crystalline product had a melting point of 151–153° (uncor.). It was recrystallized from methanol, m. p. 157–159° (uncor.); mixed melting point with L-arabinose unchanged. The initial specific rotation of a 2% aqueous solution of the material was +170 falling to +103. L-Arabinose has the specific equilibrium rotation +105.5. Precipitation with *p*-bromophenylhydrazine gave a 95% yield of almost pure L-arabinose *p*-bromo-phenylhydrazone, m. p. 152–154°; mixed melting point with authentic phenylhydrazone derivative unchanged.

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The Preparation of the Perchlorates of Some Alkanolamines

BY R. D. CADLE,[1] BETTY JANE ROBSON AND R. W. MOSHIER[1]

The preparation of the chlorides of several alkanolamines has been reported.[2,3] The usual method was to pass anhydrous hydrogen chloride into a solution of the alkanolamine in ether whereupon the desired salt precipitated. The present note concerns the preparation of the perchlorates of some alkanolamines. The salts obtained were colorless, hygroscopic, crystalline solids. The fused salts showed a strong tendency to supercool.

Experimental Part

β-Hydroxyethylamine (ethanolamine) was obtained from the Eastman Kodak Co. N,N-Diethyl-β-hydroxyethylamine, N,N-dimethyl-β-hydroxyethylamine and N-methyl-β-hydroxyethylamine were obtained from the Carbide and Carbon Chemicals Corporation. These amines were distilled at atmospheric pressure through a 24-inch Vigreux column. The boiling ranges of the fractions used are shown by Table I. They agreed well with previously reported values.[2,3,4,5]

The salts were prepared by dissolving 2 g. of the amine in 30 ml. of absolute ethanol and adding the amount of 70% perchloric acid calculated to be sufficient to neutralize the amine. Upon removal of the alcohol by evaporation under reduced pressure, a gummy residue remained. This residue could be obtained in crystalline form by repeated washing with ether and slow cooling from the fused state. However, purification was more easily achieved by dissolving the gummy residue in 15 ml. of absolute ethanol, adding anhydrous ether until the solution became cloudy, and cooling to −10°. Crystals slowly formed, and after several hours at this temperature the supernatant liquid was decanted and the crystallization repeated.

TABLE I

β-HYDROXYETHYLAMINE AND DERIVATIVES

Amine	B. p.[a] °C. (760 mm.)	Perchlorate M. p.,[a] °C.	Perchlorate Chlorine, % Calcd.	Perchlorate Chlorine, % Found
β-Hydroxyethylamine	170–171	131–132	21.8	21.7
N-Methyl-β-hydroxyethylamine	158	37.5–38.0	20.2	20.0
N,N-Dimethyl-β-hydroxyethylamine	134	40.0–40.5	18.3	18.3[b]
N,N-Diethyl-β-hydroxyethylamine	160	49.5–50.5	15.9	16.1[b]

[a] Corrected. [b] Two identical analyses.

The recrystallized salt was dried in an evacuated desiccator over phosphorus pentoxide. The dried salts were analyzed by the method of Arndt and Nachtwey.[6]

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[1] Present address: Stanford Research Institute, Stanford, California.

[2] Horne and Shriner, THIS JOURNAL, **54**, 2925 (1932).

[3] Knorr and Matthes, *Ber.*, **31**, 1069 (1898).

[4] Fränkel and Cornelius, *ibid.*, **51**, 1654 (1918).

[5] Knorr, *ibid.*, **30**, 909 (1897).

[6] Arndt and Nachtwey, *ibid.*, **59B**, 446 (1926).

Oxidation in Decarboxylation of Acids with Copper Chromite

BY WILLIAM G. DAUBEN AND PETER COAD

It has been reported[1] that when phenylacetic acid labeled in the carboxyl group with C^{14} was decarboxylated over a copper chromite catalyst in quinoline at 205°, the specific activity of the evolved carbon dioxide was slightly less than that of the original acid. We have found that this dilution of the radioactive carbon dioxide is due to non-radioactive carbon dioxide formed by the oxidation of the reaction product, toluene.

Methylene-labeled phenylacetic acid was prepared from carboxyl-labeled benzoic acid in the conventional manner and decarboxylated under various conditions. With commercial copper chromite catalyst[2] at pot temperatures of 170, 205 and 230°, the evolved carbon dioxide contained 0.07, 0.5 and 0.6%, respectively, of the C^{14} which was originally present in the methylene carbon atom. When copper chromite prepared as described by Lazier[3] was used at 205°, only 0.3%[4] was found.

This oxidation of the toluene formed in the reaction is most likely due to the cupric oxide present in the catalyst[5] since it was found that when the copper chromite was reduced with hydrogen before use only 0.1% was found and when iron or copper powder was used no trace of radioactivity could be detected.

It was also found that when β-methylene-labeled-β-phenylpropionic acid, prepared from methylene-labeled phenylacetic acid, was decarboxylated over copper chromite at 230°, 0.3% of the original C^{14} was evolved. It is interesting to note that Fries and Calvin[6] obtained similar results when methyl-labeled barium acetate was decarboxylated by pyrolysis. Thus, it is recommended that copper powder rather than copper chromite be used in decarboxylations in tracer work.

Experimental

Methylene-labeled Phenylacetic Acid.—Carboxyl-labeled methyl benzoate (31.1 g., 0.229 mole, specific

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[1] Dauben, Reid, Yankwich and Calvin, THIS JOURNAL, **68**, 2117 (1946).

[2] Copper Chromite Catalyst, No. Cu-186-powder, Harshaw Chemical Company, Cleveland, Ohio.

[3] "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., p. 142 (1944).

[4] All percentages refer to that originally present in the methylene carbon atom.

[5] Stroupe, THIS JOURNAL, **71**, 569 (1949).

[6] Fries and Calvin, *ibid.*, **70**, 2235 (1948).