell and presumably stereo electronically favorably located for reaction (*vide infra*). Thus, in effect, this is a unimolecular process in the sense that energy is not required for diffusion of the reactants. It is difficult to estimate the barrier for conformational interconversion of the carbonium ion VIII. However, this barrier may be higher than would first appear and in fact may approach that for the conformational interconversion of cyclohexane, about 10.6 kcal./mole.[16] Unlike the case of cyclohexane,[17] the transition state will be nearly planar (deviation from planarity will be at the expense of resonance energy). Moreover, relocation of water molecules in the solvation shell could contribute to the energy barrier. Thus, all things considered, the assumption concerning the relative magnitude of the energy barriers seems reasonable.

There remains now only the difference in the amount of exchange associated with the rearrangement of the isomers to account for. And this also is readily explicable by extension of the present interpretation so as to include differences in steric requirements for solvation of the carbonium ion conformers. Conversely, the exchange experiments provide information bearing on the nature of the solvation shell.

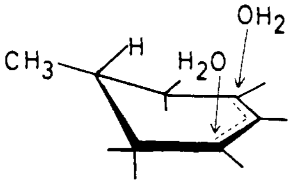
There is evidence[18] that unhindered classical carbonium ions in aqueous media are solvated so that at any instant only two water molecules in the solvation shell are eligible for bonding. Moreover, if the carbonium ion is produced from an alcohol conjugate acid, the water molecule produced in the heterolysis initially occupies one of these reactive sites. Presumably these sites are on each side of the planar cation on or near the axis of the vacant *p*-orbital.

With allylic cations (also anions and radicals) stereoelectronic requirements for bonding are best satisfied by approach along the $C\alpha$ and $C\gamma$ *p*-orbitals' axes. Thus there are four reactive sites (two on each side of the planar cation) and if steric requirements permit, these are presumably occupied by solvent molecules in the inner solvation shell.

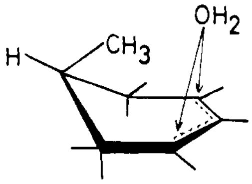
For reasons already discussed, with cyclohexenyl cations solvating water molecules on one side of the carbonium ion (the side of the out-of-plane C_5 carbon atom) are eligible for bonding. Thus, in such systems only two solvent molecules can occupy reactive sites. These will be located on or near the C_1 and C_3 *p*-orbitals' axes as illustrated for the equatorial conformer of the 5-methyl-2-cyclohexenyl cation by IX. To be sure, more than two water molecules are involved in the inner solvation shell but we are here interested only in those eligible for reaction. Now, if one of these unique molecules is formed in the heterolysis (the one nearest the carbon to which it was bonded) and if return to VIa is faster than relocation of the solvating molecules, exchange will not occur when the original optical isomer is formed but will occur when the enantiomer is formed (*i.e.*, for the racemization, $k_{\text{exc}} = {}^1/_2\, k_{\text{rac}}$). This in fact is essentially what happens with this isomer; if the rate of exchange is corrected for that associated with geometric isomerization $k_{\text{exc}} = 0.4\, k_{\text{rac}}$.

Solvation of VIIIa in a similar manner would result in serious steric interference between the C_5-methyl substituent and the two water molecules occupying the reactive sites (*cf.* non-bonding interactions in cyclohexyl systems with *cis* axial substituents). Thus it is not surprising that this conformer is solvated in a different manner.

The results show that in this case interconversion of enantiomers is substantially (93%) intramolecular. This means that one water molecule in the solvation shell is unique in that it is the most likely one to be involved in the reaction. Racemization requires that this molecule be located so that it can bond to either allylic carbon as shown by X. This reactive site is occupied by the water molecule formed in the heterolysis and the small amount of exchange shows that return is rapid relative to relocation of this unique water molecule (in this case for the racemization $k_{\text{exc}} = 0.03\, k_{\text{rac}}$).



IX



X

There are several corollaries of the present interpretation which concern reactions of 2-cyclohexen-1-yl systems in general. Only one of these, which bears on a conclusion drawn from our earlier observations, will be considered here. In the 5-methyl-2-cyclohexenyl system, ion pair return[19] in hydroxylic solvents (presumably internal return[19]) with a variety of leaving groups and solvents has in every case been found to be completely stereospecific (no geometric isomerization).[7,9c] From this it was concluded that in hydroxylic solvents internal return in general is completely stereospecific.[8] We see now that this is not necessarily so because in cyclohexenyl systems the conformational-configurational relationship between the cation and substrate favors or demands stereospecific internal return. Clearly the initially formed carbonium ion will have the counter ion

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(16) R. K. Harris and N. Sheppard, *Proc. Chem. Soc.*, 418 (1961).

(17) See J. B. Hendrickson, *J. Am. Chem. Soc.*, **83**, 4537 (1961).

(18) See H. L. Goering and R. E. Dilgren, *ibid.*, **82**, 5744 (1960).

(19) S. Winstein, E. Clippinger, A. H. Fainberg, R. Heck and G. C. Robinson, *ibid.*, **78**, 328 (1956).

in the inner solvation shell (the so-called internal ion pair[19]) on the "reactive" side. Thus return, prior to conformational interconversion of the carbonium ion, favors bond formation on the original side not only because of the location of the counter ion, but also because of conformational stereoelectronic requirements for bonding. Or to put it another way, in these systems migration of the counter ion to the other side of the cation is not sufficient for return with inversion. The cation must also adopt the proper conformation.

In this connection it is significant that ion pair return associated with the solvolysis of optically active substituted benzhydryl chlorides[20] results in racemization. Solvolysis of optically active *p*-chlorobenzhydryl *p*-nitrobenzoate involves ion pair return which is largely but not completely stereospecific, *i.e.*, racemization is detectable.[21] Thus it appears that the conformational–configurational relationship between cation and substrate in the 5-methyl-2-cyclohexenyl system may play an important role in the complete stereospecificity associated with ion pair phenomena in this system.

Experimental

Materials.—Racemic *cis*-I[22] and *trans*-5-methyl-2-cyclohexenol (II)[9c] and (−)-II,[9c] $[\alpha]^{30}\mathrm{D}$ −90.6 (35% aqueous acetone), were obtained as described earlier. All samples were shown to be homogeneous by their infrared spectra and by capillary gas chromatography (g.c.; *vide infra*). The solvent, 35% aqueous acetone, was also prepared as described earlier.[3]

cis-**5-Methyl-2-cyclohexenol-^{18}O** was prepared by lithium aluminum hydride reduction[22] of ^{18}O-enriched 5-methyl-2-cyclohexenone. The labeled ketone was prepared by stirring a mixture of 20 g. of 5-methyl-2-cyclohexenone[22] and 7.2 g. of ^{18}O-enriched water (*ca.* 4 atom % ^{18}O excess) containing a trace of *p*-toluenesulfonic acid for 21 hours at room temperature. The mixture was diluted with 50 ml. of ether and dried ($CaCl_2$). The ketone (2.08 atom % ^{18}O excess)[23] was isolated in 88% yield by distillation. The ketone was converted to labeled alcohol by reduction with lithium aluminum hydride, a method which gives a mixture containing about 95% I.[22] This isomer was purified as the *p*-nitrobenzoate derivative.[22] The resulting alcohol was shown to be configurationally homogeneous by g.c. and contained 2.06 atom % ^{18}O excess.

trans-**5-Methyl-2-cyclohexenol-^{18}O** was obtained by stirring a mixture of 19.0 g. of 5-methyl-2-cyclohexenyl chloride[10] (the configurational composition is unimportant),[9c] 25.17 g. of ^{18}O-enriched water (*ca.* 4 atom % ^{18}O excess) and 15 g. of calcium carbonate for 24 hours at room temperature. The resulting slurry was filtered and the solid material was washed several times with ether. The organic layer was separated from the combined filtrate and washings and dried (K_2CO_3). Distillation gave 10.75 g. of alcohol consisting of about 98% *trans* isomer II.[9c] The isomerically pure alcohol was obtained in the usual manner[22,9c] (homogeneity established by g.c.) and contained 3.90 atom % ^{18}O excess. This was diluted with pure unlabeled II to give alcohol containing 1.57 atom % ^{18}O excess which was used in the kinetic experiments.

Kinetic Experiments. (A) Polarimetric Rates.—Optical rotations were measured with an O.C. Rudolph and Sons model 80 high precision polarimeter equipped with a photoelectric attachment. Thermostated reaction solutions were prepared as described earlier[3] and delivered into an all-glass jacketed 4-dm. polarimeter tube (central filling) and the optical rotations were determined at appropriate time intervals. Temperature control was achieved by circulation of thermostated water through the tube jacket. Rate constants for loss of optical activity were determined as described elsewhere.[3]

(B) **Isomerization Experiments.**—One-ml. aliquots of the reaction solution (0.5 *M* in alcohol and 0.095 *M* in $HClO_4$) were withdrawn from the thermostated reaction flask (25-ml. volumetric flask) at appropriate time intervals and quenched by delivery into 2 ml. of 0.1 *M* aqueous sodium hydroxide. Solutions were prepared and rate runs initiated as described earlier.[3] The alcohols were extracted from the alkaline solution with three 1-ml. portions of pentane. The isomeric compositions of the alcohol mixtures in these extracts were determined by g.c. using a 150-foot stainless steel capillary column coated with Ucon polyglycol (LB-550-X) and an operating temperature of 120°. To show that the extraction procedure does not result in fractionation, three synthetic quenched reaction solutions of known isomeric composition (75.1%, 51.1% and 29.3% II) were prepared and the alcohol isolated by the above procedure. The compositions of the alcohol mixtures in these extracts were found to be 74.8, 52.1 and 31.8% II. Thus the analyses are good to about ±1%.

The "infinity" value was determined after equilibration for 160 hours (over 8 half-lives) found to be 55 ± 1% II and 45 ± 1% I. Thus the equilibrium constant (K_{eq}) is 1.22 ± 0.06. The results of a typical experiment are summarized in Table III.

TABLE III

ISOMERIC EQUILIBRATION OF I AND II IN 35% AQUEOUS ACETONE AT 30.2°; [II] = 0.05 *M*; [$HClO_4$] = 0.095 *M*

Time, hr.	Composition, % II	Reaction,[a] %	10^2k_{eq}[b,c] hr.$^{-1}$
0	95.6	0	
5	90.0	13.8	2.94
10	84.8	26.6	3.18
15	80.8	35.0	3.01
20	76.3	47.5	3.47
25	73.9	53.4	3.04
			3.13 ± 0.16

[a] Fraction of reactant II which was changed to equilibrium composition, 55% II and 45% I. [b] Calculated using the integrated expression for a first-order reaction. [c] Graphical analysis (least squares) gives a value of 3.01 hr.$^{-1}$ for $10^2\ k_{eq}$.

(C) **Oxygen-exchange Experiments.**—Reaction solutions were prepared as described earlier[3] except that ^{18}O-labeled I and II were used. Five-ml. samples of the reaction solution (0.5 *M* in alcohol and 0.095 *M* in $HClO_4$) were withdrawn at appropriate time intervals and quenched by delivery into 10 ml. of 0.1 *M* aqueous sodium hydroxide. The resulting alkaline solution was extracted with three 5-ml. portions of pentane. The extracts were concentrated to 1 ml. under a stream of dry nitrogen and the pure binary mixture of alcohols was isolated without fractionation by preparative g.c. A 9-ft. 20% Ucon polyglycol(LB-550-X)-on-Celite column and an operating temperature of 120° was used for this separation. That isomeric fractionation

TABLE IV

RATE OF ^{18}O-EXCHANGE ASSOCIATED WITH THE REARRANGEMENT OF *cis*-5-METHYL-2-CYCLOHEXENOL-^{18}O; IN 35% AQUEOUS ACETONE AT 30.2°; [I] = 0.5 *M* [$HClO_4$] = 0.095 *M*

Time, hr.	^{18}O Content,[23] atom % excess	10^2k_{exo},[a] hr.$^{-1}$
0	2.06	
14.5	1.46	2.23
24.0	1.28	1.98
37.0	0.94	2.12
49.5	0.65	2.33
		2.17 ± 0.12

[a] Calculated using the integrated expression for a first-order reaction.

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(20) See S. Winstein, A. Ledwith and M. Hojo, *Tetrahedron Letters*, **18**, 341 (1961), and references therein.

(21) H. L. Goering and J. F. Levy, *ibid.*, **18**, 644 (1961); R. G. Briody, unpublished results.

(22) H. L. Goering and J. P. Blanchard, *J. Am. Chem. Soc.*, **76**, 5405 (1954).

(23) The O^{18} contents were determined as described in H. L. Goering and M. M. Pombo, *ibid*, **82**, 2515 (1960).

did not occur during isolation and purification of the binary mixtures of alcohols was established by isolation of alcohol mixtures of known composition (75.1%, 51.1% and 29.3% II) from synthetic quenched reaction mixtures. The observed compositions were 73.7%, 50.3% and 27.9% II. Isolation of an alcohol mixture containing 1.57 atom % ^{18}O excess[23] by this procedure gave alcohol having 1.55 atom % ^{18}O excess. Thus the isolation does not result in change of the ^{18}O content. The results of a typical experiment are summarized in Table IV.

[CONTRIBUTION FROM EMERYVILLE RESEARCH CENTER, SHELL DEVELOPMENT CO., EMERYVILLE, CALIF., AND DEPARTMENT OF CHEMISTRY, CASE INSTITUTE OF TECHNOLOGY, CLEVELAND 6, O.]

Addition of Peroxides to Conjugated Olefins Catalyzed by Copper Salts[1]

BY JAY K. KOCHI

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t-Butyl peracetate and perbenzoate react with conjugated olefins under catalysis by copper salts to form adducts containing one or more olefin units. From butadiene, *t*-butoxybutenyl derivatives are formed which are the same as those derived from *t*-butyl hypochlorite or *t*-butyl hydroperoxide and ferrous sulfate. It is demonstrated that these *t*-butyl peresters and copper salts form *t*-butoxy radicals as intermediates, which add to butadiene to produce *t*-butoxybutenyl radicals. The similarity in the oxidation by cupric salts of *t*-butoxybutenyl radicals and butenyl radicals from butenes examined earlier is discussed. The mechanistic implications of the oxidation of allylic radicals by an electron transfer process or a ligand transfer process is further amplified. The reaction of *t*-butyl hydroperoxide and copper salts is also postulated to form *t*-butoxy radical intermediates, and no evidence for the formation of *t*-butylperoxy radicals from this system is presently at hand.

Introduction

The copper salt-catalyzed reactions of *t*-butyl peresters and benzoyl peroxide with simple olefins, represented by the normal butenes, have been studied.[2,3] The difference in behaviors between these two peroxides was attributed to the initiating radical produced from each: *t*-butoxy from *t*-butyl perester and benzoyloxy from benzoyl peroxide. Although the former radicals reacted with simple olefins primarily by allylic hydrogen abstraction,

$$t\text{-BuO}_3\text{CR} + \text{Cu}^{\text{I}} \longrightarrow t\text{-BuO}\cdot + \text{Cu}^{\text{II}}\text{O}_2\text{CR} \quad (1)$$

$$(\text{C}_6\text{H}_5\text{CO}_2)_2 + \text{Cu}^{\text{I}} \longrightarrow \text{C}_6\text{H}_5\text{CO}_2\cdot + \text{Cu}^{\text{II}}\text{O}_2\text{CC}_6\text{H}_5 \quad (2)$$

benzoyloxy radicals reacted by an addition process. Kharasch and co-workers[4] have studied the behavior of *t*-butoxy radicals toward such receptive dienes as butadiene and found that addition at the terminal positions to produce allylic radicals was the predominant reaction. Similar considerations

$$t\text{-BuO}\cdot + \text{C}_4\text{H}_6 \longrightarrow \underset{\text{I}}{t\text{-BuO—CH}_2\text{—CH}\cdots\text{CH}\cdots\text{CH}_2\cdot} \quad (3)$$

apply to benzoyloxy radicals. If *t*-butoxy radicals are formed from the catalyzed reactions of *t*-butyl peresters in the presence of butadiene, such allylic *adduct* radicals as I will result. The reaction of these allylic radicals with cupric salts should be governed by the same considerations as the simple butenyl radicals II derived from butenes by a hydrogen abstraction reaction described earlier.[2]

$$t\text{-BuO}\cdot + \text{C}_4\text{H}_8 \longrightarrow t\text{-BuOH} + \underset{\text{II}}{\text{CH}_3\text{—CH}\cdots\text{CH}\cdots\text{CH}_2\cdot} \quad (4)$$

The reactions are

$$\text{C}_4\text{H}_7\cdot + \text{Cu}^{\text{II}}\text{O}_2\text{CR} \longrightarrow \text{C}_4\text{H}_7\text{O}_2\text{CR} + \text{Cu}^{\text{I}} \quad (5)$$

and analogously

$$t\text{-BuOC}_4\text{H}_6\cdot + \text{Cu}^{\text{II}}\text{O}_2\text{CR} \longrightarrow \underset{\text{III}}{t\text{-BuOC}_4\text{H}_6\text{O}_2\text{CR}} + \text{Cu}^{\text{I}}, \text{ etc.} \quad (6)$$

The reaction between peresters and such conjugated olefins as butadiene, isoprene and styrene was investigated in the presence of copper salts to explore the behavior of these allylic radicals. The reactions of butoxybutenyl radical I postulated as an intermediate from butadiene and *t*-butyl peresters with the aid of copper salts were compared with those adduct radicals prepared unambiguously from known sources of *t*-butoxy radicals, such as *t*-butyl hypochlorite and *t*-butyl hydroperoxide and ferrous salts. Butadiene is also an effective trap for *t*-butylperoxy radicals,[5] and it was employed with *t*-butyl hydroperoxide and copper salts to attempt to obtain evidence for the formation of *t*-butylperoxy intermediates.[6]

The stoichiometry of the addition of peresters to butadiene catalyzed by copper salts is given by eq. 7.

$$t\text{-BuOO}_2\text{CR} + \text{C}_4\text{H}_6 \xrightarrow{\text{Cu}^{\text{I}}} t\text{-BuOC}_4\text{H}_6\text{O}_2\text{CR} \quad (7)$$

Results

Conjugated Olefins and Peresters.—Butadiene (1 mole) and *t*-butyl peracetate (0.25 mole) reacted readily in benzene solution (100 ml.) with catalytic amounts of cuprous bromide (1.4 meq.) to produce acetic acid (8–10%), *t*-butyl alcohol (approximately 5%) and 90–92% ester. A minor amount of polymeric butadiene (approximately 10 g.) was also produced. Distillation of the ester mixture yielded two fractions corresponding to a 1:1 (40–50%) and a 2:1 (25–30%) adduct of butadiene and *t*-butyl peracetate, in addition to higher boiling adducts which were not identified. The 1:1 adducts consisted of two isomers, 4-*t*-butoxy-3-acetoxybutene-1(V, R = CH_3) and 4-

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[1] Presented in part before the Petroleum section of the Gordon Research Conference, Colby Jr. College, New London, N. H., June, 1961. Part III, Peroxide Reactions Catalyzed by Copper Salts.

[2] J. K. Kochi, *J. Am. Chem. Soc*, **83**, 3162 (1961); **84**, 774 (1962).

[3] J. K. Kochi, *ibid.*, **84**, 1572 (1962).

[4] M. S. Kharasch, F. Arimoto and W. Nudenberg, *J. Org. Chem.*, **16**, 1556 (1951); D. H. Volman and W. M. Graven, *J. Am. Chem. Soc.*, **75**, 3111 (1953).

[5] M. S. Kharasch, P. Pauson and W. Nudenberg, *J. Org. Chem.*, **18**, 322 (1953).

[6] J. K. Kochi, *Tetrahedron*, **18**, 483 (1962).