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 $[\alpha]^{25}\text{D}$ $-31.2°$. 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

BY GORDON N. WALKER

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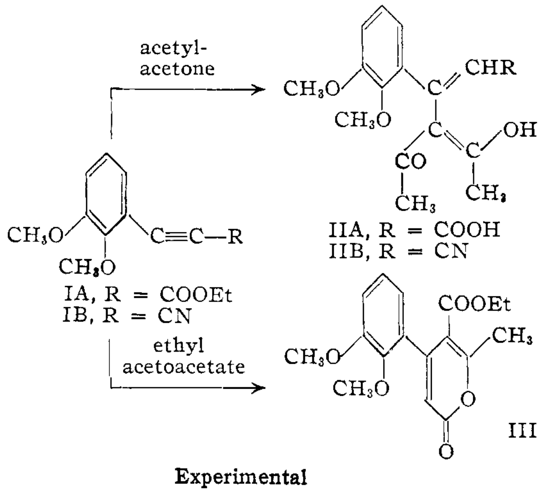
Condensation of esters of phenylpropiolic acid with ethyl acetoacetate[1] and acetylacetone[2] in the presence of sodium ethoxide leads to the formation of 4-phenyl-α-pyrones. Apparently the reaction consists in Michael addition of the methylene group of the diketone or keto ester to the triple bond 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.



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).

and refluxed for 1.5 hours. The supernatant solution was decanted, and the residue, remaining after distillation of the solvent, was distilled *in vacuo*. There was obtained 6.8 g. (46%) of crystalline material, b.p. 126–153° (1–2 mm.), sufficiently pure for further work. Recrystallization from hexane afforded colorless crystals, m.p. 52–55°.

Anal. Calcd. for $C_{11}H_9O_2N$: C, 70.53; H, 4.84. Found: C, 70.47; H, 4.85.

4-(2',3'-Dimethoxyphenyl)-5-carbethoxy-6-methyl-α-pyrone.—A solution of 2.4 g. of ethyl 2,3-dimethoxyphenylpropiolate and 2.0 g. of ethyl acetoacetate was treated with 0.25 g. of dry sodium ethoxide, and the mixture was heated on the steam-cone for 3.5 hours. After cooling, the mixture was taken up in cold water, and the neutral product was isolated as usual. Trituration with pentane gave 2.2 g. of crystals, m.p. 110–113°. Recrystallization from methanol led to colorless crystals, m.p. 114–116°.

Anal. Calcd. for $C_{17}H_{18}O_6$: C, 64.16; H, 5.70. Found: C, 63.94; H, 5.55.

The infrared spectrum (chloroform) had a peak at 5.8–5.85 μ.

Condensation of 3.2 g. of 2,3-dimethoxyphenylpropiolonitrile with 3.4 g. of ethyl acetoacetate in the presence of 0.4 g. of dry sodium ethoxide at 100° for 16 minutes afforded 0.5 g. of this α-pyrone and 3.5 g. of alkali-soluble, red oil. The latter material gave a purple color with ferric chloride and was gradually transformed to a tar upon exposure to air. It probably was an uncyclized addition product. Further treatment of the material with sodium ethoxide afforded additional pyrone, III.

An attempt to condense 2,3-dimethoxyphenylpropiolamide with ethyl acetoacetate in the presence of sodium ethoxide at 100° for 20 hours resulted in complete recovery of the amide.

Enol IIA.—A mixture of 10.5 g. of ethyl 2,3-dimethoxyphenylpropiolate, 7.0 g. of acetylacetone and 1.0 g. of dry sodium ethoxide was heated on the steam-cone for seven days. The reaction was quenched with cold water, and the aqueous solution was washed with ether. Acidification gave 4.8 g. of enol, m.p. 140–145°, after trituration with ether. Recrystallization from benzene gave colorless needles, m.p. 145.5–147°.

Anal. Calcd. for $C_{16}H_{18}O_6$: C, 62.74; H, 5.92. Found: C, 62.84; H, 5.85.

The compound gave a red-violet color with ferric chloride. The infrared spectrum (chloroform) had a band at 3.1–3.3 μ and a peak at 5.92 μ (bonded acid carbonyl).

Enol IIB.—A mixture of 3.4 g. of 2,3-dimethoxyphenylpropiolonitrile, 2.7 g. of acetylacetone and 0.35 g. of dry sodium ethoxide was heated at 100° for three hours. The mixture was treated with cold water, and the aqueous solution was washed with ether and acidified at ice temperature. The product was extracted with ether. The ether solution was dried over magnesium sulfate, and the ether was evaporated. Recrystallization from methanol afforded 2.7 g. of colorless crystals, m.p. 91.5–92.5°.

Anal. Calcd. for $C_{16}H_{17}O_4N$: C, 66.88; H, 5.97. Found: C, 66.64; H, 5.95.

This enol gave a dark red color with ferric chloride. The infrared spectrum (chloroform) had a peak at 4.55 μ. No peaks representative of hydroxyl or carbonyl groups were apparent.

The infrared spectra of IIA and IIB were virtually identical in the region 8–10 μ.

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The Preparation of the Methylmethoxygermanes

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Johnson and Fritz have recently reported the preparation and properties of seven germanium tetraalkoxides[1]; before their work only two such compounds, tetraethoxygermane[2] and tetraphenoxygermane,[3] were known. This paper reports the synthesis of the three methylmethoxygermanes. These compounds, which are apparently the first alkylalkoxygermanes to be reported, complete the series $(CH_3)_4Ge$–$Ge(OCH_3)_4$.

The methylmethoxygermanes are colorless mobile liquids, with faint pleasant odors, soluble in all organic solvents tried. They are hydrolyzed rapidly by water or moist air to polymeric alkylgermanium oxides. The compounds are monomeric in the vapor state, and unlike the methylchlorogermanes,[4] their boiling points increase almost regularly with increasing molecular weight.

Experimental[5]

Methyltrimethoxygermane.—The preparation was carried out in a 500-ml. flask fitted with a reflux condenser and a dropping funnel, both protected from atmospheric moisture with drying tubes. To a solution of 13.3 g. (0.58 gram atom) of sodium in 125 ml. of methanol was added dropwise 34.6 g. (0.178 mole) of methyltrichlorogermane.[6] The mixture was heated to reflux for two hours. The methanol solution containing the product was then filtered from the precipitated NaCl under reduced pressure, using a sintered glass filter tube. The product was separated from methanol by fractional distillation through a 40-cm. helix-packed column. The yield was 21.9 g., or 66%.

Anal. Calcd. for $C_4H_{12}GeO_3$: C, 26.58; H, 6.69; mol. wt., 181. Found: C, 26.59; H, 6.72; mol. wt., 181.

TABLE I

COMPOUNDS OF THE SERIES $(CH_3)_4Ge$–$Ge(OCH_3)_4$

Formula	B.p. °C.	B.p. Mm.	$n^{25}D$	d^{25}_4
$(CH_3)_4Ge$[7]	43.2	736	1.3863	0.9661
$(CH_3)_3GeOCH_3$	87–88	753	1.401	1.075
$(CH_3)_2Ge(OCH_3)_2$	118–118.5	763	1.4093	1.207
$CH_3Ge(OCH_3)_3$	136.5–138	760	1.4053	1.264
$Ge(OCH_3)_4$[1]	148–150	722	1.3968	1.325

Dimethyldimethoxygermane.—This compound was prepared from dimethyldichlorogermane[6] and sodium methoxide in 77% yield, in the same way as in the preparation of methyltrimethoxygermane.

Anal. Calcd. for $C_4H_{12}GeO_2$: C, 29.16; H, 7.34; mol. wt., 165. Found: C, 28.98; H, 7.38; mol. wt., 171.

Trimethylmethoxygermane.—A Grignard reagent solution prepared from 51 g. (0.40 mole) of methyl iodide was added with stirring to a solution of 66 g. (0.40 mole) of dimethyldimethoxygermane in 300 ml. of ethyl ether, under an atmosphere of nitrogen. After standing overnight, the ethereal solution was filtered from the precipitated magnesium salts under nitrogen and fractionally distilled. However, none of the expected trimethylmethoxygermane was isolated. Instead, 9.5 g. of impure trimethyliodogermane came over at 136° as a heavy oil which liberated iodine on standing. Titration with base gave 47.0% I; C_3H_9GeI requires 51.9%.

Six grams (0.024 mole) of this product was then treated with sodium methoxide in methanol as in the previous preparations. Fractional distillation now gave 2.0 g. (56%) of trimethylmethoxygermane.

Anal. Calcd. for $C_4H_{12}GeO$: C, 32.30; H, 9.14; mol. wt., 149. Found: C, 32.31; H, 9.40; mol. wt., 152.

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[3] R. Schwarz and W. Reinhardt, *Ber.*, **65**, 1745 (1932).

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