

and ethylamine hydrochloride decomposed on distillation at 1 mm. pressure.

5-Dimethylaminomethylfurfuryl Alcohol.—The amine was prepared in 12% yield from furfuryl alcohol, formaldehyde and dimethylamine hydrochloride by the method described previously¹; b. p. 110–111° (3 mm.), n_D^{25} 1.4968, d_{25}^{25} 1.07. Calcd. for $C_8H_{13}NO_2$: N, 9.0. Found: N, 9.1.

The compound was completely soluble in water. The hydrochloride crystallized as prisms from alcohol melting at 120–121°, and is hygroscopic. Calcd. for $C_8H_{14}NO_2Cl$: N, 7.3; Cl, 18.6. Found: N, 7.5; Cl, 18.6.

5-N-Morpholinomethylfurfuryl Alcohol.—This compound is a very viscous, light yellow oil that was prepared in 42% yield: b. p. 128–130° (1 mm.), n_D^{30} 1.5195; 134–135° (2 mm.), d_{20}^{20} 1.12. Calcd. for $C_{10}H_{15}NO_3$: N, 7.1. Found: N, 6.9.

This amine was also completely soluble in water. The hydrochloride crystallized as plates from alcohol that melted at 136–136.5°. Calcd. for $C_{10}H_{16}NO_3Cl$: N, 6.0; Cl, 15.2. Found: N, 5.9; Cl, 15.4. The salt is very deliquescent.

The author wishes to thank the Quaker Oats Co. for a generous supply of furfuryl alcohol and furoic acid.

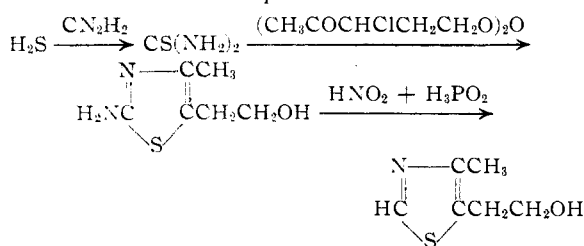
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The Reduction of 2-Amino-4-methyl-5- β -hydroxyethylthiazole in the Synthesis of Thiamin

BY J. B. HATCHER¹

In the course of studies involving the use of thiamin labelled with radioactive sulfur² the low yields, as based on sulfur, of the usual synthesis resulted in samples of the vitamin very weak in radioactivity. It is felt desirable to record the preliminary work, discontinued at the beginning of the war, which indicated the feasibility of an alternative synthesis for the thiazole portion of the vitamin. The steps are



Experimental

The first step was not studied, but should offer no particular difficulties in obtaining high yields since there are no significant side reactions. The second step was found to give yields of 80% when an excess of the acetopropyl ether was slowly run into an aqueous solution of thiourea at 100°. The third step is essentially new, since the literature records an impressive list of failures with this type reaction with various amino thiazoles. However, the first trials of the reaction step above gave good yields, *e. g.*, 31%, as follows: 2 g. of the aminothiazole dihydrochloride was dissolved in about 15 ml. of 12 *N* hydrochloric acid in a 50-ml. Erlenmeyer flask and cooled to 0° by swirling in an ice-bath. An equivalent amount (4.1 ml.) of 2 *M*

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(2) Buchman, Hatcher, Yost, and McMillan, *Proc. Natl. Acad. Sci.*, **26**, 412 (1940).

sodium nitrate solution was run in slowly drop by drop with vigorous shaking and swirling of the flask. Fifteen ml. of 30–32% H_3PO_2 was then added slowly, with the flask still in the ice-bath, and finally the mixture was allowed to warm to room temperature. It was then made alkaline with 6 *N* sodium hydroxide and diluted to about 1 liter, and extracted with five 10-ml. portions of ethyl ether. The ether extracts were combined, evaporated on a hot-plate to about 10 ml. and transferred to a distilling flask. The remainder of the ether was removed under vacuum at room temperature, and the residue vacuum distilled at 120–130° giving 0.38 g. of a colorless liquid. This liquid gave a picrate melting at 162° (uncor.) and the picrate gave no depression of the melting point when mixed with a sample of the picrate prepared from the pure thiamin thiazole prepared by the usual methods.

On the basis of these results it was concluded that the proposed synthesis would offer considerable advantages in the preparation of vitamin B₁ for the purposes, and that the removal of amino groups from thiazoles by diazotization and reduction is by no means as difficult as the literature indicates.

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2-Octyl Nitrite

BY NATHAN KORNBLUM AND EUGENE P. OLIVETO

In the course of another investigation it became necessary to know the refractive index, density, and boiling point of 2-octyl nitrite. Since the literature does not contain definitive values for these constants (*cf.* Table I) this compound was prepared by two different procedures, one involving the action of nitrosyl chloride on a pyridine solution of 2-octanol and the other the interaction of 2-octanol with sodium nitrite and sulfuric acid. The samples of 2-octyl nitrite thus obtained had n_D^{20} 1.4082 and 1.4083; d_4^{20} 0.8644 and 0.862, respectively, which values are distinctly different from those in the literature.^{1–5} Upon analysis of these preparations the correct carbon, hydrogen and nitrogen values were found.

TABLE I

Compound nitrite	B. p., °C. (mm.)	n_D^{20}	Density	Ref.
<i>dl</i> -2-Octyl	165–166°	d_4^0 0.881	1
<i>dl</i> -2-Octyl	65 (15)	d_4^0 .879	2
<i>l</i> -2-Octyl	63–65 (15)	1.4202 ^a	$d_4^{18.4}$.861	3
<i>l</i> -2-Octyl	85–90 (18)	1.4218	d_{20}^{20} .857	4
<i>l</i> -2-Octyl	70–75 (18)	1.4270	d_{20}^{20} .852	5
<i>d</i> -2-Octyl	70–75 (18)	1.4270	d_{20}^{20} .852	5
<i>dl</i> -2-Octyl	72–74 (18)	1.4272	d_{20}^{20} .852	5
<i>d</i> -2-Octyl	86–90 (18)	1.4279	d_{20}^{20} .852	4

^a Taken at 18.5°.

The nitrite ester of 2-octanol decomposes on standing at room temperature, especially in the presence of light, and this may account for the discrepancies noted.⁶

(1) Bertoni, *Gazz. chim. ital.*, **16**, 521 (1886).

(2) Bouveault and Wahl, *Bull. soc. chim.*, (3) **29**, 959 (1903).

(3) Kenyon and Young, *J. Chem. Soc.*, 965 (1938).

(4) Shriner and Young, *THIS JOURNAL*, **53**, 3332 (1930).

(5) Pezold and Shriner, *ibid.*, **54**, 4707 (1932).

(6) The instability of nitrite esters has been noted previously; *cf.* Horswell and Silverman, *Ind. Eng. Chem., Anal. Ed.*, **13**, 555 (1941).