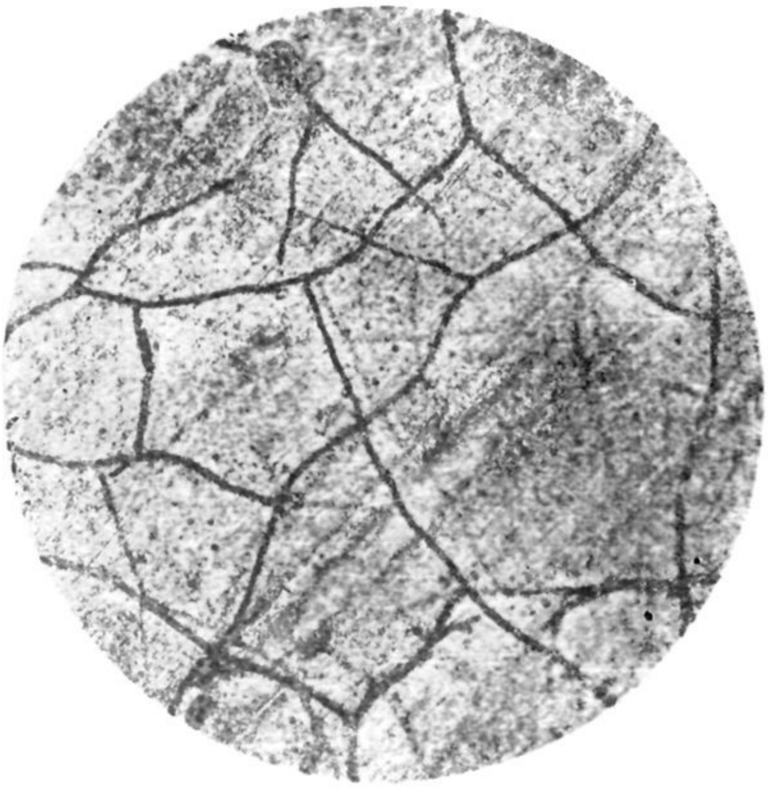

Fig. 2.—Photomicrograph (375×) of chrome-plated nickel; sample 1, thickness 0.5 mil., surface ratio—27.

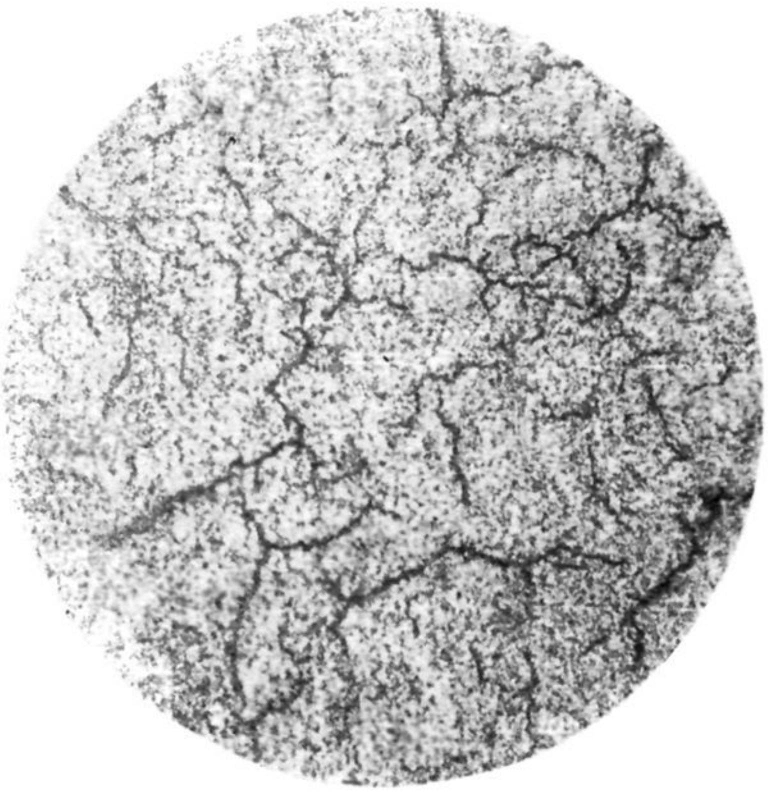

Fig. 3.—Photomicrograph (375×) of chrome-plated nickel; sample 3, thickness 1.5 mil., surface ratio—53.

plausible the previous claims of Bowden and Rideal pointing to a ratio as high as 50 of accessible to apparent area for etched silver, and a surface ratio of 12 for electrodeposited nickel, and furthermore indicate that these high ratios may apply to metals in general with similar preparation.

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Reaction of Some Furan Derivatives with Formaldehyde and Amine Hydrochlorides

BY R. F. HOLDREN

A recent communication[1] described the reaction of 2-methylfuran with formaldehyde and various amine hydrochlorides. A further study of this reaction as applied to other furan derivatives is reported herein.

Marini[2] has reported that the sulfuric acid condensation of ethyl 2-furoate and methylolphthalimide gave ethyl 5-phthalimidomethylfuran-2-carboxylate. In the present work no reaction was observed with compounds which contained a negative group attached to the furan nucleus, *e. g.*, 2-furoic acid and ethyl 2-furoate.

Although furfuryl acetate reacted slowly with formaldehyde and ethyl amine hydrochloride at 60°, no simple product could be isolated from the mixture. Apparently the ester first hydrolyzed to furfuryl alcohol which then reacted to give polymeric substances. That this is the case is inferred from the fact that furfuryl alcohol gave only resins under the same conditions. In contrast to this it was found that furfuryl acetate reacted readily with benzylamine hydrochloride at 30°. However, the product decomposed on distillation *in vacuo*, thus preventing the isolation of any pure material.

Furfuryl cyanoethyl ether reacted readily with formaldehyde andethylamine hydrochloride. Again the product was found to decompose on vacuum distillation. In these last two cases all attempts at purification by crystallization of the hydrochlorides from the reaction mixture were of no avail.

Furfuryl alcohol reacted with formaldehyde and dimethylamine hydrochloride at 30° to yield 5-dimethylaminomethylfurfuryl alcohol. Morpholine hydrochloride behaved in the same manner to give 5-N-morpholinomethylfurfuryl alcohol. The acidic nature of the hydrochlorides caused considerable polymerization of the furfuryl alcohol in both instances. Only resins could be isolated on reaction of furfuryl alcohol with ammonium chloride and ethylamine hydrochloride.

Experimental

All melting and boiling points are uncorrected. Hydrochloride salts were prepared as described in the previous communication.[1]

Furfuryl Cyanoethyl Ether.—This compound was prepared in 95% yield by the method of Bruson and Riener,[3] using 40% potassium hydroxide as a catalyst. No reaction occurred if benzyltrimethylammonium hydroxide was used as a catalyst. Since the ether has been reported only in the patent literature,[4] some physical constants are given below: b. p. 100–101° (1 mm.), $n^{30}D$ 1.4742; b. p. 109–110° (2 mm.), d_{30} 1.090.

The reaction product of the ether with formaldehyde

(1) Holdren and Hixon, THIS JOURNAL, **66**, 1198 (1946).

(2) Marini, *Gazz. chim. ital.*, **69**, 340 (1939) [*C. A.*, **33**, 8607 (1939)]. The author is grateful to the referee for calling his attention to the prior work.

(3) Bruson and Riener, THIS JOURNAL, **65**, 23 (1943).

(4) Bruson, U.S. Patent 2,280,790 (1942).

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 previously[1]; b. p. 110–111° (3 mm.), $n^{25}D$ 1.4968, d_{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.), $n^{30}D$ 1.5195; 134–135° (2 mm.), d_{30} 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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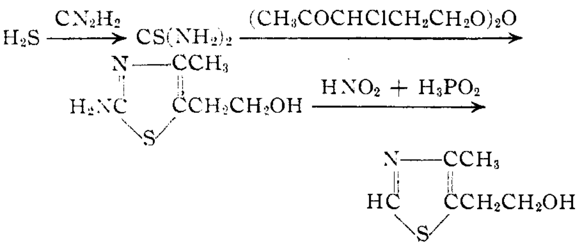
The Reduction of 2-Amino-4-methyl-5-β-hydroxyethylthiazole in the Synthesis of Thiamin

BY J. B. HATCHER[1]

In the course of studies involving the use of thiamin labelled with radioactive sulfur[2] 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* 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 B_1 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.

(1) Present address: The Argonne National Laboratory, Chicago, Illinois.

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

PASADENA, CALIFORNIA RECEIVED AUGUST 7, 1946

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 $n^{20}D$ 1.4082 and 1.4083; $d^{20}{}_4$ 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.)	$n^{20}D$	Density		Ref.
dl-2-Octyl	165–166°	....	d^0	0.881	1
dl-2-Octyl	65 (15)	....	d_4^0	.879	2
l-2-Octyl	63–65 (15)	1.4202[a]	$d^{18}{}_4$	.861	3
l-2-Octyl	85–90 (18)	1.4218	$d^{20}{}_{20}$	.857	4
l-2-Octyl	70–75 (18)	1.4270	$d^{20}{}_{20}$	.852	5
d-2-Octyl	70–75 (18)	1.4270	$d^{20}{}_{20}$	.852	5
dl-2-Octyl	72–74 (18)	1.4272	$d^{20}{}_{20}$	.852	5
d-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).