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Mechanisms of Acid-catalyzed Reactions. III. Oxotropic Rearrangement of α -Phenylallyl Alcohols

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The solvent composition-acidity function criterion^{1a,c} and the Bunnett^{1b} H₂O activity relation have been simultaneously applied as probes of the mechanism of oxotropic rearrangement of α -phenylallyl alcohols in hydroxylic solvents. The results obtained appear to describe a transition state which does not involve the nucleophilic properties of water and appears to contradict earlier interpretations^{5,8,11} of the course of reaction.

The structure of the carbonium ion intermediate in anionotropic rearrangements of uncharged allylic derivatives in non-aqueous systems has been examined in considerable detail.² Though current knowledge of the nature of the ion pairs that develop with ionization

of the —C—X bond is indeed very extensive, compar-

tively little is known about the oxotropic reaction of cationic allylic substrates in aqueous or partly aqueous systems. That is to say, the formation of carbonium ion-pair intermediates are commonly conceded to form in the solvolysis of *uncharged* phenylallyl derivatives,^{2,3} although some covalent character in the transition state bonding has been invoked on occasion to explain certain features of this reaction.⁴ There exists, however, considerable disagreement as to the course of reaction and nature of the intermediates in the solvolysis of the (charged) conjugate acids of phenylallyl alcohols, the so-called oxotropic rearrangement.

Thus, Braude, Jones and Stern⁵ have investigated the rearrangement of phenylpropenylcarbinol by determining the reaction rate as a function of medium over a wide range of ethanol-water solvent compositions. These authors applied as a kinetic criterion of mechanism a proposed medium dependence of isodielectric energy of activation^{5,6} and other criteria which led them to suggest the intramolecular or S₂' processes discussed by Braude in a series of review articles.⁷ The rearrangement of the simpler homolog phenylvinylcarbinol to cinnamyl alcohol could not be incorporated into the study since in ethanol-water solutions this substrate is partially etherified *via* displacement⁸ before the rearrangement step and the ether rearranges in acid at a slower rate. However, by extrapolation of their conclusions regarding phenylpropenylcarbinol it was suggested that phenylvinylcarbinol also rearranges *via* A₂.

Subsequently, workers in the British laboratory^{8,9} studying the solvolysis of 1-phenylallyl chloride in

aqueous dioxan and aqueous alcohol solutions inferred that a limiting S_N1 mechanism did obtain in this system as judged from its (determined) *m*-value of the Grunwald-Winstein relationship.^{10,11} But, surprisingly, nearly all of the solvolytic product was the 1-phenylallyl derivative (ether or alcohol), leading the authors to conclude that a "hot" carbonium ion¹² (reacting with solvent before it could be delocalized) was to be preferred. These results with the *uncharged* phenylallyl derivative, however, were distinctively different from those obtained through solvolysis of phenylallyl oxonium ion in aqueous dioxane (60:40, v./v.) by Bunton, Pocker and Dahn.¹³ They observed by use of H₂O¹⁸ tagging that the over-all rate of formation of carbonium ions was about 2.5 times greater than the rate of rearrangement. Furthermore, the occurrence of an A₁ reaction process was identified by the linear relation (slope = 1.3) between the Hammett acidity function *H*₀ and the rate in the dioxane-water medium. They have interpreted these data to be in contradiction with the intramolecular and S₂' processes of oxotropic rearrangement proposed by Braude⁷ as represented in Fig. 1 by paths a and/or b.

Goering and Dilgren¹⁴ have conducted some very elegant studies of the racemization, O¹⁸ exchange and rearrangement reactions taking place with optically active α -phenylallyl alcohol in aqueous acid-dioxane media. Their results serve to elaborate the earlier work¹³ by demonstrating that the rates of racemization are greater than the rates of O¹⁸ exchange, which, in turn, are greater than the rates of rearrangement.

Goering^{14b} has considered two possible mechanisms that are consistent with these data. The one chosen as the more likely is (the A₁) represented by path f (see Fig. 1). The alternative may be described as a combination of S_N2 and S_N2' displacement that are equivalent to a tandem of path d followed by path b and/or path c. In the final analysis, however, their preference for path f is based on the reported⁷ adherence of the rate (in aqueous ethanol solution) to an *H*₀ dependence.

Others have disputed the latter argument, regarding the *H*₀ criterion as dubious evidence for the choice of path f. It is particularly difficult to ignore the valid objection raised by Gutbzahl and Grunwald¹⁵ con-

(1) For previous papers in this series see: (a) H. Kwart and L. B. Weisfeld, *J. Am. Chem. Soc.*, **80**, 4670 (1958); (b) H. Kwart and A. L. Goodman, *ibid.*, **82**, 1947 (1960); (c) H. Kwart and M. B. Price, *ibid.*, **82**, 5123 (1960).

(2) See H. L. Goering, *Rec. Chem. Progr.*, **21**, 109 (1960), for a thorough review of this subject.

(3) In addition to the work so excellently summarized in ref. 2 see also: (a) R. A. Sneen, *J. Am. Chem. Soc.*, **82**, 4261 (1960); (b) R. A. Sneen and A. M. Rosenberg, *ibid.*, **83**, 895, 900 (1961).

(4) H. L. Goering, *et al.*, *ibid.*, **77**, 1129, 5026, 6249 (1955).

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

(6) E. A. Braude, *ibid.*, 443 (1944).

(7) E. A. Braude, *Ann. Reports*, **46**, 125 (1949); *Quart. Revs.*, **4**, 404 (1950).

(8) E. A. Braude, G. Wolkanas and E. S. Waight, *Chemistry & Industry*, 314 (1956).

(9) G. Wolkanas and E. S. Waight, *Proc. Chem. Soc.*, 8 (1959).

(10) E. Grunwald and S. Winstein, *J. Am. Chem. Soc.*, **70**, 846 (1948).

(11) A. Fainberg and S. Winstein, *ibid.*, **78**, 2770 (1956).

(12) D. Semenov, Chin-Hua Shih and W. G. Young, *ibid.*, **80**, 5472 (1960).

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

(14) (a) H. L. Goering and R. E. Dilgren, *J. Am. Chem. Soc.*, **81**, 2356 (1959); (b) **82**, 5744 (1960).

(15) B. Gutbzahl and E. Grunwald, *ibid.*, **75**, 559 (1953).

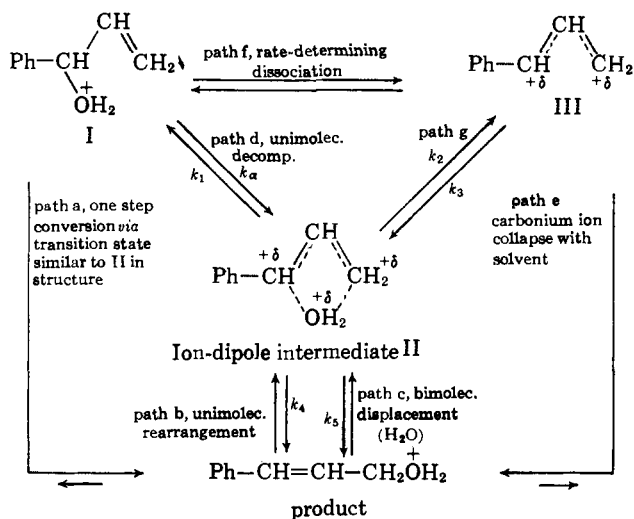


Fig. 1.—Alternative paths for oxotropic rearrangement.

cerning the existence of a genuine Hammett acidity function in other than purely aqueous media. Whalley,¹⁶ on the other hand, has formulated an alternative criterion for distinguishing the A-1 mechanism through studies of the pressure effect on the rate. By these means an estimate of the relative volume of ground and activated states can be attained. The results quoted^{16b} for the oxotropic rearrangement of α -phenylallyl alcohol indicate a volume decrease in the transition state. It was consequently inferred that a unimolecular decomposition to the resonance-stabilized cation, path f or paths d and g, was *not* the preferred mechanism. However, no obvious choice could be made on this basis between the bimolecular displacement, path c (k_5), and the unimolecular rearrangement, path b (k_4), and it was not clearly established whether the rate-determining step involved ionization to form II or the decomposition of II to products *via* k_2 , k_4 or k_5 .

To decide between these alternatives, we undertook to re-examine the examples discussed above by applying two recently developed kinetic criteria of acid-catalyzed mechanism. These methods are somewhat similar in that they seek a correlation of reaction rate with the activity of water in the medium. The first method based on the solvent composition (S.-C.) criterion,^{1a} tests the response of rate to variation of the composition of aqueous alcohol solutions. The latter is expressed in terms of an empirical measure, Y_0 , devised by Grunwald¹⁷ to estimate the ionizing power of the medium; Y_0 may also be understood to express a measure of the activity of water with variation of the mole fraction of ethanol. This criterion may be denoted in several equivalent ways, two of which are

$$\log k_\psi - H_\psi = A + \Delta m Y_0 \quad (1)$$

$$\log k_\psi - \log I = A' + \Delta m Y_0 \quad (2)$$

where k_ψ is the pseudo-first-order rate constant, and the significance of the remaining terms have been discussed in ref. 1a. A linear plot between the tabulated values of Y_0 and $\log k_\psi - H_\psi$ or $\log k_\psi - \log I$ over the full range of solvent composition verifies an A1 mechanism; severe curvature of the plot broadly signifies the operation of an A2 mechanism.

The second kinetic criterion represents a most interesting development by Bunnett¹⁸ correlating rate

(16) (a) E. Whalley, *Trans. Faraday Soc.*, **55**, 798 (1959); (b) Whalley has quoted the data of R. T. Harris and K. E. Weale, *J. Chem. Soc.*, 953 (1956).

(17) B. Gutbezahl and E. Grunwald, *J. Am. Chem. Soc.*, **75**, 565 (1953), and earlier references cited therein.

(18) J. F. Bunnett, *ibid.*, **83**, 4956 (1961), *et seq.*

and a_{H_2O} in aqueous solutions of different acid strength.

$$\log k_\psi + H_0 = w \log a_{H_2O} + \text{constant} \quad (3)$$

where H_0 is the usual Hammett acidity function. It will be noted that the terms $\Delta m Y_0$ and $w \log a_{H_2O}$ are superficially analogous. It is, however, not possible to say at this time that the value of Δm has significance similar to that which Bunnett¹⁹ has associated with the magnitude and sign of w .

Results

The data of Braude and Stern²⁰ on the rates of rearrangement of phenylpropenylcarbinol in various ethanol solutions and varying acid concentrations have been recomputed to fit the form of eq. 2 and are listed in Table I. The plot of these data according to eq. 2 gives a reasonably straight line over the entire range of solvent compositions whose least square slope $\Delta m = 0.59$ (correlation coefficient, $r = 0.99$).

TABLE I

REARRANGEMENT OF PHENYLPROPENYLCARBINOL IN ETHANOL-WATER MIXTURES AT 30° AND IN 0.1 M HCl¹¹

Wt. % EtOH	$\log I$	$\log k_2 + 1$	$1 + \log I - \log k_2$	$-Y_0$
34.7	0.909	1.940	0.969	0.13
53.9	.398	1.380	1.018	.7
64.5	.255	1.130	1.125	.37
75.6	.171	0.949	1.222	.505
87.2	.204	0.869	1.335	.70
99.5	1.820	2.398	1.422	.94

TABLE II

REARRANGEMENT OF α -PHENYLALLYL ALCOHOL^a

Mole/l. H ₂ SO ₄	$-H_0$	$k_\psi \times 10^3$, min. ⁻¹	$2 + \log k_\psi + H_0$	$-\log a_{H_2O}$
Containing 0.82 vol. % ethanol				
0.475	-0.165	4.02	0.769	0.008
0.982	+ .244	12.3	.846	.018
1.473	.570	32.0	.935	.028
1.949	.850	67.4	.979	.043
2.466	1.120	155	1.070	.060
2.983	1.370	318	1.132	.084
Containing no EtOH				
0.767	0.09	7.37	0.778	0.013
1.538	0.61	29.8	0.864	.030
2.439	1.10	133	1.014	.060
2.901	1.33	261	1.087	.080

^a In water solution at 25°, reaction pursued spectrophotometrically at 251 m μ , concn. of substrate = 5×10^{-5} mole/l.

We have interpreted this result to mean that solvent water does not enter the transition state as a nucleophile in the oxotropic rearrangement. It clearly fits an A1 mechanism of either unimolecular rearrangement (path b, k_4) or any of the unimolecular decomposition paths illustrated in Fig. 1 and contradicts the conclusion arrived at earlier by Braude and co-workers.²⁰ It is interesting, too, that the corresponding data we have recomputed for ethynylpropenylcarbinol²¹ show a similar linear relationship expected of an A1 mechanism, though having a slope, Δm , almost twice as large as that for the phenylpropenyl analog. We have, therefore, extrapolated with some confidence to the conclusion that phenylvinyl oxotropic rearrangement in aqueous solution also occurs *via* an A1 mechanism, even though the complicating factor of etherification in water-alcohol solution has prevented us from applying the same mechanistic probes (according to eq. 1 and 2).

(19) J. F. Bunnett, *ibid.*, **83**, 4968 (1961).

(20) E. A. Braude and E. S. Stern, *J. Chem. Soc.*, 1971 (1948).

(21) Unpublished work of L. B. Weisfeld from these laboratories.

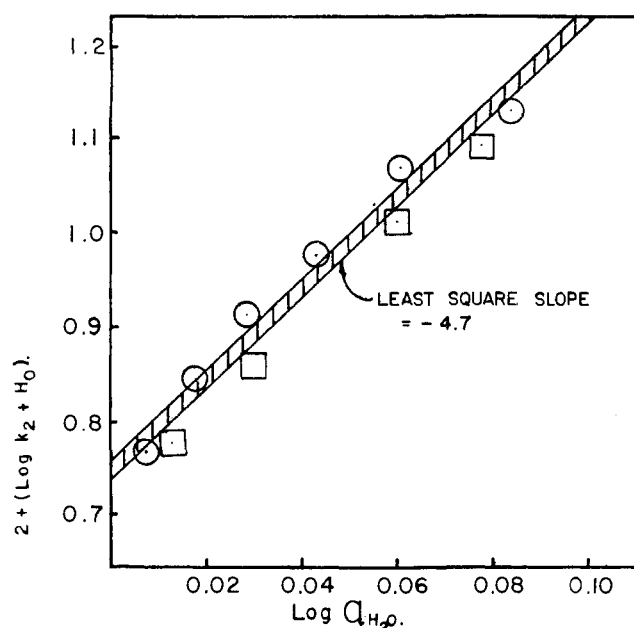


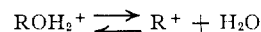
Fig. 2.—Oxotropic rearrangement of phenylvinylcarbinol in AQ H_2SO_4 : ○, 0.82 vol. % ETOH; □, no ETHO.

It is possible, however, conveniently to observe the rearrangement rates in aqueous solution over a wide range of acid concentrations (*ca.* 0.5–3.0 M H_2SO_4). Plotting the data (so obtained) according to the Bunnett eq. 3 (see Fig. 2) permits us to determine the w -parameter directly. Bunnett has characterized many acid-catalyzed mechanisms by the range and magnitude of w . The data summarized in Table II and plotted in Fig. 2 lead to $w = -4.7$ ($r = 0.97$), one of the largest negative values reported. Bunnett has demonstrated that reactions proceeding with an A1 mechanism generally exhibit w -values close to zero and ranging negatively.

Discussion

The interpretations arrived at above are apparently at variance with those advanced by Braude⁷ and by Whalley.¹⁶ For instance, both the solvent composition–acidity function criterion^{1a,b} and the Bunnett criterion¹⁸ that correlate rate data in aqueous solution seem to indicate the absence of a bimolecular substitution mechanism subscribed to previously.^{16,20} The alternative mechanism permitted by Whalley's¹⁶ interpretation of his results, *viz.*, the unimolecular rearrangement mechanism, must also be excluded as inconsistent with the large negative w -value we obtained. Some explanations that are possibly more attractive and are also consistent with both the (S.–C.) and w -criteria may be deduced from the following considerations.

The magnitude of w could be reflecting the difference in the state of hydration between the transition and ground states.¹⁰ For example, in the –OH exchange between *t*-butyl alcohol and water



the positive charge resides largely at the carbonium ion center of the *t*-butyl group. Consequently, the hydration tendency would be very large and little water if any, will be stripped away in going from the ground to the transition state. To a first approximation we can assume that hydration of the ground states of most alcohols are similar. The comparison then leads to the realization that, if the unimolecular rearrangement mechanism (Fig. 1) prevailed, regardless of whether the rate-determining step involved formation or decomposition of the intimate ion-dipole II, there would be little difference expected in the degree of hydration as the reaction proceeded. On the other hand, if the rate-determining step was a unimolecular decomposition of the nature of path for paths d and g, the transition state would experience extensive redistribution of positive charge over the entire allylic system conjugated with the benzene ring. Such diffusion of charge reduces the degree to which the water dipoles are organized in the solvation shell and consequently creates decreased hydration of the system.

This picture furthermore can be reconciled with the negative volume of activation determined by Harris and Weale.¹⁶ Clearly, a stripping away of solvent molecules in the fashion anticipated by the discussion above, and in agreement with the large negative w -parameter exhibited by the reaction, would produce a negative volume of activation. Concomitantly, if an ionic intermediate does occur in oxotropic rearrangement as suggested by the data of Bunton, *et al.*,¹³ and Goering,¹⁴ this fixes the formation of the transition state as an event occurring somewhere between the intimate ion-dipole II and the resonance stabilized allylic cation III.

Another way of arriving at essentially the same conclusion²² is to call into consideration the respective charge character of the several possible transition states. Thus, the transition state for formation of the intermediate II has more carbonium and less oxonium character than II or (even) the transition state lying astride path a. The greater degree of oxonium character must be associated with the greater extent of hydration (of the hydrogens attached to oxygen). Consequently, a lower value of w is to be anticipated for a mechanism proceeding through unimolecular decomposition than for any of the alternative possibilities considered on Fig. 1. Since the observed w -value (-4.7) is unusually low, a preference for this mechanism is indicated.

Experimental

Kinetic Measurements.—All rate runs were carried out spectrophotometrically with the technique described previously by Kwart and Price.¹⁶

α -Phenylallyl alcohol was prepared by the method described by Braude, Jones and Stern.³ The physical constants of the preparation agreed very well with those described in the literature.

(22) As suggested by an interested Referee.