with III[4] prepared from citrinin gave no depression. The bis-(*p*-nitrobenzoate) of 4-methyl-5-ethylresorcinol was prepared (m. p. 205–6°) and compared with the bis-(*p*-nitrobenzoate) of III (m. p. 205–6°). A mixed melting point determination gave 205–206°. *Anal.* Calcd. for $C_{23}H_{18}O_8N_2$: C, 61.33; H, 4.03. Found: C, 61.50; H, 4.03.

Methylation of the hydroxyl groups of 2-methyl-3,5-dihydroxybenzoic acid (prepared by the method of Jacobsen and Wierss[5]) gave 2-methyl-3,5-dimethoxybenzoic acid, m. p. 157–158° (Hetherington, *et al.*,[1] reported m. p. 142–146° for V). *Anal.* Calcd. for $C_{10}H_{12}O_4$: C, 61.21; H, 6.16; neut. equiv., 196.2. Found: C, 61.35; H, 6.55; neut. equiv., 195. This acid was converted to the amide which was treated with methylmagnesium bromide to give 2-methyl-3,5-dimethoxyacetophenone, m. p. 46–47°. Reduction of this ketone with hydrazine followed by demethylation produced 4-methyl-5-ethylresorcinol, m. p. 67–69°. Admixture of this sample with III or with the sample prepared from 5-ethylresorcinol produced no depression.

The above evidence completely eliminates the formulas advanced by Coyne, Raistrick and Robinson[6] for citrinin, II, III, IV and V.

Terminal-methyl number determinations were run on citrinin (2.68 and 2.76) and on II (2.57 and 2.51). Since II couples with two moles of benzenediazonium chloride in an apparently normal manner (Gore, *et al.*[4]), and since the molecule must have at least three terminal methyl groups, II would appear to be 4-methyl-5-(1-methyl-2-hydroxypropyl)-resorcinol. The synthesis of this substance has been undertaken.

(4) Hetherington, *et al.*,[1] reported a melting point of 97–99° which changed to 65–70° after the sample stood for some time. Gore, Panse and Venkatarumen [*Nature*, 157, 333 (1946)] reported 65–70° and Spranger and Ruoff [*J. Org. Chem.*, 11, 189 (1946)] 67–70° as the melting point of III.

(5) Jacobson and Wierss, *Ber.*, 16, 1960 (1883).

(6) Coyne, Raistrick and Robinson, *Trans. Roy. Soc.* (London), B220, 297–300 (1931).

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REDUCTION OF CARBON DIOXIDE TO METHANOL BY LITHIUM ALUMINUM HYDRIDE[1]

Sir:

Carbon dioxide is rapidly absorbed by lithium aluminum hydride in ether solution. From such mixtures formaldehyde was isolated, as the dimethone derivative and as hexamethylenetetramine, in yields not over 25%. Schlesinger and Finholt[2] found two moles of carbon dioxide absorbed per mole of hydride, which is consistent with reduction to the formaldehyde stage but does not exclude further reduction followed by partial carbonation of the resultant methoxide.

We then found that, with lithium aluminum hydride in excess, 0.75 mole of hydride is consumed per mole of carbon dioxide and hence that the reduction under these conditions proceeds to the methanol stage.

However, the isolation of methanol proved troublesome. The best of many different procedures for the recovery of small amounts of methanol from ether–water mixtures gave yields, based on carbon dioxide, of less than 50%. The conventional procedure for effecting reductions with lithium aluminum hydride was eventually abandoned in favor of one which is better with respect to yield and better adapted to isotopic synthesis since it involves fewer operations.

A relatively non-volatile solvent, diethyl carbitol, replaces diethyl ether, and a high-boiling alcohol, *n*-butylcarbitol, is used both to decompose the excess hydride and to liberate methanol by alcoholysis. Methanol, the most volatile component of the system, is then obtained in a simple distillation employing an inert entraining gas. The over-all process is shown below:

First Stage

$$4\mathrm{CO_2} + 3\mathrm{LiAlH_4} = \mathrm{LiAl(OCH_3)_4} + 2\mathrm{LiAlO_2}$$

Second Stage (R = *n*-butylcarbityl)

$$\mathrm{LiAlH_4} + 4\mathrm{ROH} = \mathrm{LiAl(OR)_4} + 4\mathrm{H_2}$$

$$\mathrm{LiAl(OCH_3)_4} + 4\mathrm{ROH} = \mathrm{LiAl(OR)_4} + 4\mathrm{CH_3OH}$$

In a typical experiment, the carbon dioxide generated from 13.0 g. of barium carbonate by the slow addition of 30% perchloric acid, and diluted by a stream of nitrogen, was passed through drierite into a solution of 3.8 g. of lithium aluminum hydride in 500 cc. of diethyl carbitol. Shortly thereafter, 120 g. of *n*-butylcarbitol was added and, with continued flow of nitrogen gas, the mixture was heated. The product, collected in a trap cooled by a Dry Ice freezing mixture,[3] was redistilled to separate a small residue of high-boiling material and there was obtained as distillate 1.71 g. of methanol, n^{20}_{D} 1.3310, identified further as the N-(α-naphthyl)-carbamate, m. p. 124°. The yield of methanol was thus 81% based on barium carbonate. A small fraction, 1.7%, of unreacted carbon dioxide was collected in an ascarite tube through which the effluent gas passed.

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(1) Experimental work started at George Herbert Jones Laboratory, The University of Chicago, and continued at Clinton National Laboratory, Oak Ridge, operating under Contract No. W-35-058-eng-71 with the Atomic Energy Project.

(2) Schlesinger and Finholt, unpublished work.

(3) An improvement in yield might result from liquid nitrogen cooling since methanol is appreciably volatile at Dry Ice temperatures.

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