

Preparation of 2-(1-Hydroxy-1-methyl-2-oxopropyl)-2,5-dimethyl-3(2H)-furanone (1).—To a solution of 51 ml of biacetyl (Fisher Scientific Co., reagent grade) in 500 ml of water was added 1 ml of acetic acid, and the reaction was heated at 70° for 13 days. The dark orange reaction mixture was evaporated under vacuum and the residual oil was extracted with petroleum ether. The extract was discarded and the remaining residue was crystallized from carbon tetrachloride in several crops, melting between 91 and 96°. The yield was 12.54 g (36% from biacetyl, assuming the conversion of 3 moles of biacetyl to 1 mole of 1; 25% from biacetyl by weight). An analytical sample, mp 95–96°, was prepared by recrystallization from carbon tetrachloride: infrared absorption (KBr) at 2.93, 3.33, 3.41, 5.84, 5.91, 6.22, 6.83, 6.91, 7.04, 7.28, 7.38, 7.48, 8.02, 8.39, 8.70, 8.87, 9.25, 9.50, 9.95, 10.38, 10.70, 11.10, 12.38 μ ; ultraviolet maximum (H₂O) at 265 m μ (ϵ 10,600); nmr spectrum (CDCl₃), singlets at τ 4.53, 5.90, 7.78, 8.52, and 8.55 with peak area ratio 1:1:6:3:3; nmr spectrum (D₂O), singlets at τ 4.45, 7.79, 7.82, 8.64, 8.67 with peak area ratio 1:3:3:3:3; mass spectrum (peaks with 10% or more of the intensity of the base peak are listed), m/e 112, 86, 68, 43 (base peak), 40, 39, and 15; the ratio of the intensities of the peaks of m/e 112, 113, and 114 was 100:7.2:0.8 (expected¹² for C₆H₈O₂, 100:6.7:0.6); thin layer chromatography (95% benzene, 5% methanol), R_f 0.44.

Anal. Calcd for C₁₀H₁₄O₄: C, 60.59; H, 7.12; CH₃, 30.2. Found: C, 60.64; H, 7.20; CH₃, 27.0; mol wt (vapor pressure), 169.

3-Acetyl-2,5-dimethyl-3(2H)-furanone (2a) and Its Derivatives.—Compound 1 (1 g) was dissolved in 50 ml of saturated sodium metaperiodate solution and allowed to stand at room temperature overnight. The solution was extracted several times with ether, and the ether solution was washed with water until the washings gave a negative starch iodide test. The ether solution was dried (Na₂SO₄) and evaporated. The resulting oil crystallized on standing to give 408 mg (56%) of 2a, mp 49–50°. An analytical sample, mp 51–52°, was prepared by recrystallizing from petroleum ether (bp 30–60°) and drying in air: infrared absorption (KBr) at 3.32, 3.38, 5.76, 5.89, 6.22, 7.00, 7.20, 7.37, 7.50, 8.15, 8.37, 8.64, 8.72, 9.07, 9.65, 9.88, 10.38, 10.58, 11.17, 11.71, 12.32, and 13.57 μ ; ultraviolet maximum (H₂O) at 263 m μ ; nmr spectrum (CDCl₃), singlets at τ 4.43, 7.60, 7.88, and 8.47 with peak area ratio 1:3:3:3; mass spectrum, molecular ion at m/e 154 (0.2% of base peak), peaks with 10% or more of the intensity of the base peak occurred at m/e 112, 97, 43, 40, 30, and 15; the ratio of the intensities of the peaks of m/e 112, 113, and 114 was 100:7.1:0.7 (expected¹² for C₈H₈O₂, 100:6.7:0.6); thin layer chromatography (95% benzene, 5% methanol), R_f 0.74.

Anal. Calcd for C₈H₁₀O₃: C, 62.33; H, 6.54. Found: C, 62.81; H, 6.61.

When 2a was dissolved in water and treated with a solution of semicarbazide hydrochloride was sodium acetate, a crystalline semicarbazone (2b) quickly separated. It was filtered and an analytical sample, mp 219–220° dec, was prepared by recrystallization from ethanol–water: infrared absorption (KBr) at 2.87, 3.15, 5.87, 6.23, 6.27 (shoulder), 6.77, 6.97, 7.26, 7.49, 7.69, 8.27, 8.54, 8.94 (shoulder), 9.10, 9.37, 10.46, 11.20, 12.00, 13.03, and 13.42 μ ; ultraviolet maximum (H₂O) at 230 and 265 m μ ; nmr spectrum (CD₃SOCD₃ with added D₂O), singlets at τ 4.25, 7.59, 8.24, and 8.39 with peak area ratio 1:3:3:3; thin layer chromatography (95% benzene, 5% methanol), R_f 0.04.

Anal. Calcd for C₉H₁₃N₃O₃: C, 51.18; H, 6.20; N, 19.89. Found: C, 50.99; H, 6.20; N, 19.40.

Treatment of 2a with a solution of sodium acetate and hydroxylamine hydrochloride led to the precipitation of an oxime. After recrystallization from ethanol–water, white crystals, mp 131–132°, were obtained: infrared spectrum (KBr) contained bands at 3.10, 5.99, and 6.31 μ ; ultraviolet maximum (H₂O) at 264 m μ ; thin layer chromatography (95% benzene, 5% methanol), R_f 0.44.

Reaction of 1 and 2a with Sodium Hydroxide. Compound 1 (50 mg) was dissolved in 20 ml of NaOH solution, pH 13.5. During the next 20 min, the absorption maximum at 265 m μ in the ultraviolet was seen to disappear, and a new well-defined peak appeared at 295 m μ , with an absorption about 25% greater than the original solution. A portion of the solution was allowed

to remain at pH 13.5 for several hours and the absorption at 295 m μ gradually disappeared. The remainder of the solution had been neutralized with HCl after 20 min. Only a weak absorption maximum in the ultraviolet, at 265 m μ , remained. A portion of this solution was distilled. The aqueous distillate was treated with 2,4-dinitrophenylhydrazine reagent and a yellow compound, mp 313–315°, precipitated. It was identical with the 2,4-dinitrophenylhydrazone of biacetyl, mp 314°. The remainder of the neutralized solution gave a strong positive ferric chloride test. Thin layer chromatography (95% benzene, 5% methanol) revealed ultraviolet-absorbing spots of R_f 0.06, 0.15, 0.27, 0.44, 0.67, and 0.90.

When dissolved in NaOH solution of pH 13.5, 2a also showed a shift of the ultraviolet maximum, from 263 to 295 m μ , over 15 min. A portion of the solvent, kept at pH 13.5 for several hours, gradually lost the absorption at 295 m μ . Another portion was neutralized after 15 min and then showed only weak absorption at 265 m μ in the ultraviolet. The solution was concentrated and revealed on thin layer chromatography (95% benzene, 5% methanol) ultraviolet-absorbing spots of R_f 0.04, 0.25, and 0.40.

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On the Mechanism of Cinnamic Acid Decarboxylation in an Acid Medium

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Johnson and Heinz¹ had demonstrated that the decarboxylation of β -phenylcinnamic acid (I) and β -methylcinnamic acid (II) to *unsym*-diphenylethylene and α -methylstyrene, respectively, is acid catalyzed but the first-order rate constants are not a linear function of the hydrobromic acid concentration. In 1961, Noyce, King, and Woo² reported that β -*p*-methoxyphenyl- β -hydroxypropionic acid undergoes a decarboxylative dehydration reaction in which the decarboxylation was nearly independent of acid concentration while the dehydration reaction closely paralleled the acidity function. This suggested the intermediacy of a β -hydroxy propionic acid in the decarboxylation of cinnamic acids. Having previously ascertained the validity of the acidity function, H_0 , for the hydrogen bromide–acetic acid–water system,³ we undertook an investigation aimed at elucidation of the mechanism of the acid-catalyzed decarboxylation of cinnamic acids. At the outset of this work however, Noyce, Brauman, and Kirby⁴ published a detailed account of the decarboxylation mechanism showing the decarboxylation is the result of hydration of the olefinic function to the β -hydroxy acid followed by a synchronous decarboxylation and dehydration reaction of the hydroxy acid. Their data predict that in the H_0 range from -0.8 to -2.4 (regardless of the mineral acid used) a plot of $\log k$ vs. H_0 should be linear with a slope of 1.0 and at higher acidities the slope of the line should

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TABLE I

Temp, °C	HBr, <i>M</i>	Solvent, compn % CH ₃ COOH	Log (<i>C</i> _{BH⁺} / <i>C</i> _B)	<i>H</i> ₀	β-Phenyl- cinnamic acid		β-Methyl- cinnamic acid	
					Log <i>k</i> ¹	Log <i>k</i> + <i>H</i> ₀	Log <i>k</i> ¹	Log <i>k</i> + <i>H</i> ₀
A 113	4.5	38.8	1.78	-2.48	-1.82	-4.30
B 108	3.6	45.2	1.40	-2.10	-2.08	-4.18
C 111	2.7	50.9	0.99	-1.69	-2.08	-3.77	-2.35	-4.04
D 109	2.2	54.3	0.72	-1.42	-2.34	-3.76	-2.66	-4.08
E 107	1.6	58.4	0.38	-1.08	-2.57	-3.65	-2.96	-4.04
F 106	1.3	60.2	0.17	-0.87	-2.80	-3.67	-3.14	-4.01

approach a limiting value of about 0.3. Table I contains the rate data of Johnson and Heinz¹ and our *H*₀ data and demonstrate that the region of acidity in which the decarboxylation was originally carried out is indeed the region in which the rate-limiting process is hydration of the double bond. If one allows for the small variations in temperature at which the reactions were carried out the agreement is even better than listed in Table I.

Since the protonation behavior of weak bases is not the same in different acid-solvent systems,^{5,6} we realize that our data do not constitute a rigorous proof that the same mechanism is operative in aqueous sulfuric acid and in aqueous hydrogen bromide-acetic acid.

Experimental Section

***H*₀ Measurements.**—The Spectrophotometric data were obtained using a Beckman DU spectrophotometer with 1-cm cells. The solutions were prepared according to Johnson and Heinz¹ except that indicator was also added. The concentration of indicator (*ca.* 10⁻³ *M*) was such that the absorbance of the solution was between 0.2 and 0.8. The indicator employed was *o*-nitroaniline (*pK*_{BH⁺} = -0.70 as previously determined⁷ for the hydrogen bromide-acetic acid-water system). Acidity functions⁷ were calculated from the following equation.

$$H_0 = pK_{BH^+} - \log \frac{C_{BH^+}}{C_B}$$

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The [3.2.1] Bicyclic Mechanism in the Acyclic Field¹

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In previous publications,^{4,5} reactions of certain derivatives of *o*-benzoylbenzoic acid were explained by a new mechanism which involved a [3.2.1] bicyclic path. Since the starting materials in these reactions

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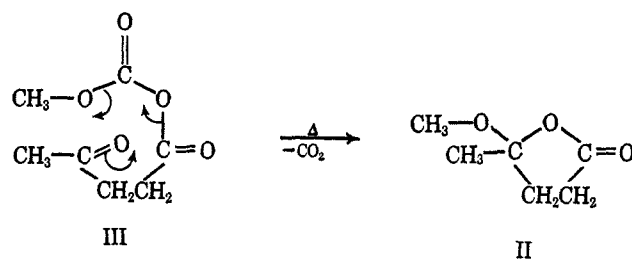
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all involved functions in the *ortho* positions the question arose as to whether similar reactions would occur in acyclic starting materials. Accordingly levulinic acid was chosen as a model compound for test.

Pure samples of methyl levulinate, I, and pseudo methyl levulinate, II, were prepared as described.⁶ These esters were characterized by their nmr spectra⁷ as this determination permits a more accurate method for analysis of mixtures of the two than that used before.⁶ When a solution rich (*ca.* 93%) in ψ -methyl levulinate, II, in pure absolute methanol was held for 14 hr at room temperature, there was no change in the ratio of ψ to *n* ester. However, if a small drop of hydrochloric acid was added, conversion to *n* ester was complete after a few minutes. The change undoubtedly takes place by acid-catalyzed addition of methanol to the carbonyl group of II followed by elimination of methanol to form I. Thus, as in the case of *o*-benzoylbenzoic acid, the *n* ester is by far more stable than the ψ ester.⁸

When a suspension of dry sodium levulinate in dry ether was stirred with methyl chlorocarbonate, a product was formed which, on the basis of its nmr spectrum, was undoubtedly the mixed anhydride, III, of levulinic and methylcarbonic acids. On pyrolysis of III at 120–140° carbon dioxide was evolved and there was obtained a mixture of II and I in the ratio of 92:8 as determined by nmr analysis. The formation of II is pictured below as taking place by the [3.2.1] bicyclic path.



When attempts were made to make III by reaction of levulinic acid with methyl chlorocarbonate in the presence of Dabco,⁹ the crude product formed was much less pure than the product obtained from the above reaction of sodium levulinate. However, on pyrolysis an excellent yield of the same methyl esters of levulinic acid was obtained. The ratio of ψ to *n* ester was about the same in both experiments.

A word concerning the preparation of the acid chloride of levulinic acid seems in order. When this acid

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(9) 1,4-Diazabicyclo[2.2.2]octane. We thank the Houdry Process Co., Marcus Hook, Pa., for a generous sample.