55. *Researches on Acetylenic Compounds. Part XXIII. The Preparation and Properties of αβ-Acetylenic γ-Keto-esters.*

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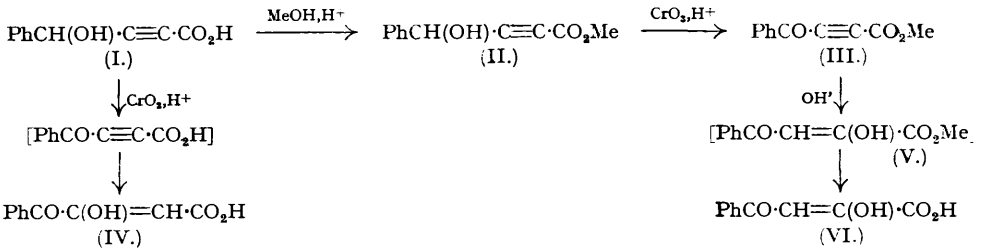
Oxidation of the esters of αβ-acetylenic γ-hydroxy-acids with chromic acid in acetone gives the γ-keto-esters. On the other hand, oxidation of the free acids is accompanied by hydration of the triple bond resulting in the formation of βγ-diketo-acids; alkaline hydrolysis of a typical γ-keto-ester leads to hydration in the opposite direction, an αγ-diketo-acid being formed. With various types of amines, the keto-esters give adducts, convertible by mild acid hydrolysis into αγ-diketo-acid derivatives, and with hydrazine, hydroxylamine, and diazomethane the keto-esters yield the expected heterocyclic compounds.

As an extension of recent work on the synthesis of acetylenic hydroxy-acids (Haynes and Jones, *J.*, 1946, 503) and on the conversion of ethynylcarbinols into the corresponding ketones (Bowden, Heilbron, Jones, and Weedon, *J.*, 1945, 39), the application of the chromic acid–acetone-oxidation procedure to the hydroxy-acids and their esters has been investigated. No general synthesis of the expected acetylenic keto-esters has been described, although Nineham and Raphael (*J.*, 1949, 118) have prepared methyl β-benzoylpropiolate (see also Ingold, *J.*, 1925, 1199) and a vinylacetylenic keto-acid has been obtained by Heilbron, Jones, and Sondheimer (*J.*, 1949, 604) by oxidation of the corresponding primary-secondary glycol.

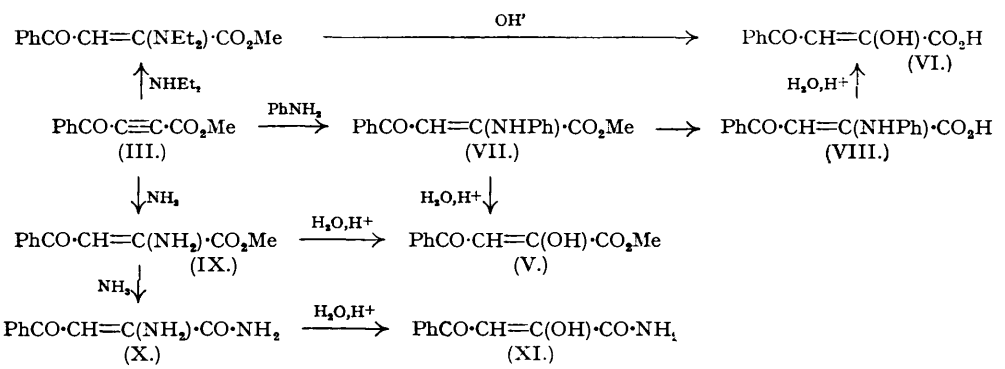
It was found that the method of Bowden, Heilbron, Jones, and Weedon (*loc. cit.*) was applicable generally to αβ-acetylenic hydroxy-esters, and *acylpropiolic esters*, $RCO{\cdot}C{\equiv}C{\cdot}CO_2Me$, have been prepared in the cases where R = Ph, Me, and Pr. They are pungent, somewhat lachrymatory, compounds which decompose readily on heating to 70—120°, and they resinify on treatment with pyridine. Their structures were confirmed by hydrogenation to known β-acylpropionic esters. Similarly, oxidation of the methyl ester of 5-hydroxyhex-3-en-1-yne-1-carboxylic acid gave the corresponding *keto*-ester ($MeCO{\cdot}CH{=}CH{\cdot}C{\equiv}C{\cdot}CO_2Me$) as a very unstable liquid. When the same method was applied to the acetylenic hydroxy-acids themselves, however, oxidation was accompanied by hydration of the triple bond. Thus the hydroxy-acid (I) derived from phenylethynylcarbinol gave, in 40% yield, a crystalline acid which, in view of its analysis, light-absorption properties, ferric chloride coloration, and reaction with *o*-phenylenediamine to give a *quinoxaline* derivative, must be formulated as *β-hydroxy-β-benzoylacrylic acid* (IV) [cf. the hydration of phenyl ethynyl ketone to 1-phenylbutane-2 : 3-dione (Bowden, Braude, and Jones, *J.*, 1946, 945), which, however, requires mercuric sulphate catalysis]. The oxidation of 3-hydroxybut-1-yne-1-carboxylic acid also apparently proceeds with concomitant hydration since the unstable acidic product gave a strong ferric chloride coloration and yielded a *quinoxaline* derivative with *o*-phenylenediamine.

An obvious alternative route to the free αβ-acetylenic γ-keto-acids was by the hydrolysis of the corresponding esters. An exothermic reaction occurred on treatment of the ester (III) with aqueous methanolic potassium hydroxide and, after 24 hours α-hydroxy-β-benzoylacrylic acid (VI) (benzoylpyruvic acid) was isolated on acidification. Variable results were obtained on repetition of this alkaline hydrolysis, probably owing to the instability of the acid (VI). The

ester (V) was presumed to be an intermediate in this reaction but attempts to isolate it were unsuccessful.



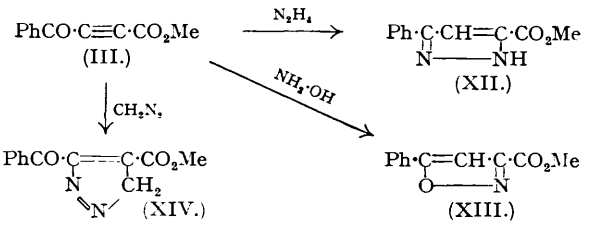
The keto-esters studied were found to react readily with amines (cf. Bowden, Braude, Jones, and Weedon, *J.*, 1945, 45). Thus methyl β-benzoylpropiolate (III), when treated with aniline, gave the crystalline *adduct* (VII) in 85% yield; the latter was hydrolysed to (V) with dilute mineral acids at room temperature, and hence has the structure shown, rather than that in which the anilino-group is in the β-position to the carbomethoxyl group. Alkaline hydrolysis gave the known acid (VIII), convertible into (VI). Treatment of methyl β-benzoylpropiolate with diethylamine gave an analogous liquid *adduct*. The reaction with ammonia was more complex; liquid ammonia caused resinification, but treatment of (III) in methanolic solution with aqueous ammonia resulted in an immediate exothermic reaction. Isolation of the product after some time gave the crystalline *amino-amide* (X) in 50% yield. When, however, the product was isolated by rapid removal of the ammonia and solvent immediately after the exothermic reaction had ceased, the *amino*-ester (IX), was obtained as a yellow oil which, after distillation at 70° (bath temp.)/10^{-4} mm., crystallised and then melted at 40°. Mild acid hydrolysis of (IX) and (X) proceeded as expected, the known enols (V) and (XI) being formed; the position of the amino-group was thus established.



The addition of ammonia to β-benzoylacrylic acid has recently been stated (Bougault and Chabrier, *Compt. rend.*, 1948, **226**, 1378), to give β-amino-β-benzoylpropionic acid, although no evidence was quoted in support of the structure assigned to the adduct. Such a result is surprising in view of an earlier discussion (Bougault, *Ann. Chim.*, 1908, **15**, 491) of the addition of nucleophilic reagents to this acid in which, by analogy with other reactions giving known α-substituted β-benzoylpropionic acids, it was considered probable that the adduct obtained from ammonia was α-amino-β-benzoylpropionic acid. Since it seems unlikely that addition of ammonia to corresponding ethylenic and acetylenic substances takes place in opposite directions, and the structure of the adduct from the latter has been unambiguously proved, the earlier interpretation of this reaction is perhaps to be preferred.

The formation of heterocyclic compounds by the reaction of ethynyl ketones with hydrazine, hydroxylamine, etc., has already been described (Bowden and Jones, *J.*, 1944, 953). The ester (III) gave with hydrazine and hydroxylamine the crystalline esters (XII) and (XIII), respectively, the reactions being smoother than those involving ethynyl ketones because of the greater stability of (III) towards alkaline reagents. Diazomethane also reacted readily with (III) in ethereal solution to yield (XIV) in good yield [its structure was not proved rigidly, and it may be the isomeric methyl 2-benzoylpyrazole-3-carboxylate. The " 3-benzoylpyrazole "

obtained from diazomethane and phenyl ethynyl ketone by Bowden and Jones (*loc. cit.*) may similarly be the 2-benzoyl compound].



It was pointed out by Bowden and Jones (*loc. cit.*) that the reactions of ethynylketones in general parallel those of the hydroxymethylene derivatives of the corresponding methyl ketones, and the ethynyl ketones can often be substituted advantageously for the latter (cf. Johnson, *J.*, 1947, 346). The examples of heterocyclic syntheses given above demonstrate that αβ-acetylenic γ-keto-esters show a similar parallelism to αγ-diketo-esters, which indeed can easily be prepared from them. Although the latter are in most cases much more readily accessible (from the condensation of oxalic ester with methyl ketones) the greater reactivity of the acetylenic compounds suggests that these may occasionally be of value.

Light-absorption data for the amine adducts described are given in Table I, the values for the nearest available analogues in the 2-aminovinyl ketone series being given for comparison. Data for the corresponding enols are given in Table II. It is clear that in alcoholic solutions

TABLE I.

Light Absorption of Adducts.

Amino-keto-acid derivative.			Corresponding amino-ketone.[1]		
	$\lambda_{max.}$, A.	$\varepsilon_{max.}$		$\lambda_{max.}$, A.	$\varepsilon_{max.}$
PhCO·CH=C(NH₂)·CO₂Me	2590	4,500	PhCO·CH=CH·NH₂ (m. p. 70°)	2420	14,000
	3520	17,000		3240	22,000
PhCO·CH=C(NH₂)·CO·NH₂	2460	7,000	PhCO·CH=CH·NH₂ (m. p. 90—91°)	2420	11,000
	2560	7,000		3240	18,000
	3430	17,500			
PhCO·CH=C(NEt₂)·CO₂Me	2470	10,500	½(PhCO·CH=CH·NH·CH₂)₂	2420	11,000
	3410	22,000		2450	11,000
				3450	17,000
PhCO·CH=C(NHPh)·CO₂Me	2400	13,000			
	3730	19,000	PhCO·CH=CH·NHPh	2420	17,500
				2540	17,500
PhCO·CH=C(NHPh)·CO₂H	2400	11,000		3740	31,000
	3680	14,000			

[1] Data from Bowden, Braude, Jones, and Weedon, *loc. cit.*, and Bowden, Braude, and Jones, *J.*, 1946, 945.

TABLE II.

Light Absorption of Enols.

	$\lambda_{max.}$, A.	$\varepsilon_{max.}$		$\lambda_{max.}$, A.	$\varepsilon_{max.}$
PhCO·CH=C(OH)·CO₂Me	3110	15,000	cf. PhCO·CH=CH·CO₂Me(*cis*) [1]	2510	12,000
PhCO·CH=C(OH)·CO₂H	3115	12,500	PhCO·CH=CH·CO₂Me(*trans*) [1]	2350	12,000
	3340 *	9,500		2680	9,000
PhCO·CH=C(OH)·CO·NH₂	2230	6,000	PhC(OH)·C(OMe)=CH [1]	2250	13,500
	3240	14,000	O——CO		
PhCO·C(OH)=CH·CO₂H	2680	13,500			

* Inflexion.

[1] Nineham and Raphael, *loc. cit.*

these compounds exist, at any rate largely, as the vinylamine and enolic forms rather than their imino- and ketonic tautomers. The powerful auxochromic effects of the amino- and hydroxyl groups in the α-substituted β-benzoylacrylic acid derivatives correspond to those observed in the vinyl ketone series (Bowden, Braude, Jones, and Weedon, *loc. cit.*). The effect

of the carbomethoxyl, carboxyl, or carbamyl group on the position and intensity of the absorption maximum is not profound, but it is unexpectedly variable. The differences between the light absorption of the methyl ester and the amide of α-hydroxy-β-benzoylacrylic acid, and of the acid itself, are especially interesting; normally the conversion of an acid into its ester or amide has little effect on its light absorption. In these compounds however, the adjacent carboxyl or similar group clearly can interact with the hydroxyl or amino-group, possibly by hydrogen bonding, thereby modifying the mobility of its free electron pair and hence its auxochromic effect (cf. Bowden, Braude, and Jones, *J.*, 1946, 748).

As would be expected the hydroxyl group in β-hydroxy-β-benzoylacrylic acid has little effect on the light absorption; the difference between this compound and the β-methoxy-β-benzoylacrylic acid described by Nineham and Raphael (*loc. cit.*), which exists in the cyclic form, is noteworthy.

The acetylene carbinols required for this work were prepared by the method of Heilbron, Jones, and Weedon (*J.*, 1945, 81) with numerous minor modifications; the preparation of phenylethynylcarbinol is described to exemplify these and because existing physical constants apparently refer to incompletely purified materials. The acetylenic hydroxy-acids were obtained by the method of Haynes and Jones (*loc. cit.*) except that the Grignard complexes were prepared without heating (cf. Jones and Whiting, *J.*, 1949, 1423). It was found that with this modification and using ether as solvent, the method could be applied to phenylethynylcarbinol, contrary to previous experience; but when it was applied to propenylethynylcarbinol the syrupy product, though obtained in good yield and light in colour, was shown by its light absorption to contain about 50% of the rearranged isomer, from which it could not be separated. The method of carboxylating phenylethynylcarbinol described by Nineham and Raphael (*loc. cit.*) gave in our hands very variable results, apparently because of the unpredictable physical state of the precipitated sodium derivative; it could not be applied to propylethynylcarbinol. An attempt to carboxylate the dipotassium derivative of phenylethynylcarbinol, prepared by treating the carbinol with the potassium hydroxide–butyraldehyde diethyl acetal complex according to the method of Weizmann (B.PP. 573,527; 580,921; see also Bergmann, " Chemistry of Acetylenic Compounds," p. 50) also failed, the isolation of a small amount of acetylenedicarboxylic ester suggesting fission of the carbinol under these conditions.

Experimental.

(Light-absorption determinations were carried out in alcohol solutions on a Hilger medium spectrograph).

Phenylethynylcarbinol.—The apparatus consisted of a three-necked, 10-l. flask fitted with an efficient stirrer (without mercury seal) and a gas inlet tube of at least 12 mm. diameter, the whole being well insulated by immersion in cork dust. To liquid ammonia (6 l.), powdered ferric nitrate (3 g.) and sodium (10 g.) were added, and after a short interval more sodium (290 g.; ½-inch cubes). When after 20—60 minutes the colour had changed from dark blue to grey, acetylene was passed in rapidly; after some hours the colour again changed, becoming clear and black. The flow of acetylene was replaced by a slow current of nitrogen and a solution of benzaldehyde (1230 g.) in dry ether (1 l.) was added during two hours. After the flask contents had been stirred for 16 hours, ether (1·5 l.) was added, and the mixture was warmed until the greater part of the ammonia had evaporated. Ice and 6N-sulphuric acid in excess were added, and the aqueous layer was extracted with ether, the extract then being washed with sodium hydrogen carbonate and dried. After the removal of ether distillation of the residue at 0·3 mm. gave a number of fractions. The forerun (*ca.* 200 g.) b. p. 35—70°, consisted mainly of benzaldehyde and was discarded; fractions, b. p. 70—100°, consisting principally of the acetylenic carbinol were then obtained. Of these the middle portion had m. p. *ca.* 25—26° and was accepted; earlier and later fractions, the former containing much benzaldehyde and benzyl alcohol and the latter benzoic acid, were combined, dissolved in ether, and washed with saturated sodium hydrogen sulphite solution (the precipitated benzaldehyde addition compound being removed by filtration) and thoroughly with sodium carbonate solution. After the ethereal solution had been dried and the solvent removed the residue was distilled, fractions having m. p. 25—27° being retained; the total yield was 875 g. A specimen recovered from an attempted carboxylation by the method of Nineham and Raphael (*loc. cit.*) was free from benzaldehyde and had b. p. 94°/0·7 mm., n_D^{20} 1·5518 (supercooled), m. p. 27·5°. After crystallisation from ether–light petroleum at *ca.* −40° it formed small prisms, m. p. 28·5°, unchanged on recrystallisation from the same solvent (Jones and McCombie, *J.*, 1942, 733, give m. p. 22°; earlier workers describe this compound as a liquid).*

In the preparation of ethynylcarbinols it has been found possible to dispense with the use of a cooling bath and control of the reaction temperature. Rigorous exclusion of water by means of a mercury-sealed stirrer, soda-lime tubes, etc., is difficult and indeed somewhat hazardous because of the risk of a blockage in the latter. It is, however, preferable to decompose the sodio-complex with ammonium chloride as described by Heilbron, Jones, and Weedon (*loc. cit.*) when the carbinol is sensitive to acids or to oxidation.

3-Hydroxy-3-phenylprop-1-yne-1-carboxylic Acid (I).—Phenylethynylcarbinol (58 g.) was added during three hours to an ethereal solution of ethylmagnesium bromide [from magnesium (25 g.)], with efficient stirring and ice-cooling. The colloidal suspension obtained was stirred at 0° for a further thirty

* Cf. Clapperton and McGregor, *J. Amer. Chem. Soc.*, 1949, **71**, 3234.

minutes and then poured on to an excess of solid carbon dioxide in an autoclave, which was then sealed. After 22 hours the Grignard complex was decomposed, and isolation of the acidic fraction gave a dark semi-solid mass (*ca.* 70 g.). Trituration with cold benzene gave the hydroxy-acid (48·5 g.), m. p. 84—85°, which after repeated crystallisation from benzene had m. p. 89—90° (Nineham and Raphael, *loc. cit.*, give m. p. 94—95°). Conversion into the methyl ester by refluxing a methanolic sulphuric acid solution followed by distillation at 0·01 mm. (b. p. 143°) gave yields of only 45—55%, and it was found more economical to esterify the crude acid, m. p. *ca.* 84°, with cold methanolic sulphuric acid for one week, and to oxidise the undistilled ester, obtained in 85% yield, directly to methyl β-benzoylpropiolate (II) by Nineham and Raphael's method (*loc. cit.*), the yield of pure keto-ester from the crude acid then being 55%.

Hydrogenation of Methyl β-Benzoylpropiolate.—When the keto-ester (1·1 g.) was shaken with hydrogen in methyl acetate solution in the presence of a palladium–calcium carbonate catalyst until absorption was complete (uptake 240 c.c. at 769 mm. and 18°) and the product was hydrolysed with excess of aqueous–methanolic potassium hydroxide solution for 60 hours at room temperature, isolation of the acid fraction gave β-benzoylpropionic acid (0·7 g.) as colourless plates, m. p. 114° undepressed on admixture with an authentic specimen (Somerville and Allen, *Org. Synth.*, 1933, **13**, 12, give m. p. 116°).

Methyl β-Butyrylpropiolate.—To a solution of methyl 3-hydroxyhex-1-yne-1-carboxylate (Haynes and Jones, *loc. cit.*) (5 g.) in acetone (20 c.c.) a solution of 6N-chromic acid [12 c.c.; the solution was prepared from chromic acid (100 g.), sulphuric acid (160 g.), and water (500 c.c.)] was added dropwise over a period of 20 minutes with stirring, the temperature being kept below 30° by cooling in water. The solution was stirred for a further 30 minutes and water (30 c.c.) was added; isolation of the neutral fraction with ether followed by careful fractional distillation gave the *keto*-ester (2·2 g.), b. p. 43—44°/0·02 mm., n_D^{19} 1·4511 (Found: C, 62·1; H, 6·35. $C_8H_{10}O_3$ requires C, 62·3; H, 6·55%), and recovered hydroxy-ester (1·2 g.), b. p. 72°/0·01 mm., n_D^{20} 1·4595. The 2 : 4-*dinitrophenylhydrazone* crystallised from methanol in yellow needles, m. p. 77—78° (Found: C, 50·25; H, 4·1. $C_{14}H_{14}O_6N_4$ requires C, 50·4; H, 4·2%).

Methyl 3-Hydroxybut-1-yne-1-carboxylate.—The crude hydroxy-acid (Haynes and Jones, *loc. cit.*) (38 g.) was esterified with methanolic sulphuric acid, giving the *ester* (27 g.), b. p. 60°/0·03 mm., 114°/12 mm., $n_D^{20\cdot5}$ 1·4579 (Found: C, 56·15; H, 6·3. $C_6H_8O_3$ requires C, 56·25; H, 6·3%).

Methyl β-Acetylpropiolate.—A solution of methyl 3-hydroxybut-1-yne-1-carboxylate (10 g.) in acetone (50 c.c.) was treated with 6N-chromic acid solution (30 c.c.) as previously described. Isolation of the product with ether, and fractional distillation gave the *keto*-ester (6·0 g.), b. p. 79°/16 mm., n_D^{20} 1·4470 (Found: C, 56·95; H, 4·6. $C_6H_6O_3$ requires C, 57·15; H, 4·8%). The 2 : 4-*dinitrophenylhydrazone* formed yellow prisms, m. p. 166°, from ethyl acetate–ethanol (Found: C, 47·75; H, 3·55. $C_{12}H_{10}O_6N_4$ requires C, 47·05; H, 3·3%).

Hydrogenation. The keto-ester (1·2 g.) in methyl acetate (20 c.c.) was shaken in hydrogen in the presence of a palladium–calcium carbonate catalyst (100 mg.; 2%) until absorption was complete (uptake 395 c.c.). After removal of the catalyst and evaporation of the solvent distillation gave methyl lævulate (1·0 g.), b. p. 83—85°/18 mm., n_D^{23} 1·4234 (Cowley and Schuette, *J. Amer. Chem. Soc.*, 1931, **53**, 3485, give b. p. 197·7°, n_D^{20} 1·4223). The 2 : 4-dinitrophenylhydrazone formed yellow needles, m. p. 140°, from ethanol (Cowley and Schuette, *loc. cit.*, give m. p. 141—142°).

Methyl 5-Ketohex-3-en-1-yne-1-carboxylate.—A solution of methyl 5-hydroxyhex-3-en-1-yne-1-carboxylate (4 g.) (Haynes and Jones, *loc. cit.*) in acetone (30 c.c.) was treated with 6N-chromic acid (10 c.c.) at 10°. Isolation with ether and distillation gave the *keto*-ester (1·8 g.), b. p. 67°/10^{-2} mm., n_D^{20} 1·5140 (Found: C, 62·6; H, 5·1. $C_8H_8O_3$ requires C, 63·15; H, 5·3%). Light absorption (in alcohol): Maxima, 2600 and 2680 A.; ε = 15,000. The 2 : 4-*dinitrophenylhydrazone* formed red prisms, m. p. 185—186° (decomp.), from ethyl acetate (Found: C, 50·45; H, 3·75. $C_{14}H_{12}O_6N_4$ requires C, 50·6; H, 3·65%).

β-Hydroxy-β-benzoylacrylic Acid (IV).—6N-Chromic acid (11 c.c.) was added during 20 minutes to a solution of 3-hydroxy-3-phenylprop-1-yne-1-carboxylic acid (5 g.) in acetone (30 c.c.), the temperature being kept at 5—10°. After being stirred for a further 10 minutes the solution was diluted with water and extracted with ether, and the extract was washed with water, dried, and evaporated. Crystallisation of the residue from benzene–light petroleum (b. p. 40—60°) gave the *acid* as plates, m. p. 54° (Found: C, 62·45; H, 3·8. $C_{10}H_8O_4$ requires C, 62·5; H, 4·2%). It gave a crimson ferric chloride coloration. The *quinoxaline* derivative was readily obtained by mixing ethereal solution of the acid and *o*-phenylenediamine; it formed golden-yellow plates, m. p. 262°, from methanol (Found: C, 72·85; H, 4·6. $C_{16}H_{12}O_2N_2$ requires C, 72·7; H, 4·55%). Light absorption: Maxima at 2670, 4130, and 4350 A.; ε = 12,500, 30,000, and 27,500, respectively.

β-Hydroxy-β-acetylacrylic Acid.—Oxidation of 3-hydroxybut-1-yne-1-carboxylic acid (0·8 g.) in acetone (10 c.c.) with 6N-chromic acid (3 c.c.) at 15° followed by isolation with ether gave the crude enolic *acid* (0·5 g.) as a syrup which gave an intense crimson coloration with ferric chloride solution. It was characterised as its *quinoxaline* derivative which formed brownish prisms, m. p. 248—250°, from ethanol (Found: C, 65·8; H, 5·65. $C_{11}H_{10}O_2N_2$ requires C, 65·3; H, 5·0%). Light absorption: Maxima, 2230, 2280, 2680, and 3910 A.: ε = 30,500, 26,500, 7,000, and 17,500, respectively.

α-Hydroxy-β-benzoylacrylic Acid (*Benzoylpyruvic Acid*) (VI).—A solution of methyl β-benzoylpropiolate (0·5 g.) and potassium hydroxide (0·5 g.) in aqueous methanol was set aside at 20° for 18 hours. After dilution with water and ether extraction acidification of the aqueous phase precipitated an oil which solidified during 2 days at 0°, and was recrystallised from benzene to give the acrylic acid (0·15 g.) as plates, m. p. 151° (decomp.) (Brömme and Claisen, *Ber.*, 1888, **21**, 1132, give m. p. 156—158°).

Methyl α-Anilino-β-benzoylacrylate (VII).—Aniline (400 mg.) was added to a solution of methyl β-benzoylpropiolate (400 mg.) in dry ether (15 c.c.). After 20 hours the solution was filtered to remove a small quantity of flocculent matter and the ether was evaporated under reduced pressure. The residual oil solidified and was crystallised from aqueous methanol to give the *anilino*-ester (508 mg., 85%) as glistening golden-yellow needles, m. p. 59°, unchanged on recrystallisation from the same solvent or light petroleum (b. p. 40—60°) (Found: C, 72·8; H, 5·5. $C_{17}H_{15}O_3N$ requires C, 72·55; H, 5·4%).

Alkaline hydrolysis. A solution of the ester (0·3 g.) and potassium hydroxide (0·2 g.) in aqueous

methanol was set aside at 20° for 12 hours. Isolation of the acid fraction gave α-anilino-β-benzoylacrylic acid (VIII) (0·2 g.) as yellow needles, m. p. 164° (decomp.) [Brömme and Claisen, *loc. cit.*, give m. p. 168—170° (decomp.)].

The anilino-acid and the ester were readily hydrolysed by dilute mineral acid to the corresponding enols. A solution of the ester (100 mg.) in methanol (3 c.c.) was treated with 2N-hydrochloric acid (1 c.c.) at toom temperature; the progress of the reaction was shown by the disappearance of the yellow colour. After 25 minutes water was added till a turbidity just formed; on storage methyl α-hydroxy-β-benzoylacrylate (V) (61 mg.) separated as cream, fine needles, m. p. 60°, unchanged on crystallisation from light petroleum (b. p. 40—60°) (Perkin, *J.*, 1872, **25**, 833, gives m. p. 61°; Drude, *Ber.*, 1897, **30**, 955, gives m. p. 62°).

Treatment of a solution of the anilino-acid (0·5 g.) in dioxan (15 c.c.) with 2N-sulphuric acid (8 c.c.) for 20 hours at room temperature gave, after dilution with water, α-hydroxy-β-benzoylacrylic acid (VI) (0·29 g.) which after crystallisation from benzene had m. p. 154° (decomp.), undepressed on admixture with a specimen prepared as above.

Methyl α-Diethylamino-β-benzoylacrylate.—Diethylamine (1 g.) was added to a solution of methyl β-benzoylpropiolate (1 g.) in methanol–ether (5 c.c.). After 20 hours at 20° evaporation of the solvent and distillation at 85° (bath temp.)/10^{-4} mm. gave the *amino*-ester (0·8 g.), n_D^{18} 1·6060 (Found: 69·05; H, 7·05. $C_{15}H_{17}O_3N$ requires C, 69·0; H, 7·35%).

Hydrolysis. The amino-ester (0·3 g.) in dioxan (15 c.c.) was treated with a solution of potassium hydroxide (5 c.c.; 0·4 N) at 20° for 20 hours. Acidification followed by isolation with ether gave an oil (0·2 g.) which solidified when kept, and was crystallised from benzene to give α-hydroxy-β-benzoylacrylic acid (VI) (0·1 g.), m. p. 156° (decomp.) undepressed on admixture with a specimen prepared as above. It is not known whether the amino-residue was removed in the alkaline hydrolysis or whether the amino-acid is so labile towards acid hydrolysis that this occurred almost immediately on acidifying the alkaline solution.

Methyl α-Amino-β-benzoylacrylate (IX).—To a solution of methyl β-benzoylpropiolate (2·0 g.) in methanol (10 c.c.) and ether (6 c.c.) ammonia (0·8 c.c.; *d* 0·88) was added. The temperature of the mixture rose quickly to 40°, then began to fall. At this point, after about 2 minutes, the reaction was stopped by the rapid removal of all volatile material under reduced pressure. Distillation of the residue at 50—70° (bath temp.)/10^{-4} mm. gave a viscous yellow oil (1·1 g.) which partly solidified after several weeks. Recrystallisation from aqueous methanol gave the *amino*-ester as large prisms, m. p. 40° (Found: C, 64·6; H, 5·25. $C_{11}H_{11}O_3N$ requires C, 64·35; H, 5·4%).

α-Amino-β-benzoylacrylamide (X).—Ammonia (2 c.c.; *d* 0·88) was added to a solution of methyl β-benzoylpropiolate (400 mg.) in methanol (6 c.c.). After 18 hours at 20° dilution with water gave the *amino-amide* (270 mg.) which after recrystallisation from benzene formed straw-coloured needles, m. p. 137° (Found: C, 63·5; H, 5·6. $C_{10}H_{10}O_2N_2$ requires C, 63·15; H, 5·3%). It crystallised well from aqueous methanol, but then retained water tenaciously and gave inaccurate analytical data.

Both the ester and the amide were readily hydrolysed by mineral acids to the corresponding enols. A solution of methyl β-benzoylpropiolate (200 mg.) in methanol (3 c.c.) was treated with ammonia (0·5 c.c.; *d* 0·88). The solution of the amino-ester obtained by allowing the reaction to continue for 15 minutes was acidified with 2N-sulphuric acid. Next morning the separated solid was recrystallised twice from aqueous methanol, giving methyl α-hydroxy-β-benzoylacrylate (V) as long needles, m. p. 59—60° undepressed on admixture with a specimen prepared as described above. Similarly α-amino-β-benzoylacrylamide (150 mg.), dissolved in methanol (6 c.c.) and 2N-sulphuric acid (2 ml.), gave, after 30 minutes at 20°, a crystalline precipitate of α-hydroxy-β-benzoylacrylamide (XI) which after recrystallisation from aqueous methanol formed pale cream needles, m. p. 140° strongly depressed on admixture with the starting material (Found: C, 62·85; H, 4·7; N, 7·2. Calc. for $C_{10}H_9O_3N$: C, 62·8; H, 4·75; N, 7·35%) [Mumm and Münchmeyer, *Ber.*, 1910, **43**, 3342, give m. p. 138° (decomp.)].

Methyl 3-Phenylpyrazole-5-carboxylate (XII).—A solution of hydrazine hydrate (0·1 g.) in methanol (2 c.c.) was added slowly to a solution of methyl β-benzoylpropiolate (0·5 g.) in methanol with ice-cooling. After dilution of the solution with water and isolation with ether the methyl ester was obtained, which after crystallisation from aqueous methanol formed prisms, m. p. 177—178° (Found: C, 65·4; H, 5·45. Calc. for $C_{11}H_{10}O_2N_2$: C, 65·35; H, 5·0%) (Buchner and Lehmann, *Ber.*, 1902, **35**, 35, give m. p. 181—182°).

Methyl 5-Phenylisooxazole-3-carboxylate (XIII).—A solution of hydroxylamine hydrochloride (0·5 g.) in methanol (5 c.c.) was neutralised with methanolic sodium methoxide (5 c.c.) and filtered from precipitated sodium chloride. A portion (8 c.c.) of the resultant solution was added to methyl β-benzoylpropiolate (0·5 g.) in methanol (5 c.c.), and the mixture was set aside for 18 hours at 20°. Isolation with ether then gave the *ester* (0·15 g.) as plates, m. p. 86—88° (Found: N, 6·65. $C_{11}H_9O_3N$ requires N, 6·9%).

Methyl 3(4?)-Benzoylpyrazole-4(3?)-carboxylate (XIV).—A solution of methyl β-benzoylpropiolate (1·0 g.) in ether (5 c.c.) was treated with an excess of ethereal diazomethane. After 18 hours at 20° evaporation of the solvent and crystallisation from aqueous methanol gave the *ester* as well-formed prisms, m. p. 138° (Found: C, 62·7; H, 4·6. $C_{12}H_{10}O_3N_2$ requires C, 62·6; H, 4·4%).

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