erization is the rate of hydration of *cis*-cinnamic acid.

Evidence from Deuterium Isotope Studies.—Further support for the addition–elimination sequence is obtained by carrying out the isomerization in deuteriosulfuric acid. The *trans*-cinnamic acid which is formed contains carbon bound deuterium. This deuterium is at the α-position as shown by comparison of the infrared spectrum (particularly the decrease in the doublet at 10.2 microns) with an authentic sample of *trans*-cinnamic acid-α-d_1. The amount of deuterium incorporated is about 80%. The mass spectrum of methyl cinnamate derived from this cinnamic acid also shows the presence of 75–80% of one deuterium atom per mole.

It may further be shown that the deuterium is incorporated during the isomerization, and not subsequent to it by the following observations.

When authentic *trans*-cinnamic acid-α-d_1 is allowed to stand in ordinary sulfuric acid, deuterium is lost slowly from the deuteriocinnamic acid. By reisolating cinnamic acid, and following the appearance of the 10.2 μ doublet, the rate of α-D–α-H exchange may be determined (Table VI).

The net rate of loss of deuterium is only 1/25 the rate of the *cis* to *trans* isomerization.

TABLE VI

RATE OF DEUTERIUM EXCHANGE OF *trans*-CINNAMIC ACID-α-d_1 IN SULFURIC ACID AT 45.00°

H_2SO_4, %	H_0	k_{exch}, sec.$^{-1}$	k_{isomer},[a] sec.$^{-1}$
69.28	−5.56	1.24×10^{-6}	35×10^{-5}

[a] Interpolated from Table II.

Conclusions.—Clearly, the isomerization of *cis*-cinnamic acid takes place by an addition–elimination sequence at the carbon–carbon double bond. It is to be noted that this mechanism differs from the one established for the isomerization of maleic acid to fumaric acid. In the latter case, no carbon-bound deuterium is incorporated during isomerization.[19,20]

It also contrasts with the mechanisms which we have established for the isomerization of unsaturated ketones.[3,5,6]

[19] C. Horrex, *Trans. Faraday Soc.*, **33**, 570 (1937).

[20] S. Seltzer, *J. Am. Chem. Soc.*, **83**, 1861 (1961).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, BERKELEY, CALIF.]

The Kinetics and Mechanism of the Dehydration of β-Phenyl-β-hydroxypropionic Acid[1-3]

BY DONALD S. NOYCE AND CHARLES A. LANE[4]

RECEIVED SEPTEMBER 29, 1961

The acid-catalyzed racemization of (+)-β-phenyl-β-hydroxypropionic acid, (+)-I, has been studied over the range 40–60% sulfuric acid. The rate of dehydration of I has been studied over the sulfuric acid concentration range 38–77%. The reaction sshow typical carbonium ion behavior; the slopes against the acidity function H_0 are substantially greater than unity; the activation parameters are concordant with a carbonium ion process.

Introduction

In the previous paper,[1] we have presented evidence showing that the acid-catalyzed isomerization of *cis*-cinnamic acid proceeds *via* an addition–elimination sequence, with β-phenyl-β-hydroxypropionic acid (I) being an intermediate.

It is the purpose of the present report to examine in some detail the behavior of I in fairly concentrated acids.

The kinetics and mechanism of the acid-catalyzed reactions of alcohols have received considerable attention in recent years. Racemization, dehydration, and O^{18} exchange have been studied for several alcohols.[5-9]

Compound I offers several advantages for a thorough study as will be clear from the results. Most particularly, the stability of the product *trans*-cinnamic acid makes studies over a wide range of acidities quite feasible.

Experimental[10]

β-Phenyl-β-hydroxypropionic acid (I) was prepared by the Reformatsky reaction[11] followed by alkaline hydrolysis; m.p. 93–94° (lit.[12] 92°, 94°, 96°).

Resolution.—Racemic I was resolved by the method of Kenyon, Phillips and Shutt[13] with some modification. Satisfactory results were not obtained using a 1:1 mixture of I and brucine, but were obtained using a 2:1 molar mixture of I and brucine and fractional crystallization from ethyl ace-

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[1] Paper XIV in the series Carbonyl Reactions; previous paper, D. S. Noyce, P. A. King, F. B. Kirby and W. L. Reed, *J. Am. Chem. Soc.*, **84**, 1632 (1962).

[2] Presented in part at the Meeting of the National Academy of Sciences, Berkeley, Calif., October, 1958; and at the 8th Conference on Reaction Mechanisms, Princeton, N. J., September, 1960.

[3] This research was supported in part by a grant from the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of this fund.

[4] National Science Foundation Coöperative Fellow, 1959–1961.

[5] R. H. Boyd, R. W. Taft, Jr., A. P. Wolfe and D. R. Christman, *J. Am. Chem. Soc.*, **82**, 4729 (1960).

[6] J. Manassen and F. G. Klein, *J. Chem. Soc.*, 4203 (1960).

[7] C. A. Bunton, A. Konasiewicz and D. R. Llewellyn, *ibid.*, 607 (1955); C. A. Bunton and D. R. Llewellyn, *ibid.*, 3402 (1957).

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

[9] D. Jeffery and A. Fry, Abstracts of 138th Meeting of the American Chemical Society, New York, N. Y., September, 1960, p. 33P.

[10] Melting points are corrected; boiling points are uncorrected. Infrared spectra were determined with a Baird infrared spectrophotometer.

[11] C. R. Hauser and D. S. Breslow, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 408.

[12] *Cf.* Beilstein, "Handbuch der Organischen Chemie," Vol. 10, p. 249.

[13] J. Kenyon, H. Phillips and G. R. Shutt, *J. Chem. Soc.*, 1663 (1935).

tate. The isolated salt, dec. 89–108°, analyzed for a solvate with ethyl acetate.

Anal. Calcd. for $(C_9H_{10}O_3)_2 \cdot C_{23}H_{26}N_2O_4 \cdot C_4H_8O_2$: C, 66.32; H, 6.68; N, 3.44. Found: C, 66.52; H, 6.78; N, 3.42.

Decomposition of the brucine salt afforded (+)-I, m.p. 116–118° (lit.[13] 117–118°), $[\alpha]^{21}D$ 18.2° (*c* 4.95, absolute ethanol), $[\alpha]^{23}D$ 58.2 (*c* 2, chloroform) after crystallization from benzene. The infrared spectrum (mull) was nearly identical with that of racemic I.

Racemization Studies.—The racemization of (+)-I was followed with an O. C. Rudolph polarimeter reading to 0.002°, using 4-dm. jacketed tubes. The concentration of (+)-I was 1 to 1.5% and the initial observed rotation was about 1°.

In making a run, sulfuric acid of the desired concentration was thermostated. A weighed, finely ground, sample of (+)-I was rapidly stirred into the sulfuric acid. The solution was quickly filtered by forcing through a sintered glass filter directly into the polarimeter tube.

Six readings were taken at each point in the slower runs. In the faster runs, rotations were taken by noting the time at which the rotation equalled a predetermined value.

Dehydration Studies.—The rate of dehydration was followed by the increase in the ultraviolet absorption at 288 and 300 mμ. The sulfuric acid solutions were approximately 3×10^{-5} molar in I, and initially had no absorption at these wave lengths. The kinetics were followed to completion. Rate constants were determined graphically by plotting the approach to the observed optical density at "infinite" time.

In the most rapid runs, a very small amount of powdered I was quickly stirred into sulfuric acid of the desired concentrations within a Beckman cell. After 10–20 seconds, readings were initiated. For these runs, the Beckman was pre-set, and the time at which the needle of the null meter swung past zero was noted by recording the information with a dictating machine. The data were then tabulated. In this way, with a final optical density of 0.6, seven or eight points were obtained through a period of 60–95% reaction when the half-life was about 7 seconds.

Product Isolation.—Cinnamic acid was isolated in 96% yield upon maintaining a solution of 3.78 g. of racemic β-phenyl-β-hydroxypropionic acid in 200 ml. of 7.39 *M* sulfuric acid for 20 hours at 45°. The isolated cinnamic acid (3.22 g.) was identified by infrared spectrum and mixed melting point.

Isolation Experiment under the Conditions of the Racemization Studies.—A solution of 0.204 g. of (+)-β-phenyl-β-hydroxypropionic acid in 30 ml. of 58.84% sulfuric acid was maintained at 25° for 25 minutes. The solution was poured on ice, partially neutralized with 26 g. of sodium carbonate and extracted continuously with ether to afford 0.200 g. of material. Chromatography on silica gel with benzene afforded 23 mg. of impure *trans*-cinnamic acid (infrared spectral identification). Elution with chloroform afforded 0.172 g. of 95.5% racemized β-phenyl-β-hydroxypropionic acid, m.p. 91–92°, $[\alpha]D$ +2.6° (*c* 2, chloroform), infrared spectrum identical to pure I. Calculations using the rate constants determined spectrophotometrically predict the isolation of 19 mg. of cinnamic acid and of 183 mg. of 99% racemized I.

Determination of the Extent of Dehydration of β-Phenyl-β-hydroxypropionic Acid.—A solution of 20 mg. of I in 100 ml. of 52% sulfuric acid was maintained at 45° for 30 hours. At the end of this time, the solution was cooled, carefully extracted twice with benzene (removal of cinnamic acid, but not of I) and the sulfuric acid solution washed with pentane. This solution was almost completely transparent in the region of the absorption maximum for cinnamic acid. Upon warming the sulfuric acid solution (at 45° for 10 hours), the absorptivity increased. This represented the formation of 1.7% of cinnamic acid. The equilibrium constant for the dehydration reaction, including the activity[14] of water (0.332), is calculated to be 19.2. A duplicate experiment gave 20.0. In a separate experiment, starting with cinnamic acid, concordant results were obtained.

Results

Racemization of (+)-β-Phenyl-β-hydroxypropionic Acid, (+)-I.—The racemization of (+)-I takes place rapidly at 25° in 50% sulfuric acid. Almost completely racemized I can be isolated after the appropriate time interval with very little cinnamic acid being formed concurrently.

The measured rates of racemization of (+)-β-phenyl-β-hydroxypropionic acid are presented in Table I.

TABLE I

RACEMIZATION OF (+)-β-PHENYL-β-HYDROXYPROPIONIC ACID

H_2SO_4, %	Temp., °C. ± 0.05	H_0	$k\alpha \times 10^5$, sec.$^{-1}$	$\log k\alpha + H_0$
39.77	25.00	−2.40	1.77	−7.15
47.40	25.00	−3.11	11.3	−7.06
52.03	25.00	−3.60	45.5	−6.94
58.84	25.00	−4.33	320	−6.82
	25.1[b]		334	−6.81
	25.1[b]		300	−6.85
39.77	44.95	−2.40	22.6	−6.05
47.00	44.92	−3.06	124	−5.97
21.19[a]	45.00	−2.30	22.6	−5.95

[a] Hydrochloric acid used. [b] Temperature 25.1 ± 0.1°.

It is to be noted that the rate of racemization increases somewhat more rapidly than the acidity function h_0, and the slope of a log *k* *vs.* H_0 plot for the data at 25° is 1.17.

This behavior is similar to that reported recently by several investigators; Boyd, Taft, Wolf and Christman[5] found that the O^{18} exchange of *t*-butyl alcohol shows a slope of the log *k* *vs.* H_0 correlation of 1.20, consistent with a carbonium ion process. A closer parallel is the work of Grunwald, Heller and Klein[8] in the study of the O^{18} exchange and racemization of 1-phenylethanol. They, likewise, observed that the racemization rate increased somewhat faster than h_0 in the region of 0.1 to 1.0 *M* perchloric acid.

The similarity of the *t*-butyl system and the 1-phenylethyl system in solvolytic reactions is well known.[15]

A greater variety of studies have been carried out on *sec*-butyl alcohol. Bunton and Llewellyn[7] reported that the rate of racemization is twice the rate of O^{18} exchange, showing clearly the important nucleophilic component (almost complete back-side attack) in the racemization. The reported slopes of log *k* *vs.* H_0 are given as 0.97 and 1.02 for racemization and O^{18} exchange. However, no mechanistic significance can be attached to the slopes because of the high (15%) alcohol concentration in the medium. It is known from the work of Bartlett and McCollum,[16] that the addition of alcohols alters the H_0 value of the solution to variable degrees at different acid concentrations.

In all of these reactions, elimination is slower than racemization or O^{18} exchange. The ratio of substitution to elimination varies considerably, being small for *sec*-butyl alcohol and larger for 1-phenylethanol and *t*-butyl alcohol.

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[14] E. M. Collins, *J. Phys. Chem.*, **37**, 1191 (1933), corrected at 25° with the data of Giauque, *et al.* (W. F. Giauque, E. W. Hornung, J. E. Kunzler and T. R. Rubin, *J. Am. Chem. Soc.* **82**, 62 (1960)).

[15] A. Streitwieser, Jr., *Chem. Revs.*, **56**, 571 (1956).

[16] P. D. Bartlett and J. D. McCollum, *J. Am. Chem. Soc.*, **78**, 1441 (1956).

Further comparison of relative rates for these compounds is instructive. We have extrapolated our rate of racemization of 1 *M* sulfuric acid and have extrapolated the other data to these conditions where necessary. Table II presents such an extrapolated comparison.

TABLE II

RELATIVE RATES OF RACEMIZATION AT 25° IN 1.00 *M* ACID

Compound	Acid	H_0	log *k*, sec.$^{-1}$
I[a]	H_2SO_4	−0.26	−7.25
1-Phenylethanol[b]	$HClO_4$	− .23	−4.70
sec-Butyl alcohol[c]	$HClO_4$	− .23	−10.0
t-Butyl alcohol[d]	H_2SO_4	− .26	−5.31

[a] Extrapolated from results in Table I. [b] Ref. 8. [c] Ref. 7. [d] O^{18} exchange rate, ref. 5.

The difference in rate between I and 1-phenylethanol is easily accommodated by an approximate calculation of the inductive effect of the carboxyl group. Using the ρ–σ^* treatment of Taft,[17–19] with a ρ[20] of −4.6 and a σ^*-value for the carboxyl group[21] of 2.9, a rate difference of about $10^{3.3}$ is calculated.

Rate of Dehydration of I.—With the rate of racemization as background and as presumptive evidence for a carbonium ion mechanism, we turn to the rate of dehydration of I in strongly acidic solution. The measured data are given in Table III. Under all of the conditions reported here, *trans*-cinnamic acid is formed in high yield, and the evidence precludes the formation of any quantity of *cis*-cinnamic acid.

TABLE III

RATE OF DEHYDRATION OF β-PHENYL-β-HYDROXYPROPIONIC ACID IN SULFURIC ACID

At 25.00°	H_0[a]	*k*, sec.$^{-1}$	log *k*	log *k* + H_0
58.05%	−4.25	5.59×10^{-5}	−4.25	−8.50
65.45	−5.09	8.24×10^{-4}	−3.08	−8.17
69.00	−5.53	3.5×10^{-3}	−2.46	−7.99
69.00	−5.53	3.34×10^{-3}	−2.48	−8.01
77.0	−6.57	9.1×10^{-2}	−1.04	−7.61
		9.1×10^{-2}		
		9.6×10^{-2}[b]		

At 44.7°	H_0[a]	ΔH_0[d]	H_0 cor.	*k*, sec.$^{-1}$[e]	log *k*	log *k* + H_0 (cor.)
38.32%[c]	−2.30	0	−2.30	3.38×10^{-6}	−5.47	−7.77
39.68	−2.39	0	−2.39	3.98×10^{-6}	−5.40	−7.79
51.87	−3.58	0.01	−3.57	1.07×10^{-4}	−3.97	−7.54
51.87	−3.58	.01	−3.57	1.07×10^{-4}	−3.97	−7.54
58.05	−4.25	.03	−4.22	7.21×10^{-4}	−3.14	−7.36
65.45	−5.09	.08	−5.01	7.2×10^{-3}[b]	−2.14	−7.15
				8.01×10^{-3}	−2.10	−7.11
69.00	−5.53	.10	−5.43	2.96×10^{-2}	−1.53	−6.96
				3.01	−1.52	−6.95
At 70.00°						
39.68%	−2.39	0	−2.39	9.8×10^{-5}	−4.01	−6.40

[a] Values from Paul and Long.[22] [b] Less precise. [c] Temp. 44.8°. [d] Calculated from the measurements of Gelbstein, Shcheglova and Temkin[23]. We have applied these corrections to the H_0 values of Paul and Long. [e] Not corrected for the 1% hydroxy acid remaining at equilibrium.

Since the rate of dehydration is only of moderate speed in fairly concentrated sulfuric acid, β-phenyl-β-hydroxypropionic acid offers a particularly favorable situation for investigating the rate over not only a wide range of acidity, but also a substantial range of water activity. Accordingly, we have expended some effort to make measurements in the highest accessible acid concentrations. Data are thus available over four H_0 units, and through a range in which the activity of water is changing by a factor of 50.

The rate measurements at the highest acid concentration (77% sulfuric acid, $H_0 = -6.57$) are in the region of protonation of carboxyl groups and above the acidity values for the protonation of many alcohols. Precise values for the *pK*'s for alcohols are scarce. For isopropyl alcohol, Bartlett and McCollum[16] have reported a value of −3.2, while Roček[24] finds that a value of −4.1 gives the best fit to the rate of oxidation of isopropyl alcohol. A value of −4.0 is given for methanol.[22] Compound I is clearly much less basic, and our kinetic data suggest that the pK_{BH^+} for I is −7.0 or even more negative. There are no data for benzyl alcohols acting as simple bases. Deno and his coworkers[25] conclude that benzyl alcohol itself is equilibrium with the carbonium ion at sufficiently high acidity, (~90% H_2SO_4) and that there is no appreciable fraction of $[C_6H_5CH_2OH_2^+]$ present at intermediate acidities. The inductive effect of the carboxyl group should decrease the basicity of the hydroxyl group in I.

Extent of Dehydration.—Though the dehydration of I to cinnamic acid is essentially complete, there is a very small amount of I remaining at equilibrium. In 52% sulfuric acid this amounts to 1.7%. Thus, the rate constants, which are determined by following the increase in optical absorption to the final equilibrium value, are too high by an amount corresponding to this 1.7%. No correction has been made for this factor.

Activation Parameters.—From the data given in Table III, we have calculated the energy of activation for the dehydration process. In order to determine $\Delta F^{\ddagger}$ and $\Delta S^{\ddagger}$ it is necessary to extrapolate the data to unit activity for the hydrogen ion. Extrapolation, using the linear log $k + H_0$ plot, gives $\Delta F^{\ddagger} = 29.7$ kcal. and $\Delta S^{\ddagger} = -13.7$ e.u. This extrapolation is fairly severe, as it extends over two H_0 units. Alternative methods of extrapolation were explored briefly. The results, taken in conjunction with the precision of the kinetic data, indicate that the uncertainty in $\Delta S^{\ddagger}$ is about 5 entropy units.

Similarly, extrapolation of the measured rates of racemization to 1.00 *M* sulfuric acid, using a log *k* vs. H_0 plot gives $\Delta F^{\ddagger} = 27.8$ kcal., $\Delta H^{\ddagger} = 25.8$ kcal. and $\Delta S^{\ddagger} = -6.7$ e.u. Alternately, using a plot of log *k* vs. (H_0 + log a_{H_2O}),[26] the activation

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(17) R. W. Taft, Jr., *J. Am. Chem. Soc.*, **75**, 4231 (1953).

(18) A. Streitwieser, Jr., *ibid.*, **78**, 4935 (1956).

(19) D. S. Noyce and H. I. Weingarten, *ibid.*, **79**, 3103 (1957).

(20) D. S. Noyce, P. A. King and W. L. Reed, *ibid.*, **84**, 1638 (1962).

(21) R. W. Taft, Jr., in M. S. Newman's "Steric Effects in Organic Chemistry," J. Wiley and Sons, Inc., New York, N. Y., 1956, Chapter 13, p. 615.

(22) M. A. Paul and F. A. Long, *Chem. Revs.*, **57**, 1 (1957).

(23) A. I. Gelbstein, G. G. Shcheglova and M. I. Temkin, *Zhur. neorg. Khim.*, **1**, 506 (1956).

(24) J. Roček and J. Krupicka, *Coll. Czechoslov. Chem., Commun.*, **23**, 2068 (1958).

(25) N. C. Deno, P. T. Groves, J. J. Jaruzelski and M. N. Lugasch, *J. Am. Chem. Soc.*, **82**, 4719 (1960).

(26) This is the definition originally used by Gold and Hawes (*J. Chem. Soc.*, 2102 (1951)) in determining the function J_0. It is to be noted that this is also equivalent to plotting the data in the manner suggested by Bunnett (*J. Am. Chem. Soc.*, **82**, 499 (1960)) with $w = -1$.

parameters for racemization are $\Delta F^{\ddagger} = 27.2$ kcal., $\Delta H^{\ddagger} = 25.6$ kcal. and $\Delta S^{\ddagger} = -5.4$ e.u.

Table IV

Comparison of Entropies of Activation for Carbonium Ion Reactions

Compound	$\Delta S^{\ddagger}$	Ref.	Compound	$\Delta S^{\ddagger}$	Ref.
t-C_4H_9OH, $-H_2O$	+19	5			
t-$C_5H_{11}OH$, $-H_2O$	+12	5	$C_6H_5CHOHCH_3$ rac.	+10	8
t-C_4H_9OH, O^{18} exch.	+15	5			
t-C_4H_9Cl, H_2O	+12	27	$C_6H_5CHClCH_3$; H_2O	+ 1	28
			I, rac.	(−6)	
			I, dehydr.	−13	

Comparison of these values with those for aliphatic alcohols shows that the entropy of activation is substantially more negative. However, this is to be expected. Table IV gives comparison data for t-butyl alcohol and t-butyl chloride, and for α-phenylethyl alcohol and α-phenylethyl chloride.

Variation of the Rate of Dehydration with Acid Concentration.—The plot of log k vs. H_0 gives a slope of 1.39 at 25°, and 1.32 at 45°. At 45° there is some indication that the slope is somewhat less at the lowest acidities.

An alternative way of treating the data is to plot log k vs. H_0 + log a_{H_2O}.[26] When plotted in this fashion, the slopes are very nearly unity. At 25° the slope is 0.98, at 45°, 0.97. The H_R function[29] does not provide a satisfactory basis for correlating the rate of dehydration. Thus, J_0, as originally defined by Gold and Hawes,[26] offers the most satisfactory method of correlating the data.

Conclusion.—Both the racemization and dehydration of β-phenyl-β-hydroxypropionic acid show behavior typical of that expected of a carbonium ion reaction. The rate-determining process in dehydration is the loss of the hydrogen from the α-carbon.

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[27] S. Winstein and A. H. Fainberg, *J. Am. Chem. Soc.*, **79**, 5937 (1957).

[28] A. H. Fainberg and S. Winstein, *ibid.*, **79**, 1602 (1957).

[29] N. C. Deno, J. J. Jaruzelski and A. Schriesheim, *ibid.*, **77**, 3044 (1955); N. C. Deno, H. E. Berkheimer, W. L. Evans and H. J. Peterson, *ibid.*, **81**, 2344 (1959).

[Contribution from the Department of Chemistry, University of California, Berkeley, Calif.]

The Kinetics of the Dehydration of Substituted β-Phenyl-β-hydroxypropionic Acids[1-3]

By Donald S. Noyce, Paul A. King,[4] Charles A. Lane,[5] and Wilmer L. Reed

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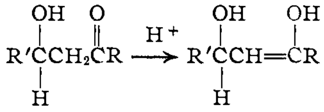
The rate of dehydration has been measured for a series of β-aryl-β-hydroxypropionic acids. An electron-donating substituent markedly accelerates the rate of dehydration, while an electron-withdrawing substituent severely slows the reaction. The rates may be correlated with σ^+, with a ρ of -4.6. Suggested mechanisms for the dehydration of β-hydroxy acids are discussed.

Introduction

In recent studies[6,7] we have investigated the rates and mechanism of the dehydration of β-aryl-β-hydroxyketones under acidic conditions.

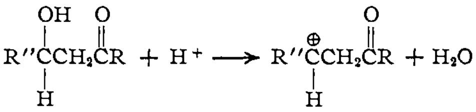
It was found that for most compounds enolization is the rate-controlling step (eq. 1). Rapid loss of the elements of water then occurs. Evidence was obtained for an alternative mechanism, in which



$$\mathrm{R'\overset{OH}{\underset{H}{C}}CH_2\overset{O}{\overset{\|}{C}}R \xrightarrow{H^+} R'\overset{OH}{\underset{H}{C}}CH{=}\overset{OH}{\overset{|}{C}}R} \qquad (1)$$

direct formation of the carbonium ion takes precedence over enolization (eq. 2).

This latter mechanism was observed with 4-(p-methoxyphenyl)-4-hydroxy-2-butanone and 4-(p-methoxyphenyl)-4-hydroxy-3-methyl-2-butanone.



$$\mathrm{R''\overset{OH}{\underset{H}{C}}CH_2\overset{O}{\overset{\|}{C}}R + H^+ \longrightarrow R''\overset{\oplus}{\underset{H}{C}}CH_2\overset{O}{\overset{\|}{C}}R + H_2O} \qquad (2)$$

A

The very effective stabilization of the carbonium ion provided by the anisyl group is responsible for the change in mechanism. Characteristic of this latter mechanism is dependence upon H_0, with unit slope or greater, and only slightly negative entropy of activation. Since the speed of dehydration is almost completely determined by the stability of the derived carbonium ion A, the carbonyl group is only a hindrance, inductively destabilizing the carbonium ion to some extent.

Pressman and Lucas have carried out studies of the rates of dehydration of β-hydroxybutyric acid[8] and of β-hydroxyisovaleric acid.[9] They pointed out the very great difference in the rate of dehydration between the hydroxy acids and the corresponding hydroxy aldehydes[10,11]: it would be expected that aliphatic hydroxy aldehydes, undergoing dehydration *via* enolization, would be far more labile than hydroxy acids. This, then, is a rational corol-

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[1] Paper XV in the series Carbonyl Reactions; previous paper, D. S. Noyce and C. A. Lane, *J. Am. Chem. Soc.*, **84**, 1635 (1962).

[2] Presented in part at the Meeting of the National Academy of Sciences, Berkeley, Calif., October, 1958; and at the 8th Conference on Reaction Mechanisms, Princeton, N. J., September, 1960.

[3] This research was supported in part by a grant from the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of these funds.

[4] Union Carbide Corp. Fellow, 1956–1957.

[5] National Science Foundation Co-operative Fellow, 1959–1960.

[6] D. S. Noyce and W. L. Reed, *J. Am. Chem. Soc.*, **80**, 5539 (1958).

[7] D. S. Noyce and L. R. Snyder, *ibid.*, **81**, 620 (1959).

[8] D. Pressman and H. J. Lucas, *ibid.*, **61**, 2271 (1939).

[9] D. Pressman and H. J. Lucas, *ibid.*, **62**, 2069 (1940).

[10] (a) S. Winstein and H. J. Lucas, *ibid.*, **59**, 1461 (1937); (b) D. Pressman and H. J. Lucas, *ibid.*, **64**, 1953 (1942).

[11] H. J. Lucas, W. T. Stewart and D. Pressman, *ibid.*, **66**, 1818 (1944).