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Oxygen Exchange Associated with the Acid-catalyzed Rearrangement of α-Phenylallyl Alcohol in Aqueous Dioxane[1]

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RECEIVED MARCH 7, 1960

The rate of oxygen exchange associated with the acid-catalyzed racemization and rearrangement of optically active α-phenylallyl alcohol in 40% dioxane has been determined. The data show that about 4% of the γ-phenylallyl alcohol and 22 ± 8% of the racemic α-phenylallyl alcohol derived from active α-phenylallyl alcohol are produced without oxygen exchange. These results are interpreted in terms of a carbonium ion mechanism in which the phenylallyl carbonium ion is common to exchange, rearrangement and racemization. The rate of production of the carbonium ion is thought to correspond to the rate of loss of optical activity rather than to the rate of oxygen exchange. The water molecule formed in the dissociation step apparently has a greater chance than the average water molecule in the solvent to be involved in the solvation of the carbonium ion and consequently a greater chance to be involved in the recombination step. Thus dissociation to form the common intermediate results in loss of optical activity but does not always result in oxygen exchange.

Introduction

The acid-catalyzed rearrangement of α-phenylallyl alcohol ($R^{\alpha}OH$) to γ-phenylallyl alcohol ($R^{\gamma}OH$) involves protonation (eq. 1) followed by a first-order rearrangement of the conjugate acid of the allylic alcohol (eq. 2).[3] The product is sufficiently more stable than the reactant so that the rearrangement is irreversible. At low acid concentrations the rate of rearrangement is first order in lyonium ion ($SH^{\oplus}$) and alcohol (eq. 3).[4]

$$R^{\alpha}OH + SH^{\oplus} \underset{}{\overset{K}{\rightleftarrows}} R^{\alpha}OH_2^{\oplus} + S \qquad (1)$$

$$R^{\alpha}OH_2^{\oplus} \xrightarrow{k_r'} R^{\gamma}OH_2^{\oplus} \qquad (2)$$

$$\text{rate} = k_{r0}[SH^{\oplus}][R^{\alpha}OH] \qquad (3)$$

However, $[SH^{\oplus}]$ is constant and the reaction is pseudo first order (eq. 4).

$$\text{rate} = k_r[R^{\alpha}OH] \qquad (4)$$

In an earlier study the pseudo first-order rate constants for rearrangement (k_r, eq. 4) and loss of optical activity (k_{α}, eq. 5) of optically active $R^{\alpha}OH$ in 40% aqueous dioxane were determined.[3] These constants are proportional to the first-order constants for loss of optical activity (k_{α}', eq. 6) and rearrangement (k_r', eq. 2) of the conjugate acid of the active alcohol as illustrated by eq. 7 and 8. The rate of loss of optical activity exceeds that of rearrangement; *i.e.*, $k_{\alpha} > k_r$. In other words, racemization of the alcohol accompanies the rearrangement. The pseudo first-order rate constant for the racemization (k_{rac}, eq. 9) is the difference between k_{α} and k_r as shown by eq. 10.

$$\text{rate} = k_{\alpha}[\text{active } R^{\alpha}OH] \qquad (5)$$

$$\text{(active) } ROH_2^{\oplus} \xrightarrow{k_{\alpha}'} \text{inactive products} \qquad (6)$$

$$k_r = k_r'K[SH^{\oplus}] \qquad (7)$$

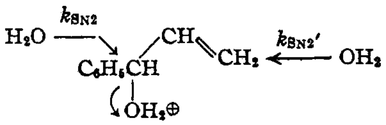
$$k_{\alpha} = k_{\alpha}'K[SH^{\oplus}] \qquad (8)$$

$$\text{(active) } R^{\alpha}OH \xrightarrow{k_{rac}} \text{(racemic) } R^{\alpha}OH \qquad (9)$$

$$k_{rac} = k_{\alpha} - k_r \qquad (10)$$

Two possible mechanisms have been suggested[3] for the rearrangement of $R^{\alpha}OH_2^{\oplus}$ to account for the excess racemization. The one which was considered to be the more likely[3,5] is the carbonium ion process illustrated by eq. 11. The other, illustrated by II, involves a combination of SN2- and SN2′-type displacements.

$$R^{\alpha}OH_2^{\oplus} \overset{k_{\alpha}'}{\rightleftarrows} \underset{\text{I}}{[C_6H_5CH\overset{\dots}{-}CH\overset{\dots}{-}CH_2]^{\oplus}} + H_2O \longrightarrow R^{\alpha}OH_2^{\oplus} \qquad (11)$$



II

In the present work we have determined the rate of oxygen exchange associated with the racemization and rearrangement to distinguish between these possibilities and to obtain more information about the rearrangement. Both the rate constant for oxygen exchange of the phenylallyl system (k^*_{exc}, eq. 12) and the rate constant for oxygen exchange of the unrearranged alcohol (k_{exc}, eq. 13) have been determined using O^{18}-labeled α-phenylallyl alcohol ($R^{\alpha}O^{18}H$).

$$R^{\alpha}O^{18}H \xrightarrow{k^*_{exc}} R^{\alpha}OH + R^{\gamma}OH \qquad (12)$$

$$R^{\alpha}O^{18}H \xrightarrow{k_{exc}} R^{\alpha}OH \qquad (13)$$

According to the carbonium ion process (eq. 11) k_{α} corresponds to the rate of production of the phenylallyl carbonium ion I which is common to racemization and rearrangement. The constant for racemization (k_{rac}, eq. 9 and 10) corresponds to the rate of formation of that fraction of the carbonium ion involved in the racemization. For this mechanism the rate of oxygen exchange should correspond to the rate of formation of the carbonium ion providing the departing water molecule in the dissociation step becomes kinetically equivalent to the water in the solvent. In this case k^*_{exc} and k_{exc} would be expected to be the same as k_{α} and k_{rac}, respectively.

For the displacement mechanism (II) the rate of oxygen exchange of the unrearranged alcohol

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[1] This work was supported by the Office of Ordnance Research, U. S. Army.

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[3] H. L. Goering and R. E. Dilgren, THIS JOURNAL, **81**, 2556 (1959).

[4] At high acid concentrations the rate parallels the acidity function, H_0; E. A. Braude, *Quart. Revs.*, **4**, 404 (1950); *Ann. Rept. Chem. Soc.*, **46**, 114 (1949).

[5] H. L. Goering and E. F. Silversmith, THIS JOURNAL, **79**, 348 (1957).

TABLE I

OXYGEN EXCHANGE AND REARRANGEMENT OF α-PHENYLALLYL ALCOHOL-O^{18} IN 40% AQUEOUS DIOXANE AT 30°

$[HClO_4] = 0.0514\ M$, $[LiClO_4] = 0.0486\ M$

			Composition (% $R^\alpha OH$)[c]		O^{18} content[d]				
t, min.	D_t[a]	$10^3 k_r$,[b] min.$^{-1}$	Reaction mixture	Isolated sample	Isolated sample	$R^\alpha OH$ + $R^\gamma OH$	$R^\alpha OH$	$10^3 k^*_{exc}$,[e] min.$^{-1}$	$10^3 k_{exc}$,[f] min.$^{-1}$
0	45.2	...	98.3	99.8	3.40	3.34	3.40	..	..
91	180	0.794	92.3	97.5	3.00	2.83	3.07	1.86	1.12
182	306	.795	86.3	98.1	2.79	2.46	2.84	1.71	0.990
270	418	.792	80.5	98.6	2.64	2.15	2.67	1.66	.894
360	529	.798	75.7	96.6	2.39	1.87	2.47	1.65	.888
540	729	.806	66.4	88.3	1.89	1.44	2.14	1.60	.856
630	813	.801	62.0	83.8	1.63	1.21	1.93	1.66	.898
720	904	.814	57.9	94.6	1.72	1.07	1.81	1.64	.875
	1980[g]		4.5	7.5	0.072	0.074	0.013[h]		
	Mean	0.800 ± 0.006					Mean	1.68 ± 0.05	0.931 ± 0.070
	$10^3 k_0$[i] =	15.5 ± 0.1					$10^3 k_0$[i]	32.6 ± 0.9	18.1 ± 1.3

[a] Optical densities of diluted (EtOH) aliquots at 251.0 mμ. [b] Pseudo first-order rate constant for disappearance of $R^\alpha OH$. [c] Composition of phenylallyl alcohol during reaction (fourth column) calculated from k_r (corrected for side reaction) and composition of isolated binary mixture of $R^\alpha OH$ and $R^\gamma OH$ (fifth column). [d] Atom % O^{18} excess of (i) isolated binary mixture, (ii) $R^\alpha OH + R^\gamma OH$ in reaction mixture and (iii) remaining $R^\alpha OH$. [e] Pseudo first-order rate constant for O^{18} exchange out of phenylallyl system (calculated from data in column 7). [f] Pseudo first-order rate constant for O^{18} exchange from unrearranged $R^\alpha OH$ (calculated from data in column 8). [g] Refers to 10 half-lives for rearrangement; other values in this row refer to 10 half-lives for exchange. [h] Estimated assuming O^{18} content to be same as that of water in the solvent at this time. [i] Second-order catalytic constants obtained by dividing above pseudo first-order constants by acid concentration; dimensions are l. mole^{-1} min.$^{-1}$.

would correspond to k_{S_N2}. In this case k_{rac} would be twice as large as k_{exc} (it is assumed that each displacement would result in inversion).

The rates of rearrangement and oxygen exchange of α-phenylallyl alcohol in aqueous dioxane have recently been investigated by Bunton and coworkers.[6] However, they used conditions different (solvent and temperature) from those we used in the earlier work[3] and thus their rate of exchange (k^*_{exc}) cannot be compared with our rate of loss of optical activity (k_α).

Results

α-Phenylallyl alcohol-O^{18} ($R^\alpha O^{18}H$) was prepared from vinylmagnesium bromide[7] and benzaldehyde-O^{18}. The labeled benzaldehyde was obtained by equilibration of benzaldehyde and O^{18}-enriched water. The O^{18}-labeled α-phenylallyl alcohol was purified by recrystallization of the acid phthalate derivative.[3]

So that the rate of exchange could be compared with the rates of rearrangement and loss of optical activity reported previously,[3] the same conditions were used; *i.e.*, 40% aqueous dioxane containing $HClO_4$ and sufficient $LiClO_4$ so that $\mu = 0.1$. Kinetic data for the rearrangement and oxygen exchange of $R^\alpha O^{18}H$ are given in Table I.

The pseudo first-order constant for rearrangement (third column) was determined by the spectrophotometric method described previously. The second-order catalytic constant shown at the bottom of the tables is the same as the average value of twelve independent experiments reported earlier.[3] Thus under these conditions the second-order catalytic constant for loss of optical activity, $k_{\alpha c}$, must also have the value reported earlier ($38.8 \pm 0.6 \times 10^{-3}$ l. mole^{-1} min.$^{-1}$).

To determine the rate of oxygen exchange pure binary mixtures of $R^\alpha OH$ and $R^\gamma OH$ were isolated from the quenched aliquots. The compositions of these mixtures were determined by ultraviolet analysis. That the samples were indeed pure binary mixtures was shown by infrared as well as by ultraviolet spectra. The compositions of the isolated samples are shown in the fifth column and O^{18} contents of these samples are given in the sixth column. The fourth column shows the composition of the phenylallyl alcohol in the reaction mixture at the times that the aliquots were quenched. These values were calculated from the ultraviolet spectra and the concentration of phenylallyl alcohol. The extinction coefficients of $R^\alpha OH$ and $R^\gamma OH$ at 251.0 mμ are 198 and 17,900, respectively. As reported earlier,[3] the rearrangement of $R^\alpha OH$ under these conditions gives 0.915 equivalent of $R^\gamma OH$; the rest is converted to an unidentified side-product. Actually k_r is the constant for disappearance of $R^\alpha OH$ and is 8.5% higher than the constant for conversion of $R^\alpha OH$ to $R^\gamma OH$. In other words, 8.5% of the phenylallyl alcohol is destroyed during the rearrangement (the rearrangement product, $R^\gamma OH$, once formed is stable) and a correction for this side reaction must be made when computing the concentration and composition of phenylallyl alcohol in the reaction mixture.

The sample isolated at "infinity" time (about 10 half-lives for exchange) consisted of 92.5% $R^\gamma OH$ and 7.5% $R^\alpha OH$. The O^{18} content of this sample was 0.072 atom % excess. At this point equilibration is complete and the O^{18} content of the $R^\alpha OH$ is about that of the water in the medium (0.013 atom % O^{18} excess). From these data it can be shown that the O^{18} content of the $R^\gamma OH$ is 0.080 atom % excess by use of the relationship

$$N = fN_\alpha + (1 - f)N_\gamma \qquad (14)$$

where N, N_α and N_γ are the O^{18} contents of the mixture, $R^\alpha OH$ and $R^\gamma OH$, respectively, and f is the mole fraction of $R^\alpha OH$ in the mixture.

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(6) C. A. Bunton, Y. Pocker and H. Dahn, *Chemistry & Industry*, 1516 (1958).

(7) H. Normant, *Compt. rend.*, **240**, 314 (1955).

In a control experiment it was found that O^{18}-labeled γ-phenylallyl alcohol does not undergo any measurable exchange under the conditions of the rearrangement during a period corresponding to 10 half-lives for exchange of $R^{\alpha}O^{18}H$. Thus the $R^{\gamma}OH$ does not undergo any exchange subsequent to its formation. It is apparent that rearrangement results in almost but not quite complete exchange; the O^{18} content of the $R^{\gamma}OH$ is slightly higher than that of the water in the medium.

The values of N_α (column 8) were calculated from the O^{18} contents of the samples (column 6) using eq. 14 and a value of 0.080 for N_γ. Actually, as will be shown later, N_γ varies during the rearrangement from about 0.180 to 0.080, however, the results obtained by assuming N_γ to be constant are well within experimental error of those obtained using the actual values. The O^{18} contents of the total phenylallyl alcohol in the reaction mixture (column 7) were also determined using eq. 14 and the values of f (column 4), N_γ (0.080) and N_α (column 8).

The pseudo first-order rate constant for O^{18} exchange out of the phenylallyl system, k^*_{exc}, was computed from the O^{18} contents of the phenylallyl alcohol in column 7. The constant for O^{18} exchange of the unrearranged $R^{\alpha}OH$, k_{exc}, was determined using the data in column 8.

That the method described above for determining the O^{18} content of the phenylallyl alcohol at various times is reliable was indicated by the following control experiment. A synthetic reaction mixture containing $R^{\alpha}O^{18}H$ and $R^{\gamma}OH$ (but no acid) was prepared. The composition of the phenylallyl alcohol in the mixture was 74.7% $R^{\alpha}OH$ and 25.3% $R^{\gamma}OH$ and the O^{18} content of the binary mixture in the solution was 2.33 atom % excess. A pure binary mixture of the isomeric phenylallyl alcohols was isolated by the method used in the kinetic experiment. This contained 97.3% $R^{\alpha}OH$ and the O^{18} content of this mixture was 3.05 atom % excess. From this information the value of N_α can be calculated using eq. 14 (N_γ is zero) and then the O^{18} content of the synthetic mixture can be determined. The value obtained in this way (2.34 atom % O^{18} excess) agrees with the known value. Thus it appears that the values in columns 7 and 8 are reliable.

The rate constants for (a) loss of optical activity ($k_{\alpha c}$), (b) rearrangement (k_{rc}), (c) racemization ($k_{rac\ c}$), (d) O^{18} exchange out of the phenylallyl system ($k^*_{exc\ c}$) and (e) O^{18} exchange out of unrearranged $R^{\alpha}OH$ ($k_{exc\ c}$) are given in Table II. For easy comparison the constants have been normalized by conversion to the second-order catalytic constants (*i.e.*, the values given correspond to the pseudo first-order constants at an acid concentration of 1 *M*).

As mentioned above, the spectrophotometric constant, k_r, is the constant for the disappearance of $R^{\alpha}OH$. Since $R^{\alpha}OH$ gives 91.5% $R^{\gamma}OH$ and 8.5% of an unidentified side product,[3] k_r is the sum of two constants, that for formation of $R^{\gamma}OH$ (corrected k_r) and that for formation of the side product (k_{sp}). The product composition corresponds to the relative magnitudes of the two constants. Thus k_{sp} is 8.5% of the spectrophotometric rate constant or 1.3×10^{-3} l. mole^{-1} min.$^{-1}$. The rate constants for rearrangement (k_{rc}) and loss of optical activity ($k_{\alpha c}$) in Table II have been corrected for the side reaction by subtracting the above value for k_{sp}. Thus k_{rc} is 8.5% lower and $k_{\alpha c}$ is also a little lower than the values reported earlier.[3] This correction simply amounts to subtraction of contributions to the rate constants by the side reaction. The constants for exchange were determined in such a manner that corrected values are obtained directly.

TABLE II

RATE CONSTANTS FOR THE REARRANGEMENT OF α-PHENYLALLYL ALCOHOL IN 40% AQUEOUS DIOXANE AT 30°, $\mu = 0.10$

Reaction	10^3k_c, l. mole^{-1} min.$^{-1}$
Loss of activity ($k_{\alpha c}$)	37.5 ± 0.6[a,b]
Rearrangement (k_{rc})	14.2 ± .1[a,c]
Racemization ($k_{rac\ c}$)	23.3 ± .7
Oxygen exchange ($k^*_{exc\ c}$)[d]	32.6 ± .9
Oxygen exchange ($k_{exc\ c}$)[e]	18.1 ± 1.3

[a] Corrected for side reaction. [b] Average value and mean deviation of 9 independent experiments at acid concentrations 0.01 to 0.1 *M*. [c] Average value and mean deviation of 13 experiments at acid concentrations 0.01 to 0.1 *M*. [d] Oxygen-18 exchange out of phenylallyl system. [e] Oxygen-18 exchange out of unrearranged α-phenylallyl alcohol.

Discussion

The most direct way to treat the present data is to focus attention on the racemization which accompanies the rearrangement. Comparison of k_{rac} and k_{exc} (the constant for exchange associated with the racemization) shows that exchange is a little slower than racemization or, in other words, racemization does not result in complete exchange. Although this discrepancy is small and the uncertainty in the latter constant is rather large, there is little doubt but that the difference is real. The observed value of k_{exc}/k_{rac} is 0.78 ± 0.08 which indicates 22 ± 8% of the initially formed racemic material has not exchanged oxygen, or to put it another way, exchange (substitution) results in a slight excess of inversion of configuration.

The fact that racemization does not result in complete exchange also causes a discrepancy between k_α and k^*_{exc}. Since rearrangement results in essentially complete exchange, ($k^*_{exc} - k_{exc}$) should equal k_r. It can be seen from Table II that this is the case within experimental error.

For the displacement process II k'_{rac} ($2k_{S_N2}$) would be twice as large as $k'_{exc}(k_{S_N2})$; *i.e.*, k_{exc}/k_{rac} would be 0.5. Clearly this can be ruled out. On the other hand, the data are consistent with the carbonium ion process (eq. 11). This mechanism for the racemization, isolated from the rearrangement, is illustrated in its simplest form by eq. 15.

$$d\text{-ROH}_2^{\oplus} \overset{k'_{rac}}{\rightleftarrows} \text{R}^{\oplus} + \text{H}_2\text{O} \overset{k'_{rac}}{\leftrightarrows} l\text{-ROH}_2^{\oplus} \quad (15)$$

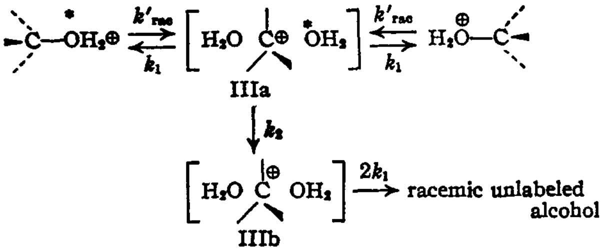
As mentioned earlier, for this process $k_{exc}/k_{rac} = 1$ (and k_α is equal to k^*_{exc}) if the water molecule formed in the dissociation becomes equivalent with the water in the solvent before the carbonium ion is converted to product. However, from other work it is not surprising that k_{exc}/k_{rac} is a little less than unity. For example, for the acid-catalyzed racemization of optically active α-phenyl ethanol in water $k_{exc}/k_{rac} = 0.86$,[8] a value similar to that observed in the present work. For the racemization of optically active *p*-methoxybenzhydrol in aqueous dioxane the rate of exchange corresponds to the rate of rearrangement; *i.e.*, $k_{exc}/k_{rac} = 1$.[9] The ratio of exchange to racemization for active *sec*-butyl alcohol is about 0.5. In this case each substitution (exchange) results in inversion.[10] This result corresponds to an SN2-type displacement mechanism for the racemization. However, there is evidence[10] that even in this case (and thus also in the others) racemization (and exchange) involves the carbonium ion mechanism (eq. 15). In this connection it is noteworthy that the rate of oxygen exchange in aqueous acid is considerably faster for *sec*-butyl alcohol[10] than for *n*-butyl alcohol.[11]

A slower rate of exchange than racemization for a carbonium ion process (eq. 15) can be interpreted in two ways. A value of 0.78 for k_{exc}/k_{rac} (the value observed in the present case) would obtain if dissociation resulted in 72% racemization and 28% inversion. In this case only 78% of the initially formed racemic material would have dissociated to form the ion (*i.e.*, the fraction which had exchanged). On the other hand, the same value for k_{exc}/k_{rac} would obtain if dissociation resulted in complete racemization but the intermediate reacted with the original water molecule 22% of the time. According to this picture all of the racemic material, including the fraction which had not exchanged, would be derived from the intermediate. The fundamental difference between these interpretations is that in the first the rate of production of the carbonium ion corresponds to k_{exc} and in the second to k_{rac}.

Bunton and co-workers[10] prefer the first interpretation; *i.e.*, when $k_{exc}/k_{rac} < 1$ they assume that the rate of formation of the carbonium ion corresponds to the rate of exchange. For example, in the case of *sec*-butyl alcohol ($k_{exc}/k_{rac} = 0.5$) they propose that the carbonium ion is converted exclusively to the opposite enantiomer from which it was formed. According to this idea the fraction of racemic product which has not exchanged has not reacted (*i.e.*, dissociated to give the intermediate).

It is difficult to visualize how or why in a reaction of this type a carbonium ion intermediate would be preferably or exclusively converted to the opposite enantiomer from which it is formed. For this and other reasons we prefer the alternate interpretation; racemization and exchange involve dissociation to give a carbonium ion intermediate which has an equal chance of being converted to either enantiomer. However, the water molecule formed in the dissociation step may be involved in the solvation shell and in the recombination step. Thus the rate of production of the carbonium ion corresponds to the rate of racemization rather than the rate of exchange. Dissociation always results in loss of optical activity but may not result in exchange.

The available data appear to be consistent with the accompanying scheme. This is a modification or elaboration of the carbonium ion mechanism (eq. 11) to include the oxygen exchange results. In this illustration optically active O^{18} labeled alcohol (the labeled atom is marked with an asterisk) dissociates to form the solvated carbonium ion III. At any instant there are only two water molecules in the solvation shell (one on each side of the plane of the cation) eligible to react with the carbonium ion. Only these two water molecules are shown in III. Presumably these molecules and the others in the solvation shell are held in position by dipole-charge interactions.



According to this picture the water molecule produced in the dissociation step occupies one of the reactive sites (*i.e.*, the initially formed carbonium ion IIIa derived from labeled alcohol is asymmetrically solvated). The carbonium ion III is converted to the two optical isomers at equal rates. However, if the carbonium ion reacts with water before the molecules occupying the active sites exchange with the solvent or other molecules in the solvation shell (*i.e.*, before IIIa is converted to IIIb) there is a 50% chance that the original water molecule will be involved in the recombination. In this case half of the racemic material derived from the intermediate (the enantiomer with the original configuration) will not have exchanged oxygen atoms.

From this model it is apparent that the value of k_{exc}/k_{rac} depends on the lifetime or stability of the carbonium ion. If $k_1 >> k_2$ a limiting situation obtains and $k_{exc}/k_{rac} = 0.5$. This is apparently the case with *sec*-butyl alcohol. The fact that the limiting value of k_{exc}/k_{rac} is 0.5 requires that only two water molecules in the solvation shell are eligible to react with the cation (one with inversion and one with retention). If there were more than two reactive sites the lower limiting value of this ratio would exceed 0.5.

In the case of *p*-methoxybenzhydrol the carbonium ion is relatively stable and the opposite limiting situation is realized; $k_1 << k_2$ and thus k_{exc}/k_{rac} is unity. With α-phenylethanol and α-phenylallyl alcohol the reactivity of the cation is such that there is partial exchange prior to return to product. According to the scheme

$$k_{exc}/k_{rac} = (k_2 + k_1)/(2k_1 + k_2)$$

From this relationship it can be shown that in a case such as the present where $k_{exc}/k_{rac} = 0.8$ the value of k_1/k_2 is $^1/_3$.

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[8] E. Grunwald, A. Heller and F. S. Klein, *J. Chem. Soc.*, 2604 (1957).

[9] C. A. Bunton, D. R. Llewellyn and I. Wilson, *ibid.*, 4747 (1958).

[10] (a) C. A. Bunton and D. R. Llewellyn, *ibid.*, 3402 (1957); (b) C. A. Bunton, A. Konasiewcz and D. R. Llewellyn, *ibid.*, 604 (1955).

[11] I. Dostrovsky and F. S. Klein, *ibid.*, 4401 (1955).

This model appears to be similar to that suggested by Grunwald and co-workers.[8] However, there are some important differences. In the first place they suggest that more than two molecules in the solvation shell can react with the ion, a proposal that is not in accord with the data for *sec*-butyl alcohol. Of more importance is the fact that they make no clear distinction between reactions of the following charge-types. On the other hand, we prefer to make a rather sharp

$$RX \longrightarrow R^{\oplus} + X^{\ominus} \tag{16}$$

$$RX^{\oplus} \longrightarrow R^{\oplus} + X \tag{17}$$

distinction between these types of reactions. In reactions of the first charge type discrete intermediates (in addition to the solvated dissociated carbonium ion) are involved which can best be described as ion pairs.[12] The so-called intimate ion pairs have well defined structures (in hydroxylic solvents providing the carbonium ion does not rearrange, optical isomers are stable) and the barrier for further separation in many cases is sufficiently high so that competing reactions (involving internal return) intervene.[13]

In reactions of the second charge type a pair of ions is not formed and ion pair intermediates involving the alkyl moiety and leaving group are not possible. In this case an asymmetrically solvated (shielded) carbonium ion is presumably involved (when the leaving group is the same as the solvent the system is symmetrical).

It should be pointed out that the model proposed for the solvated carbonium III is the same as that suggested by Doering and Zeiss[14] except for minor details such as the nature of the bonding. In fact, they suggested this model for the same reason that we have adopted it; to account for a slight excess of inversion in a carbonium ion reaction. In our view the Doering–Zeiss picture accommodates the experimental findings very nicely for reactions of the charge type illustrated by eq. 17. The Winstein picture[12] applies for reactions of the other charge type. One could argue that these two situations differ in degree rather than kind.

It is interesting to note that the γ-phenylallyl alcohol derived from $R^{\alpha}O^{18}H$ has a slightly greater O^{18} abundance than the water in the solvent.[15] In other words the rearrangement is partly intramolecular in the sense that some of the product results from recombination of the partners formed in the dissociation. This intramolecular component is analogous to ion pair return.[12]

Comparison of k_{exc} and k_r shows that most of the $R^{\alpha}O^{18}H$ exchanges oxygen before rearranging to γ-phenylallyl alcohol. The fraction of the product formed from $R^{\alpha}O^{18}H$ before and after exchange can be computed by the method used by Winstein and Trifan[16] to calculate the fractions of solvolysis product derived from an active reactant before and after racemization. The average O^{18} abundance of the α-phenylallyl alcohol is $k_r/(k_r + k_{exc})$ times the initial O^{18} abundance (k_r is the constant for disappearance of $R^{\alpha}OH$ and $(k_r + k_{exc})$ is the rate constant for disappearance of $R^{\alpha}O^{18}H$). Or to put it another way $k_r/(k_r + k_{exc})$ is the fraction of the original $R^{\alpha}O^{18}H$ converted to $R^{\alpha}OH$ before exchanging oxygen atoms. Thus 43% of the labeled alcohol rearranges before exchanging oxygen atoms or the average O^{18} content of the $R^{\alpha}O^{18}H$ is 1.52 atom % O^{18} excess. This gives rise to product having an O^{18} content about 0.06 atom % O^{18} excess higher than the water in the medium.[17] This shows that about 6 out of 152 or about 4% of the molecules rearrange intramolecularly. The intramolecular component to the rearrangement presumably is similar to that in the racemization; *i.e.*, water formed in the dissociation is involved in the solvation shell of the carbonium ion and thus has a greater chance than water in the solvent to be involved in the recombination step.

Experimental

Materials.—Benzaldehyde-O^{18} was prepared by stirring 118 g. of unlabeled benzaldehyde with 40 ml. of O^{18}-enriched water (6.10 atom % O^{18} excess) in the presence of a catalytic amount of *p*-toluenesulfonic acid for 12 hours at room temperature under nitrogen. Then the mixture was decanted into a separatory funnel and the product was taken up in ether. The ethereal solution of the product was dried over magnesium sulfate in the presence of a trace of hydroquinone. Isolation by distillation gave 106 g. of benzaldehyde-O^{18} (90.4% recovery), b.p. 72° (16 mm.), 3.69 atom % O^{18} excess.[18]

α-Phenylallyl alcohol-O^{18} was obtained by the reaction of benzaldehyde-O^{18} with vinyl Grignard reagent[7] in tetrahydrofuran solution. In the present reaction the yield was raised *ca.* 20% above that reported[7] by using a 20% excess of vinyl Grignard reagent.

In a typical preparation a solution of 1.19 moles of vinyl bromide in 750 ml. of anhydrous tetrahydrofuran (freshly distilled from lithium aluminum hydride) was added with vigorous stirring to 1.19 moles of magnesium turnings over the course of 4 hours. The rate of addition of the halide–tetrahydrofuran mixture was such that the heat of reaction maintained the temperature at 50–55°. Formation of the Grignard reagent was completed by external heating (50–55°) for an additional 4.5 hours. The tetrahydrofuran solution of vinylmagnesium bromide was allowed to cool to room temperature and then a solution of 1.00 mole of benzaldehyde-O^{18} in 300 ml. of dry tetrahydrofuran was added over the course of 2.5 hours. The reaction mixture was then stirred at room temperature for 12 hours and decomposed with 200 ml. of cold aqueous ammonium chloride. The tetrahydrofuran solution was decanted from the caked residue which was triturated with four 250-ml. portions of ether. The combined tetrahydrofuran–ether solution was dried (first Na_2SO_4, then $MgSO_4$) and the solvent was removed under reduced pressure. The residue was distilled and 116 g. (86.5% yield) of α-phenylallyl alcohol-O^{18} was obtained, b.p. 84–85° (*ca.* 2 mm.), n^{25}_D 1.5376, 3.59 atom % O^{18} excess; ultraviolet spectrum: shoulder 247.5–249 mμ (ϵ 175), λ_{max} at 252.2, 258.0 and 263.0 mμ with ϵ 242, 268 and 195, respectively.

The labeled alcohol was purified by recrystallization of the acid phthalate derivative. The method for the preparation of this derivative (83.5% yield), and the regeneration of labeled alcohol from this derivative by saponification with 50% ethanolic 5 *M* KOH (87% yield) has been described

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

(13) (a) S. Winstein and G. C. Robinson, *ibid.*, **80**, 169 (1958); (b) H. L. Goering and M. M. Pombo, *ibid.*, **82**, 2515 (1960), and earlier papers in these series.

(14) W. E. Doering and H. H. Zeiss, *ibid.*, **75**, 4733 (1953)

(15) This is in contrast to the recent report of Bunton and co-workers[6] that under slightly different conditions (60% aqueous dioxane at 25°) the O^{18} content of the rearrangement product ($R^{\gamma}OH$) was the same as that of the water in the solvent.

(16) S. Winstein and D. Trifan, THIS JOURNAL, **74**, 1154 (1952).

(17) From the relationship between the O^{18} contents of the α and γ-phenylallyl alcohols it can be seen that the O^{18} abundance of the initially formed $R^{\gamma}OH$ is about $(3.5/1.5) \times 0.080 = 0.18$ atom % O^{18} excess.

(18) The O^{18} contents were determined by the method described in ref. 13b.

previously.[3] Oxygen-18 analyses indicated that the alkyl-oxygen of the acid phthalate derivative had 3.60 atom % O^{18} excess (assuming discrete labeling) and that the pure α-phenylallyl alcohol-O^{18} had 3.54 atom % O^{18} excess.[18] Thus the purification process resulted in a loss of only *ca.* 1.4% of the oxygen-18 label. The labeled alcohol obtained by saponification of the acid phthalate derivative had b.p. 68.5–69° (0.15 mm.), $n^{25}\text{D}$ 1.5380; ultraviolet spectrum: shoulder, 248.5–249.5 mμ (ε 228), $\lambda_{\max}$ at 252.2, 258.0 and 264.0 mμ with ε 275, 287 and 213, respectively. This alcohol was redistilled twice before use in the exchange experiment.

Cinnamyl alcohol-O^{18} was prepared by the sodium borohydride reduction[19] of cinnamaldehyde-O^{18}. The cinnamaldehyde-O^{18} was prepared by equilibrating the unlabeled aldehyde with O^{18}-enriched water in the presence of a catalytic amount of *p*-toluenesulfonic acid. The cinnamyl alcohol-O^{18}, purified by recrystallization from ether–pentane, had m.p. 34.0–34.4°, $n^{25}\text{D}$ 1.5818 (supercooled liquid), and 0.54 atom % O^{18} excess; ultraviolet spectrum: $\lambda_{\max}$ at 251.0, 283.3 and 292.2 mμ with ε 17,600, 1200 and 843, respectively.

Oxygen-18 Exchange Experiments. Part A. Oxygen-18 Exchange Associated with the Rearrangement and Racemization of α-Phenylallyl Alcohol-O^{18}.—An acid ($HClO_4$) concentration of 0.0514 *M* and an initial $R^{\alpha}O^{18}H$ concentration of 0.119 *M* were used in this experiment. The reaction solution was prepared by dissolving a weighed sample of labeled alcohol in 40% aqueous dioxane.[20] The reaction mixture also contained 0.0486 *M* $LiClO_4$. Thus the ionic strength was 0.1. After a short time for temperature equilibration a 94.10-ml. aliquot was withdrawn and delivered into a 100-ml. volumetric flask containing 5.00 ml. of 1 *M* aqueous NaOH to quench the reaction. Subsequent aliquots were withdrawn at appropriate time intervals and treated in the same manner. The quenched aliquots of reaction solution were diluted to exactly 100 ml. with distilled water and sampled (1-ml. aliquots) for ultraviolet spectral analysis (k_r determination, columns 2 and 3 of Table I). The remaining 99-ml. portions of quenched reaction solutions were saturated with sodium chloride and extracted with ether (150-, 100-, 50-ml. portions). The ethereal solutions of the binary mixture of α- and γ-phenylallyl alcohols were dried over K_2CO_3. The solvent was removed under reduced pressure and *ca.* 25% of the residue was distilled. The distillation flask was then transferred to a clean semi-micro distillation apparatus and the remainder of the material was distilled. The first few drops of distillate were discarded. The main fraction from this distillation was redistilled and three roughly equal fractions were collected. The third of these fractions was that used for ultraviolet spectral analysis and oxygen-18 determinations (columns 5 and 6, respectively, of Table I). This experiment is summarized in Table I. The method used to compute the O^{18} contents of the remaining α-phenylallyl alcohol (column 8, Table I) and the total phenylallyl alcohol in the reaction mixture (column 7) from the experimentally determined values for the isolated samples (column 6) has been described in a preceding section.

Part B. Oxygen-18 Exchange between Cinnamyl Alcohol-O^{18} and the Reaction Medium.—A solution of 0.12 *M* cinnamyl alcohol-O^{18} and 0.101 *M* $HClO_4$ was prepared and thermostated at 30° for 0, 5 and 10 half-periods for loss of optical activity of active $R^{\alpha}OH$. The three samples of cinnamyl alcohol extracted from the quenched aliquots of reaction solution (isolated by distillation, and purified by recrystallization from ether–pentane) had the same melting points (34.2–34.6°) and oxygen-18 contents (0.54 atom % excess). The extinction coefficient for the absorption at 251 μ remained constant which shows that the concentration of $R\gamma OH$ did not vary during the experiment.

Isolation of Mixtures of α and γ-Phenylallyl Alcohol from Reaction Mixtures.—The following experiment was carried out to determine if the O^{18} contents of the isolated binary mixtures (column 6) and the O^{18} contents calculated from these experimental values (columns 7 and 8) were reliable. In effect this experiment is one in which known values are compared with experimentally determined values.

A mixture of *ca.* 75% α-phenylallyl alcohol-O^{18} (3.14 atom % excess) and 25% unlabeled cinnamyl alcohol was prepared. The O^{18} content of the binary mixture was 2.34 atom % O^{18} excess. This binary mixture was used to prepare a simulated reaction mixture. The solution (40% aqueous dioxane) also contained 0.1 *M* $LiClO_4$ and 0.003 *M* NaOH. A 1-ml. aliquot of this solution was withdrawn and shown to be 74.7% labeled α-isomer and 25.3% unlabeled α-isomer by ultraviolet analysis. From the composition and the O^{18} content of the α-isomer, the O^{18} content of the phenylallyl system in the reaction solution was calculated to be 2.34 atom % O^{18} excess.

The remainder of the reaction solution (99 ml.) was sampled (94.10 ml. aliquot) and a pure binary mixture of α- and γ-isomers (shown by infrared and ultraviolet spectra) was isolated as described in the kinetic experiment. The purified isolated sample consisted of 97.3% α-isomer and 2.7% γ-isomer (ultraviolet analysis) and had 3.05 atom % O^{18} excess. The calculated value of the O^{18} content of the phenylallyl alcohol in the reaction mixture (eq. 14 $N_{\gamma} = 0$) is 2.33 atom % O^{18} excess which is in excellent agreement with the known value (2.34 atom % O^{18} excess) obtained by direct analysis of the binary mixture used to make up the simulated reaction solution. Thus it appears that the isolation and analytical techniques employed in the kinetic experiment are reliable.

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[19] S. W. Chaikin and W. G. Brown, THIS JOURNAL, **71**, 122 (1949).

[20] Prepared by mixing two volumes of pure dioxane and three volumes of conductivity water at 25°; see footnote 18, ref. 3.

COMMUNICATIONS TO THE EDITOR

STEREOCHEMISTRY OF TRISUBSTITUTED DOUBLE BONDS IN TERPENOIDS

Sir:

By the use of nuclear magnetic resonance spectroscopy, it has proved possible to determine readily for the first time the stereochemistry of certain trisubstituted double bonds bearing carbonyl substituents.[1–6] A variety of trisubstituted double bond more common in nature (found in many terpenoids) is the type $A\text{-}CH_2C(CH_3){=}CHCH_2\text{-}B$; it has been stated[7] that n.m.r. cannot be used to distinguish geometrical isomers in one case of this sort. However, we have found relatively small (about 0.07 τ unit[8]) but very useful differences in the chemical shifts of the methyl hydrogens in the n.m.r. spectra of geometrical isomers for compounds with the types of double bonds shown in Table I.

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(1) L. M. Jackman and R. H. Wiley, *Proc. Chem. Soc.*, 196 (1958).

(2) J. W. K. Burrell, L. M. Jackman and B. C. L. Weedon, *ibid.*, 263 (1959).

(3) M. D. Nair and R. Adams, THIS JOURNAL, **82**, 3786 (1960).

(4) D. E. Jones, *et al.*, *J. Chem. Soc.*, 2349 (1960).

(5) R. R. Fraser, *Can. J. Chem.*, **38**, 549 (1960).

(6) S. Fujiwara, *et al.*, *Bull. Chem. Soc. Japan*, **33**, 428 (1960).

(7) R. H. Wiley and L. M. Jackman in L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, Inc., New York, N. Y., 1959, pp. 121, 124.

(8) G. V. D. Tiers, *J. Phys. Chem.*, **62**, 1151 (1958).