well registered the bath temperature. In some runs, hydrogen sulfide was added to the bomb before heating the reaction mixture, while other runs were conducted in which the hydrogen sulfide pressure was allowed to develop autogeneously. Excess hydrogen sulfide could be bled off through the valve to permit study of the reaction over a limited pressure range.

Product Separations.—The crude reaction mixture was extracted with boiling xylene to remove *p*-toluic acid, sulfur and some of the by-products, and the residue was then extracted with boiling dioxane to remove most of the remaining by-products[1] and any remaining sulfur. The insoluble material consisted of a mixture of 4,4′-stilbenedicarboxylic acid and 4,4′-bibenzyldicarboxylic acid, which were separated as follows through the potassium salts: 45 g. of crude dimer acids was boiled with 700 ml. of water and 22 g. of potassium hydroxide, the hot solution was filtered, and the filter cake washed with about 100 ml. of hot water. A clear, light yellow solution was obtained from most reactions. The hot solution was stirred with 25 g. of potassium chloride for a few minutes, and the mixture was cooled to precipitate the potassium salt of 4,4′-stilbenedicarboxylic acid, which was collected and washed with a small amount of saturated potassium chloride solution. The filtrate was heated to about 90°, and the 4,4′-bibenzyldicarboxylic acid was precipitated with an excess of hydrochloric acid. After a period of digestion the acid was collected, washed and dried. The product usually contained about 10% 4,4′-stilbenedicarboxylic acid. Further purification was effected by recrystallizations of the potassium salts, when desired.

The potassium salts of the acids were dissolved in hot water with added base, and the free acids precipitated in the same manner as the 4,4′-bibenzyldicarboxylic acid. This fraction usually contained 85 to 90% of 4,4′-stilbenedicarboxylic acid, the remainder being 4,4′-bibenzyldicarboxylic acid.

4,4′-Stilbenedicarboxylic Acid.—4,4′-Stilbenedicarboxylic acid was identified by its characteristic ultraviolet adsorption spectrum, fluorescence, solubility of its potassium salt, and its reaction with dilute solutions of permanganate in neutral or alkaline solutions.[1]

4,4′-Bibenzyldicarboxylic Acid.—The dimethyl ester, m.p. 119°,[3] was formed through the acid chloride. As 4,4′-bibenzyldicarboxylic acid reacts slowly with dilute alkaline permanganate solution, the amount of 4,4′-stilbenedicarboxylic acid in a mixture of the two acids can be determined approximately by permanganate titration in dilute caustic solution. The acid has a neutral equivalent of 135. The best samples, containing about 1.5% of 4,4′-stilbenedicarboxylic acid, melted at 378–385° in a sealed tube. Spectroscopic examination of the acid and ester showed that absorption spectra closely resemble the spectrum of *p*-toluic acid, both in the position of the absorption maxima, and in the intensity of the absorption.

Tetra-(*p*-carboxyphenyl)-thiophene.—The dioxane-soluble, xylene-insoluble brown product formed in the reaction had the same properties as the tetra-(*p*-carboxyphenyl)-thiophene previously described.[1]

Discussion

Temperature.—The reaction was studied at 288 and 315°. While the reaction was faster at the higher temperature, the yield of dimer acids decreases sharply with increasing reaction time at 315°. There is no evidence of such an effect at 288°. The products of reaction at 315° are more highly colored than the products from reaction at 288°, when the same purification technique is used.

Hydrogen Sulfide Pressure.—Increasing hydrogen sulfide pressure decreases the rate of dimerization of *p*-toluic acid considerably. While sulfur will completely react with *p*-toluic acid at a 1:2 mole ratio in two hours at atmospheric pressure and 275°, reaction was not complete at 288° in 6.5 hours with a hydrogen sulfide pressure at 27–38 atm. 4,4′-Bibenzyldicarboxylic acid is produced by treating a mixture of 4,4′-stilbenedicarboxylic acid and *p*-toluic acid with hydrogen sulfide. The *p*-toluic acid acted as a solvent for the 4,4′-stilbenedicarboxylic acid, and also reacted with the sulfur liberated in the reaction. When 4,4′-stilbenedicarboxylic acid was added to a reaction mixture with *p*-toluic acid and sulfur the ratios of stilbene- and bibenzyldicarboxylic acids obtained in the final products were similar to the ratios obtained when the stilbenedicarboxylic acid was omitted and more bibenzyldicarboxylic acid was produced from the same amount of sulfur and toluic acid. Higher conversions are obtained due to the sulfur liberated by reaction of hydrogen sulfide with stilbenedicarboxylic acid.

The presence of hydrogen sulfide pressure greatly decreased the amount of tetra-(*p*-carboxyphenyl)-thiophene formed. The reaction of *p*-toluic acid with sulfur under hydrogen sulfide pressure gave yields of dimer acids (4,4′-stilbenedicarboxylic acid plus 4,4′-bibenzyldicarboxylic acid) varying from 67.5 to 80.8% at 288°, when conversions were held below about 50% of the toluic acid. This compares[1] to yields of 50 to 60% (based on toluic acid converted) at 270–275° and similar conversions at atmospheric pressure. The fraction of 4,4′-bibenzyldicarboxylic acid in the dimer acid varies from 39% with reaction at 288° and 17 atm. for three hours to 100% with reaction at 315° and 38 atm. for six hours.

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[3] C. Liebermann and P. Mitter, *Ber.*, **45**, 1210 (1912).

Amine Glutamates

BY BRUNO VASSEL AND W. G. SKELLY

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During the course of an investigation on the properties of certain L-glutamic acid derivatives a number of previously unreported amine salts were prepared.

Table I presents the melting points of the octyl-, decyl-, dodecyl- and cyclohexylamine glutamates, analytical data on these salts, as well as the boiling points of the rectified amines used.

TABLE I

Amine glutamate	B.p. of amine cut used, °C.	M.p. (cor.) of amine glutamate,[1] °C.	α-Carboxyl-C (Van Slyke),[2] %		Nitrogen, % (Micro Kjeldahl)	
			Theory	Found	Theory	Found
n-Octylamine	176–178	150.5	4.35	4.67	10.15	9.99
n-Decylamine	216–218	160.9	3.95	4.29	9.21	9.25
n-Dodecylamine	119–122[3]	165.0	3.56	3.85	8.45	8.37
Cyclohexylamine	134	157.7	4.87	4.61	11.39	10.88

TABLE II

Amine glutamate	Solubility at 25°, in G./100 ml. soln.		Distribution coefficient
	Water	1-Butanol	
n-Octylamine	30.79	0.106	0.0035
n-Decylamine	23.08	.071	.0031
n-Dodecylamine	36.27	.064	.0018
Cyclohexylamine	6.58	.080	.012

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(1) Fisher–Johns melting point block.

(2) An excess of ninhydrin must be used because of the presence of the amine.

(3) At 5 mm.

Table II summarizes the solubilities of the amine L-glutamates in water and in dry 1-butanol at 25°. These salts are surprisingly insoluble in the alcohol.

Experimental

Materials.—The L-glutamic acid was a commercial product (International Min. and Chem. Corp.) of high purity which after crystallization at *p*H 3.2 and drying at 110° had $[\alpha]^{25}D$ −31.2°. The cyclohexylamine (Monsanto Chemical Co.) and the octyl-, decyl- and dodecylamines (Armour and Co.) were thrice distilled through a Vigreux column. The fractions distilling at the temperatures shown in Table I were used in the preparation of the glutamates.

Amine Glutamates.—One mole of amine was dissolved in 500 ml. of 1-butanol, containing 50 ml. of water in case of octylamine (129.2 g.) and 75 ml. of water when decyl- (157.3 g.) or dodecylamine (185.3 g.) was used. Each mole of cyclohexylamine (99.2 g.) was dissolved in 700 ml. of butanol containing 200 ml. of ethanol and 100 ml. of water. The solutions were heated to 70°, then 0.95 mole (139.8 g.) of powdered L-glutamic acid was added in small batches with continuous stirring. After 15 minutes all but traces of the glutamic acid had dissolved. The solutions were filtered hot, cooled to room temperature, seeded to overcome the tendency to supersaturate, and placed in the refrigerator overnight. After filtration of the crystalline mass and washing with ether, the products were dried over H_2SO_4 *in vacuo*. Yields ranged from 53 to 65% of theory. Concentration of the mother liquors *in vacuo* and reseeding increased the over-all yields to 85–90%. The almost white products were recrystallized from 75–80% aqueous ethanol which must be free from aldehydes to prevent discoloration.

Solubilities.— Excesses of the glutamates were stirred continuously in water or in absolute 1-butanol in a constant temperature bath at 25 ± 0.5° for 24 hours. After filtration by gravity the filtrates were analyzed for total nitrogen. The aqueous dodecylamine glutamate solution was, however, too viscous to be filtered; instead it was centrifuged and the clear supernatant was analyzed.

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Michael Addition Products from 2,3-Dimethoxyphenylpropiolic Acid Derivatives

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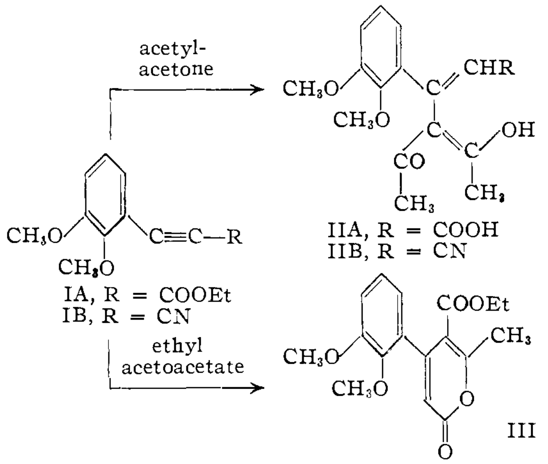
Condensation of esters of phenylpropiolic acid with ethyl acetoacetate[1] and acetylacetone[2] in the presence of sodium ethoxide leads to the formation of 4-phenyl-α-pyrones. Apparently the reaction consists in Michael addition of the methylene group of the diketone or keto ester to the triple bond of the propiolate, followed by lactonization of an enol form of the resulting keto ester. In the case of acetylacetone, an oily, enolic intermediate was isolated.[2]

This reaction was investigated for several derivatives of 2,3-dimethoxyphenylpropiolic acid. The reactions of ester IA and nitrile IB with ethyl acetoacetate were found to take this course, and the product in each case was the α-pyrone derivative, III. However, when acetylacetone was used instead of ethyl acetoacetate, pyrones were not isolated, and the non-cyclic condensation products, IIA and IIB, were obtained. In the case of IIA, the condensation was very slow and was accompanied by cleavage of the ethyl ester group to the corresponding acid. The infrared spectra of IIA and IIB (see Experimental Part) suggested that these compounds were strongly chelated enols.



IIA, R = COOH
IIB, R = CN

IA, R = COOEt
IB, R = CN

III

Experimental

Methyl 2,3-Dimethoxycinnamate.—Esterification of 65.6 g. of 2,3-dimethoxycinnamic acid with 38 g. of methanol in the presence of 200 ml. of ethylene dichloride[3] and 3 ml. of concentrated sulfuric acid (ten-hour reflux) afforded, after distillation *in vacuo*, 58.3 g. (83%) of colorless crystals, b.p. 147–148° (1.1 mm.), m.p. 52–54°.

Anal. Calcd. for $C_{12}H_{14}O_4$: C, 64.85; H, 6.35. Found: C, 65.04; H, 6.59.

2,3-Dimethoxyphenylpropiolamide and Esters. (A) Bromination.—A solution of 70 g. (0.31 mole) of methyl 2,3-dimethoxycinnamate in 600 ml. of dry ether was treated slowly with 56 g. (0.35 mole) of bromine at ice temperature. The solution was kept cold for two days and was washed with sodium bicarbonate solution and water. Evaporation of the dried ether solution afforded 123 g. of crude dibromoester.

(B) Dehydrobromination.—The crude product of A was refluxed for three hours with a solution of 125 g. of potassium hydroxide in 800 ml. of methanol. The mixture was filtered and the solution was steam distilled. The remaining aqueous solution was acidified at ice temperature, and the product was extracted with ether. The ether solution was dried over magnesium sulfate, and the solvent was evaporated. The crude acid, 64.5 g. of orange oil which crystallized slowly, was not purified further (reported[4] m.p. 108–109°).

(C) 2,3-Dimethoxyphenylpropiolamide.—The crude acid from B was treated with 130 ml. of thionyl chloride and the solution was allowed to stand overnight. The excess reagent was removed by distillation *in vacuo* at 60°. The residue was dissolved in chloroform and added slowly to excess concentrated ammonium hydroxide. After an hour the mixture was diluted with ether and the crystals were collected. Recrystallization from ethyl acetate gave 29 g. (44% from the methyl cinnamate) of colorless crystals, m.p. 148–151°.

Anal. Calcd. for $C_{11}H_{11}O_3N$: C, 64.38; H, 5.40. Found: C, 64.31; H, 5.35.

(D) Ethyl and Methyl Esters.—A sample of the crude acid chloride obtained as described in C was dissolved in chloroform and added slowly to excess absolute ethanol at ice temperature. The neutral product was isolated in the usual way and was distilled *in vacuo;* there was obtained a viscous, yellow oil, b.p. 150–159° (1.0 mm.).

Esterification of 30.9 g. of crude acid from B with 15 g. of methanol in the presence of 45 ml. of ethylene dichloride[3] and 2 ml. of concentrated sulfuric acid (four-hour reflux) afforded, after distillation of the neutral fraction, 14 g. (42%) of viscous, yellow oil, b.p. 135–142° (0.7 mm.).

These esters did not crystallize and were used as obtained.

2,3-Dimethoxyphenylpropiolonitrile.—A solution of 16.4 g. (0.080 mole) of 2,3-dimethoxyphenylpropiolamide in 250 ml. of dry trimethylbenzene was treated with 40 g. (0.28 mole) of phosphorus pentoxide, and the mixture was stirred

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(1) S. Ruhemann, *J. Chem. Soc.*, **75**, 251 (1899).

(2) S. Ruhemann, *ibid.*, **75**, 411 (1899).

(3) R. O. Clinton and S. C. Laskowski, THIS JOURNAL, **70**, 3135 (1948).

(4) S. Ruhemann, *Ber.*, **53**, 277 (1920).