

either coincide at one or two points in the positive quadrant or not at all, depending on the value of  $C$ . If they do not intersect, the sequence (4) does not converge. The limiting case will occur when the two curves osculate, *i. e.*, when  $y_1 = y_2$  and  $dy_1/dx = dy_2/dx$ , where the two roots will coincide. The first of these equations is equivalent to (5), the second is

$$d_{\infty} \ln C = 1 \quad (6)$$

Solving (5) and (6) simultaneously for  $C$  yields  $C = e^{1/e} = 1.4447$ . Thus (4) will converge as long as  $C$  is less than this value, for which  $d_{\infty} = e$ . When  $0 < C < 1$ , the slope of  $y_2$  is negative, and there will be only one point where the curves intersect. In the region  $1 < C < e^{1/e}$ , there will be two finite roots; thus, for example, when  $C = 1.2$ , equation (5) is satisfied by the two values  $d_{\infty} = 1.2577$  and  $14.7675$ . Since physically  $T_{\infty}$  and  $d_{\infty}$  must be uniquely determined, only values of  $C$  lying between zero and unity will be suitable for empirical formulas of this type.

The roots of (5) can be found by iteration or any other conventional method for solving transcendental equations. Using the value  $C = 0.13523$  chosen by Erickson,  $d_{\infty} = 0.42622$  and  $T_{\infty} = 122.6^{\circ}$ , in excellent agreement with Erickson's result and the available experimental data.

$d_{\infty}$  is independent of the value of  $d_2$ . Other functional relations of the form  $x_n = f(x_{n-1})$ , with simple restrictions on the nature of  $f(x)$ , will also give the odd-even oscillatory character of this function, converging to a limit independent of the starting value.

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SCHENECTADY, NEW YORK RECEIVED FEBRUARY 17, 1949

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## A New Method for the Preparation of the Thiazole Moiety of Thiamine

BY ALBERT J. EUSEBI, ELLIS V. BROWN AND LEOPOLD R. CERECEDO

In a previous paper, Cerecedo and Tolpin<sup>1</sup> reported the synthesis of ethyl 4-methylthiazole-5-acetate by condensation of ethyl  $\alpha$ -bromolevulinate with thioformamide. Their attempts to reduce this compound to the alcohol, 4-methyl-5- $\beta$ -hydroxyethylthiazole, were unsuccessful. This reduction has now been smoothly carried out by the use of  $\text{LiAlH}_4$ . The usefulness of this substance as a reducing agent has recently been established with a variety of organic compounds.<sup>2</sup>

### Experimental<sup>3</sup>

To a solution of 2.5 g. (0.066 mole) of  $\text{LiAlH}_4$  in 100 ml. of anhydrous ether was added a solution of 18.5 g. (0.10

mole) of ethyl 4-methylthiazole-5-acetate in 150 ml. of anhydrous ether at a rate to produce mild reflux of the ether. The reaction was allowed to continue for fifteen minutes after the last addition. The mixture was then cooled, and water added dropwise to decompose the excess of  $\text{LiAlH}_4$ . The precipitate was treated with an excess of alkali, and the mixture extracted with three 100-ml. portions of ether. The combined ether extracts were dried with sodium sulfate, and the ether removed *in vacuo*. The light brown residue was distilled under diminished pressure at  $91-95^{\circ}$  (2 mm.). The yield was 7 g. (49%). In a second run with smaller quantities of reactants a 62% yield was obtained.

Picrate of 4-methyl-5- $\beta$ -hydroxyethylthiazole (I), after recrystallization from ethanol, melted at  $162^{\circ}$  (uncor.).

*Anal.* Calcd. for  $\text{C}_{12}\text{H}_{12}\text{O}_8\text{N}_2\text{S}$ : C, 38.71; H, 3.22; N, 15.05; S, 8.60. Found: C, 39.05; H, 3.06; N, 14.95; S, 8.30.

Picrotonate of (I), recrystallized from ethanol, m. p.  $183-185^{\circ}$  (uncor.).

*Anal.* Calcd. for  $\text{C}_{16}\text{H}_{17}\text{O}_8\text{N}_2\text{S}$ : C, 47.17; H, 4.18; N, 17.19; S, 7.86. Found: C, 47.10; H, 4.18; N, 16.94; S, 7.84.

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## Preparation of 3-Ethylpyridine

BY T. I. FAND AND C. F. LUTOMSKI

The preparation of 3-ethylpyridine from 3-acetylpyridine using the general method of Wolff-Kishner has been reported by Woodward,<sup>1</sup> but the yield of pure product is not given. The need for rather large quantities of 3-ethylpyridine prompted a search for conditions giving a better yield. The method finally adopted which gave an 80% yield of 3-ethylpyridine from 3-acetylpyridine was the Huang-Minlon<sup>2</sup> modification of the Wolff-Kishner reaction. The amount of triethylene glycol used by Huang-Minlon<sup>2</sup> could be reduced to one-third without diminution of yield.

### Procedure

One liter of triethylene glycol (Carbide and Carbon Chemicals Corp.), 242 g. of 3-acetylpyridine, 270 g. of 85% hydrazine hydrate (Edwal Labs.), and 225 g. of potassium hydroxide pellets were heated in a 2-liter flask equipped with a stirrer and reflux condenser for one hour by means of an oil-bath maintained between  $110-125^{\circ}$ . The reflux condenser was then changed for distillation and the temperature of the oil-bath was raised over a period of one-half hour to  $185-190^{\circ}$  and maintained there for two hours, during which period the product distilled over. The distillate was extracted with ether, dried over potassium carbonate and finally fractionated through a 3-ball Snyder column. A main fraction was collected boiling between  $165.5-166^{\circ}$  at atmospheric pressure. The yield was 172 g. or 80%. The picrate melted at  $129-130^{\circ}$ . The boiling point of 3-ethylpyridine is reported<sup>3</sup> as  $165-165.3^{\circ}$ , and the melting point of the picrate is reported<sup>4</sup> as  $128-130^{\circ}$ .

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(2) Huang-Minlon, *ibid.*, **68**, 2487 (1946).

(3) Stoehr, *J. prakt. Chem.*, [2] **48**, 35 (1892).

(4) Stoehr, *ibid.*, [2] **48**, 38 (1892).

(1) Cerecedo and Tolpin, *THIS JOURNAL*, **69**, 1660 (1937).

(2) Nystrom and Brown, *ibid.*, **69**, 1197, 2548 (1947).

(3) Analyses by Dr. F. A. Bähler.