The spectral values after 96 hr. indicated a 38% conversion to tropone. Attempts to carry out the oxidation at pH 6, pH 8 and pH 10 were unsuccessful.

Brominative Elimination.—To a solution of 0.812 g. (0.0075 mole) of 2,4-cycloheptadienone in 20 ml. of carbon tetrachloride was added dropwise with stirring a solution of one equivalent of bromine in 38 ml. of carbon tetrachloride. The addition was carried out at 0° over a period of 2 hr.; disappearance of the bromine color was immediate. Although the intermediate bromination product was not investigated, it was noted to be somewhat volatile and extremely irritating. The brominating mixture was then refluxed, with the exclusion of atmospheric moisture, overnight, during which time a felt-like mass of tropone hydrobromide was deposited. The product, which weighed 1.04 g. (79%), was contaminated by a small amount of black powder; spectral analysis showed that the salt was, however, 95% pure (obsd. $\log \epsilon$ 4.32 $\lambda_{\max}$ 224 mμ), reported $\log \epsilon$ 4.43).

Conversion of 2,4-Cycloheptadienone Enol Acetate to Tropone. Elimination with N-Bromosuccinimide.—Using an infrared lamp as a heat source, a mixture of 0.25 g. (0.005 mole) of XVIII, 0.9 g. (0.005 mole) of N-bromosuccinimide and 25 ml. of allyl bromide was refluxed for 2 hr. After this time a mixture of solids had precipitated, spectral assay of which indicated a quantity of tropone, presumably as the hydrobromide, which corresponded to about 16% yield. The allyl bromide filtrate was extracted with dilute hydrochloric acid; the extract revealed on spectral analysis an additional amount of tropone which raised the total spectral yield to 29%.

Perbenzoic Acid Oxidation.—A chloroform solution of 0.75 g. (0.005 mole) of XVIII was made up in a 50-ml. volumetric flask with 14.5 ml. of a chloroform solution containing one equivalent of perbenzoic acid. The consumption of perbenzoic acid was complete after 6 hr. at room temperature. Twenty-five milliliters of the reaction mixture was extracted with 5% sodium carbonate; neither the aqueous extract nor the chloroform solution gave a test for tropolone (ferric chloride). The latter solution was mixed with a solution of 1 ml. of concentrated hydrochloric acid in 20 ml. of water, after which the chloroform was distilled off. Neutralization of the aqueous tropone hydrochloride solution with sodium carbonate, followed by spectral assay, indicated a 55% yield of I.

Small yields of tropone were also obtained as a consequence of the action of the following reagents on 2,4-cycloheptadienone enol ether: (1) selenium dioxide in pyridine, (2) lead tetraacetate.

Conversion of 2,4-Cycloheptadienone to Tropolone.—Through the action of two moles of perbenzoic acid on the enol acetate XVIII, tropolone was obtained, although in small yield (4.3%). The oxidation proper was carried out as described in the XVIII to tropone conversion, using perbenzoic acid, except that two equivalents of the reagent were used. The rate of consumption of the second mole was slower than that of the first. Again, a 25-ml. portion of the chloroform solution was extracted with 5% sodium carbonate, which removed no tropolone (ferric chloride test); 1 ml. of concentrated hydrochloric acid and 20 ml. of water was added to the chloroform solution and the organic solvent removed by evaporation. The aqueous solution remaining was decanted from a tarry, brown residue and then extracted with chloroform. The extract was mixed with 20 ml. of concentrated aqueous cupric acetate, the mixture warmed and the chloroform separated. After several repetitions of the hot chloroform extraction, the combined extracts were concentrated to give 33 mg. of pale green needles, m.p. 318° (lit. 320°[43]). A portion of the salt was converted to tropolone by treatment with hydrogen sulfide; sublimation of the recovered aromatic gave product which melted at 50–51°.

The yield of tropolone could be raised to 26% by oxidation with peroxytrifluoroacetic, rather than perbenzoic, acid. A solution of 3.0 g. (0.02 mole) of the enol acetate XVIII in 25 ml. of dry methylene chloride was introduced into a suspension of 25 g. of vacuum dried, powdered sodium carbonate in 80 ml. of dry methylene chloride protected from moisture. While the flask was cooled in ice, a methylene dichloride solution containing, by assay, 0.04 equivalent of peroxytrifluoroacetic acid (about 10% of the solvent was distilled from the solution before its standardization, as an aid toward drying) was added dropwise with rapid stirring. The supernatant, which did not give any coloration with ferric chloride, was decanted from the buffer, which had coalesced after about three-quarters of the peracid had been added. The methylene chloride solution, combined with three washings of the residue made with the same solvent, was mixed with 20 ml. of 20% hydrochloric acid. Evaporation of the organic solvent left a reddish-brown pungent solution, which was filtered and extracted with portions of chloroform until the extracts failed to give the green color, characteristic of tropolone, with alcoholic ferric chloride. Removal of the solvent under reduced pressure gave about 1.3 g. of a dark liquid which was converted to a precipitate of crude tropolone copper enolate on treatment with 25 ml. of saturated cupric acetate solution. The precipitate was taken up in hot chloroform; after filtration, the solvent was blown off to yield 0.807 g. of the enolate, m.p. 319–320°. The metallic derivative could be converted by the hydrogen sulfide method in 93% yield of sublimed tropolone, m.p. 50.4–51.6°. A mixed melting point taken with authentic tropolone (m.p. 50.8–51.6°) was found to be 50.6–51.6°.

---

[43] W. von E. Doering and L. Knox, THIS JOURNAL, **73**, 828 (1951).

MADISON, WISCONSIN

[CONTRIBUTION FROM AVERY LABORATORY, UNIVERSITY OF NEBRASKA]

Studies with the Amine Adducts of β-Benzoylacrylic Acid and its Methyl Ester[1]

BY NORMAN H. CROMWELL, PAUL L. CREGER AND KENNETH E. COOK

RECEIVED APRIL 2, 1956

Evidence is presented to show that amines add to both β-benzoylacrylic acid and its methyl ester to produce the α-amino-γ-ketoacids and esters. Reduction of the methyl α-amino-β-benzoylpropionates with lithium aluminum hydride produced a new class of amino diols while catalytic hydrogenation led to the new γ-phenyl-α-amino-γ-butyrolactones. γ-Phenyl-γ-butyrolactone reacted with morpholine to give γ-phenyl-γ-morpholinobutyric acid while γ-phenyl-$\Delta^{\beta,\gamma}$-butenolide under similar conditions resulted in β-benzoylpropionmorpholide. The infrared spectra of these materials were determined and analyzed.

Several investigators have reported studies of the reactions of β-benzoylacrylic acid and its esters with ammonia and amines.[2] Little or no evidence for the structures of the resulting products have been offered by these investigators and disagreement as to assignment of structures is apparent from a reading of the literature. Nevertheless, Bougault[2a] seems to have made the most logical structural assignments for the amine adducts.

The present investigation of the reactions of

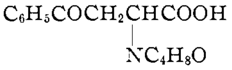
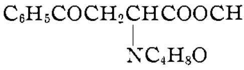
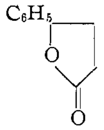
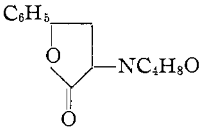
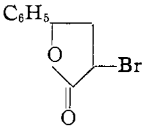
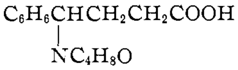
---

(1) Presented in part at the 128th meeting of the American Chemical Society, Minneapolis, Minn., Sept., 1955.

(2) (a) J. Bougault, *Ann. chim. phys.*, [8] **15**, 491 (1908); (b) P. Chabrier, *et al.*, *Compt. rend.*, **230**, 212 (1950); **226**, 1378 (1948); **237**, 1420 (1953).

TABLE I

SUMMARY OF INFRARED SPECTRA[a]

Structure	Band	Nujol mull	CCl_4 wave no.	Soln. approx. % abs.
 $C_6H_5COCH_2\underset{NC_4H_8O}{\underset{\mid}{CH}}COOH$	Ketone C=O	1677	..	..
	Ionized COO^-	1615		
	Phenyl	1600		
 $C_6H_5COCH_2\underset{NC_4H_8O}{\underset{\mid}{CH}}COOCH_3$	Ester C=O	1733	1733	50
	Ketone C=O	1681	1686	50
	Phenyl	1598	1600	10
	Lactone C=O	..	1795	85
	Lactone C=O	..	1779	64
	Lactone C=O	..	1793	75
$C_6H_5COCH_2CH_2CONC_4H_8O$	Ketone C=O	1686	1685	50
	Amide C=O	1643	1653	70
	Phenyl	1598	1600	15
 $C_6H_6\underset{NC_4H_8O}{\underset{\mid}{CH}}CH_2CH_2COOH$	Ionized COO^-	1617		
	Phenyl	1588		
	^+N-H	3430		
$C_6H_5CH_2CH_2CH_2CONC_4H_8O$	Amide C=O	1640	1657	65
	Unassigned	1610 (sh)	1605	5
	Phenyl	1585		
$CH_3CH=CHCONC_4H_8O$[b]	Amide C=O	..	1658	30
	C=C	..	1623	40

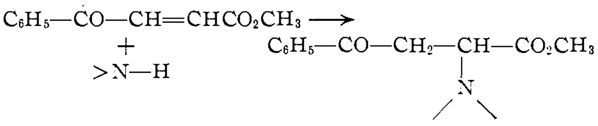
[a] The infrared spectra were recorded from 4000 to 600 cm.$^{-1}$ using a Perkin–Elmer Model 21 double-beam instrument employing sodium chloride optics and cells. The determinations in CCl_4 solution were made using matched 0.1 mm. cells and concentrations of 20–25 mg./ml. [b] N. H. Cromwell and F. Pelletier, *J. Org. Chem.*, **15**, 877 (1950).

amines with β-benzoylacrylic acid and its methyl ester were undertaken to establish the structures and to develop the chemistry of these interesting polyfunctional compounds. Evidence is presented which, in agreement with Bougault,[2a] indicates that both β-benzoylacrylic acid and its methyl ester add amines, (*i.e.*, morpholine, piperidine and benzylamine), to the more reactive ketone–carbonyl vinyl system to produce the α-amino-γ-ketoacids and esters. Thus the amino group turns up in a β-position with respect to the ketone carbonyl group.

The α-amino-γ-ketoesters were prepared in good yields by dissolving methyl β-benzoylacrylate in a mixture of petroleum ether and methanol and treating the solutions with one equivalent of the amine, using ice-bath cooling. The addition products (I–III) crystallized from the reaction mixtures and these processes appeared to be exothermic.

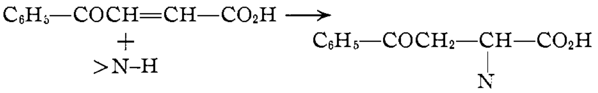
The α-amino-γ-ketoacids (IV and V) were prepared by adding one equivalent of the amine to a benzene solution of the β-benzoylacrylic acid at room temperature. The addition products formed immediately. Analytical samples of these free bases were difficult to obtain because of the easy reversal of the addition product to the starting materials. α-Morpholino-β-benzoylpropionic acid (IV) on treatment with diazomethane produced methyl α-morpholino-β-benzoylpropionate (I), identical with that obtained from the addition of morpholine to methyl-β-benzoylacrylate. Chabrier[2b] has reported that amines add in the same direction when β-benzoylacrylic acid is dissolved in aqueous base or in organic solvents (alcohol, acetone, benzene or ether). These investigators have offered no definitive evidence for the composition or structures of their products and have, as a matter of fact, assigned the unlikely β-amino-γ-ketoacid and ester structures to their compounds.

The infrared spectra, see Table I, of the morpholine adducts showed a benzoyl carbonyl stretching vibration band between 1677 and 1686 cm.$^{-1}$ and the acid displayed a carboxylate ion band at 1615 cm.$^{-1}$ while the ester had an ester carbonyl band near 1733 cm.$^{-1}$.



$$C_6H_5-CO-CH=CHCO_2CH_3 + >N-H \longrightarrow C_6H_5-CO-CH_2-\underset{\underset{\diagup\ \diagdown}{N}}{\underset{\mid}{CH}}-CO_2CH_3$$

I, >N–, NC_4H_8O
II, >N–, NC_5H_{10}
III, >N–, $HN-CH_2C_6H_5$

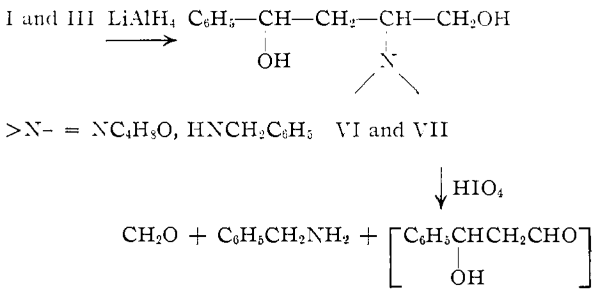


$$C_6H_5-COCH=CH-CO_2H + >N-H \longrightarrow C_6H_5-COCH_2-\underset{\underset{\diagup\ \diagdown}{N}}{\underset{\mid}{CH}}-CO_2H$$

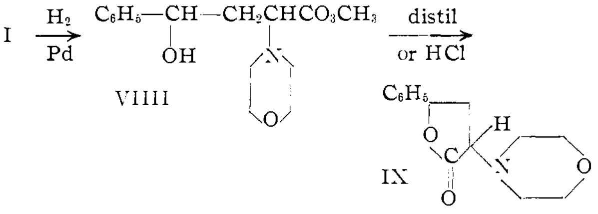
$$IV \xrightarrow{CH_2N_2} I.$$

IV, >N–, NC_4H_8O
V, >N–, NC_5H_{10}

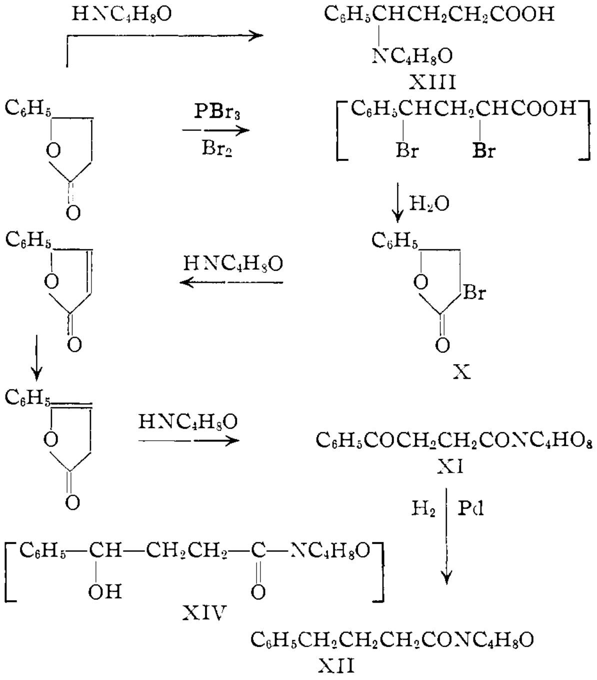
Hydrogenation of α-morpholino- and α-benzylaminomethyl-β-benzoylpropionates (I and III) with lithium aluminum hydride produced examples of an interesting new class of amino diols, 2-morpholino and 2-benzylamino-4-phenyl-1,4-butandiols (VI and VII, respectively). The structure of the latter compound VII was established by a periodic acid oxidation experiment. From this reaction mixture a good yield of formaldehyde and of benzylamine were obtained and no trace of benzaldehyde could be detected. This experiment supports our assignment of the location of the amino groups in the various compounds (I–IX).



A methanol solution of methyl-α-morpholino-β-benzoylpropionate (I) absorbed one molar equivalent of hydrogen on shaking for 30 minutes under a hydrogen pressure of three atmospheres in the presence of palladium-on-charcoal. Evaporation of the solvent produced a thick oil. Treatment of this material with dry hydrogen chloride produced a hydrochloride which was identical with the hydrochloride of a compound, m.p. 101–102°, obtained by the distillation of the thick oil. The analysis and infrared spectrum (carbonyl band at 1779 cm.$^{-1}$) of the 101–102° melting compound IX showed it to be α-morpholino-γ-phenylbutyrolactone. Thus either acid or heat causes the intermediate amino alcohol ester VIII to cyclize to the α-amino-γ-lactone.



Unsuccessful attempts to prepare the amino lactone IX, which is the first example of an interesting new class of compounds, from α-bromo-γ-phenylbutyrolactone, clearly indicates the importance of the above synthetic method. α-Bromo-γ-phenylbutyrolactone (X) was prepared from γ-phenylbutyrolactone. Treatment of the bromide X with two equivalents of morpholine in dry ether at room temperature gave an excellent yield of β-benzoylpropionmorpholide (XI), and no trace of the aminolactone IX. The structure of XI was established by comparison with the products obtained by heating β-benzoylpropionic acid with morpholine, and from the treatment of a synthesized sample of γ-phenyl-$\Delta^{\beta,\gamma}$-butenolide[3] with morpholine in dry ether at room temperature. The β-benzoylpropionmorpholide (XI) showed benzoyl–carbonyl and amide–carbonyl stretching vibration bands at 1685 and 1653 cm.$^{-1}$, respectively. This amide XI gave no reaction with hydrogen chloride gas in dry ether. These experiments indicate that the reaction of α-bromo-γ-phenyl-γ-butyrolactone with morpholine involved dehydrohalogenation to produce the unstable[4] γ-phenyl-$\Delta^{\alpha,\beta}$-butenolide which then rearranged to γ-phenyl-$\Delta^{\beta,\gamma}$-butenolide, which in turn reacted with morpholine to produce β-benzoylpropionmorpholide (XI).

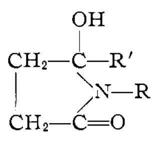


Hydrogenation of the keto amide XI produced the amide XII, γ-phenylbutyromorpholide identical with a sample synthesized from γ-phenylbutyric acid. This material gave no precipitate with dry hydrogen chloride gas in dry ether and showed an amide carbonyl stretching vibration at 1657 cm.$^{-1}$ in the infrared spectrum. Reaction of γ-phenyl-γ-butyrolactone with morpholine in dry ether produced γ-phenyl-γ-morpholinobutyric acid (XIII), instead of the hydroxyamide XIV. This new amino acid XIII formed morpholine hydrochloride with dry hydrogen chloride gas in dry ether solution. Its infrared spectrum showed no amide–carbonyl band. Our investigations with these reactions and interesting new classes of products are continuing.

Acknowledgment.—This investigation was supported in part by a grant from the National Science Foundation, NSF-G1091.

---

[3] Apparently ammonia and amines react with γ-phenyl-$\Delta^{\beta,\gamma}$-butenolide to produce β-benzoylpropionamides as primary products, as assumed by Wolff, *Ann.*, **229**, 256 (1885); Biedermann, *Ber.*, **24**, 4077 (1891); and Lukes and Prelog, *Coll. Czech. Chem. Comm.*, **1**, 119, 287, 334, 461, 617 (1929). When ammonia or a primary amine is used, the primary product, the β-benzoylpropionamide, apparently undergoes ring closure to produce isomeric products to which Walton, *J. Chem. Soc.*, 438 (1940), has assigned a cyclic structure. We are making a study of the infrared spectra of such materials in this Laboratory.



[4] See F. Ramirez and M. B. Rubin, THIS JOURNAL, **77**, 3768 (1955), for an excellent discussion of the relative stabilities of some $\Delta^{\alpha,\beta}$- and $\Delta^{\beta,\gamma}$-butenolides.

Experimental

Addition of Amines to Methyl β-Benzoylacrylate.—To a solution of 5.00 g. (0.026 mole) of methyl β-benzoylacrylate in 150 ml. of petroleum ether (b.p. 30–60°) and 10 ml. of methanol, 0.026 mole of the amine was added in one lot. The reaction mixtures were cooled in an ice water–bath with stirring. Crystallization was induced by scratching the flask. Filtration and evaporation of the filtrate resulted in the products in good yields, which were recrystallized from ether–petroleum ether mixtures. The hydrochlorides were prepared from dry hydrogen chloride gas in dry ether and recrystallized from ether and methanol.

Methyl α-morpholino-β-benzoylpropionate (I): m.p. 97–98°; yield 87%.

Anal. Calcd. for $C_{15}H_{19}NO_4$: C, 64.96; H, 6.91; N, 5.05. Found: C, 65.02; H, 6.85; N, 4.97.

Hydrochloride, m.p. 143–144°.

Methyl α-piperidino-β-benzoylpropionate (II): m.p. 66–66.5°; yield 70%.

Anal. Calcd. for $C_{16}H_{21}NO_3$: C, 69.79; H, 7.69; N, 5.09. Found: C, 69.88; H, 7.88; N, 4.99.

Hydrochloride, m.p. 200–204°.

Methyl α-Benzylamino-β-benzoylpropionate (III): m.p. 78.5–79.5°; yield 85%.

Anal. Calcd. for $C_{18}H_{19}NO_3$: C, 72.70; H, 6.44; N, 4.71. Found: C, 73.09; H, 6.57; N, 4.76.

Hydrochloride, m.p. 134.5–135.5°.

Addition of Amines to β-Benzoylacrylic Acid.—To solutions of 3.52 g. (0.02 mole) of β-benzoylacrylic acid in 100 ml. of benzene were added at once 0.02 mole amounts of morpholine and piperidine, respectively. After standing at room temperature for 10–15 minutes the products were removed by filtration and recrystallized rapidly from butanol.

α-Morpholino-β-benzoylpropionic acid (IV): m.p. 166–167° dec.; yield 99%.

Anal. Calcd. for $C_{14}H_{17}NO_4$: C, 63.86; H, 6.51; N, 5.32. Found: C, 63.84; H, 6.68; N, 5.16.

α-Piperidino-β-benzoylpropionic Acid (V): m.p. 163–164° dec.; yield 99%.

Anal. Calcd. for $C_{15}H_{19}NO_3$: C, 68.94; H, 7.33; N, 5.36. Found: C, 68.76; H, 7.41; N, 5.18.

Conversion of IV to I with Diazomethane.—A benzene solution of diazomethane containing 13.3 mmoles was added to a suspension of 3.17 g. (12.0 mmoles) of IV in 200 ml. of benzene. After standing at room temperature for 24 hours, 0.29 g. of unreacted acid was removed from the reaction mixture by filtration. From the filtrate 2.70 g. (89% yield based upon unrecovered acid) of I, 97–98°, was obtained. This compound was identical with that prepared from methyl β-benzoylacrylate as described above.

Hydrogenation of I and III with $LiAlH_4$.—To stirred slurries of 1.14 g. (22 mmoles) of lithium aluminum hydride in 150 ml. of dry ether were added solutions of 22 mmoles of I and III, respectively, in 150 ml. of dry ether at such a rate as to cause gentle refluxing (addition time 20–25 minutes). The reaction mixtures were refluxed for an additional 15 minutes, cooled in an ice-bath and the excess lithium aluminum hydride decomposed by the method of Micovic and Mehailovic.[5] The products were isolated as colorless viscous oils by evaporation of the solvent under vacuum on a steam-bath.

2-Morpholino-4-phenyl-1,4-butandiol (VI): 90% yield; twice distilled from a Hickman molecular still, b.p. 206–210° (0.2 mm.).

Anal. Calcd. for $C_{14}H_{21}NO_3$: C, 66.90; H, 8.42; N, 5.57. Found: C, 66.64; H, 8.92; N, 5.51.

2-Benzylamino-4-phenyl-1,4-butandiol (VII): 94% yield. This material was analyzed without further purification.

Anal. Calcd. for $C_{17}H_{21}NO_2$: N, 5.16. Found: N, 5.01.

These aminodiols did not form solid derivatives with acetic anhydride, acetyl chloride, picric acid, hydrogen chloride or phenyl isocyanate.

Periodic Acid Oxidation of 2-Benzylamino-4-phenyl-1,4-butandiol (VII).—A modification of a procedure published by Jeanloz[6] was used. From this experiment a 50% yield of the dimedone derivative of formaldehyde, m.p. 190–192°, was obtained. The benzylamine was isolated as the benzamide, m.p. 103°. A second dimedone derivative, m.p. 201–203°, resulted which was shown not to be identical with the dimedone derivative of benzaldehyde (m.p. 195–196°) nor with that of cinnamylaldehyde (m.p. 218–219°) nor with the octahydroxanthene of benzaldehyde (m.p. 205–206°). This product is possibly the dimedone derivative of β-hydroxy-β-phenylpropionaldehyde but has not been investigated further.

Catalytic Hydrogenation of Methyl α-Morpholino-β-benzoylpropionate. A. With Palladium-on-Charcoal.—A suspension of 0.25 g. of 10% palladium on charcoal in a solution of 2.62 g. (0.01 mole) of methyl α-morpholino-β-benzoylpropionate in 150 ml. of methanol was shaken for 1.5 hours at room temperature under a hydrogen pressure of 45 lb./in.^{2} Evaporation of the solvent left a viscous oil which resisted attempts at crystallization. Treatment of a small amount of this oil in dry ether with dry hydrogen chloride gas produced a solid hydrochloride which was recrystallized from methanol and ether, m.p. 229–230°. This compound was identical with the hydrochloride prepared from α-morpholino-γ-phenyl-γ-butyrolactone (IX).

Anal. Calcd. for $C_{14}H_{18}NO_3Cl$: C, 59.26; H, 6.39. Found: C, 59.24; H, 6.49.

Distillation of the major portion of the above mentioned oil at 194–198° (0.5 mm.) gave a colorless liquid which solidified on standing. Recrystallization from petroleum ether (b.p. 60–70°) gave colorless needles, m.p. 101–102°. The analysis and infrared spectra, see Table I, indicated this product to be α-morpholino-γ-phenylbutyrolactone (IX).

Anal. Calcd. for $C_{14}H_{17}NO_3$: C, 67.99; H, 6.93; N, 5.67. Found: C, 67.95; H, 7.00; N, 5.86.

B. With W-6 Raney Nickel.—The keto amino ester was mainly unchanged after shaking a methanol solution of it at room temperature for 3.5 hours under three atm. of hydrogen in the presence of W-6 Raney nickel catalyst.

α-Bromo-γ-phenylbutyrolactone (X).—A 5.0-g. sample of γ-phenylbutyrolactone[7] was mixed with 0.05 ml. of PBr_3. This solution was heated under reflux at 80° while 5.0 g. of bromine was added over a period of 30 minutes. Heating was continued for an additional 30 minutes after which time the straw colored, viscous liquid was mixed with 75 ml. of water. This heterogeneous mixture was heated under reflux for three hours. The cooled mixture was extracted with ether. The ether solution was extracted with dilute sodium carbonate to remove the acid by-products. Evaporation of the ether extract left an oil which after recrystallization from ether and petroleum ether produced 1.50 g. of colorless leaflets, m.p. 57–58°.

Anal. Calcd. for $C_{10}H_9O_2Br$: C, 49.81; H, 3.76; Br, 33.15. Found: C, 49.87; H, 3.81; Br, 33.18.

β-Benzoylpropionmorpholide (XI). A. From X.—A 0.5-g. sample of the bromo lactone X was dissolved in 20 ml. of wet ether and treated with 0.54 g. (3 molar equiv.) of morpholine. Morpholine hydrobromide precipitated immediately and was removed by filtration. The ether solution was washed with water, dried over anhyd. $CaSO_4$ and concentrated. Addition of a few ml. of petroleum ether caused the crystallization of a colorless product, 0.36 g., m.p. 85–87°.

Anal. Calcd. for $C_{14}H_{17}NO_3$: C, 67.99; H, 6.93; N, 5.67. Found: C, 68.20; H, 7.02; N, 5.45.

B. From γ-Phenyl-$\Delta^{\beta,\gamma}$-butenolide.[8]—A 0.20-g. (0.00125 mole) sample of the butenolide was dissolved in 30 ml. of

---

(5) V. M. Micovic and M. L. Mihailovic, *J. Org. Chem.*, **18**, 1196 (1953).

(6) R. Jeanloz, *Helv. Chim. Acta*, **27**, 1509 (1944).

(7) γ-Phenylbutyrolactone has been prepared by the catalytic hydrogenation of β-benzoylpropionic acid in the presence of ammonia; see, F. Knoop and H. Oesterlin, *Z. physiol., Chem.*, **148**, 294 (1925). For our purposes we prepared a supply of the material as follows: A 17.82-g. (0.10 mole) sample of β-benzoylpropionic acid was dissolved in 150 ml. of methanol and shaken under 45 lb./in.^{2} of hydrogen at room temperature in the presence of 0.9 g. of 10% palladium-on-charcoal catalyst. One molar equivalent (0.10 mole) of hydrogen was absorbed in 30 minutes. Removal of the catalyst and evaporation of the methanol left a viscous liquid which was distilled under reduced pressure. When the temperature reached 160–170° (11 mm.), water was evolved. The γ-lactone was then distilled b.p. 171–172° (11 mm.), as a colorless liquid, 14.21 g. (88% yield), m.p. 38°.

(8) M. Kugel, *Ann.*, **299**, 54 (1898).

ether, 0.12 g. (0.00137 mole) of morpholine was added, and the solution allowed to stand at room temperature for two days. Cooling the solution caused the crystallization of 0.205 g. (66% yield) of product, m.p. 85–87°. When admixed with the amide XI there was no depression of m.p.

C. From β-Benzoylpropionic Acid.[9]—A 0.50-g. sample of the acid and 0.50 g. of morpholine were mixed and heated in an open tube at 160–170° for two hours. The reaction mixture was cooled and mixed with water. The water insoluble crystalline material melted at 86–88°; mixed m.p. with XI, 86–87°.

γ-Phenylbutyromorpholide (XII). a.—A 0.52-g. sample of the amide XI was dissolved in 75 ml. of abs. ethanol and shaken at room temperature for 1.5 hr. under 43 lb./in.^{2} of hydrogen in the presence of 10% palladium-on-charcoal. Evaporation of the solvent left an oil which crystallized from petroleum ether (b.p. 60°), wt. 0.165 g., m.p. 41–42°.

Anal. Calcd. for $C_{14}H_{19}NO_2$: C, 72.07; H, 8.21; N, 6.00. Found: C, 72.14; H, 8.11; N, 6.19.

b.—A 2.5-g. sample of γ-phenylbutyric acid was warmed with 5.5 g. of thionyl chloride for ten minutes. The excess thionyl chloride was removed under reduced pressure and the residue treated with 5.0 g. of morpholine in benzene. After standing for a few minutes the benzene solution was washed with water and dilute sodium carbonate solution, dried over anhyd. $MgSO_4$ and evaporated to an oily residue. This oil was crystallized from petroleum ether to produce 2.6 g. (73%) of γ-phenylbutyromorpholide, m.p. 41–42°. This product gave no precipitate with dry HCl in dry ether.

γ-Phenyl-γ-morpholinobutyric Acid (XIII).—A 2.0-g. (0.0123 mole) of γ-phenyl-γ-butyrolactone[7] was dissolved in 10 ml. of dry ether and 1.075 g. (0.0123 mole) of morpholine added. After standing at room temperature for fifteen hours a colorless oil had separated. Cooling produced a solid which was recrystallized from a mixture of benzene and dry ether to give 2.55 g. of a colorless product, m.p. 94–96°.

Anal. Calcd. for $C_{14}H_{19}NO_3$: C, 67.44; H, 7.68; N, 5.62. Found: C, 67.32; H, 7.63; N, 5.31.

This amino acid produced a hygroscopic hydrochloride when treated with dry hydrogen chloride gas in ether solution. Recrystallization from methanol gave colorless crystals, m.p. 176–177°, identical with morpholine hydrochloride, as shown by a mixed m.p. experiment.

LINCOLN, NEBRASKA

---

[9] L. F. Somerville and C. F. H. Allen, "Organic Syntheses," Col. Vol. II, 2nd ed., John Wiley & Sons, Inc., New York, N. Y., 1943, p. 81.

[CONTRIBUTION FROM AVERY LABORATORY, UNIVERSITY OF NEBRASKA]

Reactions of β-Benzoylacrylic Acid and its Methyl Ester with Hydrazines. Absorption Spectra Studies[1]

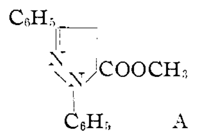
BY NORMAN H. CROMWELL, KENNETH E. COOK AND PAUL L. CREGER

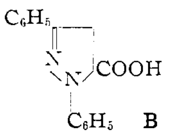
RECEIVED APRIL 5, 1956

The reaction products of phenylhydrazine with α-amino-β-benzoylpropionic acid and its methyl ester have been found to be the phenylhydrazones of β-benzoylacrylic acid and the methyl ester. Ultraviolet and infrared spectra comparisons of these products with the corresponding *unsym*-methylphenylhydrazones and with authentic pyrazolines gave definitive evidence for the structures.

In a previous study[1,2] some amine adducts of β-benzoylacrylic acid and its methyl ester were prepared and evidence was found to establish their structures as α-amino-γ-ketoacids and α-amino-γ-ketoesters. In the present study it has been found that such compounds react with phenylhydrazine to expel the amino grouping and produce the phenylhydrazones of β-benzoylacrylic acid and methyl β-benzoylacrylate, respectively, contrary to our earlier conclusions.[1]

The treatment of methyl α-morpholino-β-benzoylpropionate[2] with phenylhydrazine under mild conditions failed to yield a solid derivative. However, when this amino keto ester, or the corresponding amino keto acid,[2] was warmed with phenylhydrazine in glacial acetic acid, brilliant yellow colored products were produced which elemental analysis indicated to be the phenylhydrazones I and II of methyl β-benzoylacrylate and β-benzoylacrylic acid, respectively, or possibly the isomeric pyrazolines A and B. These products I and II failed to give positive Knorr[3] or Raiford[4] pyrazoline tests.


A


B

The same phenylhydrazine derivatives I and II resulted from the reactions of methyl β-benzoylacrylate and β-benzoylacrylic acid, respectively, and phenylhydrazine under conditions identical with those described above. The phenylhydrazine derivative I was also obtained when compound II was allowed to react with diazomethane.

Heating the phenylhydrazine derivative II of β-benzoylacrylic acid with acetic anhydride and sodium acetate gave an excellent yield of a colorless product which elemental analysis and absorption spectra studies suggested was 2,6-diphenyl-3-pyridazinone (III). Although β-benzoylacrylic acid had been reported[5] as reacting with phenylhydrazine to produce a phenylhydrazone it seemed important to obtain definitive evidence for these structures I and II, and to eliminate the possibility that these derivatives might be the pyrazolines, A and B. It appeared this could be accomplished best by careful absorption spectra comparisons with compounds of definite structure. For this purpose the methylphenylhydrazones IV and V of methyl β-benzoylacrylate and β-benzoylacrylic acid were prepared for the first time.

The infrared spectra studies (see Table I) showed some close similarities and an important difference

---

[1] Presented in part at the 128th meeting of the American Chemical Society, Minneapolis, Minn., Sept. 1955.

[2] N. H. Cromwell, P. L. Creger and K. E. Cook, THIS JOURNAL, **78**, 4412 (1956).

[3] L. Knorr, *Ann.*, **238**, 200 (1887).

[4] L. C. Raiford and W. J. Peterson, *J. Org. Chem.*, **1**, 544 (1937).

[5] T. Kozniewski and L. Marchlewski, *Chem. Zentr.*, **77** [II], 1190 (1906).