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 $k_{epim} = 1.1 \times 10^{-4}$ 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_{H_2O}/k_{D_2O}, 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_H/k_{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.

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

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

which may be chosen as models for the ground state. If these heats of hydrogenation are compared with those for models of the transition state, such as propylene and *trans*-2-butene,[13] a rate difference of 1.5 kcal can be accounted for. That is to say, the heats of hydrogenation allow one to estimate that 1-phenylpropyne is about 4 kcal more stable than ethynylbenzene in the ground state while the transition state models indicate that the methyl compound is only 2.5 kcal more stable at that point. This leads to the prediction that the energy of activation for 1-phenylpropyne hydration should be 1–2 kcal larger than that for phenylacetylene hydration.

1-Phenylpropyne differs from phenylacetylene in another way. Hyperconjugation has been shown[1,6] to make an important contribution to the factors governing the stability of the transition state leading to the vinyl cation intermediate. In any substituted phenylacetylene this stabilizing interaction is removed. If one plots the data for the relative rates of hydration of 1-phenylpropyne, phenylpropiolic acid,[4] and phenylbenzoylacetylene[5] against σ^* values, phenylacetylene is hydrated 70 times more rapidly than predicted by the correlation line. It thus appears that phenylacetylene is anomalously reactive, partly due to hyperconjugation in the transition state and partly due to bond energy differences in the initial state.

Experimental Section

1-Phenylpropyne was purified by distillation and checked by vpc. The kinetic methods used have been described previously.[6] The progress of a kinetic run was followed by observing the increase in absorbance at 256 mμ.

Registry No.—**1,** 673-32-5.

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The Preparation of Symmetrical Diaryl Sulfoxides from N,N′-Thionyldiimidazole

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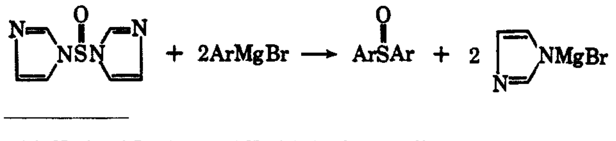
In attempting to prepare symmetrical diaryl sulfoxides we have found the existing methods to be not wholly satisfactory. We wish to report a new synthesis using N,N′-thionyldiimidazole, an intermediate described by Staab,[2] which affords reasonable yields of sulfoxide when treated with arylmagnesium halides (eq 1). In most cases the method offers a greater ease of work-up of the reaction mixtures and purification of the resultant sulfoxides. Although only *para*-substituted diaryl sulfoxides have been made in this laboratory, the method appears to be generally applicable to preparation of symmetrical diaryl sulfoxides. The only requirement is that the desired aryl halide by capable of forming a Grignard reagent.



(1)

The sulfoxides prepared are listed in Table I.

TABLE I

Diaryl sulfoxide	% yield	Mp, °C[a]	Recrystn solvent
Phenyl	35	69.5–70.5 (70.5)[b]	Ether
p-Tolyl	40	94–95 (96)[c]	Ligroin
p-Anisyl	60	97–98.5 (93–94)[d]	Acetone
Mesityl	84	153.5–154[e] (153.5–154)	Ether
p-N,N-Dimethylaminophenyl	50	155, 151.5[f]	Acetone

[a] Literature melting points are given in parentheses. [b] C. E. Colby and C. S. McLoughlin, *Ber.*, **20**, 195 (1887). [c] F. Loth and A. Michaelis, *ibid.*, **27**, 2540 (1894). [d] S. Oae and C. Zalut, *J. Am. Chem. Soc.*, **82**, 5359 (1960). [e] S. Oae, T. Kitao, Y. Kitaoka, and S. Kawamura, *Bull. Chem. Soc. Jap.*, **38**, 546 (1965). [f] A. Michaelis and P. Schindler, *Ann.*, **310**, 137 (1900).

General Preparation of Sulfoxides.—All the sulfoxides in Table I were prepared by addition of a solution of N,N′-thionyldiimidazole to a previously prepared solution of the desired Grignard reagent according to the following general directions.

Thionyl chloride (12 g, 0.10 mole) was added dropwise with stirring and cooling in an ice bath to a solution of imidazole (28 g, 0.41 mole) in 250 ml of anhydrous tetrahydrofuran. A white precipitate formed immediately. After cooling for several minutes, the reaction mixture was rapidly filtered by suction under a nitrogen atmosphere. The clear filtrate was added dropwise over a 15-min period to a Grignard solution at room temperature made from magnesium (9 g, 0.38 g-atom) in 50 ml of anhydrous tetrahydrofuran and 0.33 mole of the desired aromatic halide in 100 ml of anhydrous tetrahydrofuran. The reaction mixture was stirred at room temperature for 1 hr and then hydrolyzed by pouring into 400 ml of an ice-dilute hydrochloric acid mixture. The organic and aqueous layers were separated and the aqueous layer was extracted with three 100-ml portions of diethyl ether or chloroform. The combined extracts were washed with 100 ml of saturated sodium bicarbonate solution, separated, and again washed with 100 ml of water. The organic solution was dried over anhydrous magnesium sulfate, the drying agent filtered off, and the solvent removed using a rotary evaporator. The residue crystallized on cooling and, in most cases, merely washing with cold ether yielded pure product. Crystallization solvents are included in Table I.

Nmr and ir spectra and melting points were consistent for all the compounds listed. The sulfoxides were oxidized to the known sulfones using hydrogen peroxide in acetic acid[3] and reduced to the known sulfides using sodium iodide in hydrochloric acid solution.[4]

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(1) National Institutes of Health Predoctoral Fellow.

(2) (a) H. A. Staab and K. Wendel, *Angew. Chem.*, **73**, 26 (1961); (b) H. A. Staab, *ibid.*, **74**, 407 (1962); (c) H. A. Staab, K. Wendel, and A. Datta, *Ann.*, **694**, 78 (1966); (d) H. A. Staab and K. Wendel, *ibid.*, **694**, 86, 91 (1966).

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