TABLE I

Temp, °C	HBr, M	Solvent, compn % CH_3COOH	Log (C_{BH^+}/C_B)	H_0	β-Phenylcinnamic acid: Log k^1	β-Phenylcinnamic acid: Log $k + H_0$	β-Methylcinnamic acid: Log k^1	β-Methylcinnamic acid: Log $k + H_0$
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 Heinz[1] 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 Heinz[1] 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 determined[3] for the hydrogen bromide–acetic acid–water system). Acidity functions[7] were calculated from the following equation.

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

(5) K. Yates and M. Wai, *Can. J. Chem.*, **43**, 2131 (1965).
(6) A. J. Kresge, L. E. Hakka, S. Mylonakis, and Y. Sato, *Discussions Faraday Soc.*, **39**, 75 (1965).
(7) M. A. Paul and F. A. Long, *Chem. Rev.*, **57**, 1 (1957).

The [3.2.1] Bicyclic Mechanism in the Acyclic Field[1]

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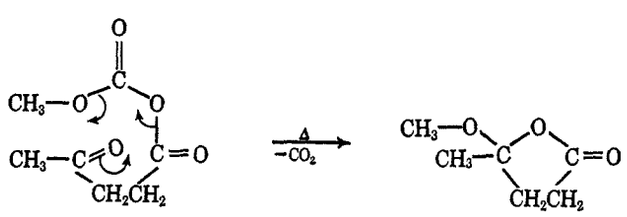
Received March 22, 1966

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 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 spectra[7] 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.



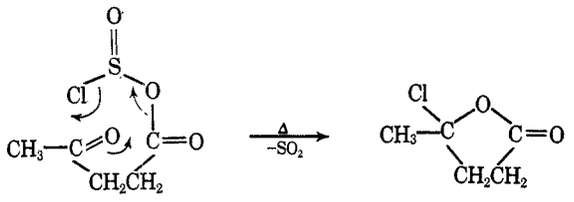
III II

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

(1) This work was supported in part by a type C grant of the Petroleum Research Fund of the American Chemical Society.
(2) Postdoctoral fellow supported by funds from a special fund of the Ohio State University.
(3) This work formed part of the Ph.D. thesis presented by Bernard Darré in 1966.
(4) M. S. Newman and C. Corduvelis, *J. Am. Chem. Soc.*, **86**, 2942 (1964).
(5) M. S. Newman and C. Corduvelis, *ibid.*, **88**, 781 (1966).
(6) D. P. Langlois and H. Wolf, *ibid.*, **70**, 2624 (1948).
(7) P. T. Lansbury and J. F. Bieron, *J. Org. Chem.*, **28**, 3564 (1963).
(8) M. S. Newman and C. Corduvelis, *ibid.*, **30**, 1795 (1965).
(9) 1,4-Diazabicyclo[2.2.2]octane. We thank the Houdry Process Co., Marcus Hook, Pa., for a generous sample.

chloride, IV, shown to be entirely cyclic by nmr analysis, is formed by the action of thionyl chloride on levulinic acid or on sodium levulinate, only the cyclic isomer is present.[10] This fact may be explained by assuming a [3.2.1]bicyclic path, as shown below. The mixed anhydride, V, would surely be expected to form from the sodium salt sequence, at least.



V IV

The formation of cyclic acid chloride of *o*-benzoylbenzoic,[11] *o*-acetylbenzoic,[11] and *o*-phthalaldehydic[11] acids may be explained similarly.

Experimental Section[12]

Normal Methyl Levulinate, I.—Esterification of levulinic acid with methanol and hydrogen chloride gave methyl levulinate which had only infrared absorption at 5.85 μ in the carbonyl region even when crude product was examined. The nmr spectrum in CCl_4 showed a singlet at δ = 2.13 ppm (keto CH_3, 3 H), a multiplet at 2.56 ($-CH_2-CH_2-$, 4 H), and a singlet at 3.63 ($-COOCH_3$, 3 H). As the methyl protons of *n* ester ($CH_3-C(=O)-$, 2.13 ppm) and ψ ester (CH_3-C-, 1.56 ppm) are both singlets, the only difference is in the chemical shift (δ).

Pseudo Methyl Levulinate, II.—This ester, bp 95° (15 mm), was prepared pure in 50% yield as described.[6] The nmr spectrum in CCl_4 showed a singlet at δ 1.56 ppm (CH_3-C, 3 H), a multiplet at 2.37 ($-CH_2-CH_2-$, 4 H), and a singlet at 3.29 ($-C-OCH_3$, 3 H). The infrared absorption spectrum showed a strong band at 5.65 μ and no other band in the carbonyl region.

Levulinyl Chloride.—A solution formed by adding 5.0 g of levulinic acid to 30 ml of pure thionyl chloride was allowed to stand for 1 hr at room temperature. The excess thionyl chloride was removed under reduced pressure on a rotary evaporator. The acid chloride thus formed had an nmr spectrum (neat) which consisted of a singlet centered at δ 2.03 ppm (CH_3-C, 3 H), and a multiplet at 2.66 ($-CH_2CH_2-$, 4 H). When vacuum distillation is attempted a certain amount of hydrogen chloride is lost and some angelica lactone is formed.[10] When levulinyl chloride is made by treating dry sodium levulinate with thionyl chloride in ether the acid chloride obtained is identical with that formed directly from the acid.

Levulinic Methylcarbonic Anhydride, III. A.—To a suspension of 5.0 g of dry sodium levulinate in 35 ml of dry ether at 0° was added dropwise a solution of 6.9 g of methyl chlorocarbonate in 10 ml of dry ether. After being stirred for 30 min at 0° and at room temperature for 2 hr the mixture was filtered. The solvent and excess methyl chlorocarbonate were removed under reduced pressure to yield 2.0 g of a colorless liquid which was essentially pure III as judged by the nmr spectrum which consisted of a singlet centered at δ 2.16 ppm ($CH_3-C=O$, 3 H), a multiplet at 2.70 ($-CH_2-CH_2-$, 4 H) and a singlet at 3.86 ($-COO-COOCH_3$, 3 H).

B.—In another experiment a solution of 4.4 g of methyl chlorocarbonate in 10 ml of dry ether was added to a stirred solution at 0° of 5.0 g of levulinic acid in 30 ml of ether. To this solution at 0° was added dropwise a solution of 2.4 g of Dabco[9] in 90 ml of ether during 45 min. After a further 30 min at 0° and 40 min at room temperature, the colorless precipitate was removed by filtration. The solvent was removed under reduced pressure on a rotary evaporator to yield 6.7 g of a colorless liquid which by nmr analysis was estimated to contain 91% of III, 8% of II, and 1% of I.

When either liquid obtained as described in A and B above was heated at 120–140° for 2 hr, the evolution of carbon dioxide was about quantitative. On analysis of the products by nmr the products were shown to consist of 91–93% II and the remainder, I.

(10) J. A. Helberger [*Ann.*, **522**, 269 (1936)] used no spectrographic proofs of structure.

(11) M. Rensen, *Bull. Soc. Chim. Belges*, **70**, 77 (1961).

(12) Every experiment and preparation described herein was repeated at least once by each co-worker. Nmr spectra were determined on a Varian A-60 spectrometer with tetramethylsilane (TMS) as internal standard. δ values are given in parts per million downfield from the TMS signal (0 ppm).

Cleavage of β-Keto Sulfones by Pyrrolidine

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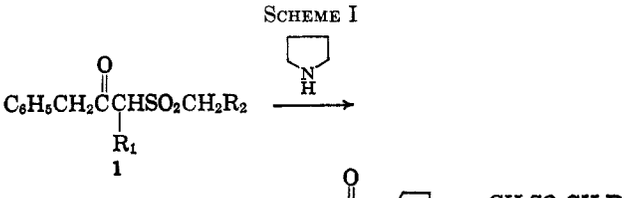
Received April 29, 1966

β-Keto sulfones can be obtained by a variety of reactions.[1-4] One reaction of these compounds which has not been investigated is enamine formation. We have found that, under normal conditions of enamine synthesis, β-keto sulfones cleave into an amide and a sulfone. For example, β-keto sulfone **1a** is converted by heating with pyrrolidine into *p*-chlorobenzyl benzyl sulfone (**2a**) and 1-(phenylacetyl)pyrrolidine. In a similar manner, the other acyclic β-keto-sulfones (Ib–d) are cleaved in good yield; **1c** and **1d** afford the same sulfone **2c** (Scheme I).

SCHEME I



1a, R_1 = C_6H_5; R_2 = *p*-ClC_6H_4 **2a**, R_1 = C_6H_5; R_2 = *p*-ClC_6H_4
b, R_1 = R_2 = C_6H_5 **b**, R_1 = R_2 = C_6H_5
c, R_1 = H; R_2 = C_6H_5 **c**, R_1 = H; R_2 = C_6H_5
d, R_1 = C_6H_5; R_2 = H

Two cyclic β-keto sulfones, containing the carbonyl group in the ring, also underwent cleavage: the product contains both the amide and the sulfone functions. Benzyl 2-ketocyclopentyl sulfone (**3a**) is converted to **4a** in high yield. The corresponding six-membered ring ketone, **3b**, is converted in cleavage product **4b** if water is not removed from the reaction mixture, and into enamine **5b** if it is removed. Either product can be isolated in about 50% yield. None of the other examples studied gave any isolable enamine. The nmr spectrum of enamine **5b** established the position of the double bond (τ 5.05 triplet, J = 3.0 cps, vinyl proton). Upon hydrolysis, this enamine was readily converted to the starting ketone **3b**. (See Scheme II.)

Formation of these products can be explained by attack of the base at the carbonyl carbon atom with formation of intermediate **7**, which has two modes of reaction: it can lose water and form enamine **5b** (Scheme III), or it can lose a carbanion and form compound **4b** upon

(1) W. E. Truce and R. H. Knospe, *J. Am. Chem. Soc.*, **77**, 5063 (1955).

(2) E. W. Truce, W. W. Banister, and R. H. Knospe, *J. Org. Chem.*, **27**, 2821 (1962).

(3) H. Becker and G. A. Russell, *ibid.*, **28**, 1896 (1963).

(4) J. J. Looker, *ibid.*, in press.