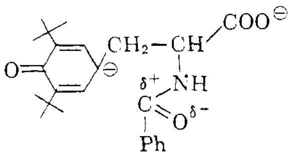
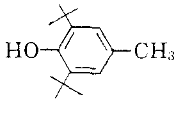
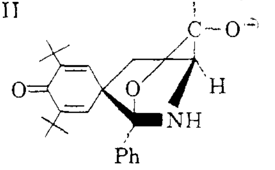
follows that any modification of the phenolate hybrid which serves to stabilize electron density at the *para* carbon atom should facilitate ionization. Whether by electrostatic effects alone, as in XVII, or by covalent bond formation as well, as in XIV, the benzamido carbonyl may serve as an electrophile to promote anion solvation at sites other than the phenolic oxygen. Such an argument is supported by the spectral data of Fig. 1, IX being more acidic than VI and both more acidic than the corresponding cresol XVIII. The fact that the ester VIa is more readily ionized than the free acid VI supports the argument used to relate the hydrolysis rates of VI and IX. Ionization constants for a variety of unhindered phenols with appropriate side chains were determined spectrophotometrically; in each case, the *pK* was found to lie within the range 10.0 to 10.1. Thus, it seems unlikely that the variations shown in Fig. 1 need be ascribed to inductive effects resulting from side-chain modification. We, therefore, attribute the enhanced ionization of VIa to the existence of an additional locus for charge solvation, as in XIX or its dipolar analog.



XVII



XVIII



XIX

[Contribution from the Department of Chemistry, University of California, Berkeley, Calif.]

The Kinetics of the Acid-catalyzed Isomerization of *cis*-Cinnamic Acid[1-3]

By Donald S. Noyce, Paul A. King,[4] Fred B. Kirby and Wilmer L. Reed

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cis-Cinnamic acid is smoothly isomerized to *trans*-cinnamic acid by moderately concentrated sulfuric acid. In the region 45–75% sulfuric acid, the rate of isomerization follows Hammett's acidity function h_0 with unit slope. Evidence is presented to show that the course of the reaction follows an addition–elimination sequence, with β-phenyl-β-hydroxypropionic acid being formed as an unstable intermediate.

Introduction

For some time we have been interested in a variety of acid-catalyzed reactions. Most recently, detailed studies of the isomerization of *cis*-benzalacetophenones[3,5,6] have been reported. Two different mechanisms were found to be operative depending upon the nature of the substituents in the benzene rings. One of these mechanisms involved addition of water to form the hydroxy-enol, while the other mechanism involved the direct rotation about the carbon–carbon double bond in the oxonium salt of the substituted benzalacetophenone.

The present paper presents a study of the acid-catalyzed isomerization of *cis*-cinnamic acid to *trans*-cinnamic acid. This study was undertaken to obtain additional information regarding reaction mechanisms to which the use of the acidity function H_0 might be applied.

The cinnamic acid system offers several advantages for a study designed to test proton addition mechanisms[7] for acid-catalyzed reactions. It is known from the thermal isomerization of methyl cinnamate[8] that the *cis*–*trans* isomerization proceeds to completion. In considering possibly useful related compounds, β-phenyl-β-hydroxypropionic acid is well known and has also been resolved. Further, the stereomutation reaction will be free of any complications of α–β,β–γ equilibria, which would not be the case with many aliphatic compounds.

We desired to obtain a body of information, which would establish with a high degree of certainty the mechanism for the isomerization of *cis*-cinnamic acid; and then finally to consider the acidity dependence (H_0 or "non-H_0") of the reaction in the light of these results.

In this and the immediately following papers, we present our experimental results and then finally the conclusions which we have drawn from these studies.

Experimental

Preparation of Materials.—Methyl *cis*-cinnamate was prepared by hydrogenation of methyl phenylpropiolate using a Lindlar catalyst. Hydrolysis of methyl *cis*-cinnamate afforded *cis*-cinnamic acid, which was crystallized to constant m.p. from ligroin; m.p. 67.5–68.0° (lit.[9] 68°), neut. equiv. 147.2 (calcd. 148.15).

Kinetic Procedures.—The progress of the reaction was followed by the increase in ultraviolet absorption at an appropriate wave length, usually 300 mμ, using a Beckman DU spectrophotometer. A weighed amount of *cis*-cinnamic

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(1) This research was supported in part by a grant from the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of this fund.

(2) Presented in part at the 8th Conference on Organic Reaction Mechanisms, Princeton, N. J., September, 1960.

(3) Paper XIII in the Series Carbonyl Reactions; previous paper, D. S. Noyce and M. J. Jorgenson, *J. Am. Chem. Soc.*, **83**, 2525 (1961).

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

(5) D. S. Noyce, W. A. Pryor and P. A. King, *J. Am. Chem. Soc.*, **81**, 5423 (1959).

(6) D. S. Noyce, G. L. Woo and M. J. Jorgenson, *ibid.*, **83**, 1160 (1961).

(7) F. A. Long and M. A. Paul, *Chem. Revs.*, **57**, 935 (1957), review much of the literature relative to such mechanisms.

(8) G. B. Kistiakowsky and W. R. Smith, *J. Am. Chem. Soc.*, **57**, 269 (1935).

(9) C. Liebermann, *Ber.*, **23**, 2510 (1890).

acid was dissolved in water and, to initiate reaction, a small aliquot of this solution was diluted with sulfuric acid of the desired concentration.

Two slightly different procedures were used at 45°. For faster runs, the optical density readings were made on a single sample maintained in a thermostated cell block. For slower runs, aliquots of a large volume of solution maintained at temperature were withdrawn and read with the Beckman. At 70°, the conventional sealed ampule technique was used.

Reactions were, in general, allowed to proceed to completion. The kinetic data were plotted in the form of apparent percentage of remaining *cis*-cinnamic acid; *i.e.*

$$\frac{\text{O.D.}_\infty - \text{O.D.}_t}{\text{O.D.}_\infty - \text{O.D}_0} \times 100$$

The infinity absorbances were reasonably stable and, in all cases, corresponded closely to those expected for complete conversion to *trans*-cinnamic acid.

Upon standing for long extended periods, a gradual decrease in absorbance occurred. This is due to slow acid-catalyzed decarboxylation of *trans*-cinnamic acid.[10]

Results of a typical kinetic run are given in Table I.

TABLE I

TYPICAL KINETIC RUN

Temp. 45.00°, H_2SO_4 62.80%, initial concn. *cis*-cinnamic acid $3.85 \times 10^{-5}M$

Time, sec. × 10^{-2}	Optical density	% Rx[a]	$k \times 10^5$, sec.$^{-1}$
0	0.219	0	....
6.2	.236	4.04	(6.64)
12.0	.248	6.89	5.95
18.0	.263	10.45	6.15
36.0	.302	19.71	6.09
49.2	.326	25.42	5.96
60.0	.345	29.93	5.93
73.2	.367	35.15	5.92
84.0	.385	39.43	5.89
97.2	.404	43.94	5.95
114.0	.427	49.41	5.98
137.4	.454	55.82	5.95
162.5	.479	61.76	5.92
174.0	.490	64.37	5.93
972.00 (∞)	.640	...	...
		Av.	5.97 ± 0.05

[a] % Rx = $(\text{O.D.}_t - \text{O.D.}_0)/(\text{O.D.}_\infty - \text{O.D.}_0) \times 100$.

Isolation of Cinnamic Acid under Conditions of the Kinetic Experiments.—A sample of *cis*-cinnamic acid (200 mg.) was dissolved in 9 *M* sulfuric acid and maintained at 45° for a period corresponding to 6 half-lives. Considerable *trans*-cinnamic acid precipitated during this period. Dilution with water, extraction with ether and work-up in the usual fashion afforded a 90% yield of *trans*-cinnamic acid, m.p. 132.4–133.5°.

***trans*-Cinnamic Acid-α-d_1.**—Benzalmalonic acid, (dec. 195–200°) was prepared by the method of Claisen and Crismer[11] and converted to the sodium salt by titration to *p*H 8.3. The solution was evaporated to dryness under reduced pressure.

Anal. Calcd. for $C_{10}H_6O_4Na_2$: C, 50.86; H, 2.56. Found: C, 50.56; H, 2.89.

Conversion to di-deuteriobenzalmalonic acid was effected by solution of 5.13 g. of the sodium salt in 10 ml. of D_2O and precipitation with 10 ml. of D_2SO_4. The precipitate was collected by filtration and placed in a 250-ml. round-bottomed flask, 100 ml. of previously dried pyridine added, and the flask fitted with a condenser and drying tube and heated under reflux for 3 hours. The colorless pyridine solution was cooled and poured onto a mixture of 100 ml. of concentrated HCl and 200 g. of cracked ice. The organic material was extracted with four 50-ml. portions of ether which were combined and washed with 5% $KHCO_3$ solution. The ethereal solution was separated and dried over anhydrous sodium sulfate and evaporated to yield 3.4 g. of *trans*-cinnamic acid-α-d_1 (85% yield), m.p. 133°. The infrared spectrum showed that the doublet at 10.2 μ, characteristic of ordinary cinnamic acid, had almost completely disappeared. Analysis of the spectra indicated that this product is 88% deuterated in the α-position.

Isomerization of *cis*-Cinnamic Acid in Sulfuric Acid-d_2.—A suspension of 300 mg. of *cis*-cinnamic acid in 100 ml. of 9.2 *M* sulfuric acid-d_2 in D_2O was maintained at 45° for 36 hours. Work-up in the usual fashion, followed by crystallization from water and then from pentane, afforded 100 mg. of *trans*-cinnamic acid-α-*d*, m.p. 133.2–134.4°. The infrared spectrum of this material compared favorably with authentic cinnamic acid-α-d_1, but the doublet at 10.2 μ was more pronounced, indicating that the material was 80% deuterated.

Results

Acidity Dependence.—The isomerization of *cis*-cinnamic acid to *trans*-cinnamic acid proceeds smoothly in moderately concentrated sulfuric acid. At 45° in the region 60–75% sulfuric acid, each kinetic run is smoothly first order from 5–90% reaction, and proceeds to completion within the precision of the spectrophotometric method (±2%).

The isomerization is smoothly acid catalyzed. The half-life at 45° decreases from nearly a week in 45% sulfuric acid to only 10 minutes in 75% sulfuric acid. The rate constants over this range of acidity are given in Table II. Also given are the sums log $k + H_0$, using both the H_0 values of Paul and Long[12] at 25°, and corrected H_0 values, applying the temperature corrections determined by Gelbstein, Shcheglova and Temkin.[13]

It is to be noted that the slope of log k *vs.* H_0 is very nearly unity throughout the entire range. The pK_{BH^+} for *cis*-cinnamic acid is thus clearly substantially more negative than −6.5. The pK_{BH^+} of *trans*-cinnamic acid is −6.2, somewhat more basic than benzoic acid.[14] To be consistent with our rate data, *cis*-cinnamic acid must be less basic than *trans*-cinnamic acid. This is, of course, in accord with the steric inhibition of resonance stabilization which manifests itself more strongly in the cation than in the free acid. A similar situation exists in *o*-methylbenzoic acid.[14]

Temperature Dependence.—Table III presents data for the rate of isomerization at 70.0°.

The energy of activation calculated from these data is 24 ± 1 kcal. In order to calculate $\Delta S^\ddagger$, it is necessary to extrapolate to some standard state for proton activity, either 1 *M* sulfuric acid or $h_0 = 1$. Such an extrapolation is fairly severe in this case. The extrapolated rate constant at $h_0 = 1$ is 1.20×10^{-9} sec.$^{-1}$ at 45°, giving $\Delta F^\ddagger = 31.5$ kcal. and $\Delta S^\ddagger = -26 \pm 3$ e.u.

It should be noted that the very negative $\Delta S^\ddagger$ obtained in this case contrasts with the entropies of activation associated with most other reactions which correlate with the acidity function. Long, Pritchard and Stafford[15] and Taft and his co-workers[16] have applied the entropy criterion to H_0

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[10] Unpublished experiments of Mr. F. B. Kirby.

[11] L. Claisen and L. Crismer, *Ann.*, **218**, 129 (1883).

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

[13] A. I. Gelbstein, G. G. Shcheglova and M. I. Temkin, *Zhur. neorg. Khim.*, **1**, 506 (1956).

[14] R. Stewart and K. Yates, *J. Am. Chem. Soc.*, **82**, 4059 (1960).

[15] F. A. Long, J. G. Pritchard and F. E. Stafford, *ibid.*, **79**, 2362 (1957).

[16] R. W. Taft, Jr., *ibid.*, **74**, 5374 (1952); R. W. Taft, Jr., E. L. Purlee, P. Riesz and G. A. DeFazio, *ibid.*, **77**, 1584 (1955).

TABLE II

RATE OF ISOMERIZATION OF *cis*-CINNAMIC ACID IN AQUEOUS SULFURIC ACID AT 45.0°

H_2SO_4, %	Molar	H_0[a]	ΔH_0[b]	Cor. H_0	$k_1 \times 10^6$, sec.$^{-1}$	log k	log $k + H_0$ Uncor.	log $k + H_0$ Cor.
46.84	6.52	−3.04	0	−3.04	0.133	−5.88	−8.92	−8.92
51.63	7.43	−3.56	0.01	−3.55	0.448	−5.35	−8.91	−8.90
62.80	9.79	−4.79	.07	−4.72	5.97	−4.22	−9.01	−8.94
67.92	10.99	−5.38	.10	−5.28	22.7	−3.64	−9.02	−8.92
68.88		−5.50	.09	−5.41	30.3	−3.52	−9.02	−8.93
69.88	11.47	−5.64	.09	−5.55	42.3	−3.37	−9.01	−8.92
75.97		−6.43	.10	−6.33	254	−2.60	−9.03	−8.93
							[c]	[d]

[a] Ref. 12. [b] From data in ref. 13. [c] Av. = −8.99 ± 0.04. [d] Av. = −8.92 ± 0.01.

TABLE III

RATE OF ISOMERIZATION OF *cis*-CINNAMIC ACID IN AQUEOUS SULFURIC ACID AT 70.0°

H_2SO_4, %	Molar	H_0	ΔH	Cor. H_0	$k \times 10^5$, sec.$^{-1}$	log k	log $k + H_0$ Uncor.	log $k + H_0$ Cor.
46.84	6.52	−3.04	0	−3.04	2.20	−4.66	−7.70	−7.70
50.0	7.11	−3.38	0	−3.38	4.13	−4.38	−7.76	−7.76
54.82	8.07	−3.91	0.03	−3.89	12.9	−3.89	−7.80	−7.77
60.69	9.32	−4.56	0.12	−4.44	61.5	−3.21	−7.77	−7.65
								[a]

[a] Av. = −7.72 ± 0.05.

reactions. We have also considered this question previously.[17]

Evidence for the Formation of an Unstable Intermediate.—While the rate of formation of *trans*-cinnamic acid shows good first-order kinetics throughout the course of an individual kinetic run at high acidities, this is not strictly true at lower acidities. In the slower runs, there is indication of a small induction period, as evidenced by a lag in the increase in optical absorption.

In a typical experiment (Table IV), the rate constant for the formation of *trans*-cinnamic acid shows a gradually rising value for the first 15–20% of the reaction. A plot of these data likewise reveals curvature at low conversions.

TABLE IV

RATE OF ISOMERIZATION, SHOWING INDUCTION PERIOD AT 45.00° IN 7.39 *M* H_2SO_4 CONTAINING 2% ETHANOL[a]

Time, sec. $\times 10^{-3}$	Optical density 300 mμ	Reaction,[b] %	$k \times 10^6$,[c] sec.$^{-1}$	$k \times 10^6$,[d] sec.$^{-1}$
0	0.126	...		
5.88	.128	0.66	1.13	
11.58	.133	2.4	2.04	
20.88	.142	5.4	2.67	...
38.88	.172	15.6	4.36	(6.32)
91.5	.230	35.2	4.75	5.30
132.5	.263	46.4	4.71	5.09
177.6	.300	59.0	5.02	5.33
266.8	.340	72.5	4.84	5.03
(∞)	.421			
			Av.	5.19 ± 0.12

[a] Ethanol added to facilitate solubility. *cis*-Cinnamic acid was dissolved in 2 ml. of ethanol and diluted to 100 ml. with aqueous sulfuric acid. The H_0 value of this solution was not determined. [b] $(\text{O.D.}_t - \text{O.D.}_0)/(\text{O.D.}_\infty - \text{O.D.}_0) \times 100$. [c] $k = \ln[(\text{O.D.}_\infty - \text{O.D.}_t)/(\text{O.D.}_\infty - \text{O.D.}_0)]t^{-1}$, starting at zero time. [d] $k = \ln[(\text{O.D.}_\infty - \text{O.D.}_t)/(\text{O.D.}_\infty - \text{O.D.}_0)]t^{-1}$, zero time taken at 20.9×10^3 sec.

This behavior is consistent with a reaction sequence in which *cis*-cinnamic is converted to an intermediate which fairly rapidly is converted to *trans*-cinnamic acid (eq. 1, with $k_2 > k_1$).

$$cis \xrightarrow{k_1} \text{intermediate} \xrightarrow{k_2} trans \qquad (1)$$

Though it is possible in principle to determine both k_1 and k_2 from the data of Table IV, the limitations of the spectrophotometric method in this case preclude any accurate determination of k_2. However, k_1 is easily obtained.

It is much more instructive to compare the rate of dehydration[18] of β-phenyl-β-hydroxypropionic acid (III) with the rate of isomerization. The rate of dehydration is uniformly greater and also of greater than unit slope *vs.* H_0. This means that the ratio changes with changing acidity, becoming smallest at the lower acidities. A comparison of the rates is given in Table V.

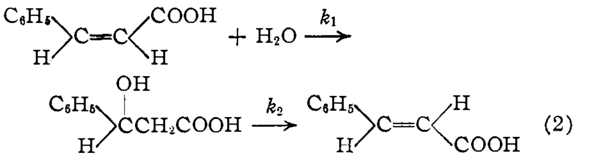
TABLE V

COMPARISON OF RATE OF DEHYDRATION OF β-PHENYL-β-HYDROXYPROPIONIC ACID WITH RATE OF ISOMERIZATION OF *cis*-CINNNAMIC ACID AT 45.00°

H_2SO_4, %	H_0[a]	k_{dehydr},[b] sec.$^{-1}$	k_{isom}, sec.$^{-1}$	$\frac{k_{dehydr}}{k_{isomer}}$	Inductn. period obsd. in formn. of *trans*
38.43	−2.30	3.4×10^{-6}	2.4×10^{-7}[c]	14 ± 1	..
51.87	−3.58	1.07×10^{-4}	4.69×10^{-6}	23 ± 2	Yes
58.05	−4.25	7.31×10^{-4}	1.61×10^{-5}	45 ± 3	Quest.
62.80	−4.79	3.2×10^{-3}	5.97×10^{-5}	54 ± 4	No
69.00	−5.53	3.0×10^{-2}	3.25×10^{-4}	92 ± 5	No
75.97	−6.43	5.3×10^{-1}	2.54×10^{-3}	~200	No

[a] From ref. 12. [b] Taken from ref. 18. [c] Extrapolated from the data in Table II.

These comparisons provide very strong evidence that β-phenyl-β-hydroxypropionic acid is an intermediate in the isomerization of *cis*-cinnamic acid. Therefore, an addition–elimination mechanism is operating (eq. 2), and the measured rate of isom-



(2)

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[17] D. S. Noyce and W. L. Reed, *J. Am. Chem. Soc.*, **80**, 5539 (1958).

[18] D. S. Noyce and C. A. Lane, *ibid.*, **84**, 1635 (1962).

erization is the rate of hydration of *cis*-cinnamic acid.

Evidence from Deuterium Isotope Studies.—Further support for the addition–elimination sequence is obtained by carrying out the isomerization in deuteriosulfuric acid. The *trans*-cinnamic acid which is formed contains carbon bound deuterium. This deuterium is at the α-position as shown by comparison of the infrared spectrum (particularly the decrease in the doublet at 10.2 microns) with an authentic sample of *trans*-cinnamic acid-α-d_1. The amount of deuterium incorporated is about 80%. The mass spectrum of methyl cinnamate derived from this cinnamic acid also shows the presence of 75–80% of one deuterium atom per mole.

It may further be shown that the deuterium is incorporated during the isomerization, and not subsequent to it by the following observations.

When authentic *trans*-cinnamic acid-α-d_1 is allowed to stand in ordinary sulfuric acid, deuterium is lost slowly from the deuteriocinnamic acid. By reisolating cinnamic acid, and following the appearance of the 10.2 μ doublet, the rate of α-D–α-H exchange may be determined (Table VI).

The net rate of loss of deuterium is only 1/25 the rate of the *cis* to *trans* isomerization.

TABLE VI

RATE OF DEUTERIUM EXCHANGE OF *trans*-CINNAMIC ACID-α-d_1 IN SULFURIC ACID AT 45.00°

H_2SO_4, %	H_0	k_{exch}, sec.$^{-1}$	k_{isomer},[a] sec.$^{-1}$
69.28	−5.56	1.24×10^{-6}	35×10^{-5}

[a] Interpolated from Table II.

Conclusions.—Clearly, the isomerization of *cis*-cinnamic acid takes place by an addition–elimination sequence at the carbon–carbon double bond. It is to be noted that this mechanism differs from the one established for the isomerization of maleic acid to fumaric acid. In the latter case, no carbon-bound deuterium is incorporated during isomerization.[19,20]

It also contrasts with the mechanisms which we have established for the isomerization of unsaturated ketones.[3,5,6]

(19) C. Horrex, *Trans. Faraday Soc.*, **33**, 570 (1937).

(20) S. Seltzer, *J. Am. Chem. Soc.*, **83**, 1861 (1961).

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

The Kinetics and Mechanism of the Dehydration of β-Phenyl-β-hydroxypropionic Acid[1-3]

BY DONALD S. NOYCE AND CHARLES A. LANE[4]

RECEIVED SEPTEMBER 29, 1961

The acid-catalyzed racemization of (+)-β-phenyl-β-hydroxypropionic acid, (+)-I, has been studied over the range 40–60% sulfuric acid. The rate of dehydration of I has been studied over the sulfuric acid concentration range 38–77%. The reaction sshow typical carbonium ion behavior; the slopes against the acidity function H_0 are substantially greater than unity; the activation parameters are concordant with a carbonium ion process.

Introduction

In the previous paper,[1] we have presented evidence showing that the acid-catalyzed isomerization of *cis*-cinnamic acid proceeds *via* an addition–elimination sequence, with β-phenyl-β-hydroxypropionic acid (I) being an intermediate.

It is the purpose of the present report to examine in some detail the behavior of I in fairly concentrated acids.

The kinetics and mechanism of the acid-catalyzed reactions of alcohols have received considerable attention in recent years. Racemization, dehydration, and O^{18} exchange have been studied for several alcohols.[5-9]

Compound I offers several advantages for a thorough study as will be clear from the results. Most particularly, the stability of the product *trans*-cinnamic acid makes studies over a wide range of acidities quite feasible.

Experimental[10]

β-Phenyl-β-hydroxypropionic acid (I) was prepared by the Reformatsky reaction[11] followed by alkaline hydrolysis; m.p. 93–94° (lit.[12] 92°, 94°, 96°).

Resolution.—Racemic I was resolved by the method of Kenyon, Phillips and Shutt[13] with some modification. Satisfactory results were not obtained using a 1:1 mixture of I and brucine, but were obtained using a 2:1 molar mixture of I and brucine and fractional crystallization from ethyl ace-

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[1] Paper XIV in the series Carbonyl Reactions; previous paper, D. S. Noyce, P. A. King, F. B. Kirby and W. L. Reed, *J. Am. Chem. Soc.*, **84**, 1632 (1962).

[2] Presented in part at the Meeting of the National Academy of Sciences, Berkeley, Calif., October, 1958; and at the 8th Conference on Reaction Mechanisms, Princeton, N. J., September, 1960.

[3] This research was supported in part by a grant from the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of this fund.

[4] National Science Foundation Coöperative Fellow, 1959–1961.

[5] R. H. Boyd, R. W. Taft, Jr., A. P. Wolfe and D. R. Christman, *J. Am. Chem. Soc.*, **82**, 4729 (1960).

[6] J. Manassen and F. G. Klein, *J. Chem. Soc.*, 4203 (1960).

[7] C. A. Bunton, A. Konasiewicz and D. R. Llewellyn, *ibid.*, 607 (1955); C. A. Bunton and D. R. Llewellyn, *ibid.*, 3402 (1957).

[8] E. Grunwald, A. Heller and F. S. Klein, *ibid.*, 2604 (1957).

[9] D. Jeffery and A. Fry, Abstracts of 138th Meeting of the American Chemical Society, New York, N. Y., September, 1960, p. 33P.

[10] Melting points are corrected; boiling points are uncorrected. Infrared spectra were determined with a Baird infrared spectrophotometer.

[11] C. R. Hauser and D. S. Breslow, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 408.

[12] *Cf.* Beilstein, "Handbuch der Organischen Chemie," Vol. 10, p. 249.

[13] J. Kenyon, H. Phillips and G. R. Shutt, *J. Chem. Soc.*, 1663 (1935).