The compound is highly viscous, quite soluble in ether, insoluble in water and petroleum ether. It crystallizes from ether–petroleum ether solution in a dry-ice bath, remelting at once on removal from the bath, $n^{25}{}_D$ 1.5072.

Anal. Calcd. for $C_{16}H_{17}O_4N$: C, 66.9; H, 5.9. Found: C, 66.5; H, 6.1.

Furfurylaminoacetic Acid.—Ethyl furfurylaminoacetate was boiled with ten times the quantity of water until solution was complete (about two and one-half hours). The solution was evaporated to incipient dryness, the residue dissolved in a minimal quantity of water and precipitated in the form of fine needles by the addition of ten volumes of dioxane. It may be recrystallized from boiling alcohol or from four parts of hot water, the latter producing thick, transparent prisms: m. p. 210–212° (corr.) in preheated baths. Slow heating results in much decomposition starting at about 180°.

Anal. Calcd. for $C_7H_9O_3N$: C, 53.8; H, 5.80; N, 9.03. Found: C, 53.7; H, 5.72; N, 8.94.

Ethyl Difurfurylaminoacetate.—B. p. 154–157° at 3 mm.; $n^{25}{}_D$ 1.4691; $d^{25}{}_{20}$ 1.135; m. p. of hydrochloride, 94–96° (corr.) (recrystallized from absolute ethanol and ether). The ester is soluble in most organic solvents.

Anal. Calcd. for $C_{14}H_{17}O_4N$: N, 5.3. Found: N, 5.6.

Difurfurylaminoacetic Acid.—The preceding ester was hydrolyzed by two methods: (A) 1 g. of ester was boiled for fifteen minutes with 3 g. of barium hydroxide octahydrate and 5 cc. of water. The barium was removed in the usual manner and the filtrate evaporated nearly to dryness; (B) 1 g. of ester was boiled with 5 cc. of 24% sodium hydroxide until solution was complete (ten minutes). It was cooled at once and an equivalent quantity of sulfuric acid was added. After evaporation to dryness the product was extracted with hot ethanol, from which it crystallizes on cooling. It may be recrystallized from hot water, or more conveniently from 10 parts of ethanol and decolorizing with bone black. It is insoluble in ether and benzene; m. p. 140–141° (corr.).

Anal. Calcd. for $C_{12}H_{13}O_4N$: C, 61.3; H, 5.53; N, 5.95. Found: C, 61.3; H, 5.60; N, 6.04.

The authors are indebted to Mr. Saul Gottlieb for the microanalyses of these compounds.

Summary

The following derivatives of glycine have been synthesized by the use of furfuryl bromide, and their properties reported: ethyl furfurylaminoacetate, ethyl benzoylfurfurylaminoacetate, furfurylaminoacetic acid, ethyl difurfurylaminoacetate and difurfurylaminoacetic acid.

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[CONTRIBUTION FROM THE WILLIAM H. CHANDLER CHEMISTRY LABORATORY, LEHIGH UNIVERSITY]

The Preparation of 2-Furanacetic Acid

BY JULIUS PLUCKER, III, AND E. D. AMSTUTZ

In the course of other work to be reported shortly, it became necessary to prepare considerable quantities of 2-furanacetic acid. This compound is not accessible by the usual avenues of approach[1] and, although it has been prepared in several ways,[2] either the methods are inconvenient or the yields are low.[3] It was therefore thought to be of interest to investigate the applicability of the rhodanine method.

Julian and Sturgis[4] have repeated some of the elegant work of Gränacher[5] on the aldehyde-rhodanine condensation products and have shown that the rhodanine method offers a valuable way of preparing the acids of one more carbon atom. Gränacher condensed furfural with rhodanine[5] and cleaved the resulting product with alkali to give β-2-furyl-α-thioketopropionic acid (II) which in turn was converted to the oximino acid (IV). In order to prove the applicability of this method therefore it was necessary only to determine whether the oximino acid could be satisfactorily decarboxylated and dehydrated to furanacetonitrile (V). This has been done and it was found that the desired nitrile is obtained in yields consistently above 80% of the theoretical. In this connection it is interesting to note that furanacetaldoxime (VII) is reported to yield only a small amount (12–15%) of the same nitrile on dehydration under essentially the same conditions.[2b] Following is a summary of the reactions involved in the rhodanine method

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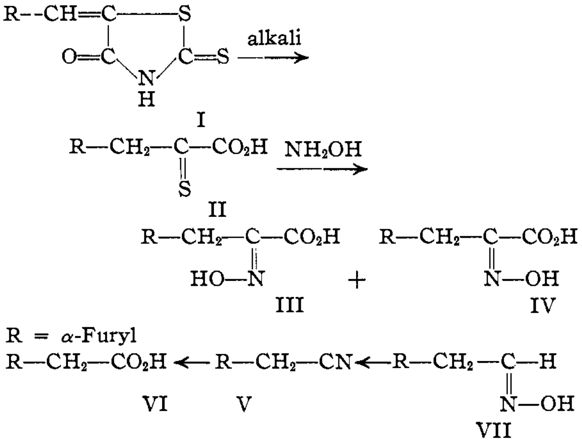
[1] (a) Johnson and co-workers, THIS JOURNAL, **52**, 1284 (1930), and Reichstein, *Ber.*, **63B**, 749 (1930), have shown that when furfuryl chloride is treated with aqueous potassium cyanide the product is composed mainly of 5-methyl-2-furonitrile instead of the expected 2-furanacetonitrile. (b) Gilman, *Rec. trav. chim.*, **51**, 93 (1932), has found that furfuryl chloride could not be made to undergo a smooth reaction leading to the Grignard reagent which, if formed, would be expected to yield the desired acid on carbonation.

[2] By the following reaction sequences: (a) Reichstein, ref. 1a; furoyl chloride → furoyl cyanide → furoyl formic acid → furanacetic acid. Sodium furylglycidate → furanacetaldehyde → furanacetic acid. (b) Johnson, ref. 1a; furfural → furyl nitro ethylene → furanacetaldoxime → furanacetonitrile → furanacetic acid.

[3] R. Robinson, *J. Chem. Soc.*, 718 (1937), mentions the lack of a satisfactory method of preparation of 2-furanacetic acid.

[4] THIS JOURNAL, **57**, 1126 (1935).

[5] *Helv. Chim. Acta*, **5**, 610 (1922).



The oxime of 2-furanpyruvic acid was obtained in two forms, both light yellow microcrystalline powders, m. p. 127–128° dec.[6] and m. p. 143.8–144° dec., tentatively designated[7] as compounds III and IV, respectively. The lower melting form is the more soluble and reacts the less vigorously with acetic anhydride but gives essentially the same yield of the nitrile as the higher melting form. They were not investigated further.

Experimental[8]

Fufuralrhodanine (m. p. 229–231° dec.; yield, 94%) was prepared and cleaved with alkali to 3-α-furyl-2-thioketopropionic acid (m. p. 114.6–115°; yield, 99%) according to the directions of Julian and Sturgis.[4]

3-α-Furyl-2-oximinopropionic Acid.—A solution of 26.6 g. of thioketo acid and 16 g. of hydroxylamine (from 33.8 g. of the hydrochloride and 11.3 g. of sodium) in 325 cc. of absolute ethyl alcohol was refluxed for one-half hour and distilled under diminished pressure till all the alcohol was removed. The brown solid remaining was dissolved in 80 cc. of 5% sodium hydroxide solution and filtered free of sulfur. Cautious acidification of the cooled filtrate with 75 cc. of 10% hydrochloric acid precipitated 8.5 g. (32%) of the acid as a light brown powder, m. p. 143.8–144° dec.; reported, m. p. 145°.[4] The filtrate was extracted with five 50-cc. portions of ether which were combined, dried over anhydrous magnesium sulfate and evaporated. There was obtained in this way an additional 13 g. (49.5%) of acid, m. p. 127–128° dec.; total yield, 21.5 g. or 81.5% of the theoretical.

In a run with twice the quantities used above the alkaline solution of the acid was acidified to congo red in the cold under ether. There was obtained a yield of 49.1 g. (93%) of acid, m. p. 121.5–122° dec.

2-Furanacetonitrile.—A mixture of 49.1 g. of oximino acid (m. p. 121.5–122.0°) and 237 g. of acetic anhydride was warmed till effervescence set in. Upon cessation of the vigorous reaction the dark reddish solution was rapidly steam distilled. The steam distillate was extracted with 300 cc. of ether in several portions which were combined, washed to neutrality with sodium carbonate solution, dried over anhydrous magnesium sulfate and distilled. There was obtained a yield of 27.3 g. (87.7%) of nitrile, b. p. (17 mm.) 84°, n^{25}_{D} 1.4691; reported,[1a] b. p. (20 mm.), 78–80°, n^{25}_{D} 1.4715.

The oximino acid (11.7 g.), m. p. 127–128°, gave 6.1 g. or an 82.5% yield of the nitrile and 7.3 g. of the acid, m. p. 143.8–144°, gave 3.5 g. or 76%. The use of a smaller quantity of the higher melting material is thought to explain the discrepancy in yields.

Hydrolysis of the nitrile in the customary way with 18% aq. potassium hydroxide gave 96% of the theoretical yield of 2-furanacetic acid, white leaflets, m. p. 66.8–67.5° (crude); m. p. authentic specimen,[9] 67–67.5°; mixed m. p. 66.5–67°.

The over-all yield of 2-furanacetic acid from furfural is about 73% of the amount required by theory.

Summary

It has been shown that 2-furanacetic acid may be conveniently prepared in very satisfactory yield from furfural by the rhodanine method.

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[6] All m. p.'s uncorrected.

[7] On the basis of Hantzsch's work on the configuration of oximes, *Ber.*, **25**, 2164 (1892). See also, "Organic Chemistry, An Advanced Treatise," H. Gilman, Ed., p. 391.

[8] The authors are indebted to Dr. F. N. Peters and the Quaker Oats Company for their generous donation of the furfural used in this work.

[9] Prepared by the reaction of α-furfuryl chloride with cuprous cyanide in acetonitrile; Johnson and Amstutz, unpublished data.