

# The Acid-Catalyzed Decarboxylation of $\beta$ -Phenylcinnamic Acid and the Intermediate Role of $\beta,\beta$ -Diphenyl- $\beta$ -hydroxypropionic Acid<sup>1,2</sup>

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In dilute sulfuric acid, the decarboxylation of  $\beta$ -phenylcinnamic acid (I) is clearly acid catalyzed. In the region of  $H_0$  from  $-0.80$  to  $-2.4$  a plot of  $\log k$  vs.  $H_0$  is linear, with a slope of 1.0. In the region of 50% sulfuric acid the rate vs.  $H_0$  profile curves very sharply, approaching a limiting slope of about 0.3. It is concluded that in dilute sulfuric acid the rate-limiting process is the protonation of the double bond, followed by rapid hydration and synchronous decarboxylation and dehydration of the formed  $\beta$ -hydroxy- $\beta,\beta$ -diphenylpropionic acid (II). In accord with this conclusion, II is shown to undergo two rapid competitive reactions in 40–50% sulfuric acid, one being simple, acid-catalyzed dehydration, and the other being synchronous dehydration and decarboxylation. Thus in 50% sulfuric acid the rate-limiting process for the formation of  $CO_2$  has shifted and has become the synchronous decarboxylation and dehydration of the small amount of  $\beta,\beta$ -diphenyl- $\beta$ -hydroxy acid formed in steady-state equilibrium with  $\beta$ -phenylcinnamic acid.

## Introduction

The decarboxylation of cinnamic acids as carried out in acidic solution has received attention sporadically since it was first observed by Miller and Kinkelin in 1889.<sup>4</sup> In 1949 Johnson and Heinz<sup>5</sup> reported kinetic studies on a variety of  $\alpha$ - and  $\beta$ -substituted cinnamic acids, and they suggested that the reactions proceeded by way of the  $\beta$ -carbonium ions. Subsequently Moyer and Johnson<sup>6</sup> undertook a more detailed and extensive study of the decarboxylation reaction, and suggested three additional alternative mechanisms which appeared attractive in the light of their experimental results.

In recent studies from these laboratories<sup>1,7,8</sup> it has been shown that many  $\beta$ -hydroxy acids undergo two concomitant reactions in aqueous sulfuric acid solutions. Besides the "normal" simple, acid-catalyzed dehydration to form unsaturated acids, a synchronous decarboxylation and dehydration occurs.<sup>8</sup>

In order to examine the possibility that the pathway for decarboxylation of substituted cinnamic acids pro-

ceeds by way of hydration (to form the  $\beta$ -hydroxy acid) followed by synchronous decarboxylation and dehydration, we have investigated the reactions of  $\beta$ -phenylcinnamic acid (I) in various sulfuric acid media, and also the behavior of the corresponding hydroxy acid,  $\beta,\beta$ -diphenyl- $\beta$ -hydroxypropionic acid (II), under similar conditions.

## Experimental Section

**Materials.**  $\beta,\beta$ -Diphenyl- $\beta$ -hydroxypropionic acid (II) was prepared by the method of Rupe and Busolt<sup>9</sup> in 74% yield, m.p. 214–215° (ethanol) (lit.<sup>9</sup> m.p. 212°).

$\beta$ -Phenylcinnamic acid (I) was prepared by the procedure of Rupe and Busolt, modified by dehydrating the crude hydroxy ester by the procedure of Johnson and Glenn,<sup>10</sup> yield, 84%, m.p. (from benzene) 160.2–162.0° (lit.<sup>9</sup> m.p. 162°).

**Product Studies.** The extremely limited solubility of  $\beta$ -phenylcinnamic acid in aqueous sulfuric acid precludes a direct determination of the products of reaction under conditions identical with those of the kinetics experiments. Using a 50% aqueous dioxane solution, containing 30% sulfuric acid, a gravimetric determination of the carbon dioxide evolved was carried out; 95% of the theoretical amount of barium carbonate was collected. The qualitative rate observed was entirely consistent with the other data, but no rate measurements were carried out under these conditions.

In a separate experiment, the organic product of decarboxylation was identified. Introduction of an appropriate stock solution into 96% sulfuric acid resulted in the absorption spectrum of the 1,1-diphenylethyl cation,  $\lambda_{\max}$  430 ( $\epsilon_{\max}$  23,500), in good agreement with the results of Deno, Groves, and Saines.<sup>11</sup>

**Kinetic Procedures.** The rate of decarboxylation of  $\beta$ -phenylcinnamic acid was measured by observing the decrease in ultraviolet absorption at an appropriate wave length (290 or 300 m $\mu$ ), using a Beckman D.U. spectrophotometer and 10-cm. cells. The cinnamic acid maximum is near this region whereas the product, 1,1-diphenylethylene, shows little absorption in this region.

Rate constants were determined graphically by plotting the data in the form of apparent fraction of remaining organic acid ( $\log [O.D.]/[O.D.]_0$ ) against time; some rate constants were determined analytically. The precision of the data was generally  $\pm 2\%$ .

(9) H. Rupe and E. Busolt, *Ber.*, 40, 4537 (1907).

(10) W. S. Johnson and H. J. Glenn, *J. Am. Chem. Soc.*, 71, 1087 (1949).

(11) N. C. Deno, P. T. Groves, and G. Saines, *ibid.*, 81, 5791 (1959).

(1) Previous paper: D. S. Noyce, L. B. Gortler, M. J. Jorgenson, F. B. Kirby, and E. C. McGoran, *J. Am. Chem. Soc.*, 87, 4329 (1965).

(2) Supported in part by grants from the National Science Foundation, NSF-13125 and GP-1572.

(3) National Institutes of Health Fellow, 1962–1965.

(4) W. J. Miller and F. Kinkelin, *Ber.*, 22, 1715 (1889).

(5) W. S. Johnson and W. E. Heinz, *J. Am. Chem. Soc.*, 71, 2913 (1949).

(6) P. H. Moyer, Ph.D. Dissertation, University of Wisconsin, 1954; cf. "Summaries of Doctoral Dissertations, University of Wisconsin, 1953–1954," Vol. 15, University of Wisconsin Press, Madison, Wis., 1955, pp. 469–471. We are deeply grateful to Professor W. S. Johnson for making available to us a copy of Dr. Moyer's dissertation.

(7) D. S. Noyce and R. A. Heller, *J. Am. Chem. Soc.*, 87, 4325 (1965).

(8) D. S. Noyce, P. A. King, and G. L. Woo, *J. Org. Chem.*, 26, 632 (1961).

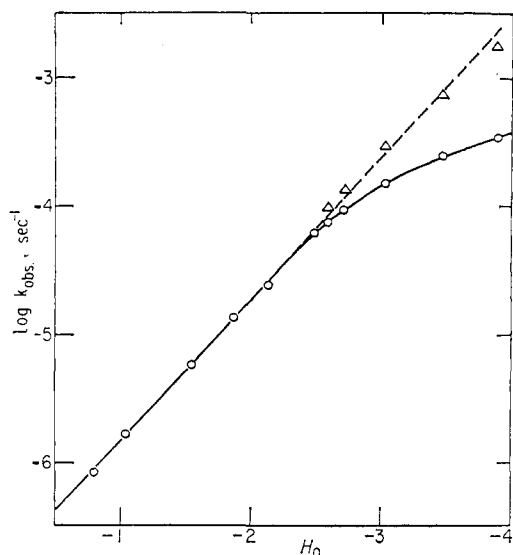


Figure 1. Decarboxylation of  $\beta$ -phenylcinnamic acid in aqueous sulfuric acid at 45°: O—, observed rate;  $\Delta$ ---, calculated for  $k_1$  (see text).

The kinetics of dehydration of  $\beta,\beta$ -diphenyl- $\beta$ -hydroxypropionic acid were determined by the methods described previously<sup>12</sup> for very fast reactions, observing the increase in ultraviolet absorption at 290 m $\mu$ . The maximum absorption was carefully determined and from this the fraction of the two competing reactions, simple dehydration and synchronous decarboxylation, was determined.

## Results and Discussion

The rate of decarboxylation of  $\beta$ -phenylcinnamic acid increases rapidly with increasing sulfuric acid concentrations up to 40% sulfuric acid. As shown in Table I

Table I. Decarboxylation of  $\beta$ -Phenylcinnamic Acid in Aqueous Sulfuric Acid at 45°

H <sub>2</sub> SO <sub>4</sub> , %	-H <sub>0</sub> <sup>a</sup>	k × 10 <sup>7</sup> , sec. <sup>-1</sup>	log k	log k + H <sub>0</sub>
16.43	0.80	8.37	-6.08	-6.88
19.93	1.04	17.2	-5.77	-6.81
27.10	1.54	58.6	-5.23	-6.77
32.12	1.86	138	-4.86	-6.72
35.96	2.13	246	-4.61	-6.74
40.63	2.47	618	-4.21	-6.68
41.90	2.58	745	-4.13	-6.71
43.27	2.70	947	-4.02	-6.72
46.26	3.02	1500	-3.82	-6.84
50.82	3.47	2510	-3.60	-7.07
54.87	3.88	3550	-3.45	-7.34
19.38 <sup>b</sup>	...	545	-4.26	...
19.37 <sup>b</sup>	...	535	-4.27	...
19.93 <sup>c</sup>	...	1.68	-6.78	...
40.63 <sup>c</sup>	...	60.0	-5.22	...

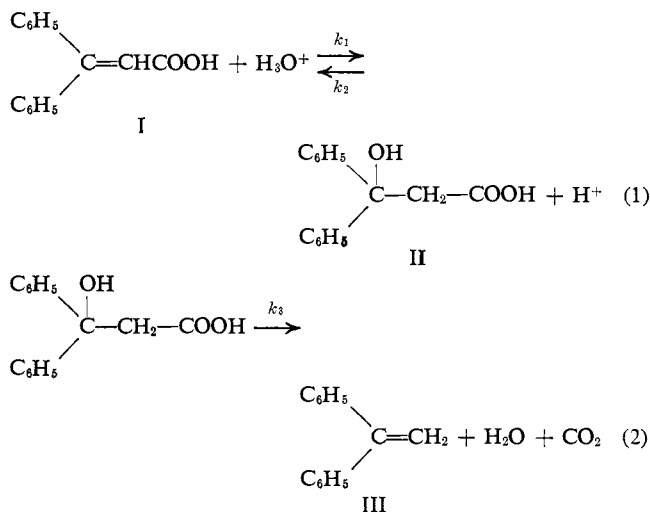
<sup>a</sup> Corrected for temperature variation. <sup>b</sup> At 79.90 ± 0.05°. <sup>c</sup> At 25.00° (extrapolated from data at other temperatures).

and Figure 1, in more concentrated sulfuric acid solutions there is a fairly abrupt change in the slope of the logarithm of the observed rate when plotted against the acidity function,  $H_0$ . This change in rate very closely resembles a change from a reaction apparently first order in acidity to one zero order in acidity.

(12) D. S. Noyce and C. A. Lane, *J. Am. Chem. Soc.*, **84**, 1635 (1962).

One possible reason for this change may be quickly discarded. Substantial conversion of  $\beta$ -phenylcinnamic acid to its conjugate acid is inconsistent with the known basicities of any of the functional centers in  $\beta$ -phenylcinnamic acid, even though the rate profile may be fit moderately well with a  $pK_{BH^+}$  of -2.8 (44% sulfuric acid). Deno, Groves, and Saines<sup>13</sup> have shown that 1,1-diphenylethylene is one-half protonated in 72% sulfuric acid. In the present situation the carboxyl group will inductively destabilize a hypothetical benzhydryl cation. Thus carbon protonation is not the explanation for the change in the rate vs. acidity profile. Similarly, protonation at the carboxyl group may be eliminated. The protonation of carboxylic acids occurs in about 80% sulfuric acid<sup>14</sup> and is of only moderate sensitivity to the effect of substituents. The  $pK_{BH^+}$  of *cis*-cinnamic acid seems to be about -7.<sup>15</sup> Prediction of the  $pK_{BH^+}$  for  $\beta$ -phenylcinnamic acid from these facts does not give a basicity sufficiently great to accord with the experimental observations of Table I. Thus carboxyl protonation is excluded. Finally, it is to be noted that there is no marked change in the initial absorption spectrum of  $\beta$ -phenylcinnamic acid in going from 20 to 50% sulfuric acid. This fact likewise indicates that conversion of  $\beta$ -phenylcinnamic acid to its conjugate acid is not the explanation for the observed rate vs. acidity profile. An entirely different explanation is attractive, and as will develop is fully in accord with the observations.

Consider the sequence represented by eq. 1 and 2.



If both the forward and reverse steps of eq. 1 are strongly acid catalyzed, while eq. 2 is not, then a predicted profile of the observed rate plotted against acidity will have the general shape observed. The above statement is correct with the additional assumption that II is present in small quantity, that is, a steady-state intermediate. The observed pseudo-first-order rate constant,  $k_{\text{obsd}}$ , under a particular set of conditions is given by eq. 3 for the assumptions just

$$k_{\text{obsd}} = \frac{k_1(\text{H}^+)k_3}{k_2(\text{H}^+) + k_3} \quad (3)$$

(13) N. C. Deno, P. T. Groves, and G. Saines, *ibid.*, **81**, 5790 (1959).

(14) R. Stewart and K. Yates, *ibid.*, **82**, 4059 (1960).

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

above. It is easy to see that at low acid concentrations eq. 3 reduces to eq. 4 and hence the observed rate is the

$$k_{\text{obsd}} = k_1(\text{H}^+) \quad (4)$$

rate-limiting, acid-catalyzed hydration of  $\beta$ -phenylcinnamic acid.

The rate of conversion of I to II may be compared very advantageously to the rate of acid-catalyzed hydration of other unsaturated acids. The best direct comparison is to the rate of the *cis* to *trans* isomerization of *cis*-*p*-methoxycinnamic acid.<sup>16</sup> As we have noted before,<sup>17</sup> the benzhydryl system is very similar to the *p*-methoxybenzyl system in its ability to stabilize a positive charge. In 36% sulfuric acid ( $H_0 = -2.13$ ) *cis*-*p*-methoxycinnamic acid isomerizes at a rate 15 times the rate of destruction of  $\beta$ -phenylcinnamic acid. As it was demonstrated that the *cis*-*trans* isomerization proceeded by way of a rate-limiting hydration, the agreement of this line of argument with the hypothesis above that rate-limiting hydration of  $\beta$ -phenylcinnamic acid occurs in sulfuric acid less concentrated than 40% is most gratifying.

At the other extreme it is advantageous to examine the limiting case of eq. 3 where the catalyzing acid concentration is very high. Equation 3 reduces to eq. 5 under these conditions

$$k_{\text{obsd}} = \frac{k_1 k_3}{k_2} \quad (5)$$

or

$$k_{\text{obsd}} = K k_3 \quad (6)$$

where  $K$  is the equilibrium constant for reaction 1 and is the equilibrium constant for hydration of the cinnamic acid. The value of  $K$  has not been directly determined in the case of the  $\beta$ -phenylcinnamic  $\rightleftharpoons$   $\beta,\beta$ -diphenyl- $\beta$ -hydroxypropionic acid system but by analogy with the situation for cinnamic acid itself<sup>12</sup> is expected to be small, *i.e.*, about 0.01 in 50% sulfuric acid. Thus this conclusion leads to two predictions, namely, first, that the reactions of  $\beta,\beta$ -diphenyl- $\beta$ -hydroxypropionic acid should be much more rapid than the observed reactions of  $\beta$ -phenylcinnamic acid, and second, that  $\beta,\beta$ -diphenyl- $\beta$ -hydroxypropionic acid should undergo largely simple dehydration above *ca.* 50% sulfuric acid and largely decarboxylation below *ca.* 40% sulfuric acid. Between these extremes the two modes of decomposition should be competitive.

**Kinetics of Reaction of  $\beta,\beta$ -Diphenyl- $\beta$ -hydroxypropionic Acid (II).** Accordingly, we have examined the reactions of II under a variety of conditions. Qualitatively,  $\beta,\beta$ -diphenyl- $\beta$ -hydroxypropionic acid in dilute (20%) sulfuric acid does not give rise to the spectrum of  $\beta$ -phenylcinnamic acid, even after an extended period of time; rather the spectrum of 1,1-diphenylethylene appears and eventually the spectrum of products from the further reaction of 1,1-diphenylethylene with aqueous acid appears. However, when  $\beta,\beta$ -diphenyl- $\beta$ -hydroxypropionic acid is introduced into 55% sulfuric acid at 45°, the spectrum of  $\beta$ -phenylcinnamic acid appears within the time to prepare the solution (less than 1 min.). This spectrum then decays at a measureable rate.

(16) D. S. Noyce and H. S. Avarbock, *J. Am. Chem. Soc.*, **84**, 1644 (1962).

(17) D. S. Noyce and M. J. Jorgenson, *J. Org. Chem.*, **28**, 3208 (1963).

Quantitative measurements have been made at 25° of the reactions of  $\beta,\beta$ -diphenyl- $\beta$ -hydroxypropionic acid in various concentrations of mineral acid. The results are recorded in Table II.

**Table II.** Rates of Reaction of  $\beta,\beta$ -Diphenyl- $\beta$ -hydroxypropionic Acid<sup>a</sup>

H <sub>2</sub> SO <sub>4</sub> , %	H <sub>0</sub> <sup>b</sup>	k <sub>obsd</sub> , sec. <sup>-1</sup>	Dehyd., % <sup>c</sup>	k <sub>-H<sub>2</sub>O</sub> , sec. <sup>-1</sup>	k <sub>-CO<sub>2</sub></sub> , sec. <sup>-1</sup>
19.93	-1.03			1.6 × 10 <sup>-5d</sup>	
40.65	-2.47			7.5 × 10 <sup>-4d</sup>	
42.95	-2.66	2.81 × 10 <sup>-3</sup>	39	1.1 × 10 <sup>-3</sup>	1.7 × 10 <sup>-3</sup>
42.98	-2.66	3.17 × 10 <sup>-3</sup>	36	1.4 × 10 <sup>-3</sup>	2.0 × 10 <sup>-3</sup>
46.57	-3.05	6.27 × 10 <sup>-3</sup>	51	3.2 × 10 <sup>-3</sup>	3.1 × 10 <sup>-3</sup>
46.59	-3.05	6.10 × 10 <sup>-3</sup>	47	2.9 × 10 <sup>-3</sup>	3.2 × 10 <sup>-3</sup>
49.90	-3.41	1.36 × 10 <sup>-2</sup>	60	8.1 × 10 <sup>-3</sup>	5.5 × 10 <sup>-3</sup>
50.13	-3.43	1.57 × 10 <sup>-2</sup>	56	8.8 × 10 <sup>-3</sup>	6.4 × 10 <sup>-3</sup>
51.52	-3.58	1.86 × 10 <sup>-2</sup>	72	1.4 × 10 <sup>-2</sup>	5.1 × 10 <sup>-3</sup>
52.52	-3.58	2.20 × 10 <sup>-2</sup>	66	1.5 × 10 <sup>-2</sup>	7.5 × 10 <sup>-3</sup>

<sup>a</sup> Solutions contained 5% ethanol by volume to improve solubility; temperature 24.96 ± 0.01°. <sup>b</sup> H<sub>0</sub> values from D. R. Hartter, Ph.D. Dissertation, University of California, 1964. <sup>c</sup> % dehydration = 100ε<sub>max</sub>(290)/12,700. <sup>d</sup> Extrapolated values.

The rates of dehydration for  $\beta,\beta$ -diphenyl- $\beta$ -hydroxypropionic acid show the typical steep increase with acid concentration; a plot of log  $k_{-\text{H}_2\text{O}}$  vs.  $H_0$  gives a slope of 1.14. The rates of decarboxylation show a lesser sensitivity to changing acid concentration; a plot of log  $k_{-\text{CO}_2}$  vs.  $H_0$  gives a slope of 0.5.

Clearly, then, the two alternative modes of reaction available to  $\beta,\beta$ -diphenyl- $\beta$ -hydroxypropionic acid are competitive in the range of 40–50% sulfuric acid, a range of acid concentrations which coincides with the change in characteristics of the observed rate of decarboxylation of  $\beta$ -phenylcinnamic acid.

The rate of dehydration of II is very substantially larger than the rate of reaction of I with mineral acid. Incidentally this observation completely validates the steady-state assumption in developing the arguments pointed out in eq. 3–6. From the reported data it is possible to obtain the ratio  $k_1/k_2$  under a variety of conditions. At 25°, in 40.65% sulfuric acid ( $H_0 = -2.47$ ) the ratio of rates observed for hydration to dehydration is 1:120; in 20% sulfuric acid, 1:100.

Further insight into the situation represented by the two sets of kinetic data given in Tables I and II is obtained as follows. The observed rate of disappearance of  $\beta$ -phenylcinnamic acid, as given in eq. 3, is of course equal to the rate of formation of the ultimate products, carbon dioxide and 1,1-diphenylethylene.

However, the term  $k_3/(k_2 + k_3)$  is simply the fraction CO<sub>2</sub> formed in the reaction of  $\beta,\beta$ -diphenyl- $\beta$ -hydroxypropionic acid. Rearranging,  $k_1 = k_{\text{obsd}}/f_{\text{CO}_2}$ .

In Figure 1, the values of  $k_1$  calculated on this basis are included as triangles. (This includes the necessary assumption, namely, that the ratio of decarboxylation to simple dehydration does not change very rapidly with temperature.)

These results clearly show that the decarboxylation of cinnamic acids is the result, not of direct replacement of carboxyl by hydrogen, but of hydration of the olefinic function to the  $\beta$ -hydroxy acid followed by the

synchronous decarboxylation and dehydration reaction which is characteristic of the hydroxy acid.

A more detailed consideration of these results is now in order. For the decarboxylation of  $\beta$ -phenylcinnamic acid eq. 3 is more properly replaced by eq. 7 where

$$k_{\text{obsd}} = \frac{k_1(h_0)^\alpha k_3(h_0)^\gamma}{k_2(h_0)^\beta + k_3(h_0)^\gamma} \quad (7)$$

associated with each of the steps  $k_1$ ,  $k_2$ , and  $k_3$  is a dependency on the acidity of the medium,  $h_0^\alpha$ ,  $h_0^\beta$ , and  $h_0^\gamma$ , respectively. For the present situation  $\gamma$  is less than  $\beta$  and eq. 7 can be simplified to eq. 8, a form in which it is easier to envisage the result to be expected.

$$k_{\text{obsd}} = \frac{k_1(h_0)^\alpha k_3}{k_2(h_0)^{\beta-\gamma} + k_3} \quad (8)$$

From eq. 8 it is apparent that  $k_{\text{obsd}}$  reduces to  $k_1(\text{H}^+)^\alpha$  when the acid concentration is very low (*i.e.*,  $k_2(\text{H}^+)^{\beta-\gamma} \ll k_3$ ).

This then results in a simple, acid-catalyzed behavior in regions of low acid concentration, completely in accord with the observations. In the region of 20–40% sulfuric acid the decarboxylation of  $\beta$ -phenylcinnamic acid shows a particularly simple form and a plot of  $\log k_{\text{obsd}}$  vs.  $H_0$  is linear and of unit slope. Hence  $\alpha$  is 1.

At the extreme of high sulfuric acid concentration eq. 8 reduces to eq. 9.

$$k_{\text{obsd}} = (k_1/k_2)k_3(h_0)^{\alpha-\beta+\gamma} \quad (9)$$

Substituting for  $k_1/k_2$  an equilibrium constant for step 1 (eq. 1) gives eq. 10, which of course is a familiar

$$k_{\text{obsd}} = K_{\text{eq}}k_3(h_0)^{\alpha-\beta+\gamma} \quad (10)$$

result for a pre-equilibrium followed by a rate-limiting step. Noteworthy in this instance, however, is the complex of acid catalysis terms which accumulate. Equation 10 results in a linear plot when the observed rate is plotted against  $H_0$ , but the slope of such a plot is a composite of the acid dependency of each of the three steps. As  $\alpha$  is known to be 1, and  $\beta$  and  $\gamma$  have been determined independently as 1.14 and 0.5, respectively, eq. 10 predicts a limiting slope (in very high concentrations of sulfuric acid) for the decarboxylation of  $\beta$ -phenylcinnamic acid of 0.36. This result is gratifyingly close to the observed result between 50 and 55% sulfuric acid (slope of 0.3).

An alternate description may be formulated. This formulation specifically takes account of the fact that the relative concentrations of  $\beta$ -phenylcinnamic acid and of  $\beta,\beta$ -diphenyl- $\beta$ -hydroxypropionic acid present in an equilibrium between the two are properly dependent on the activity of water in the solution. Such a more detailed formulation is more erudite and sophisticated, and correct. It leads to a different definition of some of the symbols and terms used. However it does not add anything to the primary conclusions or the general pattern of results to be expected. Hence it will not be presented in detail.

In summary, if the acidity of the solution is in the region (low acidity) where synchronous decarboxylation and dehydration is the dominant reaction of the hydroxy acid, then the behavior of the cinnamic acid will be characterized by a rate-determining hydration reaction followed by rapid decarboxylation–dehydration. On the other hand, if the acidity of the solution is such (very high acidity) that simple dehydration is the dominant reaction of the hydroxy acid, then the rate-limiting process will be the decarboxylation–dehydration of the very limited amount of hydroxy acid in equilibrium with the cinnamic acid.

## N-Fluoroalkylamines. I. Difluoroazomethines

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Contribution No. 1093 from the Central Research Department, Experimental Station, E. I. du Pont de Nemours and Company, Wilmington, Delaware 19898. Received May 27, 1965

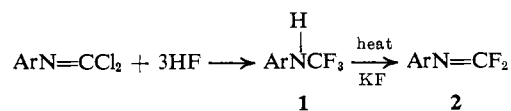
*The reaction of isothiocyanates with mercuric fluoride provides a new general route to difluoroazomethines and is particularly useful for preparing N-aryldifluoroazomethines which are trapped as N-(trifluoromethyl)-N-(fluoroformyl)anilines by carbonyl fluoride addition. Exchange reactions of N-aryldichloroazomethines with metal fluorides are also described as routes to difluoroazomethines.*

As part of a general study on the effect of fluorine substitution in organic molecules,<sup>2</sup> a synthetic program

(1) This work was presented in part at the 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept. 1964.

(2) (a) W. A. Sheppard, *J. Am. Chem. Soc.*, **84**, 3072 (1962); (b) W. A. Sheppard, *ibid.*, **85**, 1314 (1963).

was directed toward synthesis of N,N-bis(trifluoromethyl)anilines. Although a number of N-fluoroalkylamines are known<sup>3</sup> and N-(trifluoromethyl)aniline (**1**, Ar = C<sub>6</sub>H<sub>5</sub>) has been reported from reaction of N-phenyldichloroazomethine with hydrogen fluoride,<sup>4</sup>



(3) (a) A. M. Lovelace, D. A. Rausch, and W. Postelnek, "Aliphatic Fluorine Compounds," Reinhold Publishing Corp., New York, N. Y., 1958, Chapters X and XI; (b) M. Hudlicky, "Chemistry of Organic Fluorine Compounds," The MacMillan Co., New York, N. Y., 1962.

(4) (a) K. A. Petrov and A. A. Neimysheva, *J. Gen. Chem. USSR* (Eng. Transl.), **29**, 2135, 2662 (1960); (b) E. Klauke and E. Kühle, German Patent 1,170,414 (1964).