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.

[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

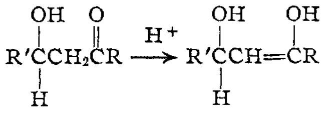
RECEIVED SEPTEMBER 29, 1961

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.

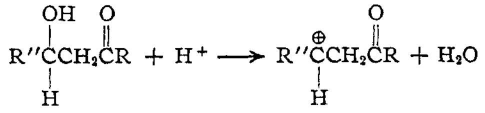
It was found that for most compounds enolization is the rate-controlling step (eq. 1). Rapid loss of the elements of water then occurs. Evidence was obtained for an alternative mechanism, in which



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

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.



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

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-

[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).

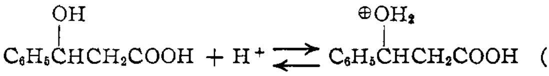
[9] D. Pressman and H. J. Lucas, *ibid.*, **62**, 2069 (1940).

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

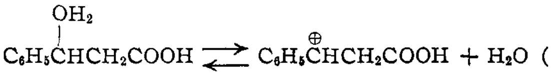
[11] H. J. Lucas, W. T. Stewart and D. Pressman, *ibid.*, **66**, 1818 (1944).

lary of our previous conclusions.[6,7] A further consequence is that the alternative mechanism involving the carbonium ion A should appear in the reactions of appropriate β-hydroxy acids.

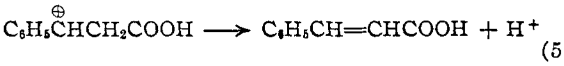
In the preceding paper[1] we have shown that the dehydration of β-phenyl-β-hydroxypropionic acid (I) shows the characteristics of a typical carbonium ion reaction sequence (eq. 3–5). Racemization of (+)-I proceeds more rapidly than dehydration.



$$C_6H_5\overset{\overset{\displaystyle OH}{|}}{C}HCH_2COOH + H^+ \rightleftarrows C_6H_5\overset{\overset{\displaystyle \oplus OH_2}{|}}{C}HCH_2COOH \quad (3)$$



$$C_6H_5\overset{\overset{\displaystyle OH_2}{|}}{C}HCH_2COOH \rightleftarrows C_6H_5\overset{\oplus}{C}HCH_2COOH + H_2O \quad (4)$$



$$C_6H_5\overset{\oplus}{C}HCH_2COOH \longrightarrow C_6H_5CH{=}CHCOOH + H^+ \quad (5)$$

In the present report we wish to show a further corollary, *i.e.*, that the rate of dehydration of β-aryl-β-hydroxypropionic acids is extremely sensitive to substituents in the aromatic ring. Accordingly, we have examined briefly the rate of dehydration of β-(*p*-methoxyphenyl)-β-hydroxypropionic acid (II), β-(*p*-chlorophenyl)-β-hydroxypropionic acid (III) and β-(*p*-nitrophenyl)-β-hydroxypropionic acid (IV).

Experimental[12]

β-(*p*-Methoxyphenyl)-β-hydroxypropionic Acid (II).—The Reformatsky reaction[13] afforded crude ethyl β-(*p*-methoxyphenyl)-β-hydroxypropionate. Distillation under reduced pressure led to extensive dehydration, so the crude ester was directly saponified. The crude ester from 84 g. of anisaldehyde was added to 300 ml. of 2.5 *N* alcoholic (15%) potassium hydroxide and allowed to stand 2 days at room temperature. After extracting the diluted (300 ml. of H_2O) alkaline hydrolysis mixture with ether, the alkaline solution was acidified to congo red with 10% sulfuric acid *while iced*. The solution was immediately extracted with ether. The dried (Na_2SO_4) ether extracts were concentrated, and the crude β-(*p*-methoxyphenyl)-β-hydroxypropionic acid crystallized from benzene–carbon tetrachloride three times to afford 46.1 g. of II, m.p. 90.2–90.8°. From the mother liquors an additional 8.3 g. of II, m.p. 89.6–90.6°, was obtained (total yield 55%).

Anal. Calcd. for $C_{10}H_{12}O_4$: C, 61.23; H, 6.12; neut. equiv , 196.2 Found: C, 61.37; H, 6.28; neut. equiv., 195.

β-(*p*-Chlorophenyl)-β-hydroxypropionic Acid (III).—The crude ester, ethyl β-(*p*-chlorophenyl)-β-hydroxypropionate, was obtained in 80% yield. It was not distilled, but hydrolyzed directly by boiling with 120 ml. of 1 *N* sodium hydroxide to which 50 ml. of 95% ethanol had been added. Acidification and work-up in the usual manner afforded a 90% yield of crude III. Two crystallizations from benzene–pentane afforded pure III, m.p. 81.5–82.5°.

Anal. Calcd. for $C_9H_9O_3Cl$: C, 53.88; H, 4.52; Cl, 17.67; neut. equiv., 200.6. Found: C, 54.26; H, 4.84; Cl, 17.65; neut. equiv., 200.0.

β-(*p*-Nitrophenyl)-β-hydroxypropionic acid (IV) was prepared by the method of Basler.[14] Ethyl *p*-nitrocinnamate (2 g.) was dissolved in acetic acid (12 ml.) and the cooled solution saturated with gaseous HBr. After sealing in a heavy-walled tube, the solution was heated at 100° for 3 hours. After cooling, the mixture was poured onto ice and filtered. The crude β-(*p*-nitrophenyl)-β-hydroxypropionic acid was dissolved in 100 ml. of 5% sodium carbonate solution and allowed to stand overnight. The alkaline solution was extracted with ether to remove neutral material, presumably *p*-nitrostyrene, and acidified to precipitate crude IV. Three crystallizations from benzene afforded pure IV, m.p. 131.2–132.2° (lit.[14] 130–132°).

Anal. Calcd. for $C_9H_9O_5N$: C, 51.20; H, 4.26; N, 6.63; neut. equiv., 211.1. Found: C, 51.40; H, 4.33; N, 6.65; neut. equiv., 212.

Isolation of Products under Conditions of the Kinetic Experiments. A. *p*-Methoxycinnamic acid was obtained in excellent yield from β-(*p*-methoxyphenyl)-β-hydroxypropionic acid. A solution of 300 mg. of II in 500 ml. of 3 *M* sulfuric acid was maintained at 45° for 10 hours. Extraction with ether and isolation of the acidic fraction afforded 0.25 g. (95%) of crude *p*-methoxycinnamic acid, m.p. 169.6–171.6°. A small sample was crystallized from ether, and the purified material was identical in infrared spectrum with authentic *p*-methoxycinnamic acid, m.p. and mixed m.p. 172.7–173.5°.

B. *p*-Chlorocinnamic Acid.—A solution of 1.33 g. of III in 1 liter of 62.3% sulfuric acid was maintained at 45° for 6.5 hours. The initial solution was clear, but gradually turned milky as the product started to precipitate. At the end of the heating period, the cooled solution was filtered, and the filtrate diluted with water to permit continuous extraction with ether. The ether extract and the precipitate were combined, and the *p*-chlorocinnamic acid was extracted into dilute sodium hydroxide solution. The acid was precipitated with dilute sulfuric acid and filtered. There was obtained 1.18 g. (97%) of *p*-chlorocinnamic acid, m.p. 248–251°. No depression was observed on admixture with an authentic sample of *p*-chlorocinnamic acid.

Results

β-(*p*-Methoxyphenyl)-β-hydroxypropionic Acid (II).—At room temperature and in 50% sulfuric acid II undergoes extremely rapid dehydration, with a half-life of less than one-half minute. At 45°, in 0.1*M* sulfuric acid, the main course of reaction is the synchronous dehydration and decarboxylation upon which we have reported briefly.[15]

Between these two extremes we have obtained data on the rate of dehydration of II over a range of acidities (Table I).

TABLE I

RATE OF DEHYDRATION OF β-(*p*-METHOXYPHENYL)-β-HYDROXYPROPIONIC ACID

H_2SO_4, *M*	$k_{-H_2O} \times 10^5$, sec.$^{-1}$	H_0[c]		log $k + H_0$[d]
		$T = 45.00°$		
0.10[a]	0.43	0.83		−4.55
0.50[a]	3.46	.13		−4.39
1.00	6.5	− .26		−4.45
1.83	26	− .74		−4.32
2.13	34	− .91		−4.37
2.39	40	−1.05		−4.45
2.54[b]	56	−1.03		−4.27
2.62	67	−1.18		−4.36
2.97	107	−1.37		−4.34
	H_0	k, sec.$^{-1}$	log k	log $k + H_0$
		$T = 25.00°$		
24.18	−1.33	8.2×10^{-5}	−4.09	−5.42
38.43	−2.30	1.75×10^{-3}	−2.76	−5.06
47.00	−3.06	1.72×10^{-2} 1.8×10^{-2}[e]	−1.76	−4.82

[a] Followed by CO_2 evolution; other runs by the spectrophotometer method. [b] $HClO_4$ used in this run. [c] Values from Paul and Long[17] at 25°. [d] Average, excluding $HClO_4$ datum, −4.40 ± 0.06. [e] Less precise; range of optical density change quite small.

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

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

[14] A. Basler, *Ber.*, **16**, 3001 (1883).

[15] D. S. Noyce, G. L. Woo and P. A. King, *J. Org. Chem.*, **26**, 632 (1961).

The data at 45° show satisfactory correlation with H_0, though with considerable scatter (implicit in a situation where a total rate must be divided between two reactions).

The data at 25° have been taken in the highest acidities at which it is convenient to work, and also under conditions where the simple dehydration reaction predominates to the almost complete exclusion of the synchronous dehydration and decarboxylation. The data at 25° show clearly that the slope of the $\log k + H_0$ plot is greater than unity, being 1.34. A plot of $\log k$ *vs.* J_0, as defined by Gold and Hawes,[16] gives a slope of 1.15. Similar results were obtained with I[1] and also for the dehydration of 4-(*p*-methoxyphenyl)-4-hydroxy-2-butanone.[6]

The activation parameters (E_a = 23. kcal., $\Delta S^{\ddagger} = -5 \pm 3$ e.u.) are similar to those obtained for many carbonium ion mechanisms.

Rate of Dehydration of III and IV.—Measurements of the rate of dehydration of β-(*p*-chlorophenyl)-β-hydroxypropionic acid (III) were made over a convenient range of acidity, sufficient to establish that the dehydration is strongly acid catalyzed. The rate parallels the acidity function with greater than unit slope (1.25). The data, determined in both sulfuric acid solution and perchloric acid solution, are given in Table II.

TABLE II

RATE OF DEHYDRATION OF β-(*p*-CHLOROPHENYL)-β-HYDROXYPROPIONIC ACID AT 45.00°

45° H_2SO_4, %	Long and Paul 25°, H_0	ΔH_0	H_0 cor.	$k \times 10^5$, sec.$^{-1}$	log k	log $k + H_0$ (cor.)	log $k + H_0$ (25°
53.46	−3.76	0.02	−3.74	6.82	−4.17	−7.91	−7.93
59.61	−4.42	.05	−4.37	35.1	−3.45	−7.82	−7.87
64.09	−4.93	.08	−4.85	185	−2.73	−7.58	−7.66
64.13	−4.94	.08	−4.86	185	−2.73	−7.59	−7.67
$HClO_4$, %							
55.50	−4.36			30.9	−3.51		−7.87
57.95	−4.82			82.3	−3.08		−7.90
59.42	−5.11			189	−2.72		−7.83
60.63	−5.32			348	−2.46		−7.78

A single measurement was made of the rate of dehydration of β-(*p*-nitrophenyl)-β-hydroxypropionic acid (IV) at 45° in 65.85% sulfuric acid. Under these conditions the observed pseudo-first-order rate constant is 1.42×10^{-6} sec.$^{-1}$. Solubility difficulties severely hamper the application of our usual methods to IV, and hence further experiments were not pursued.

Discussion

Variation of Rate with Structure.—The data presented above show very clearly the extreme sensitivity of the reaction to structure. This is precisely what would be expected from the reaction scheme 1–3

$$\text{ArCHOHCH}_2\text{COOH} + \text{H}^+ \rightleftarrows \text{ArCH(O}^{\oplus}\text{H}_2\text{)CH}_2\text{COOH} \quad (1)$$

$$\text{ArCH(O}^{\oplus}\text{H}_2\text{)CH}_2\text{COOH} \rightleftarrows \text{ArC}^{\oplus}\text{HCH}_2\text{COOH} + \text{H}_2\text{O} \quad (2)$$

$$\text{Ar}\overset{\oplus}{\text{C}}\text{HCH}_2\text{COOH} \xrightarrow{\text{slow}} \text{ArCH=CHCOOH} + \text{H}^{\oplus} \quad (3)$$

in which formation of the carbonium ion is rapid and reversible, and the rate of loss of the proton from the carbonium ion is rate determining.

It is useful to make comparison of the rates for I, II, III and IV at a common acidity. When compared at 60% sulfuric acid ($H_0 = -4.44$) at 45°, the rates cover a range of 10^7 (Table III).

TABLE III

COMPARATIVE RATES OF DEHYDRATION IN 60% SULFURIC ACID AT 45°

Compound, ArCHOHCH$_2$COOH	log k, sec.$^{-1}$	σ^{+a}
p-Methoxyphenyl	+0.5 ± 0.5	−0.778
Phenyl	−2.89	.00
p-Chlorophenyl	−3.43	.114
p-Nitrophenyl	−6.6 ± 0.1	.790

[a] From ref. 18.

Using the σ^+-values of Brown and Okamoto[18] a linear ρ–σ^+ plot is obtained with a slope of −4.6.

This slope is similar to that for several other reactions which have been correlated with the σ^+-values for the aromatic substituents. Particularly germane is the fact that the solvolysis of the substituted cumyl chlorides in aqueous acetone[18] shows a ρ of −4.62.

Comparison of β-Hydroxy Acids and β-Hydroxy Ketones.—The carbonium ion mechanism predicts that the rate of dehydration of II will be quite similar to that of 4-(*p*-methoxyphenyl)-4-hydroxy-2-butanone (V) and of 4-(*p*-methoxyphenyl)-4-hydroxy-3-methyl-2-butanone (VI) which we concluded previously[6,19,20] undergo dehydration *via* a carbonium mechanism.

The inductive effects of the carboxyl group (in II) and of the acetyl group (in V and VI) are very similar, and hence the ease of formation of the carbonium in each compound should be similar.[21]

The rates would be expected to show some difference, due to differences in conformation (*cf.* V and VI) and to differences in ease of loss of hydrogen. Rates are compared at three different acidities in Table IV.

TABLE IV

COMPARISON OF RATES OF DEHYDRATION OF SUBSTITUTED ANISYLCARBINOLS

H_0	log k for II	log k for V[a]	log k for VI[b]
−1.33	−4.09	−3.42	−5.07
−2.30	−2.76	−2.28	−4.10
−3.06	−1.76	−1.48	−3.30

[a] Interpolated from data in Table I, ref. 6. [b] Interpolated from data in Table IV, ref. 20, and Table I, ref. 19.

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[16] V. Gold and B. W. V. Hawes, *J. Chem. Soc.*, 2102 (1951). We have recalculated this function using H_0 values from the review of Paul and Long,[17] and the activity of water 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)).

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

[18] H. C. Brown and Y. Okamoto, *J. Am. Chem. Soc.*, **80**, 4979 (1958).

[19] D. S. Noyce and W. L. Reed, *ibid.*, **81**, 624 (1959).

[20] D. S. Noyce and L. R. Snyder, *ibid.*, **80**, 4324 (1958).

[21] There is an error of naivete in the designation of the rate-determining step in our studies on compound V (ref. 6, p. 5542). Clearly, in accord with the results of this paper, eq. 3, p. 5542, is best designated as the rate-determining step; *cf.* also ref. 22, footnote 4.

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

The rates of dehydration of II and V differ by a small factor (2 to 5 depending upon the acidity of the medium), while the difference in rate between V and VI is somewhat larger.

In fact, if in addition, one makes a correction for the difference in the σ-values for $-COOH$ and $-COCH_3$, the rate difference shows gratifying concordance with the mechanism advanced.

Comparison with other Hydroxy Acids.—It is now possible to offer a further interpretation of the results of Lucas and his co-workers.[8-11] The premise which we wish to put forward is that most β-hydroxy acids will undergo dehydration *via* a carbonium ion mechanism (eq. 1–3). This mechanism also appears to be most concordant with the facts for β-hydroxyisovaleric acid. The behavior of β-hydroxybutyric acid, on the other hand, is not in line with these conclusions; *e.g.*, the change from an aliphatic tertiary alcohol to an aliphatic secondary alcohol is not attended by a corresponding drop in rate; the activation parameters show deviation and the dehydration of *sec*-butyl alcohol appears to be slower than that of β-hydroxybutyric acid.

It, therefore, appears that β-hydroxybutyric acid undergoes acid-catalyzed dehydration by a different mechanism, *i.e.*, one similar to the enolization mechanism for dehydration of β-hydroxy ketones. Naturally this mechanism would be expected to apply also to β-hydroxypropionic acid.[10b]

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

Primary and Secondary Deuterium Isotope Effects on the Dehydration of β-Phenyl-β-hydroxypropionic Acid[1-3]

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

RECEIVED SEPTEMBER 29, 1961

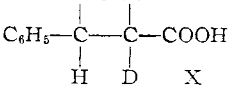
The kinetics of racemization of (+)-β-phenyl-β-hydroxypropionic-α-d_1 acid have been determined. The secondary isotope effect in this reaction is 1.11 ± 0.02. The rate of dehydration of β-phenyl-β-hydroxypropionic-α-d_1 acid is markedly less than that of the analogous protium compound. It is concluded that the kinetic isotope effects support a mechanism in which the rate-determining step is the direct loss of the α-proton to give cinnamic acid.

Introduction

Deuterium isotope effects have been of marked value in elucidating the more precise detail of many solvolytic carbonium ion reactions. In the hydrolysis of tertiary halides, Shiner[5] has shown that introduction of deuterium on the adjacent carbon has a decelerating influence upon the rate, which varies somewhat as this carbon is primary, secondary or tertiary. Lewis and Boozer[6] and Streitwieser, Jagow, Fahey and Suzuki[7] and Winstein and Takahashi[8] have examined secondary alkyl tosylates, observing a decrease in rate of 10 to 20% for each deuterium introduced when no other questions of participation are involved. A similar decrease in rate is observed in the acetolysis of methyl *p*-tolylcarbinyl chloride.[9]

Coupled with these secondary kinetic isotope effects are additional primary kinetic isotope effects if one of the pathways of reaction is elimination. In the examples studied by Shiner, the fraction of olefin formed drops from 36% for *t*-amyl chloride to 23% for *t*-amyl chloride-d_8. Similarly, when hydrogen participation is important, the observed rate of reaction is decreased by a greater fraction; in the case of acetolysis of 3-methyl-2-butyl-3-*d* *p*-toluenesulfonate[8] the rate decreases by a factor of $k_H/k_D = 2$. The product ratios likewise change, *e.g.*, more *t*-amyl acetate is formed and less 3-methyl-2-butene.[8]

In conjunction with our studies of the acid-catalyzed racemization and dehydration of β-phenyl-β-hydroxypropionic acid,[10] we have examined some deuterium isotope effects in this system in order to obtain more information about carbonium ion formation, and about the elimination step. In particular, we have prepared β-phenyl-β-hydroxypropionic-α-d_1 acid (X), and studied the rate of racemization, the rate of dehydration and the product composition. This system is of particular advantage for study of these acid-catalyzed reactions because of the demonstrated[11] stability of the product, *trans*-cinnamic acid under the conditions of the experiments. There is the further advantage that the single deuterium substitution makes possible evaluation of several secondary isotope effects.



$$C_6H_5-\overset{OH}{\underset{H}{C}}-\overset{H}{\underset{D}{C}}-COOH$$

X

Results

The addition of deuterium bromide to lithium cinnamate suspended in carbon tetrachloride afforded β-phenyl-β-bromo-propionic-α-*d* acid-*d* (XI); use of a non-polar solvent minimized the possibility

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(1) Paper XVI in the Series Carbonyl Reactions; previous paper, D. S. Noyce, P. A. King, C. A. Lane and W. L. Reed, *J. Am. Chem. Soc.*, **84**, 1638 (1962).

(2) Presented in part at the Eighth Conference on Organic Reaction Mechanisms, Princeton, N. J., September, 1960.

(3) 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.

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