of the distillation residue and treatment of the extract with alcoholic picric acid. The total yield of picrate is 0.3 g. (0.66%).

Total Dehydrogenation with Selenium.—3-*p*-Tolylmenthene-3 (22.8 g., 0.1 mole) is dehydrogenated with 32 g. of selenium added over thirty-six hours. Heating for an additional seventy-two hours with gradual increase of the temperature from 290 to 360° gives a product which on ether extraction and distillation yields: 3,4[1]-dimethyl-6-isopropyldiphenyl, 3.0 g.; 2,6,9,9-tetramethylfluorene, 4.0 g.; fraction 130–210°, 1.5 g. From the latter and also the distillation residue 0.9 g. of picrate, m. p. 169–170°, is obtained (yield, 2%).

2,6,9-Trimethylphenanthrene.—The hydrocarbon is obtained from its picrate by the method described in the previous paper: yield, 1.4% of calculated from 3-*p*-tolylmenthene-3; m. p. 78.5°. Both the picrate and the hydrocarbon show no depression in mixed melts with the corresponding products from dipinene dehydrogenation.

2,6,9,9-Tetramethylfluorene.—B. p. 123–125° (2 mm.); d^{25}_4 0.9893; $n^{25}D$ 1.5811; mol. wt. (Rast, camphor) 225, calcd. 222. *Anal.* Calcd. for $C_{17}H_{18}$: C, 91.89; H, 8.11. Found: C, 91.80; H, 8.20. Monobromo derivative, m. p. 94.5°. *Anal.* Calcd. for $C_{17}H_{17}Br$: C, 67.77; H, 5.64. Found: C, 67.75; H, 5.15. Dinitro derivative (mixed acid at room temperature), m. p. 218° (from alcohol). *Anal.* Calcd. for $C_{17}H_{16}N_2O_4$: N, 8.97. Found: N, 9.15.

Summary

2,6,9-Trimethylphenanthrene has been synthesized, characterized, and shown to be identical with the product of dipinene dehydrogenation.

WASHINGTON SQUARE COLLEGE
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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF COLUMBIA UNIVERSITY]

Mono- and Di-α-furfuryl Glycines

BY J. E. ZANETTI AND J. T. BASHOUR

We have shown the pronounced reactivity of furfuryl bromide in ether solution on the amino group[1] and it appeared of interest to investigate whether the neighboring presence of a carbethoxy group would influence the reaction. Accordingly we have studied its action on the amino group of α-aminoacetic ethyl ester and found it to proceed quite satisfactorily. The free α-furfurylamino acid can be obtained readily from the ester by hydrolysis. We have found that excess of the ethyl aminoacetate to liberate the furfuryl addition compound from its hydro bromide gave better results than the use of sodium or potassium hydroxides for similar purposes. The reaction may then be written as

$$C_4H_3OCH_2Br + 2NH_2CH_2COOC_2H_5 \longrightarrow C_4H_3OCH_2NHCH_2COOC_2H_5 + NH_2HBrCH_2COOC_2H_5$$

The glycine ester hydrobromide precipitates out of the ether, leaving in solution the furfuryl glycine ethyl ester.

As explained in the experimental part, both the mono- and di-α-furfurylglycines can be obtained in one operation by using varying ratios of α-furfuryl bromide to the amino acetate, a procedure which we found unsatisfactory when working with free amines.

Experimental

The general procedure was similar to that already described for the preparation of furfurylalkyl amines.[1] The hydrobromide precipitated and was filtered off in the usual manner. It was also found that the difurfurylaminoacetic ester could be obtained in one operation by slightly increasing the ratio of furfuryl bromide to amine. Two and one-half cc. of ethyl aminoacetate per cc. of furfuryl alcohol used in the bromide synthesis, gives a product consisting of 80% monofurfuryl derivative and 20% difurfuryl derivative. Two cc. of amine per cc. of furfuryl alcohol resulted in approximately equivalent quantities of secondary and tertiary products. Yields were over 80% on the basis of 70% yield of furfuryl bromide.

Ethyl aminoacetate was prepared from glycine through the ester hydrochloride by the methods of Curtius[2] and Fischer.[3] Over-all yields of 65% were readily obtained.

Ethyl Furfurylaminoacetate.—In contrast to glycine ester, this product is quite stable, long standing causing only a slight yellowing with very slight decomposition as determined by redistillation. No diketopiperazine formation was observed. It is soluble in most organic solvents: b. p. 99–101° at 3 mm.; $n^{25}D$ 1.4735; d^{25}_{20} 1.096. The hydrochloride melted at 68–70°. It was recrystallized from absolute alcohol by addition of absolute ether to incipient cloudiness.

Anal. Calcd. for $C_9H_{13}O_3N$: N, 7.65. Found: N, 7.70.

Ethyl Benzofurfurylaminoacetate.—Three cc. of ethyl furfurylaminoacetate was dissolved in 4.2 cc. of benzoyl chloride with cooling in an ice-bath. Thirty cc. of 2.5 *N* sodium hydroxide, ice-cold, was added at once and the mixture shaken for twenty minutes. Ether was added and the aqueous layer discarded. The ether layer was washed with dilute hydrochloric acid and water, and dried overnight with sodium sulfate. After removal of the ether, the product was collected at 157–162° at approximately 1 mm.

(1) Zanetti and Bashour, THIS JOURNAL, **61**, 3133 (1939); **62**, 742 (1940).

(2) Curtius and Goebel, *J. prakt. Chem.*, *N. F.*, **37**, 159 (1888).

(3) Fischer, *Ber.*, **34B**, 436 (1901).

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

(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).