[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

# The Acid-catalyzed Rearrangement of $\alpha$-Phenylallyl Alcohol in Aqueous Dioxane[1]

BY HARLAN L. GOERING AND RICHARD E. DILGREN[2]

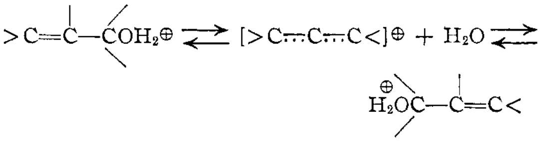
RECEIVED OCTOBER 24, 1958

The rates of (a) acid-catalyzed rearrangement ($k_r$) of $\alpha$-phenylallyl alcohol to cinnamyl alcohol and (b) acid-catalyzed loss of optical activity ($k_a$) of optically active $\alpha$-phenylallyl alcohol in 40% aqueous dioxane have been determined. The rates of rearrangement and loss of optical activity are both proportional to the acid concentration over the range of concentrations investigated (to 0.1 $M$). The two pseudo first-order rate constants, $k_r$ and $k_a$, are steady throughout the reaction and $k_a > k_r$ at the seven acid concentrations at which the two were compared. The present observations, together with information recorded in the literature, suggest that the first-order isomeric rearrangement of the conjugate acid of $\alpha$-phenylallyl alcohol involves a carbonium-ion mechanism. If this interpretation is correct, the ratio of the rates at which the phenylallyl cation is converted to (a) cinnamyl alcohol and (b) $\alpha$-phenylallyl alcohol can be determined from the value of $k_a/k_r$.

From earlier work, *viz.*, the kinetic studies of Braude and co-workers,[3] it is clear that the acid-catalyzed rearrangement of allylic alcohols involves protonation (eq. 1) followed by a first-order isomeric rearrangement of the conjugate acid of the allylic alcohol (eq. 2). Available information concerning the mechanism of the rearrangement (eq. 2) and various mechanisms which have been proposed were discussed in a previous paper,[4] and it was concluded that the most likely (or most general) mechanism for reactive allylic systems is a dissociation–recombination carbonium ion process (eq. 3).

$$\mathrm{ROH} + \mathrm{SH}^{\oplus} \rightleftarrows \mathrm{ROH_2}^{\oplus} + \mathrm{S} \qquad (1)$$

$$\mathrm{ROH_2}^{\oplus} \rightleftarrows \mathrm{R'OH_2}^{\oplus} \qquad (2)$$



(3)

In order to obtain additional information concerning mechanistic details of this reaction we have reinvestigated the acid-catalyzed rearrangement of $\alpha$-phenylallyl alcohol ($\mathrm{R^aOH}$) to cinnamyl alcohol ($\mathrm{R^\gamma OH}$).

$$\underset{(\mathrm{R^aOH})}{\mathrm{C_6H_5CHOHCH{=}CH_2}} \longrightarrow \underset{(\mathrm{R^\gamma OH})}{\mathrm{C_6H_5CH{=}CHCH_2OH}}$$

The rearrangement of $\mathrm{R^aOH}$[5] and similar alcohols[3] has been investigated previously by Braude and co-workers. Systems of this type are well suited for kinetic studies because (a) the product, $\mathrm{R^\gamma OH}$, is sufficiently more stable than the reactant so that the reaction for all practical purposes is irreversible, and (b) the reaction can be followed spectrophotometrically.

It has been shown that for $\alpha$-phenylallyl alcohol ($\mathrm{R^aOH}$) and other allylic alcohols[3,4] the rate of rearrangement is first order in alcohol and lyonium ion ($\mathrm{SH}^{\oplus}$)—at high acid concentrations the rate parallels the acidity function, $H_0$.[3] Thus at low acid concentrations

$$\text{rate} = k_{rc}\,[\mathrm{SH}^{\oplus}]\,[\mathrm{R^aOH}] \qquad (4)$$

However, since $[\mathrm{SH}^{\oplus}]$ is constant the reaction is pseudo first order and the rate expression in its simplest form is

$$\text{rate} = k_r\,[\mathrm{R^aOH}] \qquad (5)$$

As has been emphasized previously,[3] this kinetic behavior corresponds to the process

$$\mathrm{R^aOH} + \mathrm{SH}^{\oplus} \overset{K}{\rightleftarrows} \mathrm{R^aOH_2}^{\oplus} + \mathrm{S} \qquad (6)$$

$$\mathrm{R^aOH_2}^{\oplus} \xrightarrow{k'_r} \mathrm{R^\gamma OH_2}^{\oplus} \qquad (7)$$

Thus

$$k_r = k_{rc}\,[\mathrm{SH}^{\oplus}] = k'_r\,K[\mathrm{SH}^{\oplus}] \qquad (8)$$

If the first-order rearrangement of $\mathrm{R^aOH_2}^{\oplus}$ (eq. 7) involves the carbonium ion mechanism illustrated by equation 9, the pseudo first-order constant, $k_r$, is a composite as shown by equation 10.

$$\mathrm{R^aOH_2}^{\oplus} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} [\mathrm{C_6H_5CH{\cdots}CH{\cdots}CH_2}]^+ + \mathrm{H_2O} \xrightarrow{k_2} \mathrm{R^\gamma OH_2}^{\oplus} \qquad (9)$$

$$k_r = [\mathrm{SH}^{\oplus}]K\,k_1k_2/(k_{-1} + k_2) \qquad (10)$$

Since there are no asymmetric centers in the product $\mathrm{R^\gamma OH}$, it is obvious that rearrangement of optically active $\mathrm{R^aOH}$ would result in complete loss of optical activity. Moreover, regardless of mechanism, the rate would be expected to be pseudo first order as illustrated by equation 11 where $k_a$ is the pseudo first-order rate constant for loss of optical activity. In other words the process

$$\text{rate} = k_{ac}\,[\mathrm{SH}^{\oplus}][\mathrm{R^aOH}] = k_a\,[\mathrm{R^aOH}] \qquad (11)$$

would be expected to involve formation of the conjugate acid of $\mathrm{R^aOH}$ followed by the first-order process shown below.

$$\text{(active) } \mathrm{R^aOH_2}^{\oplus} \xrightarrow{k'_a} \text{inactive products} \qquad (12)$$

If rearrangement involves the carbonium ion mechanism (eq. 9) the rate of loss of optical activity will correspond to the rate of production of the carbonium ion in which case

$$k_a = [\mathrm{SH}^{\oplus}]Kk_1 \qquad (13)$$

From the above equations it can be shown that

$$k_a/k_r = k'_a/k'_r = 1 + (k_{-1}/k_2) \qquad (14)$$

The latter equation shows that if $(k_{-1}/k_2) > 0$, the polarimetric rate constant ($k_a$) will exceed the spectrophotometric rate constant ($k_r$) and in fact if the carbonium ion mechanism operates ex-

---

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

[2] United States Rubber Co. Fellow, 1958–1959; du Pont Summer Research Assistant 1956.

[3] E. A. Braude, *Quart. Revs.*, **4**, 404 (1950); *Ann. Rept. Chem. Soc.*, **46**, 114 (1949).

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

[5] E. A. Braude, E. R. H. Jones and E. S. Stern, *J. Chem. Soc.*, 396 (1946).

clusively, $(k_a/k_r)$ will provide a measure of $(k_{-1}/k_2)$, *i.e.*, the fate of the carbonium ion. In the present work the polarimetric $(k_a)$ and spectrophotometric $(k_r)$ rates for the rearrangement of α-phenylallyl alcohol in 40% aqueous dioxane have been determined at acid ($HClO_4$) concentrations up to 0.1 molar.

That the phenylallyl carbonium ion might be converted to $R^aOH_2^{\oplus}$, the least stable of the two possible products, at a rate comparable to the rate at which it is converted to $R^{\gamma}OH_2^{\oplus}$ was indicated by several observations recorded in the literature. Meisenheimer and co-workers observed that the initially formed product from the solvolysis of cinnamyl chloride in acetic acid, ethanol and water contained substantial amounts (as high as 45%) of the corresponding α-phenylallyl derivative.[6] Similarly, ethanolysis of cinnamyl bromide gives a mixture of α- and γ-phenylallyl ethyl ether containing as much as 30% of the α-phenylallyl isomer.[6a] It has also been observed[5] that the initial product from the acid-catalyzed rearrangement of α-phenylallyl alcohol in aqueous ethanol contains α-phenylallyl ethyl ether which subsequently rearranges to the γ-phenylallyl isomer. Finally, it has been observed[7] that the acid-catalyzed rearrangement of α-phenylallyl *p*-nitrobenzoate in chlorobenzene in the presence of $C^{14}$-labeled *p*-nitrobenzoic acid results in exchange with and without rearrangement. It seems likely that the phenylallyl carbonium ion is an intermediate in some or all of these reactions and in each case the two products (*i.e.*, the α- and γ-phenylallyl isomers) are formed at comparable rates.

## Results

α-Phenylallyl alcohol ($R^aOH$) was prepared from phenylmagnesium bromide and acrolein.[5,8] When purified by the method used in the earlier work[5,8] (distillation) the product contained a small amount of cinnamyl alcohol (shown to be present by the ultraviolet spectrum) and an unidentified impurity. Cinnamyl alcohol ($R^{\gamma}OH$) does not interfere in the kinetic experiments. However, the unidentified substance caused a downward drift in the pseudo first-order constants $(k_r)$ after two half-lives. The latter material could be removed by fractionation and the alcohol used in one of the experiments was purified in this way. The α-phenylallyl alcohol used in all but one of the rest of the kinetic experiments was purified by recrystallization of the acid phthalate derivative. What appears to be pure α-phenylallyl alcohol, $\lambda_{max}$ 247 mμ (165), 252 mμ (206), 258 mμ (232), 264 mμ (173), was obtained by reduction of the acid phthalate with lithium aluminum hydride. These extinction coefficients are from *ca.* $^1/_5$[5] to $^1/_8$[8b] of the values reported previously. That the low extinction coefficients were not due to partial reduction of the double bond was shown by the fact that the optical densities of solutions after rearrangement at 251 mμ (styrene chromophore) were the same for this material as for samples of $R^aOH$ (a) obtained by saponification of the acid phthalate, and (b) purified by distillation.

The alcohol used in some of the experiments was obtained by saponification of α-phenylallyl acid phthalate with concentrated alkali. The spectral data, shoulder at 247 mμ (285), $\lambda_{max}$ 252 mμ (331), indicated the presence of trace amounts (*ca.* 0.8%) of cinnamyl alcohol.

α-Phenylallyl alcohol was also prepared by reduction of phenylethynyl acid phthalate with lithium aluminum hydride.[9] This material had lower extinction coefficients for the maxima than that obtained by the lithium aluminum hydride reduction of α-phenylallyl acid phthalate. However, the extinction coefficients of the rearrangement product after ten half-lives for rearrangement were also lower than those observed when pure $R^aOH$ was used. Evidently the $R^aOH$ prepared by this method contained α-phenylpropanol or phenylethynylcarbinol. The rate constants for the various samples of $R^aOH$ described above were indistinguishable.

The acid-catalyzed ($HClO_4$) rearrangement of α-phenylallyl alcohol ($R^aOH$) to cinnamyl alcohol ($R^{\gamma}OH$) in 40% aqueous dioxane was followed by a modification of the spectrophotometric method developed by Braude and co-workers.[5] Pseudo first-order rate constants were determined for seven acid concentrations (from 0.01 to 0.1 *M*) by use of equation 15 where $D_0$, $D_t$ and $D_\infty$ are optical densities at zero time, time *t* and ten half-lives. Lithium perchlorate was added as required so that the ionic strength (μ) was the same (0.1) in all of the experiments.

$$k_r = (1/t)\ln[(D_\infty - D_0)/(D_\infty - D_t)] \qquad (15)$$

The results of the pertinent kinetic experiments are summarized in Table I. The reactions were

TABLE I

RATE CONSTANTS FOR ACID-CATALYZED REARRANGEMENT OF α-PHENYLALLYL ALCOHOL IN 40% AQUEOUS DIOXANE AT 30.02°; IONIC STRENGTH = 0.10 μ

| Expt. | [ROH] ($10^2$ *M*) | [HClO$_4$] ($10^2$ *M*) | [LiClO$_4$] ($10^2$ *M*) | $\epsilon_\infty$ $10^{-3}$ | $10^3 k_r$, min.$^{-1}$ | $10^3 k_{rc}$, l. mole$^{-1}$ min.$^{-1}$ |
|---|---|---|---|---|---|---|
| 1 | 7.1[a] | 10.00 | 0.00 | 16.6 | 1.55 ± 0.01 | 15.5 |
| 2 | 12[a] | 10.00 | .00 | 16.4 | 1.54 ± .02 | 15.4 |
| 3 | 14[a] | 10 00 | .00 | 16.7 | 1.56 ± .02 | 15.6 |
| 4 | 12[b] | 10.00 | .00 | 15.8 | 1.56 ± .01 | 15.6 |
| 5 | 12[c] | 9.11 | 1.00 | 16.6 | 1.41 ± .02 | 15.5 |
| 6 | 12[a] | 7.68 | 2.50 | 16.3 | 1.19 ± .01 | 15.5 |
| 7 | 12[a] | 5.09 | 5.00 | 16.3 | 0.778 ± .01 | 15.3 |
| 8 | 12[d] | 3.70 | 6.25 | 16.8 | .566 ± .007 | 15.3 |
| 9 | 12[a] | 2.52 | 7.50 | 16.2 | .401 ± .007 | 15.9 |
| 10 | 12[a] | 2.52 | 7.50 | 16.4 | .391 ± .008 | 15.5 |
| 11 | 12[e] | 2.52 | 7.50 | 16.0 | .385 ± .006 | 15.3 |
| 12 | 12[a] | 1.44 | 8.50 | 16.2 | .225 ± .002 | 15.6 |
| | | | | | | 15.5 ± 0.1 |

[a] *dl*-α-Phenylallyl alcohol obtained by saponification of the pure *dl*-acid phthalate. [b] *dl*-α-Phenylallyl alcohol obtained by $LiAlH_4$ reduction of phenylethynyl acid phthalate. [c] (−)α-Phenylallyl alcohol obtained by reduction ($LiAlH_4$) of the (+)-acid phthalate. [d] (−)α-Phenylallyl alcohol obtained by saponification of the (+)-acid phthalate. [e] α-Phenylallyl alcohol purified by fractionation.

---

(6) (a) J. Meisenheimer and J. Link, *Ann.*, **479**, 211 (1930); (b) J. Meisenheimer and G. Beutter, *ibid.*, **508**, 58 (1934).

(7) E. A. Braude and D. W. Turner, *J. Chem. Soc.*, 2404 (1958).

(8) (a) D. I. Duveen and J. Kenyon, *ibid.*, 1697 (1939); (b) A. Hillmer and P. Schorning, *Z. physik. Chem.*, **168A**, 81 (1934).

(9) It has been shown previously that acetylenic alcohols are reduced to allylic alcohols by lithium aluminum hydride; J. D. Chanley and H. Sobotka, THIS JOURNAL, **71**, 4140 (1949); W. Oroshnik, G. Karmas and A. D. Mebane, *ibid.*, **74**, 3807 (1952).

followed to from 80 to 93% completion and no trends in $k_r$ were observed. The clean pseudo first-order behavior throughout the reaction is illustrated by the upper line in Fig. 1 and by the data for a typical kinetic experiment included in the Experimental section. It is clear from the constancy of the second-order catalytic constants ($k_{rc}$) in the last column of Table I that the rate is proportional to the acid concentration over the range 0.01 to 0.1 $M$.

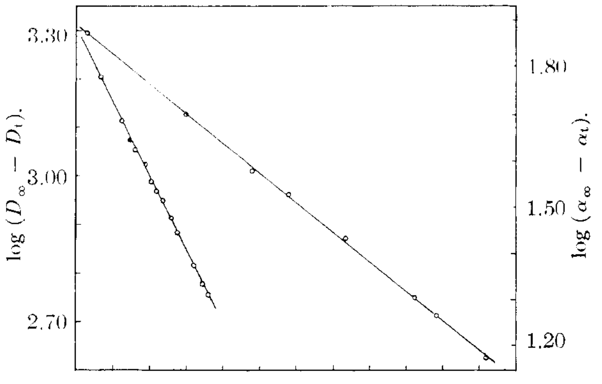


Fig. 1.—Pseudo first-order rates of rearrangement (upper line, left-hand scale), expt. 5, and loss of optical activity (lower line, right-hand scale), expt. 14, of (−)-α-phenylallyl alcohol in 40% aqueous dioxane, [$HClO_4$] = 0.0911 $M$, at 30°.

As shown by Table I the extinction coefficients of the reaction solutions after ten-half periods, $\epsilon_\infty$ (calculated from $D_\infty$) at 251 mμ (styrene chromophore) were about 16,400. This is about 8% lower than the value observed for pure *trans*-cinnamyl alcohol, $\lambda_{max}$ 251.0 mμ (17,900). This discrepancy was noticed earlier and attributed to (a) the formation of a mixture of *cis*- and *trans*-$R^\gamma OH$[5] or (b) establishment of equilibrium between $R^aOH$ and $R^\gamma OH$ rather than complete conversion of $R^aOH$ to $R^\gamma OH$.[5,10] The data presented in Fig. 2 show that neither of these interpretations is correct. These data show how the extinction coefficients of 0.12 $M$ solutions of α-phenylallyl alcohol (lower curve) and *trans*-cinnamyl alcohol (upper line) in 40% aqueous dioxane ($HClO_4$ = 0.1 $M$) at 30° vary with time. Solvent (containing acid) from the same batch was used for this pair of experiments and the data were reproducible.

If equilibrium were established at *ca.* 92% conversion, $k_r$ would be the sum of the forward and reverse rate constants—the observed, rather than the calculated, values of $D_\infty$ were used to compute the constants. Clearly the rate constant and thus half-period for equilibration would be the same for the two isomers. The data, however, show that at 10 half-lives for rearrangement, *ca.* 72 hr., the value of $\epsilon$ for $R^\gamma OH$ has decreased only slightly, *ca.* 1%. This shows that destruction of $R^\gamma OH$ subsequent to its formation is negligible at ten half-lives for the rearrangement of $R^aOH$. Thus it is clear that the low value for $\epsilon_\infty$ is due to the fact that $R^aOH$ is converted in part (*ca.* 8%) to some product other than $R^\gamma OH$ (perhaps phenylallene which polymerizes). This by-product evidently does not absorb stronger at 251 mμ than the reactant and consequently does not interfere with the kinetic measurements. Apparently $R^\gamma OH$ is also converted to this material but at a much slower rate. The data suggest that the rate of formation of the unknown material from the isomeric alcohols may be proportional to the relative rates of conversion of the alcohols to the phenylallyl carbonium ion.

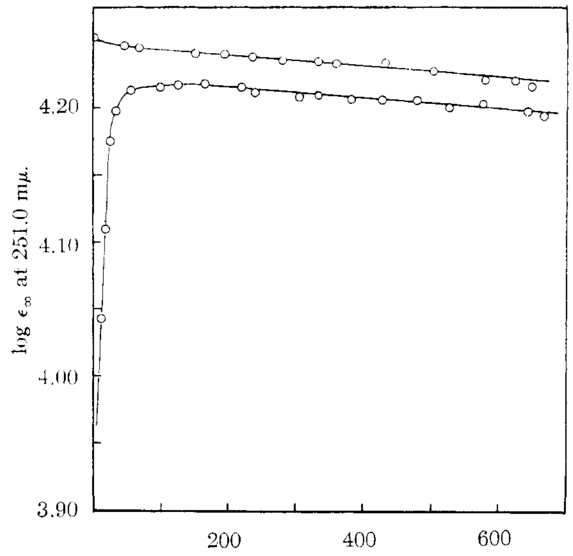


Fig. 2.—Plots of log $\epsilon$ *versus* time for α-phenylallyl alcohol (lower curve) and cinnamyl alcohol (upper curve) in 40% aqueous dioxane at 30°, [ROH] = 0.12 $M$, [$HClO_4$] = 0.100.

Since rearrangement of $R^aOH$ gives less than an equivalent amount of $R^\gamma OH$ it is apparent that the pseudo first-order constant for the disappearance of $R^aOH$ will be obtained using the observed rather than the calculated value of $D_\infty$. The constants given in Table I were calculated in this manner. These constants have not been corrected for the side reaction and thus are presumably about 8% higher than the true value for the conversion of $R^aOH$ to $R^\gamma OH$.

Optically pure (−)-$R^aOH$ was prepared by saponification or by lithium aluminum hydride reduction of optically pure (+)-α-phenylallyl acid phthalate.[8a] The pseudo first-order rate constants for loss of optical activity ($k_a$) were determined from the rate of loss of optical activity. Concentrations of (−)-$R^aOH$ were chosen so that the total observed change in rotation would be at least 0.5° and individual rotations were reproducible to within 0.004°. In these experiments the loss of optical activity was complete and the polarimetric constants ($k_a$) were steady over the range that the reaction was followed (70% to 75% completion). As with the spectrophotometric experiments, the ionic strength was 0.1, *i.e.*, [$HClO_4$] + [$LiClO_4$] = 0.1. The first-order behavior is illustrated by the lower line in Fig. 1 and by the data for a typical experiment in the Experimental section. The pertinent kinetic experiments are summarized

---

(10) E. A. Braude and E. S. Stern, *J. Chem. Soc.*, 1096 (1947).

in Table II. These data (column 6) show that the rate of loss of optical activity is proportional to the acid concentration.

TABLE II

RATE CONSTANTS FOR ACID-CATALYZED LOSS OF OPTICAL ACTIVITY OF (−)-α-PHENYLALLYL ALCOHOL IN 40% AQUEOUS DIOXANE AT 30.02°; IONIC STRENGTH = 0.10 μ

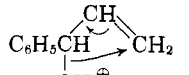
| Expt. | [ROH] ($10^2$ $M$) | [HClO$_4$] ($10^2$ $M$) | [LiClO$_4$] ($10^2$ $M$) | $10^3 k_a$, min.$^{-1}$ | $10^3 k_{ac}$, l. mole$^{-1}$ min.$^{-1}$ | $k_a/k_r$[a] |
|---|---|---|---|---|---|---|
| 13 | 12[b] | 10.00 | 0.00 | 3.87 ± 0.10 | 38.7 | 2.50 ± 0.08 |
| 14 | 12[b] | 9.11 | 1.00 | 3.57 ± .10 | 39.2 | 2.53 ± .11 |
| 15 | 12[b] | 7.68 | 2.50 | 3.02 ± .10 | 39.3 | 2.54 ± .10 |
| 16 | 12[b] | 5.09 | 5.00 | 1.98 ± .04 | 38.9 | 2.54 ± .05 |
| 17 | 12[c] | 3.70 | 6.25 | 1.39 ± .05 | 37.6 | 2.46 ± .12 |
| 18 | 15[b] | 2.52 | 7.50 | 0.981 ± .029 | 38.9 | |
| 19 | 12[b] | 2.52 | 7.50 | 1.01 ± .02 | 40.1 | 2.54 ± 0.12 |
| 20 | 14[c] | 2.52 | 7.50 | 0.994 ± .035 | 39.4 | |
| 21 | 12[c] | 1.44 | 8.50 | 0.542 ± .013 | 37.6 | 2.41 ± .08 |
| | | | | | 38.8 ± 0.6 | 2.50 ± 0.04 |

[a] Values of $k_r$ taken from column 6, Table I; the indicated uncertainties were estimated from the limiting values of the rate constants. [b] (−)-Alcohol obtained by LiAlH$_4$ reduction of (+)-acid phthalate. [c] (−)-Alcohol prepared by hydrolysis of (+)-acid phthalate.

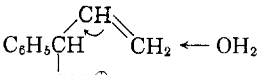
As shown in the last column of Table II, $k_a > k_r$ and the ratio $k_a/k_r$ is independent of acid concentration. The same reaction solution was used for experiments 5 and 14 and also for experiments 8 and 17, *i.e.*, the spectrophotometric as well as the polarimetric rates were determined using optically active material. In these two pairs of experiments $k_a$ and $k_r$ were obviously determined for identical conditions, *i.e.*, solvent and concentrations. The results of experiments 5 and 14 are shown graphically in Fig. 1. In cases where the same reaction solution was not used to measure $k_a$ and $k_r$, one of the constants was corrected (less than 1%) to account for the slight difference in the acidity of the two reaction solutions.

## Discussion

The fact that $k_a > k_r$ clearly shows that the rearrangement does not proceed exclusively by the intramolecular process (I)[3] and/or the S$_N$2′ type process II[3]; both of these require that $k_a = k_r$.



I

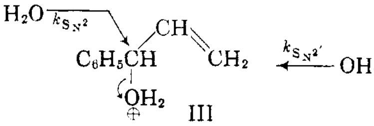


II

The data appear to be consistent with the carbonium ion mechanism shown by equation 9. If this interpretation is correct the fate of the carbonium ion, *i.e.*, $k_{-1}/k_2$, can be determined from the value of $k_a/k_r$ (eq. 14). Under the present conditions (40% aqueous dioxane, 30°) the calculated value of $k_{-1}/k_2$ is 1.50 ± 0.04, *i.e.*, the carbonium ion returns to $R^aOH_2^{\oplus}$ 50% faster than it is converted to $R^{\gamma}OH_2^{\oplus}$.

It should be pointed out that in this treatment (eq. 14) the assumption is made that racemic $R^aOH_2^{\oplus}$ results from the recombination step. In other words, it is assumed that the departing water molecule becomes kinetically equivalent with the water in the solvent. If recombination to give $R^aOH_2^{\oplus}$ involves excess retention of configuration the calculated value of $k_{-1}/k_2$ will be low because that fraction of the process which is stereospecific will not be detected by the present method. Conversely, if recombination involves excess inversion of configuration the calculated value of $k_{-1}/k_2$ will be too high.

In addition to the carbonium-ion mechanism there is another process which could account for the excess racemization. As indicated above, the S$_N$2′ type mechanism requires that $k_a = k_r$. However, the simultaneous operation of S$_N$2 and S$_N$2′ attack by water (III) would result in excess racemization.



III

For this process

$$k_a' = 2k_{S_N2} + k_{S_N2'} \qquad (16)$$

$$k_r' = k_{S_N2'} \qquad (17)$$

$$k_a'/k_r' = k_a/k_r = 2(k_{S_N2}/k_{S_N2'}) + 1 \qquad (18)$$

Thus if $k_{S_N2}/k_{S_N2'} = 0.75$ the observed value of 2.50 for $k_a/k_r$ will obtain.

For several reasons the carbonium ion mechanism is more attractive than the process illustrated by III. In the first place, as has been pointed out,[4] for the latter process one would expect the rate to be proportional to the acid concentration rather than $H_0$. On the other hand, a specific water molecule from the medium is not involved in the transition state for the carbonium ion process and the rate would be expected to parallel $H_0$, which is the case.[3] Another difficulty with the displacement process (III) is that the primary isomer, $R^{\gamma}OH$, would be expected to undergo displacement more rapidly than the secondary isomer ($R^aOH$). However, there is evidence that the primary isomer undergoes exchange at a rate that is slow relative to that of the rearrangement (with exchange) of the secondary isomer. For example, it has been observed[5] that the acid-catalyzed rearrangement of $R^aOH$ in 80% aqueous ethanol gives a mixture of cinnamyl ethyl ether (60%) and cinnamyl alcohol (40%). Under similar conditions cinnamyl alcohol is not converted to cinnamyl ethyl ether. Perhaps the most convincing evidence in this connection is the recent observation[11] that cinnamyl alcohol exchanges oxygen in aqueous dioxane containing acid very much slower than $R^aOH$ undergoes rearrangement (with oxygen exchange).

In another problem the rate of $O^{18}$ exchange between the phenylallyl system and the medium under the conditions used in the present work is being investigated. It appears that it will be possible to distinguish between the displacement (III) and carbonium ion (eq. 9) mechanisms by comparing the rate of $O^{18}$ exchange with the rates of rearrangement and loss of optical activity. For the carbonium ion mechanism the rate of exchange should equal the rate of carbonium ion formation and the following relative rates would be predicted, $k_a$ (2.50) = $k_{exc}$ (2.50) > $k_r$ (1). For the displacement mechanism

$$k_{exc}' = k_{S_N2} + k_{S_N2'} \qquad (19)$$

---

[11] Private communication from Drs. C. A. Bunton and Y. Pocker, University College, London.

From equations 17 and 19 and the value for $k_{SN2}/k_{SN2}'$ (calculated from the observed value of $k_a/k_r$) it can be shown that

$$k_{exc}'/k_r' = k_{exc}/k_t = (k_{SN2}/k_{SN2}') + 1 = 1.75$$

Thus for the latter process (III) the predicted sequence is $k_a$ (2.50) $k_{exc}$ (1.75) $k_r$ (1).

## Experimental[12]

**Materials.**—*dl*-α-Phenylallyl alcohol was prepared by the Grignard reaction in 65–72% yield according to a previously described method.[5,8] One distillation of the crude product, however, did not yield homogeneous material. A center-cut from the first distillation of the crude product was carefully refractionated and a small middle fraction was collected. A sample of this alcohol was used in expt. 11 and had b.p. 91.5° (5 mm.), $n^{25}$D 1.5390; ultraviolet spectrum: shoulder, 247.5–249.0 mμ (ε 508), $\lambda_{max}$ at 252.0, 257.5 and 263.5 mμ with ε 549, 543 and 418, respectively (lit.[5] b.p. 53–54° (0.15 mm.), $n^{14.5}$D 1.5464; ultraviolet spectrum: $\lambda_{max}$ at 248.0 and 251.0 mμ with ε 830 and 820, respectively).

*dl*-α-Phenylallyl acid phthalate was prepared in a crude yield of 90%, m.p. 71.4–72.6°, according to a previously described method.[8a] After two recrystallizations from $CS_2$–pentane (*ca.* 85% recovery) it had m.p. 72.2–73.2° (lit.[8a] m.p. 73–74°) and a neutral equivalent of 282.4 (calcd. 282.3).

(+)-α-Phenylallyl acid phthalate was obtained by the method of Duveen and Kenyon[8a] as a viscous semi-solid with $[\alpha]^{22}$D +51.3° (*l* 4.0, *c* 1.53 in $CS_2$) (lit.[13] $[\alpha]^{22}$D +51.0° (*l* 2.0, *c* 5.03 in $CS_2$) and neutral equivalent 281. (calcd. 282). The infrared spectra of carbon disulfide solutions of the optically active acid phthalate and authentic *dl*-acid phthalate were indistinguishable.

**Saponification of *dl*-α-Phenylallyl Acid Phthalate.**—A solution of 0.633 mole of *dl*-α-phenylallyl acid phthalate in 500 ml. of aqueous 8 *M* NaOH was steam-distilled. Isolation of the product[8a] resulted in a 90.4% yield of α-phenylallyl alcohol, b.p. 78–79° (0.75 mm.), $n^{25}$D 1.5392; ultraviolet spectrum: $\lambda_{max}$ at 247.3, 251.6, and 257.2 mμ with ε 640, 656 and 563, respectively. Apparently this product contained trace amounts of cinnamyl alcohol.

**Lithium Aluminum Hydride Reduction of (+)-α-Phenylallyl Acid Phthalate.**—A solution of 6.12 g. of lithium aluminum hydride in 300 ml. of dry ether was added to 22.75 g. of the (+)-α-phenylallyl acid phthalate described above in 400 ml. of dry ether at −10°. The addition required 2.5 hours. The reaction mixture was then stirred for an hour at 0° and decomposed with 150 ml. of aqueous ammonium chloride solution. The product was taken up in ether and dried over $K_2CO_3$. After removal of the solvent the residue was distilled and 6.60 g. (61%) of (−)-α-phenylallyl alcohol was obtained, b.p. 78–79° (1 mm.), $n^{25}$D 1.5386, $[\alpha]^{22}$D −5.19° (*l* 0.5, neat) (lit.[13] $[\alpha]^{17}_{5893}$ −5.12°); ultraviolet spectrum: $\lambda_{max}$ at 247.4, 252.1, 257.8 and 263.8 mμ with ε 165, 206, 232 and 173, respectively.

*Anal.* Calcd. for $C_9H_{10}O$: C, 80.56; H, 7.51. Found: C, 80.93; H, 7.51.

**Saponification of (+)-α-Phenylallyl Acid Phthalate.**—The method of Duveen and Kenyon[8a] was employed. (+)-α-Phenylallyl acid phthalate (9.80 g.) was treated with a slight excess of 50% ethanolic 5 *M* KOH for 11 hours at 30°. The (−)-α-phenylallyl alcohol (2.63 g., 56.5%) isolated by steam distillation had b.p. 76° (0.6 mm.), $n^{25}$D 1.5385, $[\alpha]^{22}$D −5.17° (*l* 0.5, neat); ultraviolet spectrum: shoulder 247.5–249.0 mμ (ε 285), $\lambda_{max}$ at 252.0, 257.7 and 263.7 mμ with ε 331, 329 and 240, respectively.

**Cinnamyl Alcohol.**—The method of Chaikin and Brown[14] was utilized for the sodium borohydride reduction of cinnamaldehyde to cinnamyl alcohol; a 90% yield of the crude product was obtained, b.p. 128.5° (10 mm.), m.p. 27.0–28.5°, $n^{25}$D 1.5804; ultraviolet spectrum: $\lambda_{max}$ at 250.5, 283.5 and 292.2 mμ with ε 17,300, 1170 and 824, respectively. After recrystallization from ether–pentane to constant m.p., $n^{25}$D (taken on the super-cooled liquid), ultraviolet and infrared spectra (total of 4 recrystallizations required), the pure cinnamyl alcohol had m.p. 34.4–34.6°, $n^{25}$D 1.5818; ultraviolet spectrum: $\lambda_{max}$ at 251.0, 283.5 and 292.2 mμ with ε 17,900, 1210 and 840, respectively (lit.[5] b.p. 139° (16 mm.), $n^{22}$D 1.5805, m.p. 33°; ultraviolet spectrum: $\lambda_{max}$ at 248.0, 251.0, 282.0 and 291.0 mμ with ε 19,000, 19,500, 1350 and 1050, respectively).

**Phenylethynylcarbinol** was prepared in 40% yield by the reaction of benzaldehyde and sodium acetylide in liquid ammonia.[15,16] After distillation the product had b.p. 87–88° (0.4 mm.), $n^{25}$D 1.5492 (lit. b.p. 114° (12 mm.),[15] $n^{20}$D 1.5508[15]; b.p. 115–116° (16 mm.),[16] $n^{21}$D 1.5482[16]).

**Phenylethynyl Acid Phthalate.**—Phenylethynyl acid phthalate was obtained in a crude yield of 82% by the method used to prepare α-phenylallyl acid phthalate. The crude product had m.p. 100–101.5°, and after three recrystallizations from carbon tetrachloride the pure acid ester melted at 103.4–103.6° (lit.[16] m.p. 94°); another recrystallization did not change the melting point; neutral equivalent calcd. 280.3, found 281.0.

**Lithium Aluminum Hydride Reduction of Phenylethynyl Acid Phthalate.**—Reduction by the method described by Doering and Zeiss[17] ("normal" addition) resulted in a 67% yield of α-phenylallyl alcohol, b.p. 73.0–73.5° (0.6 mm.), $n^{25}$D 1.5371; ultraviolet spectrum: $\lambda_{max}$ at 247.5, 252.2, 258.0 and 264.0 mμ with ε 138, 178, 210 and 159, respectively.

*Anal.* Calcd. for $C_9H_{10}O$: C, 80.56; H, 7.51. Found: C, 80.66; H, 7.24.

**Rates of Rearrangement.**—Reaction solutions were prepared by dissolving weighed samples of α-phenylallyl alcohol (containing at the most a few per cent. of $R^{\gamma}OH$) in 40% aqueous dioxane.[18] If the experiment extended over several days the reaction mixture was distributed into ampules; otherwise the reactions were carried out in volumetric flasks. After temperature equilibration 1-ml. aliquots were withdrawn at appropriate time intervals and quenched with a slight excess of alcoholic NaOH; appropriate dilutions were then made with 95% ethanol, and the resultant solutions analyzed with a Cary recording spectrophotometer in 1-cm. cells. The pseudo first-order rate constants were calculated from the optical densities at 251.0 mμ by use of equation 15. Aliquots of the reaction solution were titrated with standard base to determine the perchloric acid concentration. From 8 to 21 "points" were determined during a

TABLE III

REARRANGEMENT OF *dl*-α-PHENYLALLYL ALCOHOL AT 30° IN 40% AQUEOUS DIOXANE

$[HClO_4]$ = 0.0509 *M*, μ = 0.10 (Expt. 7)

| *t*, min. | $D_t$ | $10^3 k_r$, min.$^{-1}$ |
|---|---|---|
| 0 | 105.4 | |
| 90 | 231.9 | 0.793 |
| 150 | 310.4 | .786 |
| 375 | 571.9 | .779 |
| 450 | 565.3 | .789 |
| 1230 | 1229 | .764 |
| 1320 | 1284 | .772 |
| 1420 | 1356 | .798 |
| 1570 | 1403 | .775 |
| 2610 | 1694 | .757 |
| 2760 | 1738 | .784 |
| 3030 | 1766 | .761 |
| ∞ | 1950 | |
| | Av. | 0.778 ± 0.011 |

---

(12) All melting points are corrected. Ultraviolet spectra were obtained with a Cary recording spectrophotometer (model 11MS) with 1-cm. cells; samples for spectral analysis were dissolved in 95% ethanol.

(13) C. L. Arcus and H. E. Strauss, *J. Chem. Soc.*, 2669 (1952).

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

(15) K. N. Campbell, B. K. Campbell and L. T. Eby, *ibid.*, **60**, 2882 (1938).

(16) E. R. H. Jones and J. T. McCombie, *J. Chem. Soc.*, 733 (1942).

(17) W. E. Doering and H. H. Zeiss, THIS JOURNAL, **72**, 147 (1950).

(18) The 40% aqueous dioxane was prepared by mixing two volumes of anhydrous dioxane (L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath and Co., New York, N. Y., 1955, p. 284) with three volumes of conductivity water containing appropriate amounts of perchloric acid (Baker and Adamson; 60%, reagent grade) and lithium perchlorate (G. Frederic Smith Co., reagent grade, dried *in vacuo* for 24 hours at 120°); the volumes of the components of the reaction solvent were measured at 25°.

reaction; the average deviation of $k_r$ in a single run was approximately 1 to 1.5%. Data obtained in a typical run are shown in Table III.

**Rates of Loss of Optical Activity.**—The loss of optical activity experiments were performed with an O. C. Rudolph and Sons high precision model 80 polarimeter; individual rotations were measured with a precision of ±0.004°. The polarimetric rate determinations were carried out either in a specially constructed (American Instrument Co.) 4.038-dcm. all-glass jacketed polarimeter tube of *ca.* 23-ml. capacity or in a 4-dcm. metal-jacketed polarimeter tube of *ca.* 7.3-ml. capacity.

Reaction solutions were prepared by dissolving a known weight of optically active alcohol in 40% aqueous dioxane. After temperature equilibration, from 8 to 16 "points" were determined in an experiment. Each of the 8 to 16 "points" was the average observed rotation at the average time of 4 to 7 readings taken over a time interval of 4–10 minutes. That this method was satisfactory is indicated by the good linear plots obtained when log ($\alpha_\infty$-$\alpha_t$) was plotted against $t$ (see Fig. 1, lower line). Aliquots of the reaction solution were titrated with standard base to determine the perchloric acid concentration.

The rate constants for the loss of optical activity were calculated by use of equation 20 where $\alpha_0$ is the rotation at zero time (after temperature equilibration) and $\alpha_t$ and $\alpha_\infty$

$$k_a = (1/t)\ln(\alpha_\infty - \alpha_0)/(\alpha_\infty - \alpha_t) \qquad (20)$$

are the observed rotations at time $t$ and after ten half-lives. In all of the experiments the loss of optical activity was complete. A typical kinetic experiment is summarized in Table IV.

TABLE IV

LOSS OF OPTICAL ACTIVITY OF (−)-$\alpha$-PHENYLALLYL ALCOHOL AT 30° IN 40% AQUEOUS DIOXANE

[$HClO_4$] = 0.0370 $M$, $\mu$ = 0.10 (Expt. 17)

| $t$, min. | $\alpha^{30}_D$ | $10^3k_\alpha$, min.$^{-1}$ |
|---|---|---|
| 0 | −0.586° | |
| 334 | .357 | 1.48 |
| 380 | .332 | 1.50 |
| 524 | .299 | 1.28 |
| 611 | .252 | 1.38 |
| 684 | .234 | 1.34 |
| 786 | .202 | 1.36 |
| 846 | .183 | 1.38 |
| 881 | .172 | 1.39 |
| ∞ | .000 | |
| | | Av. 1.39 ± 0.05 |

MADISON, WIS.

---

[CONTRIBUTION FROM THE ISTITUTO DI CHIMICA INDUSTRIALE DEL POLITECNICO DI MILANO]

# The Reaction between Styrene and Triisobutylaluminum

BY G. NATTA, P. PINO, G. MAZZANTI, P. LONGI AND F. BERNARDINI

RECEIVED JULY 7, 1958

The reactions of styrene with triisobutylaluminum and with dialkylaluminum monohydride have been investigated. Oxidation and hydrolysis of the products of these reactions give 1-phenylethanol and 2-phenylethanol in good yields, as well as small quantities of acetophenone. Moreover, a study of the products obtained from tris-(phenylethyl)-aluminum, obtained in the above reactions with styrene, indicates that about 22–24% of the phenylethyl groups are attached to the aluminum through the carbon adjacent to the phenyl group.

Two isomeric compounds, I and II, have been obtained by the reaction of styrene with organometallic compounds or metallic hydrides.

$$\begin{tikzcd}[row sep=small] C_6H_5CH(R)CH_2\text{Metal} \quad \text{(I)} \\ C_6H_5CH{=}CH_2 + \text{Metal–R} \qquad R = \text{H or alkyl} \arrow[u] \arrow[d] \\ C_6H_5CH(\text{Metal})CH_2R \quad \text{(II)} \end{tikzcd}$$

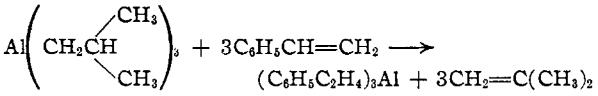
By use of an alkali metal derivative, products of type II predominate[1]; the reaction of trialkyltin hydride to styrene, on the other hand, gives a product of type I.[2]

The reaction of compounds of metals of the third periodic group with styrene has received little attention. Ziegler[3] reported the reaction of styrene with triisobutylaluminum and the oxidation of the product, tris-(phenylethyl)-aluminum, to give 2-phenylethanol. Brown[4] indicated that the same alcohol is obtained by oxidation of tris-phenylethylboron.

This paper presents a study of the reactions of styrene with triisobutylaluminum and with diethylaluminum hydride. The structure and composition of the products have been deduced by oxidation with oxygen, by hydrolysis of the resulting alcoholates, and by analysis of *the phenylethanol* thus obtained by infrared absorption spectroscopy.

## Results

The reaction between triisobutylaluminum and styrene was carried out both in the absence and the presence of solvents. Nickel, prepared *in situ* by the decomposition of nickel acetylacetonate, was used as a catalyst.[5]



$$\text{Al}\left(CH_2CH\begin{matrix}CH_3\\ CH_3\end{matrix}\right)_3 + 3C_6H_5CH{=}CH_2 \longrightarrow (C_6H_5C_2H_4)_3\text{Al} + 3CH_2{=}C(CH_3)_2$$

The tris-(phenylethyl)-aluminum obtained was oxidized at a low temperature (0–25°) but, even at 0°, the reaction does not proceed as smoothly as the oxidation of the trialkylaluminum compounds.[3] The oxidation products include 1-phenylethanol, 2-phenylethanol and acetophenone, using either ether or hexane as a solvent.

Since the secondary alcohol could be produced by isomerization during the oxidation, tris-(1-phenylethyl)-aluminum etherate and tris-(2-phenyl-

---

[1] E. Krause and A. von Grosse, "Die Chemie der metall-organischen Verbindungen," Berlin, 1937, pp. 95–96.

[2] G. J. M. van der Kerk, J. G. Noltes and J. G. A. Luijten, *J. Appl. Chem.*, **7**, 356 (1957).

[3] K. Ziegler, F. Krupp and K. Zosel, *Angew. Chem.*, **67**, 425 (1955).

[4] H. C. Brown and B. C. SubbaRao, THIS JOURNAL, **78**, 5694 (1956).

[5] K. Ziegler, H. G. Gellert, K. Zosal, W. Lehmkuhl and W. Pfohl, *Angew. Chem.*, **67**, 424 (1955).