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The Structures and the Reactions of Acetyl- and Benzoylacrylic Acids and Their Esters

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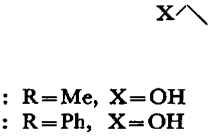
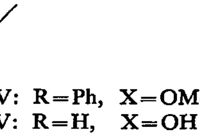
The Structures and properties of α,β-unsaturated γ-oxo acid, acetyl- and benzoylacrylic acid, and their esters are studied.

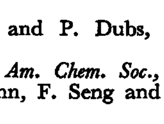
It can be considered that the α,β-unsaturated γ-oxo acid exists in three isomeric forms, the *trans*-form (A), the *cis*-form (B), and the angelica lactone form (C). Scheffold has established[1] that acetylacrylic acid (I) has two forms, A and C, which convert to each other. However, according to Shaw, the compound (mp 59°C)[2] produced by the reaction of I with diazomethane was not a simple methyl ester of I, but 5-methyl-5-methoxy-2,5-dihydro-2-oxofuran (III-C). The compound (mp 60.5°C),[3] synthesized from bromoacetone and triphenylphosphine carbomethoxymethylene, was a simple methyl ester of I, methyl acetylacrylate (III-A).



A



B



C

I: R=Me, X=OH IV: R=Ph, X=OMe
II: R=Ph, X=OH V: R=H, X=OH
III: R=Me, X=OMe VI: R=Me, X=Cl

On the other hand, it has been reported that the compound obtained by the Friedel-Crafts reaction of maleic anhydride with benzene was benzoylacrylic acid of the A form.[4] Furthermore, one of the simplest α,β-unsaturated γ-oxo acids, fumaraldehydic acid (V), is not present in the form of V-A, but in the form of V-C, 5-hydroxy-2,5-dihydro-2-oxofuran.[5]

Thus, there still remain some uncertainties about the structures and properties of α,β-unsaturated γ-oxo acid and their derivatives. In spite of this situation, recently, several natural products with a partial structure of the A, B, or C form have been reported, for example, Cytochalasine A,[6] Pyrenophorin,[7] and (±)-2-acetamido-2,5-dihydro-5-oxofuran.[8,9]

This paper will describe the structure of typical substances, acetylacrylic acid (I), benzoylacrylic acid (II), methyl acetylacrylate (III) and methyl benzoylacrylate (IV), on the basis of chemical and spectral studies.

Results and Discussion

Acetyl- and Benzoylacrylic Acid. Scheffold described[1] how *trans* acetylacrylic acid (I-A) was

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[1] R. Scheffold and P. Dubs, *Helv. Chim. Acta*, **50**, 798 (1967).

[2] E. Shaw, *J. Am. Chem. Soc.*, **68**, 2510 (1946).

[3] H. J. Bestmann, F. Seng and H. Schulz, *Chem. Ber.*, **96**, 465 (1963).

[4] E. I. Becker and C. Miesse, "Organic Syntheses," Coll. Vol. III, p. 109 (1955).

[5] N. Hellström, *Nature*, **187**, 146 (1960).

[6] D. C. Aldridge, J. J. Armstrong, R. N. Speake and W. B. Turner, *Chem. Commn.*, **1967**, 26.

[7] S. Nozoe, K. Hirai, K. Tsuda, K. Ishibashi, M. Shirasaka and J. F. Grove, *Tetrahedron Letters*, **1965**, 4675.

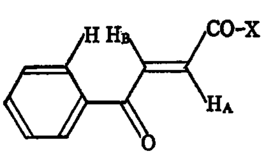
[8] S. G. Yetes, H. L. Tookey, J. J. Ellis and H. Burkhardt, *Tetrahedron Letters*, **1967**, 621.

[9] E. P. White, *J. Chem. Soc.*, **1967**, 346.

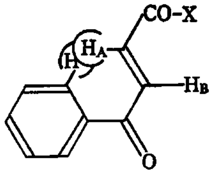
obtained from acetone and glyoxylic acid, and how the NMR spectrum of this acid showed the signal of olefinic protons at τ 3.20 (J=16.2 cps). The I compound, which we obtained by the elimination of hydrogen bromide from β-bromolevulinic acid,[10] showed the same NMR signal as I-A. The ultravioletspectrum showed λ_{max} 220 mμ.

Benzoylacrylic acid (II), which was obtained by the Friedel-Crafts reaction of maleic anhydride and benzene,[4] showed infrared absorption bands at 1700, 1670 and 1635 cm^{-1}, and no absorption between 1800 and 1750 cm^{-1}. In the ultraviolet absorption spectrum bands were observed at λ_{max} 238 mμ and λ_{max} 272 mμ. In the NMR spectrum, the signals of a pair of sharp doublets at τ 3.12 and 1.98 for the olefinic protons were observed. From the fact that the coupling constant, J=15.4 cps, of these olefinic proton signals is nearly equal to the J=16.2 cps of I-A, the structure of benzoylacrylic acid must be a II-A *trans* form.

Since the benzene ring and the remaining part of the molecule should be on the same plane as a result of the conjugation, two isomers, II-A′ and II-A″, are possible. However, inspection of the molecular model of II-A shows that II-A″ is not probable because of the steric hindrance between H_A and an ortho-H of the benzene ring. In II-A′, the deshielding effect of the benzene ring for H_B is expected to be present on account of its proximity to the benzene ring, but no such effect is expected for H_B in II-A″. From the NMR data for olefinic protons of methyl fumarate at τ 3.17,[11] the signal at τ 3.12 was assigned to H_A, and that at τ 1.98, to H_B. From the fact that H_B is more deshielded by the benzene ring, the II-A′ *trans* form is preferred as the structure of benzoylacrylic acid.



II-A′: X=OH
IV-A′: X=OMe



II-A″: X=OH
IV-A″: X=OMe

Methyl Acetylacrylate and Methyl Benzoylacrylate. *By the Elimination of Hydrogen Bromide.* Methyl acetylacrylate (III) was obtained by the elimination of hydrogen bromide from methyl β-bromolevulinate.[12] In the NMR spectrum of this product, an AB quartet signal for the olefinic protons, centered at τ 3.29 (J=15.4 cps), was observed. The infrared absorption spectrum showed carbonyl absorptions at 1725 and 1675 cm^{-1}, and no absorption in the region of the lactone carbonyl band. The ultraviolet absorption spectrum showed a λ_{max} of 220 mμ, similar to that of I-A. These data suggest that the structure of the product which we obtained by this method is in the III-A *trans* form.

By the elimination of hydrogen bromide from methyl β-bromo-β-benzoylpropionate, IV was prepared. In the NMR spectrum of IV we observed a pair of sharp doublets of the olefinic protons at τ 3.12 and 2.16 (J=15.4 cps). The infrared absorption spectrum of IV showed carbonyl absorption bands at 1725 and 1670 cm^{-1} and an olefinic double-bond absorption band at 1630 cm^{-1}, but no absorption band was observed in the lactone carbonyl region. Much as in II-A, the ultraviolet absorption spectrum of IV showed a λ_{max} value of 232 mμ and a λ_{max} value of 270 mμ. These results suggest that methyl benzoylacrylate was in the IV-A′ form.

By the Acid-Catalyzed Esterification. In the presence of sulfuric acid, II-A was esterified to IV.[13] The product was identified with IV-A′ on the basis of the spectral data and by thin-layer chromatography. In the case of the acid-catalyzed esterification of I-A, III-A was obtained in a 10% yield, and methyl α-methoxylevulinate,[14] in a 16% yield. These results suggest that the esterification of I-A and II-A by the acid catalyst occurs.

Isomerization. The treatment of III-A or IV-A with aqueous sodium hydroxide gave a hydrolyzed product, I-A or II-A. In the reaction mixture, the isomerized products were not detected. Thus, acetyl- and benzoylacrylic acids did not isomerize under the basic conditions.

It has been reported that I-A was isomerized by thionyl chloride to 5-methyl-5-chloro-2,5-dihydro-2-oxofuran (VI-C), which, in turn, was converted to I-C with an aqueous alkali.[1] Therefore, it is interesting to examine the reaction of II-A with thionyl chloride, followed by the reaction of methanol instead of an aqueous alkali.

In the NMR spectrum of the reaction mixture of II-A with thionyl chloride, followed by the reaction of methanol, we observed the signals corresponding to three substances, the normal esterified product, IV-A, and two anomalous products, 5-phenyl-5-methoxy-2,5-dihydro-2-oxofuran (IV-C) and methyl α-methoxy-β-benzoylpropionate. The molar ratio of these products was 49 : 21 : 30. The structure of IV-C was deduced from the spectral data. In the infrared absorption spectrum of IV-C absorption bands were observed at 1770 and 1630 cm^{-1}. The NMR spectrum showed olefinic proton signals at τ 3.98 and 2.82, J=5.5

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[10] L. Wolff, *Ann.*, **264**, 246 (1891).

[11] N. S. Bhacca, L. F. Johnson and J. N. Shoolery, "Varian High Resolution NMR Spectra Catalog," Vol. I, ed by Varian associates, Palo Alto, California (1962), p. 213.

[12] R. E. Lutz and G. W. Scott, *J. Org. Chem.*, **13**, 284 (1949).

[13] H. Pauly, R. Gilmour and G. Will, *Ann.*, **403**, 119 (1914).

[14] L. Birkofer and R. Dutz, *ibid.*, **608**, 7 (1957).

TABLE 1. THE NMR SPECTRA

Comp.	R	X	τ_{Ph}	τ_{Me}	τ_{OMe}	τ_{OH}	τ_{HA}	τ_{HB}	J_{AB}
I-A	Me	OH		7.60		0.27	3.20		16.2
II-A	Ph	OH	1.8—2.8			−1.36	3.12	1.98	15.4
III-A	Me	OMe		7.67	6.22		3.29		15.4
IV-A	Ph	OMe	1.9—2.8		6.19		3.21	2.16	15.4
II-B	Ph	OH	1.9—2.8			−0.92	3.70	2.90	12.0
III-B	Me	OMe		7.73	6.28		3.84		12.5
IV-B	Ph	OMe	2.0—2.8		6.42		3.76	3.13	12.0
I-C	Me	OH		8.23		4.41	3.91	2.77	6.0
IV-C	Ph	OMe	2.0—2.8		6.73		3.98	2.82	5.5

cps. The corresponding J value of I-C was 6 cps. These results suggest that II-A is partly esterified, but also partly isomerized to lactone.

Reaction of II-A with Diazomethane. When II-A was treated with diazomethane, neither IV-A nor IV-C was detected by thin-layer chromatography in the reaction mixture. The reaction of of diazomethane with carboxylic acid frequently does not lead to the expected methyl ester. For example, the reaction of diazomethane with I-A gave the isomerized product III-C,[2] while that with *trans-p*-bromobenzoylacrylic acid gave 4-(*p*-bromobenzoyl)-3-carbomethoxypyrazoline.[13] Thus, α,β-unsaturated γ-oxo acids do not afford the simple methyl ester by reaction with diazomethane.

Photoisomerization. By the photoreaction, the *cis* isomer (B) was produced from the *trans* isomer (A). The details of the photoreactions of α,β-unsaturated γ-oxo acid and their derivatives will be reported in another paper.

Experimental

Acetylacrylic Acid. This acid was prepared by the mehtod of Wolff[10] and was recrystallized from benzene to give colorless crystals, mp 125—126°C.

IR (KBr): 1700, 1670, 1625 cm^{-1}.

UV (EtOH): 220 mμ (ε 13800), 340 mμ (ε 40).

Benzoylacrylic Acid. This acid was prepared by the method of Becker,[4] and was crystallized from benzene to give colorless crystals, mp 95.5—96°C.

IR (KBr): 1700, 1670, 1635 cm^{-1}.

UV (EtOH): 238 mμ (ε 11000), 272 mμ (ε 8900).

Methyl Acetylacrylate. This was prepared by the method of Pauly[12] and was recrystallized from an ether and hexane (1 : 1 v/v) mixture, mp 58.5—60°C.

IR (KBr): 1725, 1675, 1645 cm^{-1}.

UV (EtOH): 220 mμ (ε 14400), 338 mμ (ε 40).

In the presence of sulfuric acid, acetylacrylic acid was esterified, and the product was identified on silica-gel thin-layer chromatography (Wakogel B-5) with a benzene and ethyl acetate (9 : 1 v/v) mixture.

Methyl Benzoylacrylate. This ester was prepared by two methods, by the method of Kohler[15] and by the esterification of the corresponding free acid in the presence of sulfuric acid. In both cases, the crude product was purified by chromatography on silica-gel (Merk 7734) with a benzene and ethyl acetate (9 : 1 v/v) mixture; mp 34°C.

IR (liquid film): 1725, 1670, 1630 cm^{-1}.

UV (EtOH): 232 mμ (ε 15400), 270 mμ (ε 9800).

Base-catalyzed Hydrolysis of III-A and IV-A. To a solution of the III-A or IV-A ester (100 mg) in methanol (2 m*l*), potassium hydroxide (25 mg) in water (1 m*l*) was stirred over a 2-hr period at room temperature. The reaction mixture was then worked up by the usual method, and the product was identified by thin-layer chromatography and by a study of its absorption spectrum.

Isomerization of II-A by Thionyl Chloride. One gram of II-A was dissolved in 2 m*l* of thionyl chloride, after which the mixture was kept for 10 min at 50°C. The mixture was then poured into excess methanol at 0°C. The ratio of the products in the reaction mixture was measured by means of the NMR spectrum and was found to be 49 : 21 : 30.

NMR ($CDCl_3$): τ 6.20 (1.5 H) ester methyl of IV-A. 6.29 (0.9 H) ester methyl of methoxypropionate. 6.59 (0.9H) methoxy of methoxypropionate. 6.71 (0.6 H) methoxy of IV-C.

Reaction with Diazomethane. Benzoylacrylic acid was reacted with diazomethane in ether in the usual manner. The reaction product was chromatographed on a thin layer of silica gel (Wakogel B-5) with a benzene and ethyl acetate (9 : 1 v/v) mixture. No spot corresponding to IV-A or IV-C was observed.

NMR Spectra. The NMR spectra were measured on a Hitachi H-60 High-resolution Nuclear Magnetic Resonance Spectrometer. The solvent was deuterochloroform, and TMS was used as the internal standard. The spectral data are listed in Table 1.

The authors wish to express their thanks to Mr. Kyuzaburo Furuhashi of Department of Chemistry, Tokyo Kyoiku University, for his measurement of the NMR spectra.

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15) E. P. Kohler and H. Engelbrecht, *ibid.*, **41**, 764 (1919).