

# The Mechanism of the Acid-Catalyzed Dehydration of 1,2-Diphenylethanol<sup>1,2</sup>

Donald S. Noyce, Donald R. Hartter,<sup>3</sup> and Ralph M. Pollack

Contribution from the Department of Chemistry, University of California, Berkeley, California 94720. Received January 15, 1968

**Abstract:** The acid-catalyzed dehydration of 1,2-diphenylethanol (**1**) proceeds readily in 50–60% sulfuric acid, and affords *trans*-stilbene. The reaction is very sharply acid catalyzed, a plot of  $\log k$  vs.  $-H_0$  having a slope of 1.32. Racemization of active 1,2-diphenylethanol is 58 times more rapid than dehydration. In deuteriosulfuric acid, dehydration is more rapid. The rate of dehydration of 2-deuterio-1,2-diphenylethanol is smaller than that of **1**,  $k_H/k_D$  being 1.83. All of these facts are consistent with a reaction pathway involving the reversible formation of the 1,2-diphenylethyl cation followed by rate-limiting proton loss to give *trans*-stilbene.

A study of the acid-catalyzed dehydration of alcohols, as the reverse of the acid-catalyzed hydration of olefins, provides a way of gaining much pertinent information regarding the mechanism of proton transfer to unsaturated systems. In previous studies from these laboratories the acid-catalyzed dehydrations of  $\beta$ -hydroxy acids and of  $\beta$ -hydroxy ketones have been examined to compare with proton-initiated reactions of unsaturated acids and unsaturated ketones. The related pair, cinnamic acid and  $\beta$ -hydroxy- $\beta$ -phenylpropionic acid, have been examined in detail<sup>4</sup> and it was shown that these reactions are characterized by rate-limiting proton transfer to or from carbon.

In order to gain more insight into these reaction mechanisms and their generality, we have undertaken a study of the kinetics and mechanisms of the reactions of stilbene and 1,2-diphenylethanol (**1**). It is the purpose of the present report to present the evidence which serves to establish the mechanism of the acid-catalyzed dehydration of 1,2-diphenylethanol in reasonable detail.

## Experimental Section<sup>5</sup>

**Preparation of Materials.** 1,2-Diphenylethanol (**1**), mp 67.0–67.5°, was prepared by reduction of deoxybenzoin with sodium borohydride in methanol. Partial resolution of **1** was carried out following the procedure of Gerrard and Kenyon.<sup>6</sup> Material with  $[\alpha]^{25}_D +4.29^\circ$  was used to determine the rate of racemization of **1**. Following the procedure of Curtin and Kellom,<sup>7</sup> reduction of *cis*-stilbene oxide with lithium aluminum deuteride gave *threo*-2-deuterio-1,2-diphenylethanol (**2**), mp 65.8–66.4° (lit.<sup>7</sup> mp 64.4–65.4°). *Anal.* Found: 6.87 atom % excess D, corresponding to 96.2% monodeuteration. Similarly, reduction of *trans*-stilbene oxide with lithium aluminum deuteride afforded *erythro*-2-deuterio-1,2-

diphenylethanol (**3**), mp 66.0–66.2° (lit.<sup>7</sup> mp 64.4–65.4°). *Anal.* Found: 6.98 atom % excess D, corresponding to 97.8% monodeuteration. The infrared spectra were identical with those reported by Curtin and Kellom. The nmr spectra were distinctive and in accord with the structural assignments.

1-Deuterio-1,2-diphenylethanol (**4**) was prepared by reduction of deoxybenzoin with lithium aluminum deuteride. Deoxybenzoin- $\alpha,\alpha$ -*d*<sub>2</sub> was prepared by exchange in alkaline solution. A solution of 10 g of deoxybenzoin in 70 ml of purified dioxane was added to 70 ml of D<sub>2</sub>O in which 2 g of sodium had been dissolved. The mixture was refluxed overnight. On cooling, two layers formed. The aqueous layer was extracted with three 100-ml portions of ether, and the combined organic fractions were concentrated under reduced pressure. The exchange was repeated. Deoxybenzoin- $\alpha,\alpha$ -*d*<sub>2</sub> was reduced with lithium aluminum hydride and 1,2-diphenylethanol-2,2-*d*<sub>2</sub> (**5**) was isolated, mp 65.3–65.8° (from hexane). *Anal.* Found: 13.80 atom % excess D, corresponding to 96.5% deuteration.

**Preparation of Solutions and Kinetic Methods.** For all studies in 5% ethanolic solutions, the following method was used. To 5 ml of 95% ethanol in which a weighed quantity of the organic substrate was dissolved, sufficient aqueous sulfuric acid of the requisite strength was added to give a final volume of 100 ml. The final solution was titrated in duplicate against standardized base. For determination of the acidity function, a similar procedure was used, dissolving the Hammett indicators in the original ethanol. A like procedure was used to prepare 20% ethanol-sulfuric acid solutions and 50% ethanol-sulfuric acid solutions. The 30% acetic acid-sulfuric acid solutions were prepared by mixing weighed portions of acetic acid and standardized sulfuric acid. Other kinetic methods have been described previously.<sup>8</sup> Kinetic measurements were generally made using 10-cm cells.

**Acidity Function in 5% Ethanol.** The extremely low solubility of stilbene in aqueous sulfuric acid dictated the use of a mixed solvent system for the kinetic medium. Measurements of the acidity function in this mixed medium, described above, were carried out in the usual manner, and the results of these measurements are recorded in Table I. It is to be noted that from 10 to 40% sulfuric acid, the alcoholic solution is slightly less acidic than aqueous sulfuric acid; above 40% sulfuric acid the 5% alcoholic solution is more acidic.

**Exchange of *trans*-Stilbene- $\alpha$ -*d*<sub>1</sub>.** *trans*-Stilbene- $\alpha$ -*d*<sub>1</sub> was prepared by the method of Curtin and Harris.<sup>9</sup> A mixed solvent was prepared by diluting 70 ml of 95% ethanol with aqueous sulfuric acid to a total volume of 200 ml. To this solution was added 40 mg of *trans*-stilbene- $\alpha$ -*d*<sub>1</sub>. The solution was maintained at 45.00°, and then quenched by the addition of cold water. Stilbene was isolated by extraction with ether. The extracts were dried over anhydrous sodium sulfate and evaporated to dryness *in vacuo*. The solid residue, 30–40 mg, was purified by chromatography on neutral alumina. The fraction of deuterium remaining was determined by infrared spectroscopy, using a Perkin-Elmer Model 421 spectrophotometer, by measuring the 2235-cm<sup>-1</sup> band on an expanded scale setting. Known mixtures of *trans*-stilbene and *trans*-stilbene- $\alpha$ -*d*<sub>1</sub> were used to construct a calibration curve.

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(2) A portion of this work has been reported in a preliminary communication: D. S. Noyce, D. R. Hartter, and F. B. Miles, *J. Am. Chem. Soc.*, **86**, 3584 (1964).

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

(4) (a) D. S. Noyce and C. A. Lane, *J. Am. Chem. Soc.*, **84**, 1635 (1962); (b) D. S. Noyce, P. A. King, F. B. Kirby, and W. L. Reed, *ibid.*, **84**, 1632 (1962).

(5) Analyses are by the Microanalytical Laboratory, University of California, Berkeley, Calif. Deuterium analyses were carried out by Mr. Josef Németh, Urbana, Ill.

(6) W. Gerrard and J. Kenyon, *J. Chem. Soc.*, 2564 (1928).

(7) D. Y. Curtin and D. B. Kellom, *J. Am. Chem. Soc.*, **75**, 6011 (1953).

(8) D. S. Noyce and M. J. Jorgenson, *ibid.*, **84**, 4312 (1962).

(9) D. Y. Curtin and E. E. Harris, *ibid.*, **73**, 4519 (1951).

Table I.  $H_0$  Values for 5% EtOH-95% H<sub>2</sub>O-H<sub>2</sub>SO<sub>4</sub>

H <sub>2</sub> SO <sub>4</sub> , %	$H_0$ (alcohol) <sup>a</sup>	Indicator <sup>c</sup>	$\Delta H_0^b$	H <sub>2</sub> SO <sub>4</sub> , %	$H_0$ (alcohol)	Indicator <sup>c</sup>	$\Delta H_0^b$
10	-0.29	a	0	44	-2.76	c, d	-0.01
12	-0.44	a	+0.01	46	-2.98	c, d	-0.02
14	-0.59	a	+0.01	48	-3.22	c, d	-0.03
16	-0.73	a	+0.02	50	-3.42	c, d	-0.04
18	-0.86	a	+0.03	52	-3.64	d	-0.04
20	-0.98	a, b	+0.05	54	-3.83	d, e	-0.04
22	-1.10	a, b	+0.06	56	-4.08	e	-0.07
24	-1.23	a, b	+0.07	58	-4.33	e	-0.09
26	-1.37	a, b	+0.07	60	-4.58	e, f	-0.10
28	-1.51	b	+0.07	62	-4.80	e, f	-0.10
30	-1.64	b, c	+0.08	64	-5.07	e, f	-0.13
32	-1.80	b, c	+0.06	66	-5.40	f	-0.20
34	-1.93	b, c	+0.06	68	-5.74	f	-0.24
36	-2.08	b, c	+0.05	70	-6.07	f, g	-0.27
38	-2.23	b, c	+0.03	72	-6.41	g	-0.31
40	-2.39	b, c	+0.02	74	-6.74	g	-0.33
42	-2.56	c, d	0	76	-7.08	g	-0.37
				78	-7.41	g	-0.38

<sup>a</sup>  $H_0$  in the 5% EtOH-95% H<sub>2</sub>SO<sub>4</sub> system. <sup>b</sup>  $\Delta H_0 = H_0$  (alcohol) -  $H_0$ . The  $H_0$  values of M. A. Paul and F. A. Long [*Chem. Rev.*, **57**, 1 (1957)] for aqueous acid were used up to 60% H<sub>2</sub>SO<sub>4</sub>; above 60% sulfuric acid, the values of M. J. Jorgenson and D. R. Hartter [*J. Am. Chem. Soc.*, **85**, 878 (1963)] were used. <sup>c</sup>  $H_0$  (alcohol) determinations used the following indicators: a, 2-nitro-4-chloroaniline; b, 2,5-dichloro-4-nitroaniline; c, 2-chloro-6-nitroaniline; d, 2,4-dichloro-6-nitroaniline; e, 2,4-dinitroaniline; f, 2,6-dinitroaniline; g, 2,6-dinitro-4-chloroaniline.

## Results and Discussion

The dehydration of 1,2-diphenylethanol may be conveniently followed kinetically by observing the appearance of the characteristic ultraviolet absorption of *trans*-stilbene. In aqueous sulfuric acid the extremely limited solubility of *trans*-stilbene creates some experimental problems which are overcome by carrying out studies with a small fraction of organic cosolvent (we settled on the use of 5% added ethanol) and by using more dilute solutions (about  $10^{-6}$  M) in 10-cm cells. Scrupulous care to have the glassware clean was necessary in order to obtain excellent first-order behavior.

The dehydration of 1,2-diphenylethanol is very sharply acid catalyzed. The reaction rate increases more than 100-fold in changing from 46 to 62% sulfuric acid. The reaction proceeds essentially to completion. Careful measurements in 50% sulfuric acid of the ultimate production of *trans*-stilbene gave values of  $98.7 \pm 0.5\%$  dehydration. The measured rates of dehydration (which were followed to a stable "infinity" spectrum) have not been corrected for the very small amount of back reaction. Measured rates at 25 and 45° are presented in Table II. It is to be noted that the reaction rate increases more rapidly than the increase in the acidity of the medium. When the logarithm of the pseudo-first-order rate constant is plotted vs.  $-H_0$ , the slope is 1.32. A high slope such as this appears to be characteristic of reactions proceeding *via* carbonium ion intermediates, particularly benzyl cations. Similar slopes were observed in the dehydration of  $\beta$ -aryl- $\beta$ -hydroxypropionic acids<sup>4,10</sup> and by Grunwald, Heller, and Klein<sup>11</sup> in the oxygen exchange of 1-phenylethanol. Schubert and Lamm<sup>12</sup> and Deno, Kish, and Peterson<sup>13</sup> have made similar observations in the dehydration of

Table II. Rates of Dehydration of 1,2-Diphenylethanol in 5% EtOH-95% H<sub>2</sub>O-H<sub>2</sub>SO<sub>4</sub>

H <sub>2</sub> SO <sub>4</sub> , %	$k$ , sec <sup>-1</sup>	Log $k$	$-H_0$ (alcohol)	Log $k + H_0$ (alcohol)
$T = 25.00 \pm 0.01^\circ$				
46.43	$2.70 \times 10^{-5}$	-4.57	3.01	-7.58
50.23	$1.04 \times 10^{-4}$	-3.99	3.43	-7.42
53.56	$2.74 \times 10^{-4}$	-3.56	3.80	-7.36
55.66	$5.68 \times 10^{-4}$	-3.25	4.04	-7.29
57.66	$1.24 \times 10^{-3}$	-2.91	4.28	-7.19
57.97	$1.49 \times 10^{-3}$	-2.83	4.32	-7.15
58.03	$1.37 \times 10^{-3}$	-2.86	4.33	-7.19
59.73	$3.15 \times 10^{-3}$	-2.50	4.55	-7.05
59.94	$3.20 \times 10^{-3}$	-2.50	4.56	-7.06
61.12	$5.47 \times 10^{-3}$	-2.26	4.70	-6.96
62.70	$9.36 \times 10^{-3}$	-2.03	4.90	-6.93
$T = 45.00 \pm 0.01^\circ$				
36.26	$2.72 \times 10^{-5}$	-4.57	2.10	-6.67
42.30	$1.29 \times 10^{-4}$	-3.89	2.60	-6.49
46.50	$3.98 \times 10^{-4}$	-3.40	3.04	-6.44
49.80	$1.12 \times 10^{-3}$	-2.95	3.40	-6.35
52.26	$2.18 \times 10^{-3}$	-2.66	3.65	-6.31

benzyl alcohols. Plots of the observed rates in the present study vs.  $J_0$ <sup>14</sup> give a slope of 1.02. These results are completely concordant with a carbonium ion intermediate for the dehydration reaction.

**Racemization of 1,2-Diphenylethanol.** The racemization of 1,2-diphenylethanol is quite facile in moderately concentrated sulfuric acid. In order to measure the rate of racemization it is necessary to use solutions much more concentrated in 1,2-diphenylethanol. Hence we have used a medium containing a substantially larger fraction of ethyl alcohol. Data obtained are given in Table III, along with rates of dehydration

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

(11) E. Grunwald, A. Heller, and F. S. Klein, *J. Chem. Soc.*, 2604 (1957).

(12) W. M. Schubert and B. Lamm, *J. Am. Chem. Soc.*, **88**, 120 (1966).

(13) N. C. Deno, F. A. Kish, and H. J. Peterson, *ibid.*, **87**, 2157 (1965).

(14) The  $J_0$  function [V. Gold and B. W. V. Hawes, *J. Chem. Soc.*, 2102 (1951)] has been estimated by using the activity of water in purely aqueous sulfuric acid. As rate measurements have been made over a relatively narrow range of acidity, ignoring the 5% ethanol content of the medium should introduce only a constant error in  $-J_0$ . This treatment also is equivalent to plotting the data in the manner suggested by Bunnett [J. F. Bunnett, *J. Am. Chem. Soc.*, **83**, 4956 (1961)] with  $w = -1$ .

in the same medium, and also the apparent<sup>15</sup> acidity function of the medium as determined by the Hammett indicators.

**Table III.** Rate of Racemization of 1,2-Diphenylethanol in 50% Alcoholic Sulfuric Acid at 25.00°

Wt % acid	$k_{\text{racem}}$ , sec <sup>-1</sup>	$k_{-\text{H}_2\text{O}}$ , sec <sup>-1</sup>	$H_0$	$k_{\text{racem}}/k_{-\text{H}_2\text{O}}$
37.50	$1.96 \times 10^{-5}$		-1.45	
40.47	$5.06 \times 10^{-5}$	$8.64 \times 10^{-7}$	-1.73	59
43.34	$1.39 \times 10^{-4}$	$2.4 \times 10^{-6}$	-2.03	57
45.33	$3.03 \times 10^{-4}$	$5.19 \times 10^{-6}$	-2.27	58

Noteworthy is the fact that racemization is 58 times faster than dehydration. This ratio is very similar to that observed in the study of the reactions of  $\beta$ -hydroxy- $\beta$ -phenylpropionic acid.<sup>16</sup> The racemization of 1-phenylethanol also proceeds at least 100 times more rapidly than dehydration.<sup>11,12</sup>

**Isotope Effects in the Dehydration of 1,2-Diphenylethanol.** Both *erythro*- and *threo*-2-deuterio-1,2-diphenylethanols are dehydrated at the same rate, as would be expected from the results of the study of the racemization rate. Rate data are given in Table IV. The rate of dehydration is less than that of the protium compound. The observed kinetic isotope effect, correcting for partial deuteration, is  $k_{\text{H}}/k_{\text{D}} = 1.83$ .

**Table IV.** Rates of Dehydration of Isomeric 2-Deuterio-1,2-diphenylethanols in 5% EtOH-95% H<sub>2</sub>O-H<sub>2</sub>SO<sub>4</sub> at 25.00°

Compound	H <sub>2</sub> SO <sub>4</sub> , %	-H <sub>0</sub> (alcohol)	10 <sup>4</sup> k <sub>obsd</sub> , sec <sup>-1</sup>	$k_{\text{H}}/k_{\text{D}}^a$
<b>3</b> ( <i>erythro</i> )	53.08	3.75	1.54	1.66
	55.29	3.98	3.05	
	57.15	4.22	5.63	1.88
	58.05	4.33	8.77	1.79
	58.90	4.44	12.8	
<b>2</b> ( <i>threo</i> )	59.54	4.52	16.1	1.83
	57.97	4.32	8.47	1.83
	59.54	4.52	16.1	1.85

<sup>a</sup> Corrected for partial deuteration.

Both *erythro*- and *threo*-2-deuterio-1,2-diphenylethanols were dehydrated on a preparative scale in 5% ethanolic aqueous sulfuric acid (58%), and the stilbenes isolated. The *trans*-stilbene which was formed retained 78.5% of the deuterium. This result shows that in the product-forming step, loss of H or D from the carbonium ion,  $P_{\text{H}}/P_{\text{D}}$ , is  $3.69 \pm 0.06$ . This product isotope effect, if transformed into an expected observed kinetic isotope effect on the rate of the over-all reaction,

(15) It is to be noted that the apparent acidity in the 50% alcoholic medium is less than in a purely aqueous medium of the same weight per cent sulfuric acid. Also to be noted is the fact that the rates of dehydration are not the same in media of the same measured  $H_0$  values. These facts suggest that in a medium containing this much organic cosolvent, the acidity function concept is no longer valid. This conclusion is of course in accord with the view of Grunwald and Gutbezahl [B. Gutbezahl and E. Grunwald, *J. Am. Chem. Soc.*, **75**, 559, 565 (1953)] and of Rosenthal, Hetzer, and Bates [D. Rosenthal, H. B. Hetzer, and R. G. Bates, *J. Am. Chem. Soc.*, **86**, 549 (1964)]. The apparent acidity is a useful strategem for comparing rates and for comparing reactivity in such media, but is not useful as a criterion of mechanism.

(16) D. S. Noyce and C. A. Lane, *J. Am. Chem. Soc.*, **84**, 1641 (1962).

predicts  $k_{\text{H}}/k_{\text{D}} = 1.57$ . In fact, however (Table IV), this observed rate ratio is 1.83. Assuming a secondary isotope effect on the generation of the carbonium ion of 1.17 satisfactorily reconciles these observations. This information is very similar to that obtained earlier in the study of the dehydration of  $\beta$ -hydroxy- $\beta$ -phenylpropionic acid.<sup>16</sup>

Further, 1,2-diphenylethanol-2,2-*d*<sub>2</sub> was also examined under similar conditions. The rate of dehydration of **5** by sulfuric acid in 30% aqueous acetic acid is given in Table V along with rates measured under the same conditions for the protium compound.

**Table V.** Rate of Dehydration of 1,2-Diphenylethanol-2,2-*d*<sub>2</sub> in 30% Aqueous Acetic Acid-Sulfuric Acid

H <sub>2</sub> SO <sub>4</sub> , %	10 <sup>4</sup> k <sub>obsd</sub> , sec <sup>-1</sup> (for <b>5</b> )	10 <sup>4</sup> k <sub>obsd</sub> , sec <sup>-1</sup> (for <b>1</b> )	$k_{\text{H}}/k_{\text{D}}$
47.8	2.05	8.50	4.16
47.8	2.08	7.85	3.75
47.8	2.03	8.15	3.94
40.4	0.159	0.518	3.26

The slightly reduced rate of dehydration of **2** and **3**, and the markedly reduced rate of **5**, clearly show that the rate-limiting process is the elimination of a proton from the carbonium ion, and that this step has associated with it a primary isotope effect,  $k_{\text{H}}/k_{\text{D}}$ , of nearly 4.

Further information with regard to the nature of this step comes from two other experiments. One of these involves an examination of the possibility of hydride transfers. The dehydration of 1,2-diphenylethanol-1-*d*<sub>1</sub> gives *trans*-stilbene which retains all of the deuterium. This result shows that in this system hydride rearrangements do not compete with straightforward elimination. Were a proton  $\pi$  complex to be involved in this reaction sequence, one might expect to see some evidence for hydride rearrangement.

Another confirming experiment involves measuring the rate of dehydration of **1** in deuteriosulfuric acid. Dehydration is faster in the deuterated medium, as shown by the results in Table VI. This information shows that proton transfer from the isotopic medium does not enter the rate-limiting step.

**Table VI.** Rate of Dehydration of 1,2-Diphenylethanol in 5% EtOH-95% H<sub>2</sub>O-H<sub>2</sub>SO<sub>4</sub>-*d*<sub>2</sub> at 25.00°

Wt % acid	10 <sup>4</sup> k <sub>obsd</sub> , sec <sup>-1</sup>	$k_{\text{D}_2\text{O}}/k_{\text{H}_2\text{O}}^a$
51.22	4.17	1.62

<sup>a</sup> Comparison made with media containing the same mole fraction of sulfate;  $N_{\text{SO}_4} = 0.1736$ .

**Equilibrium Extent of Dehydration of 1.** The dehydration of **1** in 50% sulfuric acid is essentially complete. A much more precise evaluation of the rate of the reverse (hydration) reaction can be made by determining the exchange rate of *trans*-stilbene- $\alpha$ -*d*<sub>1</sub> (**6**) in sulfuric acid.

The rate of loss of deuterium from **6** is given in Table VII, with the rate of dehydration under the same con-

**Table VII.** Rate of Exchange of *trans*-Stilbene- $\alpha$ - $d_1$  in 5% EtOH-95% H<sub>2</sub>O-H<sub>2</sub>SO<sub>4</sub> at 45.00°

H <sub>2</sub> SO <sub>4</sub> , %	$k_{\text{exch.}}$ , sec <sup>-1</sup>	$k_{-\text{H}_2\text{O}}$ , sec <sup>-1</sup>
43.52	$2.77 \times 10^{-6}$	$6.30 \times 10^{-3}$
43.54		$6.26 \times 10^{-3}$

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<sup>1,2</sup>

Donald S. Noyce, Donald R. Hartter,<sup>3</sup> and Frank B. Miles<sup>4</sup>

Contribution from the Department of Chemistry, University of California, Berkeley, California 94702. Received January 15, 1968

**Abstract:** The rates of the acid-catalyzed dehydration of several 1,2-diarylethanols (X-C<sub>6</sub>H<sub>4</sub>CHOHCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>-Y) have been measured. The rates of dehydration in 55% sulfuric acid are well correlated by the equation  $\log k_{\text{X,Y}} = -3.78(\sigma_{\text{X}^+} + 0.23\sigma_{\text{Y}}) - 3.19$ , 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- $\pi$  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  $\beta$ -carbon, from which the proton is ultimately lost. This structural situation is thus much more versatile than that afforded by the  $\beta$ -hydroxy- $\beta$ -arylpropionic acids which we have studied previously.<sup>5</sup>

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.

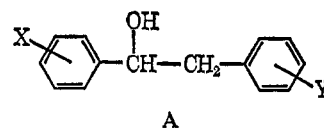
(1) Previous paper: D. S. Noyce, D. R. Hartter, and R. M. Pollack, *J. Am. Chem. Soc.*, **90**, 3791 (1968). A part of this work has been reported in a preliminary communication: D. S. Noyce, D. R. Hartter and F. B. Miles, *ibid.*, **86**, 3584 (1964).

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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).



### 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,<sup>6</sup> 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  $J_0$ <sup>7,8</sup> 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.

(6) J. F. Bunnett, *ibid.*, **83**, 4956, 4978 (1961).

(7) V. Gold and B. W. V. Hawes, *J. Chem. Soc.*, 2102 (1951).

(8) Since data for the activity of water in sulfuric acid media containing 5% ethanol are not known,  $a_{\text{H}_2\text{O}}$  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) +  $\log a_{\text{H}_2\text{O}}$  will be in error only by a constant term.