The rates of dehydration of II and V differ by a small factor (2 to 5 depending upon the acidity of the medium), while the difference in rate between V and VI is somewhat larger.

In fact, if in addition, one makes a correction for the difference in the σ-values for $-COOH$ and $-COCH_3$, the rate difference shows gratifying concordance with the mechanism advanced.

Comparison with other Hydroxy Acids.—It is now possible to offer a further interpretation of the results of Lucas and his co-workers.[8-11] The premise which we wish to put forward is that most β-hydroxy acids will undergo dehydration *via* a carbonium ion mechanism (eq. 1–3). This mechanism also appears to be most concordant with the facts for β-hydroxyisovaleric acid. The behavior of β-hydroxybutyric acid, on the other hand, is not in line with these conclusions; *e.g.*, the change from an aliphatic tertiary alcohol to an aliphatic secondary alcohol is not attended by a corresponding drop in rate; the activation parameters show deviation and the dehydration of *sec*-butyl alcohol appears to be slower than that of β-hydroxybutyric acid.

It, therefore, appears that β-hydroxybutyric acid undergoes acid-catalyzed dehydration by a different mechanism, *i.e.*, one similar to the enolization mechanism for dehydration of β-hydroxy ketones. Naturally this mechanism would be expected to apply also to β-hydroxypropionic acid.[10b]

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

Primary and Secondary Deuterium Isotope Effects on the Dehydration of β-Phenyl-β-hydroxypropionic Acid[1-3]

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

RECEIVED SEPTEMBER 29, 1961

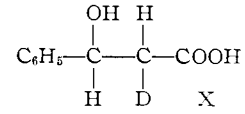
The kinetics of racemization of (+)-β-phenyl-β-hydroxypropionic-α-d_1 acid have been determined. The secondary isotope effect in this reaction is 1.11 ± 0.02. The rate of dehydration of β-phenyl-β-hydroxypropionic-α-d_1 acid is markedly less than that of the analogous protium compound. It is concluded that the kinetic isotope effects support a mechanism in which the rate-determining step is the direct loss of the α-proton to give cinnamic acid.

Introduction

Deuterium isotope effects have been of marked value in elucidating the more precise detail of many solvolytic carbonium ion reactions. In the hydrolysis of tertiary halides, Shiner[5] has shown that introduction of deuterium on the adjacent carbon has a decelerating influence upon the rate, which varies somewhat as this carbon is primary, secondary or tertiary. Lewis and Boozer[6] and Streitwieser, Jagow, Fahey and Suzuki[7] and Winstein and Takahashi[8] have examined secondary alkyl tosylates, observing a decrease in rate of 10 to 20% for each deuterium introduced when no other questions of participation are involved. A similar decrease in rate is observed in the acetolysis of methyl *p*-tolylcarbinyl chloride.[9]

Coupled with these secondary kinetic isotope effects are additional primary kinetic isotope effects if one of the pathways of reaction is elimination. In the examples studied by Shiner, the fraction of olefin formed drops from 36% for *t*-amyl chloride to 23% for *t*-amyl chloride-d_8. Similarly, when hydrogen participation is important, the observed rate of reaction is decreased by a greater fraction; in the case of acetolysis of 3-methyl-2-butyl-3-*d* *p*-toluenesulfonate[8] the rate decreases by a factor of $k_H/k_D = 2$. The product ratios likewise change, *e.g.*, more *t*-amyl acetate is formed and less 3-methyl-2-butene.[8]

In conjunction with our studies of the acid-catalyzed racemization and dehydration of β-phenyl-β-hydroxypropionic acid,[10] we have examined some deuterium isotope effects in this system in order to obtain more information about carbonium ion formation, and about the elimination step. In particular, we have prepared β-phenyl-β-hydroxypropionic-α-d_1 acid (X), and studied the rate of racemization, the rate of dehydration and the product composition. This system is of particular advantage for study of these acid-catalyzed reactions because of the demonstrated[11] stability of the product, *trans*-cinnamic acid under the conditions of the experiments. There is the further advantage that the single deuterium substitution makes possible evaluation of several secondary isotope effects.


$$C_6H_5-\overset{\overset{OH}{|}}{\underset{\underset{H}{|}}{C}}-\overset{\overset{H}{|}}{\underset{\underset{D}{|}}{C}}-COOH$$
X

Results

The addition of deuterium bromide to lithium cinnamate suspended in carbon tetrachloride afforded β-phenyl-β-bromo-propionic-α-*d* acid-*d* (XI); use of a non-polar solvent minimized the possibility

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(1) Paper XVI in the Series Carbonyl Reactions; previous paper, D. S. Noyce, P. A. King, C. A. Lane and W. L. Reed, *J. Am. Chem. Soc.*, **84**, 1638 (1962).

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

(3) 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) V. J. Shiner, Jr., *J. Am. Chem. Soc.*, **75**, 2925 (1953); **76**, 1603 (1954).

(6) E. S. Lewis and C. E. Boozer, *ibid.*, **76**, 791 (1954).

(7) A. Streitwieser, Jr., R. H. Jagow, R. C. Fahey and S. Suzuki, *ibid.*, **80**, 2326 (1958).

(8) S. Winstein and J. Takahashi, *Tetrahedron*, **2**, 316 (1958).

(9) E. S. Lewis and G. M. Coppinger, *J. Am. Chem. Soc.*, **76**, 4495 (1954).

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

(11) D. S. Noyce, P. A. King, F. B. Kirby and W. L. Reed ,*ibid.*, **84**, 1632 (1962).

TABLE I

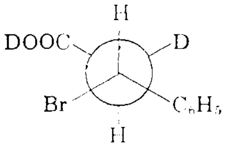
ISOTOPE EFFECT ON RATE OF RACEMIZATION OF (+)-X AT 45.0°

Compound	H_2SO_4, %	$k$rac,[a] sec.$^{-1}$	$k$rac (cor.),[b] sec.$^{-1}$	k_H/k_D
(+)-$C_6H_5CHOHCH_2COOH$	39.80	2.26×10^{-4}	2.21×10^{-4}	1.13
(+)-$C_6H_5CHOHCHDCOOH$	39.80	1.98×10^{-4}	1.95×10^{-4}	
(+)-$C_6H_5CHOHCH_2COOH$	47.00	1.24×10^{-3}	1.21×10^{-3}	1.09
(+)-$C_6H_5CHOHCHDCOOH$	47.00	1.13×10^{-3}	1.11×10^{-3}	

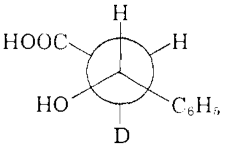
[a] Total rate of loss of optical activity. [b] Total rate corrected for the very small amount of cinnamic acid formed concurrently.

of any further hydrogen–deuterium exchange at the α-position. Hydrolysis of XI with water (slightly acid to avoid the synchronous loss of CO_2 and bromide ion[12,13] which occurs readily in alkaline solution) afforded β-phenyl-β-hydroxy-propionic-α-d_1 acid (X). X was resolved using the morphine salt.

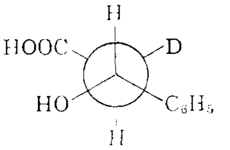
The stereochemistry of the addition and hydrolysis are of no concern in studying the dehydration for the following reason: racemization at the β-carbon is many times faster than the rate of dehydration[10] and, therefore, practically the entire elimination will proceed from material already stereochemically equilibrated at the β-carbon. On the other hand, the stereochemistry of addition and hydrolysis are of concern in studying the racemization. In the sequence two asymmetric centers are generated. The *trans* addition of deuterium bromide gives isomer a (represented by one enantiomorph in the most probable conformation).



a



b



c

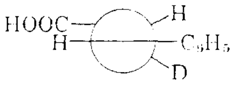
Solvolytic hydrolysis of the bromine leads to material about 50% racemized at the β-carbon.[14,15] The resolved deuterio acid (+)-X is, therefore about a 1:3 mixture of b and c.

Secondary Isotope Effect on the Rate of Racemization.—The rate of racemization of (+)-X is 11% slower than that of its protium analog. The relevant data are compared in Table I. These data are given in terms of the total rate of loss of optical activity and also corrected to give the rate of formation of racemic X and its protium analog.

The magnitude of the secondary isotope effect is a weighted composite for b and c, and is within the range to be expected for a typical carbonium ion process. In the case of *t*-amyl chloride, Shiner[5] observes that the isotope effect per deuterium (k_H/k_D) is 1.10 for replacement of the primary hydrogens and 1.18 for replacement of the secondary hydrogens. In secondary halides Lewis and Coppinger[9] find 1.10 in methyl-d_3 *p*-tolylcarbinyl chloride, while Streitwieser, *et al.*, observe 1.15–1.25 per deuterium in deuterated cyclopentyl tosylates.

The geometrical requirements of the β-deuterium isotope effect have recently been elucidated. Shiner[16] observes that when the carbon–deuterium bond is in the nodal plane of the carbonium ion, there is essentially no secondary isotope effect. However, when the projection of the carbon–deuterium bond is 30° to the nodal plane, the secondary isotope effect is $k_H/k_D = 1.07$.

In the present instance, the β-deuterium may be *gauche* or *trans* (b) or (c). The conformation of the preferred carbonium ion may well be as in d.



d

In such a case, the secondary β-deuterium isotope effect would be the same for both the *threo* and *erythro* isomers b and c.

As further confirmation of the reaction sequence, it was established that racemic β-hydroxy-β-phenylpropionic acid isolated from the kinetic experiments with (+)-X still contained one deuterium per mole.

Kinetic Isotope Effect on Rate of Dehydration.—The rate of dehydration of β-hydroxy-β-phenylpropionic-α-d_1 acid is markedly slower than of the undeuterated analog. The comparison of the over-all observed rates is given in Table II.

TABLE II

RATE OF DEHYDRATION OF β-PHENYL-β-HYDROXYPROPIONIC-α-d_1 ACID

Compound	H_2SO_4, %	$k$dehyd., sec.$^{-1}$	k_H/k_D
$C_6H_5CHOHCH_2COOH$	51.90	10.7×10^{-5}	
$C_6H_5CHOHCHDCOOH$	51.90	6.20×10^{-5}	1.72
		6.15×10^{-5}	
		6.19×10^{-5}	
		6.30×10^{-5}	

The ratio of rates for the deuterated and undeuterated compound is a composite of several kinetic isotope effects, both primary and secondary. We have determined the ratio of products formed in the dehydration of β-phenyl-β-hydroxypropionic-α-d_1 acid, and find that the resulting cinnamic acid contains 0.744 ± 0.013 atom D/molecule. This corresponds to a net kinetic isotope effect of 2.91 ± 0.2 in the loss of the proton from the α-carbon.

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(12) R. Grovenstein and D. E. Lee, *J. Am. Chem. Soc.*, **75**, 2639 (1953).

(13) S. J. Cristol and W. P. Norris, *ibid.*, **75**, 2645 (1953).

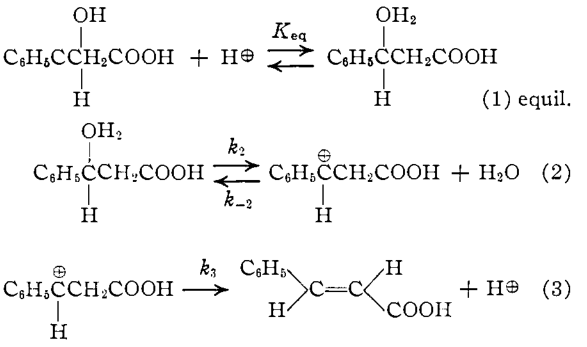
(14) A. McKenzie and H. B. P. Humphries, *J. Chem. Soc.*, **97**, 121 (1910).

(15) A. McKenzie and F. Barrow, *ibid.*, **99**, 1910 (1911); *cf.*, G. Senter and A. M. Ward, *ibid.*, **125**, 2137 (1924); **127**, 1847 (1925).

(16) V. J. Shiner, Jr., *J. Am. Chem. Soc.*, **82**, 2655 (1960).

In order to evaluate more completely the isotope effects in this system, we need to consider the secondary isotope effect on the step directly involving hydrogen loss (eq. 6).

The following reaction scheme is used in the steady state treatment below

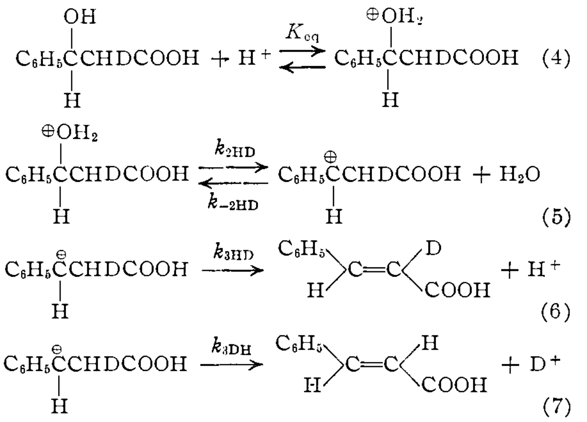


$$\mathrm{C_6H_5\overset{OH}{\underset{H}{C}}CH_2COOH + H^{\oplus} \overset{K_{eq}}{\rightleftharpoons} C_6H_5\overset{OH_2}{\underset{H}{C}}CH_2COOH} \tag*{(1) equil.}$$

$$\mathrm{C_6H_5\overset{OH_2}{\underset{H}{C}}CH_2COOH \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} C_6H_5\overset{\oplus}{\underset{H}{C}}CH_2COOH + H_2O} \tag{2}$$

$$\mathrm{C_6H_5\overset{\oplus}{\underset{H}{C}}CH_2COOH \xrightarrow{k_3} (C_6H_5)(H)C{=}C(H)(COOH) + H^{\oplus}} \tag{3}$$

and correspondingly for the reaction of the deuterium compound



$$\mathrm{C_6H_5\overset{OH}{\underset{H}{C}}CHDCOOH + H^+ \overset{K_{eq}}{\rightleftharpoons} C_6H_5\overset{\oplus OH_2}{\underset{H}{C}}CHDCOOH} \tag{4}$$

$$\mathrm{C_6H_5\overset{\oplus OH_2}{\underset{H}{C}}CHDCOOH \underset{k_{-2HD}}{\overset{k_{2HD}}{\rightleftharpoons}} C_6H_5\overset{\oplus}{\underset{H}{C}}CHDCOOH + H_2O} \tag{5}$$

$$\mathrm{C_6H_5\overset{\ominus}{\underset{H}{C}}CHDCOOH \xrightarrow{k_{3HD}} (C_6H_5)(H)C{=}C(D)(COOH) + H^+} \tag{6}$$

$$\mathrm{C_6H_5\overset{\ominus}{\underset{H}{C}}CHDCOOH \xrightarrow{k_{3DH}} (C_6H_5)(H)C{=}C(H)(COOH) + D^+} \tag{7}$$

where the choice of symbols is transparent.

The following further symbols are introduced

$S_2 = k_2/k_{2HD}$, secondary isotope effect in ionization step

$S_3 = (1/2)(k_3/k_{3HD})$, secondary isotope effect in elimination (eq. 6)

We assume, further, that K_{eq} is identical for the deuterated and undeuterated compounds. Using the usual steady state treatment, the observed rate of formation of cinnamic acid is

$$k_{obs} \text{ (for normal cpd.)} = K_{eq} \times k_2k_3/(k_{-2} + k_3) \tag{8}$$

and

$$k_{HD\ obs} \text{ (for deuterio cpd.)} = [K_{eq} \times k_{2HD}(k_{3HD} + k_{3DH})]/(k_{-2HD} + k_{3HD} + k_{3DH}) \tag{9}$$

Taking the ratio, we obtain

$$k_{obs}/k_{HD\ obs} = 10.7/6.20 = \frac{k_2}{k_{2HD}} \times \frac{k_3}{(k_{3HD} + k_{3DH})} \times \frac{k_{-2} + k_3}{(k_{-2HD} + k_{3HD} + k_{3DH})} \tag{10}$$

Since $k_{-2} >> k_3$ and $k_{-2HD} >> (k_{3HD} + k_{3DH})$

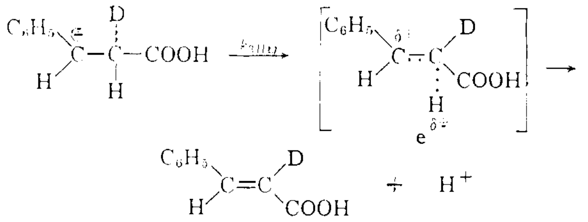
$$\frac{10.7}{6.20} \cong \frac{k_2}{k_{2HD}} \times \frac{k_3}{k_{3HD} + k_{3DH}} \times \frac{k_{-2}}{k_{-2HD}} \tag{11}$$

With the assumption that $k_{-2}/k_{-2HD} = 1.00$, eq. 11 reduces to

$$\frac{10.7}{6.20} = S_2 \times S_3 \times 2k_{3HD}/(k_{3DH} + k_{3HD}) \tag{12}$$

Putting in the experimental values, $S_2 = 1.11$ and $k_{3HD}/k_{3DH} = 2.91$, S_3 is seen to be 1.05 ± 0.02.

In the step from the carbonium ion to cinnamic acid, the transition state e is quite closely described by these results.



The modest primary isotope effect of 2.77 (2.91/1.05) shows that bond breaking has proceeded some, but not an inordinate amount. In other words, the C–H bond is still fairly strong. Concordant with this is the small magnitude of the secondary isotope effect, S_3, of 1.05. Comparisons with the recent studies of Seltzer[17] on the secondary isotope effect in the isomerization of maleic acid, and of Stewart, *et al.*,[18] on the ionization of benzhydrol show that the change from tetrahedral to trigonal at the α-carbon has not progressed very far. This conclusion, of course, leads to the observed result that the dehydration reaction has a great deal of positive charge localized at the benzylic carbon as shown by the large negative ρ-value.[19]

Conclusions.—We conclude from these studies that the rate-determining step in the dehydration of β-phenyl-β-hydroxypropionic acid is the direct loss of the proton from the α-carbon.

Experimental

β-Bromo-β-phenylpropionic-α-*d* Acid-*d* (XI).—A suspension of 3.09 g. of lithium cinnamate in 75 ml. of carbon tetrachloride was saturated with deuterium bromide[20] at the boiling point in a carefully dried, all-glass apparatus. The silvery luster of the lithium salt changed rapidly to a more powdery suspension. The suspension was then saturated at 0° with deuterium bromide and sealed in a heavy-walled tube. The sealed tube was heated at 110–120° for 4 days.

After cooling, the contents of the tube were filtered, the residue washed with hot carbon tetrachloride, and the filtrate evaporated to dryness (excess DBr present) to give crude β-bromo-β-phenylpropionic-α-*d* acid-*d*.

β-Phenyl-β-hydroxypropionic-α-*d* Acid.—The crude bromo acid was hydrolyzed by stirring with 200 ml. of acidified (1 drop H_2SO_4) water for 2 days. The suspension was chilled, filtered, and extracted three times with benzene. The filtrate was saturated with potassium chloride and extracted repeatedly with ether; from the ether extracts there was obtained 1.54 g. (46%) of crude β-phenyl-β-hydroxypropionic-α-*d* acid. Recrystallization from benzene afforded colorless crystals, m.p. 90.8–92.2°.[10]

Anal.[21] Calcd. for $C_9H_9DO_2$: 10.00 atom % excess D. Found: 10.04, 10.15 from two separate preparations.

Resolution of β-Phenyl-β-hydroxypropionic-α-*d* Acid.—The deuterio acid was resolved using the morphine salt, following the method of McKenzie and Humphries.[14] The regenerated acid was crystallized three times from benzene

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[17] S. Seltzer, *Chemistry & Industry*, 1313 (1959); *J. Am. Chem. Soc.*, **83**, 1861 (1961).

[18] R. Stewart, A. L. Gatzke, M. Mocek and K. Yates, *Chemistry & Industry*, 331 (1959).

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

[20] H. C. Brown and C. Groot, *ibid.*, **64**, 2223 (1942); benzoyl bromide was substituted for benzoyl chloride.

[21] All deuterium analyses were performed by Dr. J. Nemeth, 303 Washington Ave., Urbana, Ill., except as noted.

and then from water to yield (+)-β-phenyl-β-hydroxypropionic acid- α-d_1, m.p. 115–118°.[10] A less completely resolved sample of the (−)-acid was also obtained, m.p. 113–118°.

Kinetic Procedures.—The kinetic procedures have been described in a previous paper.[10]

Product isolation studies were carried out as described previously.[10]

A. **Racemization.**—From a sample of (+)-β-phenyl-β-hydroxypropionic acid, there was isolated *rac*-β-phenyl-β-hydroxypropionic-α-*d* acid, m.p. 90-92°.

Anal.[22] Found: 10.05 ± 0.3 atom % excess D.

B. **Dehydration.**—Samples of cinnamic-α-*d* acid were isolated under the conditions described previously.[10] The cinnamic acid was purified by crystallization from heptane and sublimation.

Anal. Calcd. for $C_9H_7DO_2$: 12.5 atom % excess D. Found: 9.14, 9.46 from two separate preparations.

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[22] Deuterium analysis by Dr. C. W. Koch, Department of Chemistry, University of California, Berkeley.

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

The Effect of Substituents upon the Rate of Isomerization of Substituted *cis*-Cinnamic Acids[1-3]

BY DONALD S. NOYCE AND HARVEY S. AVARBOCK

RECEIVED SEPTEMBER 29, 1961

The rates of isomerization of *cis-p*-methoxycinnamic acid and of *cis-p*-chlorocinnamic acid as catalyzed by sulfuric acid have been studied. Each of the isomerizations parallels the acidity function H_0 with unit slope. The corresponding β-aryl-β-hydroxypropionic acid is an intermediate. The rate of isomerization is sensitive to the electronic nature of the substituent. Correlation with σ^+ gives a ρ of −4.3. These data support a mechanism in which there is a large electron deficiency at the benzylic carbon in the transition state.

Introduction

The isomerization of *cis*-cinnamic acid as catalyzed by sulfuric acid[4] has been shown to be closely involved with the behavior of the related hydroxy acid, β-phenyl-β-hydroxypropionic acid.[1,4,5] It was also shown that the series of β-aryl-β-hydroxypropionic acid gave a very steep ρ–σ^+ correlation for the dehydration reaction, indicating the high degree of carbonium ion character at the benzylic carbon.[6]

In the present report we wish to present results on the kinetics of the acid-catalyzed isomerization of two substituted *cis*-cinnamic acids. These results show that in this reaction also there is a high degree of positive charge at the β (benzylic) carbon.

Experimental[7]

Materials.—*trans-p*-**Methoxycinnamic** acid was crystallized to constant m.p. and ultraviolet spectrum from methanol; m.p. 173.4–174.8°; neut. equiv.: calcd. 178.2, found 177.

cis-p-**Methoxycinnamic acid** was prepared by ultraviolet irradiation of a sodium carbonate solution of the *trans* isomer in a quartz flask. Separation of the *cis* and *trans* isomers was easily effected by fractional crystallization from benzene, the *cis* isomer being more soluble than the *trans* isomer by a factor of at least 300 at 25°. The product obtained in 20% yield was recrystallized to constant m.p. from a mixture of benzene and petroleum ether; m.p. 69.2–69.4° (lit.[8] 66°).

Anal. Calcd. for $C_{10}H_{10}O_3$: C, 67.41; H, 5.66; neut. equiv., 178.2. Found: C, 67.51; H, 5.78; neut. equiv., 179.

trans-p-**Chlorocinnamic acid** was prepared from *p*-chlorobenzaldehyde and malonic acid following the procedure of Pandya and Pandya.[9] A sample was crystallized to constant m.p. and spectrum from ethanol; m.p. 251.2–251.6° (lit. 247°,[9] 250°[10]); neut. equiv. calcd. 182.6, found 183.

cis-p-**Chlorocinnamic Acid.**—Ultraviolet irradiation of the *trans* isomer and separation of isomers in the manner described in the preparation of *cis-p*-methoxycinnamic acid produced *cis-p*-chlorocinnamic acid in 25% yield. It was recrystallized to constant m.p. from distilled water; m.p. 112.0–112.3° (lit.[11] 113.8–116.2°).

Anal. Calcd. for $C_9H_7O_2Cl$: C, 59.19; H, 3.86; Cl, 19.42; neut. equiv., 182.6. Found: C, 58.93; H, 3.68; Cl, 19.56; neut. equiv., 184.

Product Isolation under Conditions of the Kinetic Experiments. A. *p*-**Methoxycinnamic Acid.**—A solution of 104 mg. of *cis-p*-methoxycinnamic acid in 1000 ml. of 43.57% sulfuric acid was maintained at 25.0° for a period corresponding to eight half-lives; during the course of reaction, 75 mg. of material precipitated from solution. After being worked up in the usual manner, it was recrystallized to constant m.p. from methanol; m.p. 173.1–173.6°; neut. equiv. calcd. 178.2, found 177.0. A mixed melting point with known *trans-p*-methoxycinnamic acid showed no depression. Dilution of the reaction solution with water followed by extraction with ether on a continuous extractor yielded 15 mg. of material, m.p. 171–173°. The infrared spectra of both portions was identical with that of pure *trans-p*-methoxycinnamic acid. The combined yield was 90 mg., 87%.

B. *p*-**Chlorocinnamic Acid.**—A solution of 109 mg. of *cis-p*-chlorocinnamic acid in 160 ml. of 53.18% sulfuric acid was maintained at 90° for a period corresponding to 6 half-lives. During the course of reaction, 96 mg. of material precipitated from solution. After isolation in the usual manner, it was recrystallized from ethanol; m.p. 251.1–251.7°. The infrared spectrum was identical with that of pure *trans-p*-chlorocinnamic acid. Extraction of the reaction solution with ether yielded no further product. The yield of 96 mg. was 88% of theoretical.

cis-trans **Isomerization in Sulfuric Acid-d_2.**—A solution of 400 mg. of *cis-p*-chlorocinnamic acid in 216 g. of 51% sulfuric acid-d_2 was maintained at 90° for a period corresponding to 1 half-life. The solution was then immediately chilled at −10° and filtered through a sintered glass funnel. The precipitate was dissolved in 25 ml. of 1 *M* sodium hydroxide

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[1] Paper XVII in the Series Carbonyl Reactions; previous paper, D. S. Noyce and C. A. Lane, *J. Am. Chem. Soc.*, **84**, 1641 (1962).

[2] 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.

[3] Presented in part at the Eighth Conference on Organic Reaction Mechanisms, Princeton, N. J., September, 1960.

[4] D. S. Noyce, P. A. King, F. B. Kirby and W. L. Reed, *J. Am. Chem. Soc.*, **84**, 1632 (1962).

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

[6] D. S. Noyce, P. A. King, C. A. Lane and W. L. Reed, *ibid.*, **84**, 1638 (1962).

[7] Analyses are by the Microanalytical Laboratory of the University of California. Melting points are corrected.

[8] W. A. Roth and R. Stoermer, *Ber.*, **46**, 260 (1913).

[9] K. C. Pandya and R. B. Pandya, *Proc. Indian Acad. Sci.*, **14A**, 112 (1941).

[10] J. K. Kochi, *J, Am. Chem. Soc.*, **78**, 1228 (1956).

[11] S. Lindenfors, *Arkiv. Kemi*, **10**, 561 (1957).