raphy:[17] $\lambda_{\max}^{\mathrm{KBr}}$ 5.81 (CO), 6.77, 7.17, 7.70, 7.98, 8.18, 8.68, and 9.81 μ; $\delta_{\mathrm{TMS}}^{\mathrm{CCl_4}}$ 0.95 (singlet, 6 H) and 0.84 ppm (singlet, 6 H).

Anal. Calcd for $C_{15}H_{26}O$: C, 81.02; H, 11.79. Found: C, 81.2; H, 12.0.

9α,10α-Dimethyl-7α-isopropyldecal-2-one (14).—A solution containing 90 mg of ketone **5** in 5.0 ml of ethanol was stirred with 50 mg of palladium on charcoal in an atmosphere of hydrogen. After 11 ml of gas was taken up, the mixture was filtered and the product was isolated with ether[7b] and sublimed at room temperature (0.05 mm) affording moist white crystals, mp 33–36°, which were 97% pure by vpc.[18] The infrared and nmr spectra were superimposable on those of decalone **13** and the vpc retention times were identical by peak enhancement.

Registry No.—**1**, 15188-30-4; **2**, 4895-25-4; **3**, 5208-62-8; **4**, 13085-23-9; **5**, 15188-34-8; **7**, 15188-35-9; **8**, 15215-81-3; **9**, 15188-36-0; **10**, 15188-37-1; **11**, 5208-63-9; **11** 2,4-dinitrophenylhydrazone, 5208-64-0; **12**, 15188-39-3; **13**, 15188-40-6; **14**, 15188-41-7.

Acknowledgments.—We thank the Public Health Service for a Research Grant (AI-04965, Division of Allergy and Infectious Diseases) and a Predoctoral Fellowship (5-F1-GM-29, 696 to H. R.).

[17] A 0.25 in. × 15 ft column of 5% Carbowax 20 M on acid-washed DMCS 70–80 Chromosorb G was employed at 190°.

[18] The carbowax column was employed.[17]

Concerning the Kinetics of the Acid-Catalyzed Dehydration of α-Methyl-β-hydroxy-β-arylpropionic Acids[1]

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There has been a great deal of study devoted to the solvolytic behavior of alkyl halides and alkyl sulfonates, as influenced by numerous structural parameters.[2] However, there is somewhat less information regarding structural effects on the rates of E1 elimination. We have previously reported the results of studies of the kinetics of the acid-catalyzed dehydration of a variety of β-hydroxy acids[3–5] and β-hydroxy ketones.[6–9] These studies delineated the sensitivity of the dehydration reaction to electronic effects, and to structural changes at the alcoholic carbon. The present report is concerned with a brief examination of the effect of branching at the carbon β to the alcoholic moiety on the rate of dehydration of hydroxy acids. For this purpose we have examined the rates of dehydration of α-methyl-β-hydroxy-β-arylpropionic acids in moderately concentrated sulfuric acid. In each case the product is the *trans*-α-methylcinnamic acid.

In the solvolysis of tertiary halides chain branching generally leads to a modest increase in reactivity. Studies of the concomitant elimination reaction are somewhat less extensive. It has been reported that in 80% ethanol[10] *t*-butyl chloride gives 16% elimination, *t*-amyl chloride gives 33% elimination,[11] and 2,3-dimethyl-2-chlorobutane gives 62% elimination.[12] These results suggest that branching increases the rate of E1 reactions in aliphatic systems even more than it increases the rate of SN1 reactions. These strain interactions are more fully discussed by Brown and Fletcher.[12]

However, the situation appears to be different for benzyl systems. Baddeley, Chadwick, and Taylor[13,14] have observed that both for secondary and tertiary chlorides, branching reduces the rate of solvolysis. 2-Methyl-1-phenyl-1-chloropropane solvolyzes more slowly than 1-phenyl-1-chloropropane,[13] and 2-phenyl-2-chlorobutane solvolyzes more slowly than cumyl chloride.[14] These authors attributed these changes to steric hindrance to fully developed resonance interaction on ionization. A related situation is that discussed by Curtin.[15] In the study of elimination and rearrangement reactions which prefer a *trans* coplanar arrangement for the transition state, Curtin has observed a decreased rate of reaction for the *cis* isomer, and has attributed this "*cis*" effect to developing crowding in the transition state.

We have measured the rates of dehydration of **1**, **2**, and **3**. The results are given in Table I.

ArCHOHCH(CH$_3$)COOH
1, Ar = C$_6$H$_5$
2, Ar = p-CH$_3$C$_6$H$_4$
3, Ar = p-CH$_3$OC$_6$H$_4$

TABLE I
RATES OF DEHYDRATION OF
α-METHYL-β-ARYL-β-HYDROXYPROPIONIC ACIDS AT 25.0°

Compd	% H_2SO_4	$-H_0$	10^5k_{obs}, sec^{-1}
1[a]		4.61	0.50[b]
	63.60	4.90	1.10
	68.71	5.60	6.64
	72.66	6.21	32.1
	73.22	6.29	39.3
	75.72	6.66	135
	78.87	7.17	492
2[c]	60.30	4.61	15.0[d]
	61.89	4.79	23.4
	64.08	5.07	52.3
	66.66	5.50	142
	69.01	5.90	366
3[c]	60.30	4.61	1030

[a] In aqueous sulfuric acid. [b] Extrapolated using $\log k + H_0 = -10.60$. [c] In aqueous sulfuric acid containing 5% ethanol. [d] Extrapolated value.

The acid-catalyzed dehydrations of **1**, **2**, and **3** show typical carbonium ion characteristics. The rates increase sharply with increasing sulfuric acid concentration. They are extremely sensitive to the electron-

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[1] Previous paper: D. S. Noyce, L. M. Gortler, F. B. Kirby, and M. D. Schiavelli, *J. Am. Chem. Soc.*, **89**, 6944 (1967).

[2] A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962.

[3] D. S. Noyce, P. A. King, C. A. Lane, and W. L. Reed, *J. Am. Chem. Soc.*, **84**, 1638 (1962).

[4] D. S. Noyce and R. A. Heller, *ibid.*, **87**, 4325 (1965).

[5] D. S. Noyce, S. K. Brauman, and F. B. Kirby, *ibid.*, 4335 (1965).

[6] D. S. Noyce, W. A. Pryor, and P. A. King, *ibid.*, **81**, 5423 (1959).

[7] D. S. Noyce and W. L. Reed, *ibid.*, **80**, 5539 (1958).

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

[9] D. S. Noyce and M. J. Jorgenson, *J. Org. Chem.*, **28**, 3208 (1963).

[10] K. A. Cooper, E. D. Hughes, and C. K. Ingold, *J. Chem. Soc.*, 1280 (1937).

[11] E. D. Hughes and B. J. MacNulty, *ibid.*, 1283 (1937).

[12] H. C. Brown and R. S. Fletcher, *J. Am. Chem. Soc.*, **70**, 1223 (1950).

[13] G. Baddeley, J. Chadwick, and H. T. Taylor, *J. Chem. Soc.*, 2405 (1954).

[14] G. Baddeley, J. Chadwick, and H. T. Taylor, *ibid.*, 448 (1956).

[15] D. Y. Curtin, *Record Chem. Progr.* (Kresge-Hooker Sci. Lib.), **15**, 111 (1954).

donating nature of the aromatic substituent, and correlations of reactivity are in general completely analogous to those obtained earlier for β-aryl-β-hydroxypropionic acids.[3]

Furthermore, by studying the rate of interconversion of the two diastereoisomers of 2, we have found that this epimerization is far more facile than the dehydration. This parallels the studies of the rate of racemization of β-phenyl-β-hydroxypropionic acid[16] (4). In 42% sulfuric acid the half-life for the conversion of the *threo* isomer of 2 (mp 117°) to the equilibrium composition (63:37, *threo–erythro*) is 1.8 hr at room temperature. It is to be noted that the half-life for racemization of 4 under these conditions is 0.75 hr, and that the predicted half-life for the racemization of β-(*p*-tolyl)-β-hydroxypropionic acid (5) would be less than 5 min. Hence, the branching effect substantially decreases the rate of ionization to the carbonium ion in this system just as it does in Baddeley's[13] system.

Turning now to a consideration of the over-all rate of dehydration it is observed that the ultimate formation of α-methylcinnamic acid from 1 is substantially slower than the formation of cinnamic acid from 4. Interpolation from the data[16] for the rate of dehydration of 4, gives a rate ratio of 40 to 45. Likewise, extrapolation of the reported data[3] for the dehydration of β-(*p*-methoxyphenyl)-β-hydroxypropionic acid (6) to an H_0 of −4.61 reveals that 6 undergoes dehydration 60 times more rapidly than 3. These results suggest that in the activated complex for the dehydration process there develop substantial crowding interactions which raise the activation energy and, hence, reduce the rate of dehydration. As the substituted cinnamic acids necessarily have present one *cis* interaction, this reduced rate of dehydration for 1, 2, and 3 is clearly reminiscent of the "*cis*" effect which has been discussed by Curtin.[15]

Experimental Section[17]

Preparation of Materials. α-Methyl-β-hydroxy-β-phenylpropionic acid (1) was prepared by the method of Zimmerman and English,[18] mp 93.5–95.0°. These authors have established the configuration of the 95° melting isomer as the *threo* isomer. Following the suggestions of Cancielli, Basselier, and Jacques[19] regarding the use of nuclear magnetic resonance (nmr) for configurational assignments based on the chemical shift of H_β and the magnitude of the coupling constants between H_α and H_β, we observe that using ethyl α-bromopropionate in the original Reformatsky reactions, the two diastereoisomeric esters are formed in a 1:1 ratio; using methyl α-bromopropionate in the Reformatsky reaction, they are formed in a 3:2 ratio (*erythro–threo*).

In a similar manner, **ethyl α-methyl-β-hydroxy-β-(*p*-tolyl)-propionate** was prepared, and shown to be a mixture of the *threo* and *erythro* isomers in a 41:59 ratio. Saponification provided a mixture of the acids.

A total of 170 g of crude, partially crystalline α-methyl-β-hydroxy-β-(*p*-tolyl)propionic acid was separated by fractional crystallization into two distinct hydroxy acid fractions. The two pure acids were obtained from toluene: a high-melting acid (mp 118.5–119.5°) and a low-melting one (mp 107.0–108.5°).

The isomer separation was not a systematic fractional crystallization. The two isomeric acids individually crystallized from toluene in distinctly different crystalline forms; the low-melting acid in large prisms and the high-melting acid in rosettes. When the two acids crystallized from solution as a conglomerate of two different solid forms, isolation of the isomers was most conveniently effected by manual separation. Frequently, however, crystallization led to a broad-melting mixture, mp 85 to >100°. Instead of yielding one pure isomer, repeated crystallization of such material most often led to a mixture of crystalline forms which were separated by hand. When one pure isomer was obtained from a broad-melting mixture, the isomer isolated was not consistently the same one. Only small amounts of either isomeric acid were obtained pure at only one time. These samples were combined and finally crystallized from water. In this solvent both isomers gave prisms. Approximately 25 g of each acid was obtained pure by this method.

Anal. Calcd for $C_{11}H_{14}HO_3$: C, 68.02; H, 7.26; neut equiv, 194.2. Found for 118.5–119.5° acid: C, 67.82; H, 7.19; neut equiv, 197.0. Found for 107.0–108.5° acid: C, 68.03; H, 7.25; neut equiv, 196.6.

On the basis of the nmr spectrum the high-melting acid has been assigned the *threo* configuration and the low-melting acid the *erythro* configuration.

Ethyl α-methyl-β-(*p*-anisyl)-β-hydroxypropionate was also prepared *via* a Reformatsky reaction. Attempted purification of the hydroxy ester or free acid usually resulted in extensive decomposition. Elution of the ester on neutral alumina, grade 1, caused some dehydration; little separation of the resulting ester mixture was obtained. However, saponification of the early fractions did yield an oil which solidified on standing in the refrigerator for 1 month. Sublimation of this material again afforded an oil which solidified on prolonged standing in the cold; mp 52–87°. Purification was attempted by dissolving this solid in excess diethyl ether and allowing the solvent to evaporate slowly from the stoppered flask in the refrigerator. The material (approximately 60% dehydrated) obtained in this manner was used directly in the pseudo-first-order rate studies of the dehydration of α-methyl-β-(*p*-anisyl)-β-hydroxypropionic acid.

Epimerization of *threo*-α-Methyl-β-hydroxy-β-phenylpropionic Acid.—*threo*-α-Methyl-β-hydroxy-β-phenylpropionic acid (0.19 g) was added to 50 ml of 61.5% sulfuric acid and stirred at room temperature for 25 min. The organic acid never completely dissolved. The reaction mixture was poured into ice water, partially neutralized with sodium carbonate, and ether extracted. After drying over magnesium sulfate and concentrating the ether extracts, the residue was taken up in benzene and introduced onto a water-saturated silica gel column. Any cinnamic acid was eluted with petroleum ether (bp 30–60°); only a very small amount of uncharacterized oil was obtained. The hydroxy acid, eluted with chloroform, was obtained as a broad-melting white solid (mp 72–88°). After one recrystallization (mp 81.5–91.5°), the nmr of the hydroxy acid ($CDCl_3$) revealed the presence of 26.7 ± 0.9% of the *erythro* diastereo isomer. This experiment serves to establish that even in very acidic media, epimerization is more rapid than dehydration.

Epimerization of *threo*-α-Methyl-β-hydroxy-β-(*p*-tolyl)propionic Acid. A. Equilibrium Ratio.—The equilibrium ratio of *threo*- and *erythro*-α-methyl-β-hydroxy-β-(*p*-tolyl)propionic acid was determined as follows. The *threo* acid (0.683 g) was dissolved in 25 ml of 95% ethanol in a 500-ml volumetric flask and diluted to the mark with aqueous sulfuric acid of appropriate strength. A separate sulfuric acid solution, made up from the same stock aqueous sulfuric acid and 5% by volume in 95% ethanol, was titrated to 41.9% sulfuric acid, $H_0 = -2.57$.[20] After stirring at room temperature for 14 hr, the reaction mixture was diluted with ice water and washed with two 250-ml portions of mixed hexanes. After concentration of the mixed hexanes extracts, the residue contained 0.219 g (47%) of styrenic material; the integrated rate constant for decarboxylation is $k_{-CO_2} = 1.3 \times 10^{-5}$ sec^{-1}, $\tau_{1/2}$ 15 hr. The aqueous phase was ether extracted and the combined ether extracts were dried over magnesium sulfate and concentrated to yield 0.319 g (47% recovery) of material. The nmr spectrum (pyridine) of this material integrated in the α-methyl and β-hydrogen regions for an average value of 36.8 ± 1.4% *erythro* isomer and 63.2 ± 1.4% *threo* isomer at equilibrium.

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[16] D. S. Noyce and C. A. Lane, *J. Am. Chem. Soc.*, **84**, 1635 (1962).

[17] Melting points were determined on a Kofler micro hot stage and are uncorrected. Analyses were performed by the Microanalytical Laboratory, University of California, Berkeley, Calif.

[18] H. E. Zimmerman and J. English, Jr., *J. Am. Chem. Soc.*, **76**, 2291 (1954).

[19] J. Cancielli, J. Basselier, and J. Jacques, *Bull. Soc. Chim. France*, 1906 (1963).

[20] D. R. Hartter, Ph.D. Dissertation, University of California, Berkeley, Calif.

B. Rate of Epimerization.—*threo*-α-Methyl-β-hydroxy-β-(*p*-tolyl)propionic acid (0.369 g) was dissolved in ethanol and aqueous sulfuric acid as described above. A separate sulfuric acid solution, made up from this same stock aqueous sulfuric acid and 5% by volume in 95% ethanol, was titrated to 41.7% sulfuric acid, $H_0 = -2.55$. After stirring at room temperature for 2 hr, the reaction mixture was worked up as above. There was recovered 0.318 g (86%) of acidic material which analyzed in the α-methyl and β-hydrogen regions of the nmr (pyridine) for an average value of 21.5 ± 0.4% *erythro* isomer, 78.5 ± 0.4% *threo* isomer. The integrated rate constant for epimerization is $k_{\text{epim}} = 1.1 \times 10^{-4}$ sec^{-1}, $\tau_{1/2}$ 1.8 hr.

Kinetic Methods.—The rate of dehydration of **1**, **2**, and **3** was followed by observing the increase in absorption due to the formation of the substituted *trans*-α-methylcinnamic acid. In all cases the spectrum corresponded to the *trans* isomer. With **2**, it was observed that at the lower acidities dehydration was not complete; corrections were therefore made for the amount of hydroxy acid remaining at equilibrium.

Registry No.—**1** (*erythro*), 14366-87-1; **1** (*threo*), 14366-86-0; **2** (*erythro*), 15080-31-6; **2** (*threo*), 15080-32-7; **3**, 15084-04-5.

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The Kinetics of the Acid-Catalyzed Hydration of 1-Phenylpropyne[1,2]

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The effect of substituents upon reactivity has provided much useful information regarding the mechanism for many different types of systems. In conjunction with our studies[4-6] of the mechanism of the acid-catalyzed hydration of acetylenes, we have examined the hydration of 1-phenylpropyne (**1**) catalyzed by sulfuric acid.

The hydration of **1** proceeds smoothly in 50% sulfuric acid to give a quantitative yield of propiophenone as shown by the ultimate spectrum of the solution. The reaction is strongly acid catalyzed and a plot of the logarithm of the observed rate constants against $-H_0$ is linear with a slope of 1.30. Determination of the rate of hydration in deuteriosulfuric acid shows that the solvent isotope effect, $k_{\text{H}_2\text{O}}/k_{\text{D}_2\text{O}}$, is 2.0 in the region of 50% sulfuric acid. The solvent isotope effect is somewhat higher in the more concentrated acid media. This information shows that the hydration of **1**, in common with that of the other acetylenic compounds which we have studied, is characterized by a rate-determining proton transfer and undoubtedly proceeds through a vinylic cation. The rate data are summarized in Table I.

TABLE I

RATE OF HYDRATION OF 1-PHENYLPROPYNE

A. In H_2SO_4 at 25.00°

Wt % acid	10^4k_{obs}, sec^{-1}	$-H_0$	Log $k + H_0$
48.74	1.31	3.26	−7.14
50.20	2.03	3.42	−7.11
51.51	3.04	3.56	−7.08
52.90	5.17	3.72	−7.01
53.56	5.69	3.76	−7.01
55.78	14.1	4.04	−6.89
56.72	18.3	4.16	−6.90

B. In D_2SO_4 at 25.00°

Wt % acid	10^4k_{obs}, sec^{-1}	$-D_0{}^a$	Log $k + D_0$
43.03	0.239	2.89	−7.51
47.94	0.945	3.41	−7.43
51.52	2.82	3.80	−7.35
52.60	4.28	3.92	−7.29
54.70	8.60	4.16	−7.23
56.74	18.8	4.42	−7.15

[a] For definition, see ref 6.

It is to be noted that the hydration of 1-phenylpropyne is substantially slower than the hydration of phenylacetylene. At an H_0 of −3.0, this ratio ($k_{\text{H}}/k_{\text{CH}_3}$) is 28. Similar retardations have previously been observed upon addition of an alkyl group β to a carbonium ion center in the acid-catalyzed hydration of unsaturated systems. In studies of the hydrolysis of vinyl ethers, Jones and Wood[7] observed that the hydration of ethyl vinyl ether is 5.8 times more rapid than the hydration of ethyl propenyl ether. The introduction of a second methyl group β to the oxygen further reduces the rate by a factor of 10. On the other hand, Taft, Purlee, Riesz, and DeFazio[8] have reported that the hydration of trimethylethylene is slightly faster than that of isobutylene.

The extensive studies by Drenth and his coworkers on the acid-catalyzed hydration of alkynyl ethers and alkynyl thioethers show that the acid-catalyzed hydration of ethyl ethynyl ether[9] is 26 times faster than the hydration of ethyl propynyl ether[10] and that the hydration of ethyl ethynyl thioether is 24 times more rapid than that of ethyl propynyl thioether.[11] Thus, the hydration of the more highly substituted acetylenic systems seems to be substantially slower.

Hogeveen and Drenth[11] have discussed the possible reasons for these rate patterns. Examination of two possible sources for the rate differences is very instructive.

On the one hand the bond hybridization changes are not the same. In one case the rehybridization involves the change sp–s to sp^2–s while the other case involves the change sp–sp^3 to sp^2–sp^3. Data on heats of hydrogenation support such an argument. The difference in rate of hydration parallels the difference in heats of hydrogenation of 2-butyne and propyne[12]

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[1] Previous paper, D. S. Noyce and M. D. Schiavelli, *J. Am. Chem. Soc.*, in press.

[2] Supported in part by a grant from the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgement is made to the donors of these funds.

[3] National Science Foundation Predoctoral Fellow, 1964–1966; National Institutes of Health Predoctoral Fellow, 1966–1967.

[4] D. S. Noyce, M. A. Matesich, and P. E. Peterson, *J. Am. Chem. Soc.*, in press.

[5] D. S. Noyce and K. E. DeBruin, *ibid.*, **90**, 372 (1968).

[6] D. S. Noyce and M. D. Schiavelli, *ibid.*, in press.

[7] D. M. Jones and N. F. Wood, *J. Chem. Soc.*, 5400 (1964).

[8] R. W. Taft, Jr., E. L. Purlee, P. Riesz, and C. A. DeFazio, *J. Am. Chem. Soc.*, **77**, 1584 (1955).

[9] E. J. Stamhuis and W. Drenth, *Rec. Trav. Chim.*, **80**, 797 (1961).

[10] G. L. Hekkert and W. Drenth, *ibid.*, **82**, 405 (1963).

[11] H. Hogeveen and W. Drenth, *ibid.*, **82**, 375 (1963).

[12] T. L. Flitcroft and H. A. Skinner, *Trans. Faraday Soc.*, **54**, 47 (1958).