Anal. Calcd. for $C_{14}H_{12}N_2O_4$ (II'''): N, 10.29. Found: N, 9.94.

Attempted Isomerization of I and II (Action of Dinitrogen Tetroxide).—*meso*-1,2-Dinitro-1,2-diphenylethane (I, 0.1 g., m.p. 225° uncor.) was stirred for 8 hours in ethyl ether (200 ml.) at 0° containing excess dinitrogen tetroxide. After the mixture had been poured on ice, allowed to stand, washed with water, dried over magnesium sulfate and evaporated. Compound I was recovered essentially quantitatively, m.p. 220-225°; the product was colored by trace amounts of α-nitrostilbene.

In a similar experiment, *d,l*-1,2-dinitro-1,2-diphenylethane (II, 0.5 g., m.p. 138–145°) was stirred for 2 hours in ethyl ether (100 ml.) at 0° containing dinitrogen tetroxide (2 g.). After the mixture had been handled as in a preparative experiment, II was recovered almost completely (0.49 g.), m.p. 140–145°.

(Action of Acetic Acid).—A solution of I (0.4 g.. m.p. 237° cor.) in glacial acetic acid (60 ml.) was refluxed for 1 hour. Upon cooling the mixture, compound I (0.31 g., 77.5% recovery) was recovered as long white needles, m.p. 237°. Upon addition of water to the acetic acid solution, α-nitrostilbene, a yellow solid, m.p. 61–62°, was recovered contaminated with traces of I.

Compound II (1.0 g., m.p. 150–152°) was also refluxed in glacial acetic acid (30 ml.) for 40 minutes. After cooling the mixture, unisomerized II (0.855 g.) was isolated, m.p. 150°. Upon diluting the acid solution with water, additional II (0.05 g.) was obtained. The total amount of II (0.905 g) isolated corresponded to a recovery of 90.5%. The remaining product obtained was α-nitrostilbene, m.p. 65°, containing traces of II.

Infrared Analysis of Reaction Products from *cis*- and *trans*-Stilbenes and Dinitrogen Tetroxide.—The following four separate reactions were effected simultaneously under identical conditions: experiment 1, dinitrogen tetroxide (0.115 g., 0.00125 mole) in ethyl ether (10 ml.) was added dropwise in 15 minutes at 0° to a solution of *trans*-stilbene (0.45 g., 0.0025 mole) in ethyl ether (50 ml.); experiment 2, dinitrogen tetroxide (0.115 g., 0.00125 mole) in ethyl ether (10 ml.) was added dropwise in 15 minutes at 0° to a solution of *cis*-stilbene (0.45 g., 0.0025 mole) in ethyl ether (50 ml.); experiment 3, dinitrogen tetroxide (0.69 g., 0.0075 mole) in ethyl ether (10 ml.) was added dropwise in 15 minutes at 0° to a solution of *trans*-stilbene (0.45 g., 0.0025 mole) in ethyl ether (50 ml.); and experiment 4, dinitrogen tetroxide (0.69 g., 0.0075 mole) in ethyl ether (10 ml.) was added dropwise in 15 minutes at 0° to a solution of *cis*-stilbene (0.45 g., 0.0025 mole) in ethyl ether (50 ml.).

After the additions were completed, each reaction mixture was stirred for 75 minutes. Ten drops from each reaction mixture was mixed with potassium bromide (450 mg.); the ethyl ether and the excess dinitrogen tetroxide were immediately evaporated under vacuum. On using the potassium bromide pellets, the complete infrared spectrum of each reaction mixture was determined. The spectra of the products from experiments 1 and 2 (excess stilbene) are identical and practically superimposable; the infrared spectra of the products from experiments 3 and 4 (excess dinitrogen tetroxide) also are identical and superimposable.

The region between 10.8 and 11.2 μ was used for further comparison. *trans*-Stilbene absorbs at 11.07 μ whereas *cis*-stilbene has an absorption band at 10.83 μ. The products from experiments 3 and 4 (excess dinitrogen tetroxide) do not absorb at 10.83 or 11.07 μ. The products from experiments 1 and 2 (excess stilbenes) exhibit absorption at 11.07 μ, not at 10.83 μ. It is thus apparent that excess *cis*-stilbene in experiment 2 is isomerized essentially completely to *trans*-stilbene under the conditions of nitration.

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

Carbonyl Reactions. X. The Acid-catalyzed Isomerization of *cis*-Benzalacetophenone[1,2]

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The isomerization of *cis*-benzalacetophenone (I) to *trans*-benzalacetophenone (II) is subject to smooth acid catalysis and proceeds to completion. The rate of the isomerization does not parallel the acidity function H_0 in aqueous sulfuric acid or perchloric acid. However, the rate may be correlated with the measured acidity function values in anhydrous acetic acid. The acid-catalyzed reaction of β-phenyl-β-hydroxypropiophenone (III) does not give complete dehydration at the higher acidities. Furthermore the rate of dehydration is slower than the rate of isomerization of *cis*-benzalacetophenone. These results exclude III as an intermediate in the *cis*- to *trans*-isomerization. It is concluded that the rate-determining process in aqueous solution is the addition of water to the conjugate acid of I to produce the enol of III, which suffers rapid loss of water before ketonization. A very similar mechanism obtains in acetic acid.

Introduction

The *cis* to *trans* isomerization of unsaturated compounds has been the subject of extensive study from several points of view. Investigations of thermal gas phase reactions have been carried out for dimethyl maleate,[5] methyl *cis*-cinnamate,[6] stilbene[7] and more recently for dideuterioethylene[8] and *cis*-2-butene[9]; comparison with reaction rate theory has been made.[10] Isomerization in solution has also been studied.[11] Catalyzed isomerization has been observed with a wide range of catalysts,[12] but fewer quantitative kinetic studies have been carried out under these conditions. The isomerization of maleic acid to fumaric acid has received the most attention.[13–16] The reaction is complex; formation of either malic acid or chlorosuccinic

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(3) Union Carbide and Carbon Fellow, 1952–1953; U. S. Rubber Co. Fellow, 1953–1954.

(4) Union Carbide and Carbon Fellow, 1956–1957.

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(15) K. Nozaki and R. Ogg, *ibid.*, **63**, 2583 (1941).

(16) M. Davies and F. P. Evans, *Trans. Faraday Soc.*, **52**, 74 (1956)

acid competes with simple isomerization. The reaction is strongly acid-catalyzed[15] and shows definite sensitivity to the nature of the acid used. There is strong acceleration by certain anions.[15] The order of the reaction in maleic acid has been reported to be both first order[13,15] and second order.[14,16] The observation of Horrex[17] that carbon-bound deuterium is not incorporated during the isomerization with HCl severely limits acceptable mechanistic interpretations.

In conjunction with studies of the acid-catalyzed condensation of benzaldehyde and acetophenone[18,19] we have undertaken a study of the isomerization of *cis*-benzalacetophenone to *trans*-benzalacetophenone. The reaction has been followed spectrophotometrically, and proceeds to completion. The isomerization has been studied under four conditions: in aqueous sulfuric acid, in aqueous perchloric acid, in acetic acid containing sulfuric acid and in acetic acid containing small amounts of water and added sulfuric acid. We feel that our results provide valuable additional information concerning catalyzed isomerizations, and offer possible explanations for the previous observations.

Experimental

Materials.—*cis*-Benzalacetophenone (I) was prepared by the procedure of Lutz and Jordan.[20] The method was somewhat capricious in our hands, succeeding only during the month of June in Berkeley. Reduction of phenylbenzoylacetylene with Lindlar catalyst was much more successful. *trans*-Benzalacetophenone (II) was crystallized from ethanol to constant spectrum and melting point. Acetic acid and sulfuric acid were prepared as previously reported.[18]

Light Sensitivity.—The spectrum of II in anhydrous acetic acid containing 0.20 *M* sulfuric acid does not change if the solution is stored in glass out of direct sunlight, with no other precautions taken to exclude light. However, if this solution is exposed to sunlight in a quartz Beckman cell, it is converted within 8 minutes to a photochemical equilibrium mixture of the *cis* and *trans* isomers containing 80% of the *cis* isomer. Kinetic runs carried out in ordinary glass vessels, or with precautions to exclude artificial light, showed no differences.

Kinetic Procedure.—For kinetic runs carried out in acetic acid, a sample of I of about 2 mg. was accurately weighed and dissolved in a small amount of acetic acid, then mixed with acetic acid containing the desired concentration of sulfuric acid. Samples were removed at appropriate time intervals, and the progress of the reaction was followed by observing the increase in absorption at 310 mμ due to II. In this fashion rate data were obtained through the first half-life, and in some instances for two half-life periods. The spectrum of the reaction solution after 10 half-life periods agreed completely with that of authentic II. The final spectrum was stable in the absence of light for as much as 40 half-life periods. The isomerization proceeds to 100% completion within the precision of our methods.

The spectrum of II changes slightly as the reaction medium is changed. At 300 mμ there is a decrease in extinction coefficient of 5% with increasing sulfuric acid concentrations, but no appreciable decrease at 320 mμ.

For the kinetic runs in water a slightly modified procedure was adopted. The rate of solution of *cis*- benzalacetophenone in water is extremely slow. Therefore an accurately weighed sample of about 1 mg. was dissolved in 0.2 to 0.3 ml. of ethanol and sulfuric acid of the desired concentration added to a final volume of 100 ml. In calculating the H_0 value of the solution, the ethanol was regarded as replacing an equivalent volume of water. At these concentrations the correction is minor.[21] The H_0 values given in Table I do not include any correction for this effect. It was possible in aqueous solution to follow the disappearance of the absorption of I at 250 mμ as well as the appearance of II at 300 or 310 mμ. Data were consistent at both wave lengths, and the spectrum of the reaction mixture after several half-lives was consistent with that of II. The apparent percentage reaction was again 100% at the higher acidities where it could be conveniently reached.

Rate of Dehydration of β-Phenyl-β-hydroxypropiophenone (III).—Solutions were prepared by dissolving an accurately weighed quantity of III, about 1 mg., in 2 ml. of ethanol, and then diluting to a total volume of 100 ml. with sulfuric acid of the appropriate concentration. The appearance of *trans* was followed spectrophotometrically at 310 mμ. From the optical density after completion of the reaction the fraction of dehydration was determined, and by difference the percentage of the reversal of the condensation which occurred simultaneously.

Results and Discussion

Isomerization in Aqueous Acids.—An individual kinetic run showed smooth first-order behavior, both in the disappearance of *cis*-benzalacetophenone and in the appearance of *trans*-benzalacetophenone. There was no indication of the formation of any quantity of an intermediate. The reaction proceeded to completion within the precision of the spectrophotometric method of analysis.

The results of the rate measurements carried out in sulfuric acid and perchloric acid solution are presented in Table I.

TABLE I

RATE OF ISOMERIZATION OF *cis*-BENZALACETOPHENONE IN AQUEOUS ACID

H_2SO_4, *M*	H_0[a]	k_1, sec.$^{-1}$	log $k + H_0$
H_2SO_4, 25.95°			
0.00		$<8 \times 10^{-9}$	
.0322	1.44	1.75×10^{-7}	−5.32
.0959	1.00	4.58×10^{-7}	−5.34
.525	0.08	2.75×10^{-6}	−5.48
1.086	− .31	5.67×10^{-6}	−5.56
2.32	−1.01	2.02×10^{-5}	−5.70
3.72	−1.72	7.05×10^{-5}	−5.87
5.30	−2.41	1.72×10^{-4}	−6.17
H_2SO_4, 38.00°			
0.0959	1.00	1.55×10^{-6}	4.81
0.0525	0.08	1.02×10^{-5}	4.91
1.086	− .31	2.18×10^{-5}	4.97
5.30	−2.41	5.08×10^{-4}	5.70
$HClO_4$, 25.95°			
0.101	0.96	3.83×10^{-7}	−5.46
.590	.08	2.37×10^{-6}	−5.54
.985	− .21	3.86×10^{-6}	−5.62
1.254	− .38	5.37×10^{-6}	−5.65
2.60	−1.05	1.60×10^{-5}	−5.85
3.26	−1.35	2.17×10^{-5}	−6.01
3.93	−1.68	4.38×10^{-5}	−6.04
5.36	−2.43	1.23×10^{-4}	−6.34

[a] Values interpolated from Paul and Long.[22]

Three features of the rate data are to be noted: (1) unit slope correlation with H_0 is not obtained; (2) the rate of reaction depends upon the nature of the catalyzing acid; (3) close parallelism to the rate of halogenation of acetophenone is observed (see below).

The plot of the rate data at 26° against H_0 shows distinct curvature. As common for almost all acid-

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[17] C. Horrex, *Trans. Faraday Soc.*, **33**, 571 (1937).

[18] D. S. Noyce and W. A. Pryor, THIS JOURNAL, **77**, 1397 (1955).

[19] D. S. Noyce and W. A. Pryor, *ibid.*, **81**, 618 (1959).

[20] R. E. Lutz and R. E. Jordan, *ibid.*, **72**, 4090 (1950).

[21] P. D. Bartlett and J. C. McCollum, *ibid.*, **78**, 1441 (1956).

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

catalyzed reactions, the slope is nearly unity in dilute acid solution (less than 1 molar). At higher acidities, the slope decreases, and at the highest acidities studied, has decreased to about 0.8. The downward curvature cannot be due to appreciable protonation of the reagent *cis*-benzalacetophenone, since the pK_a of *trans*-benzalacetophenone is -5.73[22] and the pK_a of *cis*-benzalacetophenone will not differ greatly. We conclude that these observations are inconsistent with a simple, direct H_0 type of reaction.

Secondly, reactions which show good correlation with the acidity function are in general insensitive to the nature of the catalyzing acid. The depolymerization of paraldehyde[23] shows *very* little sensitivity to the nature of the catalyzing acid, with sulfuric acid and perchloric acid giving almost identical rates at the same H_0. In the hydrolysis of sucrose,[24] perchloric acid solutions tend to be about 20% more effective, while in the hydrolysis of methylal[25] sulfuric acid appears to be about 20% more effective at the same H_0. Noyce and Reed[26] have recently reported a similar observation in the dehydration of 4-(*p*-methoxyphenyl)-4-hydroxy-2-butanone.

Quite in contrast, the halogenation of acetophenone proceeds three times more rapidly in sulfuric acid than in perchloric acid of the same acidity.[27]

The third facet of the data is best presented by comparing the rate of the *cis–trans* isomerization with the rate of halogenation of acetophenone (Table II).

TABLE II

COMPARISON OF RELATIVE RATES FOR ACID-CATALYZED REACTIONS

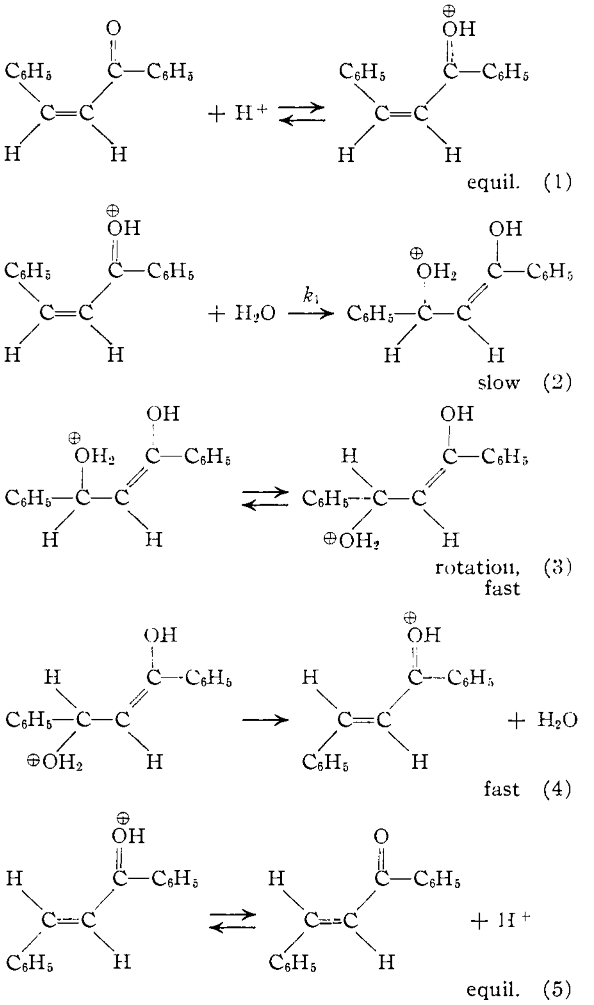
H_2SO_4, *M*	*cis–trans*	I_2–AcPh	Dehydration of[a] $C_6H_5CHOHCH_2COCH_3$	Predicted rate, H_0
0.0322	(1.00)			(1.00)
.0959	2.62	(2.62)		2.74
.525	15.7	14.6	(14.6)	22.9
1.086	32.4	38.2	39	56.2
2.32	115	129	116	282
3.72	404	310	255	1440
5.30	981	568	540	7100

[a] Interpolated from data of Noyce and Reed, ref. 26.

The rate of *cis–trans* isomerization shows a much more satisfactory correlation with the "non-H_0" reactions. At the higher acidities the rate of isomerization increases somewhat more rapidly than does the rate of enolization of acetophenone. Both the rate of isomerization and rate of enolization increase more rapidly than would be predicted by the increase in molar concentrations of the catalyzing acid, which would be the basis for evaluation using the Zucker–Hammett hypothesis.[27]

We thus reach the conclusion that the data support the mechanism outlined in Chart I, with step 2, the addition of water to the salt of *cis*-benzalacetophenone, representing the rate-determining process.

CHART I



Behavior of β-Phenyl-β-hydroxypropiophenone (III) in Aqueous Acid.—To further examine the validity of the reaction sequence above, we have investigated the behavior of β-phenyl-β-hydroxypropiophenone in aqueous acid. The relevant data are summarized in Table III.

TABLE III

RATE OF REACTION OF β-HYDROXY-β-PHENYLPROPIOPHENONE

H_2SO_4 molar	*R*[b]	*T*[c]	$k_{obs} \times 10^5$, sec.$^{-1}$	$k_1 \times 10^5$, sec.$^{-1}$,[d]	$k_1 \times 10^5$, sec.$^{-1}$,[e]
			$T = 25.06°$		
2.28	0	100	0.927	0.927	0.927
3.68	6	94	2.55	2.40	2.35
5.16	12	88	6.03	5.31	5.28
5.96	21.9	78.1	10.2	7.97	8.02
6.60	19.8	80.2	17.0	13.6	12.8
			$T = 45.00°$		
2.28	0	100	6.98	6.98	6.98
3.73	8.6	91.4	19.0	18.2	17.7
2.55[a]			3.87	3.87	3.87

[a] Perchloric acid used in this case. The dehydration was assumed to be quantitative. [b] Percentage reverse aldol reaction. [c] Percentage *trans*-chalcone formed. [d] First-order rate constant for the formation of *trans*- chalcone. [e] First-order rate constant for the formation of *trans*- chalcone from initial rates.

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(24) A. Hantzsch and A. Weissberger, *Z. physik. Chem.*, **125**, 251 (1927).

(25) D. McIntyre and F. A. Long, THIS JOURNAL, **76**, 3240 (1954).

(26) D. S. Noyce and W. L. Reed, *ibid.*, **80**, 5542 (1958).

(27) L. Zucker and L. P. Hammett, *ibid.*, **61**, 2791 (1939).

Two features of the data are immediately apparent. In the first instance the rate of dehydration is slower than the rate of isomerization. Correction for the somewhat larger quantity of ethanol which was used for solubility purposes makes an exact ratio of rates uncertain. In the second place the hydroxyketone III does not give *trans*-benzalacetophenone as the sole product. Instead it undergoes two competitive reactions, in which there is some cleavage to benzaldehyde and acetophenone in addition to normal dehydration. Both these differences effectively exclude β-phenyl-β-hydroxypropiophenone as an intermediate in the *cis–trans* isomerization.

Comparisons of the data on III with previously reported information on related hydroxy ketones reveal close similarity. We conclude that the rate-controlling step in the dehydration of III is enolization. The acidity dependence for the dehydration pathway very closely parallels the results of Noyce and Reed[26] and of Noyce and Snyder.[28]

The rate of dehydration of β-phenyl-β-hydroxypropiophenone is somewhat less than the rate of dehydration of 4-phenyl-4-hydroxy-2-butanone, as would be expected. For comparison, the rate of enolization of acetophenone is less than that of acetone.

The changing proportion of the cleavage reaction closely parallels the results which Noyce and Snyder[28] obtained on the rate of reaction of 4-phenyl-4-hydroxy-3-methyl-2-butanone. Tabulation of the rate of the cleavage reaction againt H_0 uncorrected for the small change due to the added ethanol, reveals that the cleavage reaction is closely parallel to the acidity function (Table IV).

TABLE IV

COMPARISON OF RATE OF CLEAVAGE WITH H_0 AT 25.06°

H_2SO_4, molar	R, %	$k_R \times 10^6$, sec.$^{-1}$	H_0	log $k_R + H_0$
2.28	0	..	−0.94	....
3.68	6	1.5	−1.71	−7.53
5.16	12	7.2	−2.35	−7.49
5.96	21.9	22.3	−2.74	−7.39
6.60	19.8	34.0	−3.08	−7.55

The parallelism with H_0 of the rate of cleavage (reverse aldol reaction) is further support for the mechanism of the condensation reaction presented earlier.[18,28]

Comparison with Other Reactions.—The reaction sequence suggested in Chart I is that which has been suggested by Nozaki and Ogg[15] for the maleic-fumaric acid conversion. It accommodates the data of Lucas and co-workers[29–32] on the hydration–dehydration of aldol, β-hydroxyisovaleraldehyde,[30] β-hydroxypropionaldehyde[31] and diacetone alcohol.[32] It is to be noted that the apparent heats and entropy of the isomerization and dehydration processes are similar to the values determined by Lucas and co-workers (Table V).

TABLE V

ACTIVATION PARAMETERS FOR ISOMERIZATION AND DEHYDRATION IN AQUEOUS SULFURIC ACID

Reaction	$\Delta H^{\ddagger}$, kcal.	$\Delta S^{\ddagger}$, e.u.
Isomerization of *cis*-benzalacetophenone	18.1	−22.5
Dehydration of β-phenyl-β-hydroxypropiophenone	18.4	−23.6

The outlined mechanism furthermore accommodates the observations of Horrex,[17] that carbon-bound deuterium is not incorporated in the case of maleic to fumaric isomerization. It appears pos-

TABLE VI

RATE OF ISOMERIZATION OF *cis*-BENZALACETOPHENONE IN ACETIC ACID

H_2SO_4, molar	k_1, sec.$^{-1}$	H_0[a]	log $k_1 + H_0$
A. Anhydrous acetic acid–sulfuric acid, T = 25.95°			
0.00	2.98×10^{-6}	+3.5, +1.4[b]	−2.0
.00	3.20×10^{-6}		−2.0
.0050	6.67×10^{-6}	−0.40	−5.58
.0100	1.03×10^{-5}	− .64	−5.63
.0200	1.75×10^{-5}	− .94	−5.70
.0401	2.75×10^{-5}	−1.19	−5.75
.100	6.50×10^{-5}	−1.64	−5.83
.200	1.41×10^{-4}	−1.93	−5.78
.401	3.43×10^{-4}	−2.38	−5.84
.801	1.00×10^{-3}	−2.84	−5.84
B. Anhydrous acetic acid, T = 38.00°			
0.00	9.26×10^{-6}	+3.5	−1.53
0.00	8.33×10^{-6}	3.5	−1.58
4.97×10^{-4}	1.17×10^{-5}	0.54	−4.39
9.95×10^{-4}	1.25×10^{-5}	.27	−4.63
4.99×10^{-3}	2.10×10^{-5}	− .40	−5.08
9.99×10^{-3}	2.92×10^{-5}	− .64	−5.17
0.0199	4.55×10^{-5}	− .94	−5.28
.1002	1.87×10^{-4}	−1.64	−5.37
.2005	3.50×10^{-4}	−1.93	−5.39
.401	9.79×10^{-4}	−2.38	5.38
C. Acetic acid, 0.97% H_2O, T = 25.95°			
0.00	4.65×10^{-6}	+3.5	−1.83
.112	4.87×10^{-5}	−1.30	5.61
.224	9.05×10^{-5}	−1.60	5.64
.242	9.67×10^{-5}	−1.67	5.68
.449	2.24×10^{-4}	−2.12	−5.77
.485	2.75×10^{-4}	−2.19	−5.75
.800	5.91×10^{-4}	−2.58	−5.81
.897	6.93×10^{-4}	−2.67	−5.83
1.20	1.20×10^{-3}	−2.80	−5.72

[a] The values of H_0 for anhydrous acetic acid–sulfuric acid solutions were taken from the determination of Smith and Elliott[33] at low acidities, and from the work of Gold and Hawes[34] at high acidities. A correction was applied to the data of Hall and Spengeman[35] for H_0 values in the intermediate acidity range, applying a correction of 0.28 at 0.005 molar sulfuric acid and a correction of 0.02 at 0.2 molar. H_0 values for acetic acid solutions containing small amounts of water were interpolated from the data of Gold and Hawes. [b] The value of H_0 for pure acetic acid is reported as +3.5 by Hammett[36] and as +1.4 by Hall and Meyer.[37]

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(28) D. S. Noyce and L. R. Snyder, THIS JOURNAL, **81**, 620 (1959).

(29) S. Winstein and H. J. Lucas, *ibid.*, **59**, 1461 (1937).

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

(31) D. Pressman and H. J. Lucas, *ibid.*, **64**, 1953 (1942).

(32) D. Pressman, L. Brewer and H. J. Lucas, *ibid.*, **64**, 1122 (1942).

(33) T. L. Smith and J. H. Elliott, *ibid.*, **75**, 3566 (1953).

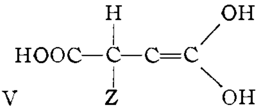
(34) V. Gold and B. W. U. Hawes, *J. Chem. Soc.*, 2102 (1951).

(35) N. F. Hall and W. F. Spengeman, THIS JOURNAL, **62**, 2489 (1940).

(36) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 270.

(37) N. F. Hall and F. Meyer, THIS JOURNAL, **62**, 2493 (1940); footnote 3.

sible that the data are also in accord with the somewhat divergent results obtained by Davies and Evans,[16] Nozaki and Ogg,[15] and Terry and Eichelberger.[14] The conjugate acid of maleic acid must suffer a nucleophilic attack to give species IV.



$$\mathrm{HOOC{-}\overset{H}{\underset{Z}{C}}{-}C{=}C(OH)_2}$$

IV

In hydrochloric acid solution chloride ion may act as the nucleophile Z; in concentrated solutions of maleic acid alone one of the carboxylic acid species may act as nucleophile, or water may act as nucleophile. In this manner stereomutation may be initiated. However, in competition with the processes analogous to rotation and loss of water is a process analogous to ketonization. In such fashion variable amounts of chlorosuccinic acid and of malic acid may be formed.

Isomerization in Acetic Acid.—The results of the stereomutation of *cis*-benzalacetophenone in acetic acid–sulfuric acid solutions are given in Table VI. At high acidities the rate approaches a linear unit-slope correlation with the indicator acidity function. There is, however, a rate observed in pure acetic acid *far* in excess of that expected from acidity considerations alone. It is possible in fact to correlate the observed rate of reaction smoothly with equation 6

$$k_{1\mathrm{obs}} = k_{\mathrm{HOAc}} + k'H_0 \qquad (6)$$

In Fig. 1 the curves drawn are those for $k_{\mathrm{HOAC}} = 2.98 \times 10^{-6}$ sec.$^{-1}$ and 4.18×10^{-5} sec.$^{-1}$ at temperatures of 26° and 38°, respectively.

The rate of isomerization in pure acetic acid appears to be the result of catalysis by undissociated acetic acid, in which acetic acid acts both as the proton source and nucleophile. At variance with this conclusion is the apparent smooth correlation with the acidity function in solutions containing larger quantities of sulfuric acid. This apparent discrepancy is discussed at greater length in the following section.

We wish now to consider the fate of the β-hydroxyketone III in acetic acid. Noyce, Pryor and Bottini[38] have shown that in wet acetic acid, III undergoes competitive cleavage and dehydration, similar to that reported here for aqueous solutions. The rate of formation of *trans*-benzalacetophenone from the β-hydroxyketone (through the acetate ester[38]) is slower than the rate of isomerization. These comparisons effectively exclude either III or the acetate ester as an intermediate in the *cis–trans* isomerization.

With the facts at hand we wish to propose that the isomerization in acetic acid solution proceeds by a mechanism entirely analogous to the pathway in aqueous solution. The rate-determining process is the formation of the acetate ester of the enol of β-phenyl-β-hydroxypropiophenone, in most solutions from the conjugate acid of *cis*-benzalacetophenone by addition of acetic acid.

The Utility of H_0 in Acetic Acid Solutions.—The conclusion that essentially identical mechanisms

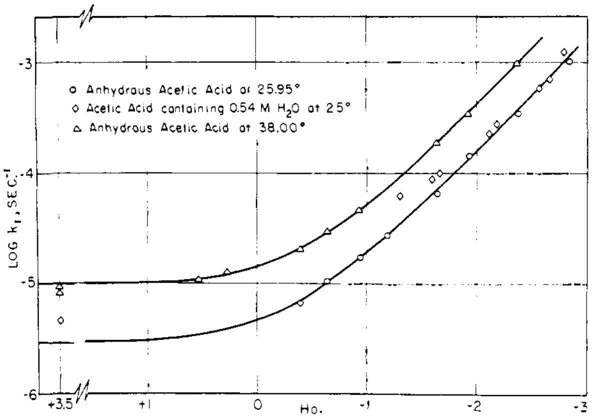


Fig. 1.—Rate of isomerization of *cis*-benzalacetophenone in acetic acid.

are operating in both aqueous and acetic acid solutions throws considerable light upon rate and acidity correlations in acetic acid.

Recently several reactions have been studied in mixed and non-aqueous solvents. Ethanol–water solvent mixtures have been used for a study of the iodination of acetone[39] and for the study of the depolymerization of paraldehyde.[40] Satchell has shown that the iodination of acetone, a "non-H_0" reaction in aqueous media, becomes much more closely parallel with the acidity function in ethanol–water as the percentage of ethanol is increased. Satchell concludes[39] that "the variation of the reaction rate with acidity in such a solvent (40 moles per cent. of ethanol) will be inadequate for diagnostic purposes." However, 24 moles per cent. ethanol appears to be suitable.[40]

Bunton, Ley, Rhind-Tutt and Vernon[41] have examined methanol–water mixtures and dioxane–water mixtures and conclude that the "Zucker–Hammett criterion of mechanism can be usefully applied to 40 and 60% aqueous dioxane solvents."

There are several reports of correlation of rates with the indicator acidity function in acetic acid. Paul and Hammett[42] observed that the slope for the acid-catalyzed bromination of *m*-nitroacetophenone was much greater than unity, but they were unable to offer any explanation for this result. More recently it has been shown that the rate of depolymerization of trioxane in acetic acid may be correlated with H_0[43] with the rate data for both aqueous and acetic acid solutions falling near the same correlation line. Roček[44] has observed that the slope of the log *k vs.* H_0 correlations vary over a wide range in the region of 85–100% acetic acid as solvents for the oxidation of methylcyclohexane. Noyce and Snyder[45] observed variation in the slopes for the rates of acid-catalyzed dehydration of some 4-

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aryl-4-hydroxy-3-methyl-2-butanones. The variation in slope is less than that observed for the same compounds in aqueous solution. The observations of rate–acidity function correlation cover both reactions which do not follow H_0 in aqueous sulfuric acid (the halogenation of ketones and the dehydration of some hydroxyketones[26]) and reactions which do parallel the acidity function (the depolymerization of trioxane and pina col rearrangement[46]). From the fairly wide range of slopes observed, it is apparent that the interpretation of acidity dependence in anhydrous acetic acid needs to be approached with a great deal of caution. We conclude at the present time that the acidity function will be useful for correlating rates in acetic acid solvent, but that the acidity function will not be valuable as a criterion of detailed mechanism in this solvent. In other words, the usual result will be correlation with the measured acidity function regardless of the detailed mechanism for acid catalysis. If a reaction specificially involves water (as the hydrolysis of an ester) then deviations will be observed which may be correlated with the changing activity of water as reported by Noyce and Snyder.[45]

Further studies in 50% aqueous acetic acid would be useful.

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[CONTRIBUTION NO. 280 FROM THE RESEARCH DIVISION, JACKSON LABORATORY, ORGANIC CHEMICALS DEPARTMENT, E. I. DU PONT DE NEMOURS AND CO.]

The Preparation of Olefins from Arylsulfonate Esters of Alcohols[1]

BY HAROLD R. NACE[2]

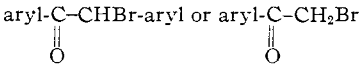
RECEIVED MARCH 28, 1959

Dimethyl sulfoxide, hexamethylphosphoramide and, to a lesser extent, dimethyl- and diethylformamide, have been found to be excellent non-reacting solvents for the decomposition of (−)-menthyl, β-cholestanyl, cyclohexyl and 2-octyl arylsulfonates to the corresponding olefins.

The solvolysis of an aryl sulfonate ester of a secondary alcohol to give the corresponding olefin is a well-known and widely employed reaction.[3–7] However, the reaction is frequently complicated by nucleophilic attack of the solvent on the carbinol carbon, causing the formation of varying amounts of substitution product, and thus lowering the yield of olefin. Indeed, in certain cases the substitution product predominates.[4,6]

Several solvents are reported here which, while promoting decomposition to the olefin, appear to be non-nucleophilic with respect to the carbinol carbon and thus lead to high yields of olefins. These are the highly polar solvents dimethyl sulfoxide, hexamethylphosphoramide, dimethylformamide and diethylformamide.

Dimethyl sulfoxide has been known for some time as an excellent solvent[8] for many classes of organic compounds. In recent publications Kornblum[9] and Major and Hess[10] reported one of the few cases in which dimethyl sulfoxide reacted with the solute, *viz.*, the conversion of an α-bromoketone to the corresponding diketone. In all of the cases reported the halo-ketone was of the type



$$\text{aryl-}\underset{\substack{\|\\ \text{O}}}{\text{C}}\text{-CHBr-aryl or aryl-}\underset{\substack{\|\\ \text{O}}}{\text{C}}\text{-CH}_2\text{Br}$$

where elimination was not possible. Tien and Hunsberger[11] reported that ethyl bromoacetate and dimethyl sulfoxide reacted to give ethyl glyoxylate in excellent yield. Although the mechanism of this reaction is not well understood at present, Tien and Hunsberger[11] and Major and Hess[10] have presented evidence that the dimethyl sulfoxide was undergoing change in the reaction, since dimethyl sulfide and trimethylsulfonium bromide were isolated from the reaction mixture.

In the case of arylsulfonates of secondary alcohols, a smooth decomposition to the olefin is accomplished by simply heating, at temperatures in the neighborhood of 100°, a solution of the sulfonate ester in dimethyl sulfoxide. The progress of the reaction can be conveniently followed by titration of the arylsulfonic acid produced, and the olefin is readily isolated by adding the reaction mixture to water, and collecting the insoluble olefin by filtration or extraction. Isomerization or decomposition of olefins sensitive to sulfonic acids can be minimized by the addition of sodium bicarbonate to the reaction mixture in an amount at least equivalent to the quantity of sulfonate ester used.

The decomposition of (−)-menthyl arylsulfonates (Table I) in dimethyl sulfoxide afforded a mixture of (+)-Δ^2- and (+)-Δ^3-menthenes, in which the Δ^3-isomer predominated. The olefin

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