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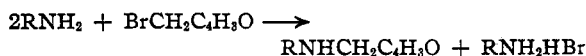
Secondary Alpha Furfuryl Amines

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

Little has been published on secondary furfuryl amines. The methyl and ethyl furfuryl amines were first prepared by Schwabbauer,¹ by the reduction of the condensation products of methyl and ethyl amine with furfural. This work was repeated by Litterschied.² No further work was done on these compounds until 1921 when von Braun and Braunsdorf³ stated that they had prepared the furfurylethylamine by the action of furfuryl bromide on ethylamine but did not describe their procedure. The Goodyear Tire and Rubber Company⁴ took a patent in 1934 for a method of preparing secondary furfuryl amines by reducing the corresponding condensation products of amines and furfural with hydrogen under pressure but although their claims extend to a large number of amines, the only product described was the di- α -furfurylamine which had been prepared by Zanetti and Beckmann⁵ by the action of furfuryl bromide on ammonia.

In connection with a study of furfuryl bromide already published in part it seemed of interest to study its reactions on amines which had been but briefly touched upon by von Braun and Braunsdorf. In this study we employed the ether solution of α -furfuryl bromide since as we have demonstrated the pure product is so unstable as to be unmanageable.⁶

The action of the bromide on a primary amine in ether solution is rapid. In a few minutes a crystalline precipitate appears which we thought at first was the hydrobromide of the secondary amine but proved to be the hydrobromide of the primary amine, the action proceeding according to the equation



The secondary amine being a much weaker base than the primary amine is released from its hydrobromide formed by the addition of the furfuryl bromide, by the primary compound. In order, therefore, to make the addition complete

mole with mole we carried the reaction in the presence of potassium hydroxide, which proved to be a satisfactory method. The yields were only fair, varying from 50 to 65% assuming the yield of the bromide to be 70% of theoretical. In all cases varying amounts of what appears to be the tertiary amines were formed but these condensation products have not yet been investigated.

The secondary amines are colorless liquids turning yellowish in a few days as do most furan compounds, except α -furfurylphenylamine, which is yellow even when repeatedly distilled. They are soluble in ethanol, ether, acetone, carbon tetrachloride, but only slightly soluble in boiling petroleum ether. The specific gravities and the indices of refraction of these compounds, none of which has been previously reported, are given in Table I.

TABLE I

Amine	B. p. °C.	Mm.	Sp. gr., 25/25	n_D^{20}	M. p. of hydrochloride, °C.
α -Furfurylmethyl	149-149.5	761	0.992	1.4729	144-146
α -Furfurylethyl	165-167	761	.963	1.4688	127-128
α -Furfuryl- <i>n</i> -butyl	198-200	768	.935	1.4669	189-191
α -Furfuryl- <i>n</i> -amyl	214-216	756	.927	1.4668	185-188
α -Furfurylphenyl	109-110	0.5	1.110	1.5834	150-151, dec.

The amines decompose slightly when boiled under ordinary atmospheric pressure but distil readily under reduced pressure. The boiling point of the phenylamine derivative could not be determined as at atmospheric pressure decomposition is too great.

These amines readily form hydrochlorides and the aliphatic ones also form picrates. The furfurylphenylamine, however, did not form a picrate.

Experimental

General Procedure.—The ethereal furfuryl bromide solution was added at once to the ethereal solution of the amine standing over crushed potassium hydroxide. The mixture was stirred continuously from one to two hours and then allowed to stand overnight. After filtration and washing of the potassium hydroxide and bromide with ether, the ether was distilled off and products separated by fractional distillation *in vacuo*.

Furfurylmethylamine, $\text{C}_4\text{H}_3\text{OCH}_2\text{NHCH}_3$.—Methylamine was generated from the hydrochloride (81 g.) by the addition of 50% potassium hydroxide solution. The

(1) Schwabbauer, *Ber.*, **35**, 410 (1902).(2) Litterschied, *Ann.*, **335**, 368 (1904).(3) Von Braun and Braunsdorf, *Ber.*, **54**, 2081 (1921).

(4) Brit. Pat. No. 412,914, July 2, 1934.

(5) Zanetti and Beckmann, *This Journal*, **50**, 2031 (1928).(6) Zanetti and Bashour, *ibid.*, **61**, 2249 (1939).

vapors were driven through an upright water-cooled condenser, a long drying tube containing potassium hydroxide pellets into a receiver containing crushed potassium hydroxide (80 g.) covered with dry ether, the receiver being immersed in a dry-ice-ethylene trichloride bath. Heating was continued until the bulk of the amine had distilled over. Furfuryl bromide solution (prepared according to the method of Zanetti⁷ from 38 g. of furfuryl alcohol) was cooled to minus 10° and siphoned into the solution of the amine. The mixture was rocked for several minutes, then removed from the bath and shaken frequently for two hours. It was then allowed to stand overnight. After filtration, the ether was removed by distillation and the product was fractionally distilled *in vacuo*. The fraction boiling 50–57° at 16.5–18 mm. was redistilled; yield, 15 g. (50% of theoretical, assuming 70% yield of bromide). As this amine had been prepared before no analysis was made.

Furfurylethylamine, $C_6H_5OCH_2NHC_2H_5$.—Ethylamine was generated from the hydrochloride (50 g.) in an apparatus consisting of the following train: an ordinary distilling flask equipped with a dropping funnel, a long slightly inclined drying tube containing potassium hydroxide pellets, a water-cooled condenser, and the same receiver as in the preparation of the methylamine. The ethereal furfuryl bromide solution prepared from 25 g. of furfuryl alcohol and precooled to minus 10° was introduced by siphon as before, and the product separated as in the preceding case. The fraction boiling at 63–65° at 17–18 mm. was redistilled; yield, 13 g. (58% on basis of 70% yield of the bromide). This amine having been prepared previously no analysis was made.

Furfurylbutylamine, $C_6H_5OCH_2NHC_4H_9$.—Twenty-five grams of normal butylamine, previously dried over potas-

sium hydroxide and distilled, was added at once to a 20-g. batch of the ethereal furfuryl bromide solution over 50 g. of crushed potassium hydroxide. The whole was stirred for one hour and then allowed to stand overnight. After filtration and removal of the ether, the fraction boiling at 92–95° at 16–18 mm. was redistilled; yield, 13 g. (60% on basis of 70% yield of furfuryl bromide).

Anal. Calcd. for $C_{10}H_{14}ON$: C, 70.58; H, 9.80; N, 9.15. Found: C, 70.40; H, 9.96; N, 9.29.

Furfurylamylamine, $C_6H_5OCH_2NHC_5H_{11}$.—The procedure was similar to the preceding: 8 g. of amylamine and a 4-g. batch of the furfuryl bromide solution were used. The fraction boiling at 108–111° at 16–18 mm. was redistilled; yield, 3.0 g. (65% on basis of 70% yield of bromide).

Anal. Calcd. for $C_{16}H_{21}ON$: N, 8.48. Found: N, 8.66.

Furfurylphenylamine, $C_6H_5OCH_2NHC_6H_5$.—Forty-five grams of aniline and a 20-g. batch of furfuryl bromide were used in this case. On distillation, the main fraction came over at 113–120° at approximately 1 mm. On redistillation this fraction boiled at 109–110° under 0.5 mm.

Anal. Calcd. for $C_{11}H_{11}ON$: C, 76.30; H, 6.36; N, 8.09. Found: C, 76.51; H, 6.47; N, 8.26.

Summary

1. The action of α -furfuryl bromide in ether solution on primary amines has been studied and found to form secondary amines.

2. The methyl, ethyl, butyl, amyl and phenyl α -furfuryl amines have been prepared by the above method and their properties reported.

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(7) Zanetti, *THIS JOURNAL*, **49**, 1065 (1927).

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Derivatives of Aminomethanethiol

BY ARTHUR BINZ AND LELAND H. PENCE

Hydroxymethanethiol, $HOCH_2SH$, was assumed by Baumann¹ to be formed as an unstable intermediate on treating formaldehyde with hydrogen sulfide, and he showed that the reaction proceeds to insoluble trithioformaldehyde, $HCHO + H_2S \rightarrow HOCH_2SH \rightarrow (CH_2S)_3$. Since trithioformaldehyde because of its low solubility and reactivity is of no particular interest for biochemical research, it was considered advantageous to investigate hydroxymethanethiol, either as such or in the form of easily soluble and reactive products obtained from it. For these reasons Binz, R  th, and Walter² attempted to isolate hy-

droxymethanethiol by reducing formaldehyde-sulfoxylate with hypophosphorous acid, $HOCH_2SO_2H \rightarrow HOCH_2SH$, and obtained a product which appeared to be the desired thiol, but the yield was very small.

In taking up this work again we endeavored to obtain a derivative of the corresponding aminomethanethiol which would be stable, by first condensing formaldehyde-sulfoxylate with piperidine and then reducing the product with hypophosphorous acid in the presence of hydriodic acid according to the reaction $C_6H_{10}NCH_2SO_2H \rightarrow C_6H_{10}NCH_2SH$. Hydrogen sulfide was also used as a reducing agent, but in both cases the yields of a compound showing the reactions of a thiol were very small.

(1) Baumann, *Ber.*, **23**, 1869 (1890).

(2) Binz, R  th and Walter, *ibid.*, **57**, 1398 (1924).