and tricarballylic acids. A small quantity of an unknown acid represented by a hydrazide melting at 173–175° was found.

WASHINGTON, D. C.

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ALPHA-FURFURYL AMINES

BY J. E. ZANETTI AND C. O. BECKMANN

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The furfuryl amines have been but little investigated. Wallach[1] was the first to prepare α-furfuryl amine by the reduction of α-furoylnitrile with zinc and sulfuric acid. Tafel[2] prepared it also by the reduction of phenylfurfurazide with sodium amalgam in alcohol solution and Goldschmidt[3] by the reduction of furfuraldoxime. Since then but little work has been done upon them[4] until recently Williams[5] prepared the hydrochloride of di-α-furfuryl amine by reducing furfuraldoxime with palladinized animal charcoal and hydrogen.

One of the reasons which has held back synthetic work in this field has been the absence of a convenient method of preparing the 2-methyl halogen furans. Since one of us[6] developed recently a convenient method of preparing α-furfuryl bromide in its ether solution, the ordinary methods of preparing these amines have become applicable.

The synthesis of the mono-, di- and tri-α-furfuryl amines was accomplished by a method similar to that employed in preparing the benzyl amines,[7] namely, by adding a solution of α-furfuryl bromide in ether to absolute alcohol saturated with dry ammonia gas (for details see experimental part). On allowing to stand for several days, a mixture of the three amines was obtained which was then fractionated.

The yields were very poor and considerable amounts of tarry material were obtained. We have been able, however, to prepare the three amines in a pure condition and have identified them by preparing some of their derivatives.

The amines when freshly distilled are colorless, oily liquids with an ammoniacal odor but rapidly turn yellow. They do not crystallize even when cooled in liquid air, passing through stages of increasing thickening

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[1] Wallach, *Ber.*, **14**, 752, 1058 (1881); *Ann.*, **214**, 227 (1882); Ciamician and Dennsted, *Ber.*, **14**, 1059, 1475 (1881).

[2] Tafel, *Ber.*, **20**, 399 (1887).

[3] Goldschmidt, *Ber.*, **20**, 730 (1887).

[4] Marquis, *Compt. rend.*, **136**, 1454 (1903).

[5] Williams, *Ber.*, **60B**, 2509 (1927).

[6] Zanetti, THIS JOURNAL, **49**, 1066 (1927).

[7] Mason, *J. Chem. Soc.*, **63**, 1311 (1893); Limpricht, *Ann.*, **144**, 305 (1867); Cannizzaro, *Ann. Suppl.*, **4**, 24 (1865).

until they finally solidify to a glassy mass with no trace of crystallization. They show the ordinary properties of amines, giving well defined salts and addition compounds with gold and platinum chlorides.

Williams[5] obtained the hydrochloride of di-α-furfuryl amine in what appears to us to be an impure condition. He gives a melting point of 170–172°, whereas we have prepared a product melting at 186–187°. The salt prepared by him was yellow in color whereas ours is pure white. Our chlorine determinations give us a higher chlorine content and a further determination of nitrogen leaves no doubt that our compound was quite pure. We had, moreover, no difficulty in preparing the gold and platinum chloride salts, whereas he states that his hydrochloride reduced the platinum chloride to platinum.

Since α-furfuryl amine has already received considerable attention, we have confined ourselves to the preparation of derivatives of the di- and tri-α-furfuryl amines and merely report the synthesis of the mono-α-furfuryl amine by the new method.

Experimental

Preparation of the Amines.—An ether solution of α-furfuryl bromide was prepared from 80 g. of α-furfuryl alcohol and 80 g. of phosphorus tribromide by the method of Zanetti. The best results were obtained when this was made in two parts. This ether solution was added in small portions with cooling to 1 liter of absolute alcohol saturated with ammonia at 0° (about 100–110 g. of NH_3). The mixture was allowed to stand in the cold for one week. The alcohol and excess ammonia were evaporated under reduced pressure and the residue, consisting of the amine hydrobromides and ammonium bromide and probably some α-furfuryl ethers, was treated with dilute sodium hydroxide in the cold. The mixture was extracted with ether, dried and distilled. α-Furfuryl amine distilled over at 144–146° at 760 mm. Distillation was continued under reduced pressure. During this distillation no attempt was made to separate the secondary and tertiary amines. The distillate, consisting of the two amines with some furfuryl ethers, was dissolved in anhydrous ethyl ether. Dry hydrogen chloride was passed through this solution to precipitate the amine hydrochlorides. These were filtered off and washed with ether; yield about 15 g.

The amine hydrochlorides were dissolved in water, dilute sodium hydroxide added in the cold, the mixture extracted with ether, dried and distilled. The amines were separated by fractional distillation under vacuum. Di-α-furfurylamine boils at 102–103° at 1 mm., tri-α-furfurylamine at 136–138° at 1 mm. The amines are colorless oils which turn yellow on standing. Analyses are recorded in Table I.

Table I

Analyses

	Amine		Hydrochloride		Chloroplatinate		Chloro-aurate	
	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
Difurfuryl amine	C, 67.80	67.35	Cl, 16.62	16.49	$C_{20}H_{24}O_4N_2PtCl_6$		$C_{10}H_{12}O_2NAuCl_4$	
$C_{10}H_{11}O_2N$		67.37		16.54	Pt, 25.55	25.45	Au, 38.11	37.99
	H, 6.21	6.38	N, 6.56	6.75				
		6.30	M. p., 186–187°					
Trifurfuryl amine	C, 70.04	69.83	Cl, 12.08	12.01	$C_{30}H_{32}O_6N_2PtCl_6$		$C_{15}H_{16}O_3NAuCl_4$	
$C_{15}H_{15}O_3N$		69.98		12.06	Pt, 21.20	21.18	Au, 33.00	33.24
	H, 5.84	6.04	N, 4.77	4.81				
		5.78	M. p., 156–157°					

Preparation of the Hydrochlorides.—The amines were dissolved in anhydrous ethyl ether and dry hydrogen chloride was passed through the solution. White crystals precipitated; these were filtered off and washed with ether. They were recrystallized by dissolving in the least amount of absolute alcohol possible and precipitating with anhydrous ether. They are white crystalline compounds. Analyses are recorded in Table I.

Preparation of the Chloroplatinates.—The amines were dissolved in small amounts of concd. hydrochloric acid and the theoretical amount of chloroplatinic acid added. Upon stirring and scratching the glass dish, the chloroplatinates crystallized out. The chloroplatinate of the di-α-furfuryl amine crystallized in red crystals, while that of the tri-α-furfuryl amine formed orange crystals. Analyses are recorded in Table I.

Preparation of the Chloro-aurate.—The method is the same as for the chloroplatinates. Both chloro-aurates are yellow, crystalline solids.

Summary

1. The mono-, di- and tri-α-furfuryl amines have been prepared in a pure condition and their properties, as well as those of some of their salts, are reported.

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NEW DERIVATIVES OF BARBITURIC ACID

BY ARTHUR W. DOX AND EDWARD G. JONES

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Although more than sixty 5,5-dialkyl and 5,5-arylalkyl derivatives of barbituric acid, exclusive of homologs with further substitution on the nitrogen or substitution of oxygen or halogen in one or both of the alkyls, have been described, their variations in hypnotic potency and type of action are sufficient to warrant the preparation of additional members of the series as new alkyl halides become available. Among the alcohols which until very recently have not been obtainable for the preparation of halides required for such syntheses are tetrahydrofurancarbinol and *n*-amyl alcohol. The present paper describes the preparation of certain 5,5-disubstituted barbituric acids containing a tetrahydrofuranmethyl or a *n*-amyl group.

Tetrahydrofuranmethyl Bromide.—The alcohol used was a pure preparation supplied by the Miner Laboratories of Chicago. Although this alcohol, in contrast to the non-hydrogenated furancarbinol, is quite stable under ordinary conditions of light, air and moisture, it was found to be unstable to mineral acids, in the presence of which it showed a strong tendency to form tarry products. For this reason the yields of bromide obtained by treatment with hydrobromic acid, with or without sulfuric acid, or with phosphorus tribromide were small. The best yield of bromide thus far obtained was only 25%. It is not improbable that the yield might be much improved by suitable modifications of the usual methods of preparing alkyl bromides. The product was