Table VII. Rate of Exchange of *trans*-Stilbene-α-d_1 in 5% EtOH–95% H_2O–H_2SO_4 at 45.00°

H_2SO_4, %	k_{exch}, sec^{-1}	k_{-H_2O}, sec^{-1}
43.52	2.77×10^{-6}	6.30×10^{-3}
43.54		6.26×10^{-3}

ditions. These results, when corrected for the statistical factors, for estimates of the secondary isotope effects, and for the primary isotope effect, lead to the conclusion that at equilibrium in this medium there is 0.31% 1,2-diphenylethanol remaining.

These data provide a relatively complete picture for the acid-catalyzed dehydration of 1,2-diphenylethanol. Acid-catalyzed formation of the carbonium ion, followed by rate-limiting loss of a proton to directly give stilbene, is the preferred reaction sequence.

The Effect of Substituents on the Rate of the Acid-Catalyzed Dehydration of 1,2-Diarylethanols[1,2]

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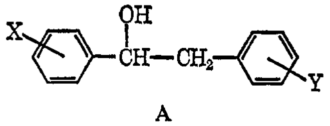
Abstract: The rates of the acid-catalyzed dehydration of several 1,2-diarylethanols (X–$C_6H_4CHOHCH_2C_6H_4$–Y) have been measured. The rates of dehydration in 55% sulfuric acid are well correlated by the equation $\log k_{X,Y} = -3.78(\sigma_X^+ + 0.23\sigma_Y) - 3.19$, showing the very strong sensitivity of the reaction rate to the electronic nature of the substituent X. The influence of substituent Y is very modest. No evidence for the possible intervention of a symmetrical proton–π complex was obtained.

In the preceding paper it has been shown that the acid-catalyzed dehydration of 1,2-diphenylethanol to form *trans*-stilbene is characterized by a rate-limiting loss of a proton from the carbonium ion. The carbonium ion is formed relatively rapidly, and it undergoes reaction with solvent with attendant racemization about 60 times more rapidly than it forms *trans*-stilbene. The reaction rate correlates well with the acidity function, and shows typical carbonium ion characteristics.

In the present report we wish to present the results of studies of a variety of substituted 1,2-diarylethanols. The diarylethanol system offers the possibility of making changes in the general electronic environment not only at the carbinol carbon but also at the β-carbon, from which the proton is ultimately lost. This structural situation is thus much more versatile than that afforded by the β-hydroxy-β-arylpropionic acids which we have studied previously.[5]

Two types of structural variation have been made. In one instance variation of the substituent X in the 1-aryl ring allows a test of the sensitivity of reaction rate to the direct influence of the effect of the substituent on the carbonium ion center. Alternatively, variation of the substituent Y in the 2-aryl ring allows test of more indirect influences on the rate of reaction. Finally, the symmetrical compounds represent a further point of interest which will be amplified below.



A

Results and Discussion

1-Aryl-2-phenylethanols. The rate of dehydration of six selected 1-aryl-2-phenylethanols has been measured. The data are presented in Tables I and II. All of the compounds show good correlation with the acidity function, H_0, and a plot of the logarithm of the observed rate *vs.* $-H_0$ is linear with a slope greater than unity. The slopes cluster around 1.3. Further examination of the response of the rate of dehydration to the acidity of the medium by accounting as well for the changing activity of water in the medium is instructive. Using the plotting technique of Bunnett,[6] the "*w*" values generally are about -1. For 1-*p*-anisyl-2-phenylethanol "*w*" is -2. A nearly equivalent fashion of examining the data is to estimate J_0[7,8] for our medium, and then to plot the observed rates ($\log k$) *vs.* $-(J_0)$. When treated in this fashion the slopes of the plots are all close to unity.

The data for 1-*p*-nitrophenyl-2-phenylethanol when plotted against $-J_0$ shows distinct curvature in the region above 76% sulfuric acid. This behavior is suggestive of the possibility that a substantial fraction of 1-*p*-nitrophenyl-2-phenylethanol is protonated, and exists as the oxonium salt in the most acidic media.

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(3) Shell Fellow in Chemistry, 1963–1964.

(4) National Science Foundation Cooperative Fellow, 1962–1964.

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

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(8) Since data for the activity of water in sulfuric acid media containing 5% ethanol are not known, a_{H_2O} for purely aqueous sulfuric acid solutions have been used. This should be a very good approximation; further, if the relative values are correct, then $J_0 = H_0$ (alcohol) + $\log a_{H_2O}$ will be in error only by a constant term.

Table I. Rate of Dehydration of 1-Aryl-2-phenylethanols in 5% Ethanolic Sulfuric Acid at 25.00°

Compound	H_2SO_4, %	$-H_0$ (alcohol)	10^5k, sec^{-1}	Log k + H_0
1-*p*-Anisyl-2-phenylethanol, X = *p*-OCH_3 (**2**)	8.37	0.12	0.467	−5.45
	11.50	0.40	0.979	−5.41
	15.55	0.68	2.07	−5.36
	20.05	0.99	5.55	−5.25
	25.83	1.36	15.2	−5.18
	31.60	1.76	51.9	−5.04
	36.00	2.08	141	−4.93
	38.26	2.24	218	−4.91
	40.06	2.40	358	−4.85
	42.15	2.59	697	−4.75
	43.84	2.74	988	−4.75
	55.4	4.00	(60,000)[a]	−4.22
1-*p*-Tolyl-2-phenylethanol, X = *p*-CH_3 (**3**)	45.84	2.97	58.3	−6.20
	48.26	3.22	115.0	−6.16
	50.60	3.48	247	−6.09
	51.82	3.60	348	−6.06
	55.4	4.00	(1,130)[a]	−5.95
1,2-Diphenylethanol, X = H (**1**)	55.4	4.00	56.0[b]	−7.25
1-*p*-Bromophenyl-2-phenylethanol, X = *p*-Br (**4**)	55.4	4.00	(17.4)[a]	−7.76
	59.69	4.53	86.6	−7.59
	61.76	4.77	181	−7.51
	63.77	5.03	411	−7.42
1-*m*-Chlorophenyl-2-phenylethanol, X = *m*-Cl (**5**)	55.4	4.00	(2.52)[a]	−8.60
	63.44	4.99	55.6	−8.25
	66.33	5.45	252	−8.05
	67.90	5.70	495	−8.01
1-*p*-Nitrophenyl-2-phenylethanol, X = *p*-NO_2 (**6**)	55.4	4.00	(0.016)[a]	−10.80
	67.72	5.68	2.48	−10.29
	70.61	6.16	10.5	−10.14
	72.83	6.54	34.2	−10.01
	74.52	6.83	85.3	−9.90
	75.88	7.05	197	−9.76
	77.22	7.28	360	−9.72
	78.14	7.43	513	−9.72
	78.37	7.47	562	−9.72

[a] Extrapolated values. [b] Interpolated from the data in the previous paper.

Table II. Rates of Dehydration of 1-Aryl-2-phenylethanols in 5% Ethanolic Sulfuric Acid at 45.00°

Compound	H_2SO_4, %	10^5k, sec^{-1}
1-Anisyl-2-phenylethanol, X = *p*-OCH_3 (**2**)	8.41	6.09
	9.62	7.96
	13.57	17.3
	19.85	55.0
	23.05	96.5
	28.57	277
	33.53	902
1-*p*-Nitrophenyl-2-phenylethanol, X = *p*-NO_2 (**6**)	63.09	4.47
	66.23	16.9
	70.50	124
	72.79	418

The rates of dehydration for compounds **1**–**6** have been extrapolated to a common acidity, 55.4% sulfuric acid, $H_0 = -4.00$. The relative rates correlate well with σ^+ substituent constants, and ρ is -3.77. This is somewhat higher than the value of ρ reported by Deno, Kish, and Peterson[9] for the relative rates of dehydration of substituted cumyl alcohols. A similar ρ was obtained by Schubert, Lamm, and Keeffe[10] and similar results are reported by Durand, *et al.*[11] In the dehydration of β-aryl-β-hydroxypropionic acids,[5] ρ was observed to be somewhat more negative. The large negative ρ is of course in complete accord with the mechanism presented in the previous paper.

Dehydration of 1-Phenyl-2-arylethanols. The rates of dehydration of four substituted alcohols, 1-phenyl-2-*p*-anisylethanol (**7**), 1-phenyl-2-*p*-methylphenylethanol (**8**), 1-phenyl-2-*p*-chlorophenylethanol (**9**), and 1-phenyl-2-*p*-nitrophenylethanol (**10**), are very much more nearly the same at a given acidity. Data given in Table III show that the rate difference between **7** and **10** is only a factor of 10 in 55% sulfuric acid ($H_0 = -4.00$), quite in contrast to the rate difference between **2** and **6** (*cf.* Table I).

Table III. Rates of Dehydration of 1-Phenyl-2-arylethanols in 5% Ethanol Sulfuric Acid at 25.00°

Compound	H_2SO_4, %	$-H_0$ (alcohol)	10^4k, sec^{-1}	Log k + H_0
2-*p*-Anisyl (**7**)	47.89	3.20	1.28	−7.09
	53.86	3.84	8.88	−6.90
	55.4	4.00	(14.1)[a]	−6.85
	55.88	4.06	16.1	−6.85
	57.34	4.24	29.2	−6.77
2-*p*-Methylphenyl (**8**)	52.37	3.66	3.20	−7.15
	55.4	4.00	(9.5)[a]	−7.03
	56.13	4.09	11.5	−7.03
	58.16	4.32	25.3	−6.92
	59.85	4.55	50.8	−6.85
2-*p*-Chlorophenyl (**9**)	55.4	4.00	(2.88)[b]	−7.54
	58.09	4.33	8.13	−7.42
	59.78	4.54	15.5	−7.35
	61.73	4.77	32.3	−7.26
2-*p*-Nitrophenyl (**10**)	55.4	4.00	(1.12)[b]	−7.95
	57.87	4.31	2.62	−7.89
	62.83	4.91	13.7	−7.78
	62.92	4.93	14.7	−7.76
	64.97	5.22	28.6	−7.76
	66.38	5.46	60.8	−7.68

[a] Interpolated value. [b] Extrapolated from rates at higher acidities.

These data correlate somewhat better with σ constants than with σ^+ constants. For correlation with σ constants, ρ is -1.0.

Multiply Substituted Diarylethanols. In addition to the ten compounds discussed above, the rate of dehydration of 1,2-bis(*p*-anisyl)ethanol (**11**) and of 1-*p*-anisyl-2-*p*-nitrophenylethanol (**12**) were determined. The results are given in Table IV.

The relative rates of compounds **11**, **3**, and **12** show a similar sensitivity to the effects of the substituents as the set of compounds **7**, **8**, **9**, and **10**, suggestive of better correlation with σ than with σ^+ and a ρ of about -1.

The results for all compounds studied are very well correlated by an equation of the form

$$\log k_{X,Y} = \rho(\sigma_X^+ + \epsilon\sigma_Y) + C \qquad (1)$$

in which ϵ represents an attenuation factor reflecting the fact that the substituent in the 2-aryl ring is one carbon further removed from the carbonium ion center, and also σ_Y is used, as this substituent is not directly

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Table IV. Rates of Dehydration of 1,2-Diarylethanols in 5% Ethanolic Sulfuric Acid

Substituted ethanol	Temp, °C	H_2SO_4, %	$-H_0$ (alcohol)	10^4k, sec^{-1}
1,2-Bis(*p*-anisyl) (**11**)	25.00	23.68	1.18	1.25
		28.65	1.54	3.60
		33.31	1.87	10.4
		36.12	2.06	18.9
		55.4	4.00	(7430.0)[a]
1-*p*-Anisyl-2-*p*-nitrophenyl (**12**)	25.00	25.98	1.38	.641
		33.49	1.90	3.25
		37.90	2.22	10.0
		40.71	2.45	19.6
		45.72	2.95	64.1
		55.4	4.00	(1550.0)[a]
	45.00	18.58	0.86	1.70
		23.59	1.20	4.53
		26.01	1.38	7.41
		28.60	1.55	13.6

[a] Extrapolated rates.

conjugated with the carbonium ion center. Attenuation factors typically have values of 0.3–0.4.[12]

In a recent study of solvolysis reactions in trifluoroacetic acid, Peterson, *et al.*,[13] have observed attenuation factors as large as 0.6, representing an unusually small diminution of the inductive effect with distance.

The best correlation is given by eq 2 for the rates of

$$\log k_{X,Y} = -3.19 - 3.78(\sigma_X^+ + 0.233\sigma_Y) \qquad (2)$$

dehydration in 55% H_2SO_4 ($H_0 = -4.00$). The value of ϵ, the attenuation factor, is smaller than in previous studies;[12] it should be noted that the particular set of compounds studied here does not provide an ultimately critical definition of ϵ. If instead of $\epsilon = 0.233$ a value of $\epsilon = 0.29$ is used, the correlation coefficient changes only from 0.998 to 0.997.

Concerning the Symmetrical Diarylethanols. It should finally be pointed out that the two symmetrical compounds, **11** and 1,2-diphenylethanol itself, show no deviations from the correlations presented above. Were the latter stages of the dehydration to involve the formation of a symmetrical proton π complex from the carbonium ion, accelerated rates of reaction might have been expected. This is not observed. Hence in interpreting the results of the present study there is no evidence requiring a proton π complex intermediate.

Experimental Section[14]

1-*p*-Anisyl-2-phenylethanol (2). Acylation of anisole with phenylacetyl chloride following the procedure of Buck and Ide[15] afforded α-phenyl-*p*-methoxyacetophenone, mp 77° (lit.[15] mp 74–75°). Reduction with sodium borohydride in methanol gave **2** in 92% yield (needles from water-alcohol), mp 58.5–59.5° (lit.[16] mp 58°).

1-*p*-Tolyl-2-phenylethanol (3) was prepared in similar fashion, mp 69–70° (lit.[17] mp 66.8–68.2°). Reduction of α-phenyl-*p*-bromoacetophenone with sodium borohydride in methanol afforded **1-*p*-bromophenyl-2-phenylethanol (4)**, mp 51–52° (from heptane). A small sample was sublimed for analysis.

Anal. Calcd for $C_{14}H_{13}BrO$: C, 60.67; H, 4.73; Br, 28.84. Found: C, 60.63; H, 4.50; Br, 28.98.

1-*m*-Chlorophenyl-2-phenylethanol (5). To the Grignard reagent from benzyl chloride, *m*-chlorobenzaldehyde in ether was added slowly. The mixture was hydrolyzed by pouring onto ice and hydrochloric acid. The two layers were separated, and the ether layer worked up in the usual manner to afford **5** as a colorless oil in 54% yield, bp 157° (0.15 mm).

Anal. Calcd for $C_{14}H_{13}ClO$: C, 72.26; H, 5.63; Cl, 15.24. Found: C, 72.29; H, 5.48; Cl, 15.10.

1-*p*-Nitrophenyl-2-phenylethanol (6). *trans-p*-Nitrostilbene was oxidized with perbenzoic acid to give *trans-p*-nitrostilbene epoxide, mp 125–126° (lit.[18] mp 125°). A solution of *p*-nitrostilbene epoxide (5 g) in 300 ml of toluene containing 3.0 g of *p*-toluenesulfonic acid was heated under reflux for 8 hr. The toluene solution was washed with 1 *N* sodium hydroxide, dried, and concentrated. The yellow residue was treated with Girard's reagent T to separate ketonic material. Hydrolysis afforded **α-phenyl-*p*-nitroacetophenone**, mp 158–160° (from benzene) (lit.[19] mp 157–158°), in 35% yield. Reduction of the ketone with sodium borohydride in methanol afforded **1-*p*-nitrophenyl-2-phenylethanol (16)**, which was purified by sublimation, mp 109–110°.

Anal. Calcd for $C_{14}H_{13}NO_3$: C, 69.12; H, 5.39; N, 5.76. Found: C, 69.11; H, 5.29; N, 5.98.

Reduction of α-(*p*-methoxyphenyl)acetophenone with sodium borohydride afforded **1-phenyl-2-(*p*-methoxyphenyl)ethanol (7)**, mp 61.5–62.0° (lit.[20] mp 62°). From the Grignard reagent of *p*-methylbenzyl chloride and benzaldehyde was obtained **1-phenyl-2-(*p*-methylphenyl)ethanol (8)**, mp 44–45° (lit.[17] mp 44.6–46.2°). In similar fashion **1-phenyl-2-(*p*-chlorophenyl)ethanol (9)**, mp 55° (lit.[17] mp 55.0–56.5°), was prepared.

Acylation of benzene with *p*-nitrophenylacetyl chloride afforded α-(*p*-nitrophenyl)acetophenone, mp 141–143° (lit.[21] mp 145°). Reduction of this ketone with sodium borohydride in methanol afforded **1-phenyl-2-(*p*-nitrophenyl)ethanol (10)**, mp 91–92° (from ethanol).

Anal. Calcd for $C_{14}H_{13}NO_3$: C, 69.12; H, 5.39; N, 5.76. Found: C, 68.87; H, 5.14; N, 5.91.

1,2-Bis(*p*-methoxyphenyl)ethanol (**11**) was prepared by sodium borohydride reduction of deoxyanisoin, mp 112.0–113.5° (lit.[22] mp 110.4°).

Reduction of α-(*p*-nitrophenyl)-*p*-methoxyacetophenone with sodium borohydride afforded **1-(*p*-methoxyphenyl)-2-(*p*-nitrophenyl)ethanol (12)**, mp 117–119° (from ethanol) (lit.[23] mp 113–115°).

Anal. Calcd for $C_{15}H_{15}NO_4$: C, 65.92; H, 5.53; N, 5.13. Found: C, 65.99; H, 5.52; N, 5.28.

Kinetic methods have been described previously.[1]

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