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.

PORTLAND, OREGON
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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).

CHEMISTRY DIVISION, RESEARCH DEPARTMENT
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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).

activity × 8[7]:3,300 cts./min./mg. barium carbonate) was reduced with 8.7 g. (0.228 mole) of lithium aluminum hydride following the procedure of Nystrom and Brown.[8] The benzyl alcohol was obtained in a yield of 21.1 g. (85.5%), b. p. 114–115° (32 mm.).

Methylene-labeled Benzyl Chloride.—In an all-glass apparatus closed with a calcium chloride tube, 10.3 g. (6.6 cc., 0.075 mole) of phosphorus trichloride was added to 21.1 g. (0.195 mole) of benzyl alcohol (prepared above) at zero degrees. The mixture was allowed to stand at room temperature for thirty minutes and at 50° for one hour. The excess phosphorus trichloride was removed and the benzyl chloride distilled, b. p. 60–61° (12 mm.), yield 21.8 g. (88.1%).

Methylene-labeled Phenylacetic Acid.—Benzylmagnesium chloride was prepared from 21.8 g. (0.172 mole) of methylene-labeled-benzyl chloride and 4.2 g. (0.172 atom) of magnesium turnings. The Grignard reagent was carbonated at −5° with gaseous carbon dioxide and the reaction mixture processed in the usual manner. The phenylacetic acid was recrystallized from petroleum ether, m. p. 76–77° (cor.), yield, 17.3 g. (74%), specific activity × 8:3,300 cts./min./mg. barium carbonate.

β-Methylene-labeled β-Phenethyl Alcohol.—Phenylacetic acid (11.1 g.) was reduced with lithium aluminum hydride as above and β-phenethyl alcohol was obtained in a yield of 8.5 g. (85.6%), b. p. 114° (9 mm.).

β-Methylene-labeled β-Phenethyl Chloride.—β-Phenethyl alcohol (8.5 g.) was allowed to react with 4.8 g. of phosphorus trichloride in the normal manner and the chloride was received in a yield of 3.3 g. (33.8%), b. p. 55° (2 mm.).

β-Methylene-labeled β-Phenylpropionic Acid.—β-Phenethylmagnesium chloride was prepared from 3.3 g. of β-phenethyl chloride (prepared above) and 0.63 g. of magnesium and the Grignard reagent carbonated with gaseous carbon dioxide, yield 1.82 g. (51.5%), m. p. 48–49°, specific activity × 9:3,300 cts./min./mg. barium carbonate.

Decarboxylation Procedure.—A mixture of 0.25 g. of the acid and 0.25 g. of the catalyst and 5 cc. of quinoline was heated for forty minutes in a salt-bath. The reaction mixture was flushed continuously with nitrogen and after the heating the aeration continued for one hour at room temperature. The evolved carbon dioxide was collected in 50 cc. of 0.14 *M* barium hydroxide. The barium carbonate was collected by filtration under nitrogen and the precipitate washed with water, alcohol and ether and dried at 110°. The yields varied from 40–80%.

All samples of barium carbonate were regenerated to carbon dioxide and reprecipitated to check for radioactive impurities. In all cases, a constant specific activity was obtained.

Radioactivity Determination.—The procedure of Dauben, Reid and Yankwich[9] was employed for sample preparation and counting.

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(7) This value was obtained by combustion of a microsample of the ester, precipitation of the carbon dioxide as barium carbonate and counting the barium carbonate. To correct for the dilution of activity in the compound, the observed specific activity was multiplied by eight.

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

(9) Dauben, Reid and Yankwich, *Anal. Chem.*, **19**, 828 (1947).

DEPARTMENT OF CHEMISTRY
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Reaction of Thiophenealdehyde Derivatives with Maleic Anhydride

BY WERNER HERZ[1]

The present note describes the reaction of two derivatives of 2-thiophenealdehyde with maleic anhydride. Parallel reactions of benzylidene[2] and furfurylidene[3] derivatives have been reported previously.

Experimental

Thiophenealdehyde-1-maleylphenylhydrazone.—A solution of 3 g. of thiophenealdehyde phenylhydrazone[4] in 20 ml. of ether was treated with 1.8 g. of maleic anhydride. The solution was warmed until solution of the anhydride occurred. The crude product which separated after standing overnight was washed with ether and weighed 4.5 g. Several recrystallizations from ethanol raised the m. p. of the yellow needles to 119–120°.

Anal. Calcd. for $C_{15}H_{12}N_2O_3S$: C, 59.99; H, 4.03; neut. equiv., 300. Found: C, 59.95; H, 4.09; neut. equiv., 301.

Under the same conditions pyrrolealdehyde phenylhydrazone on treatment with maleic anhydride yielded golden-yellow needles which decomposed immediately on exposure to air and could not be recrystallized satisfactorily.

N-*p*-Tolylmaleamic Acid.—A solution of 1.8 g. of thiophenealdehyde *p*-toluidine[5] in 15 ml. of ether on treatment with 1.2 g. of maleic anhydride gave yellowish-green needles, m. p. 201° with gas evolution after recrystallization from ethanol, which did not depress the m. p. of authentic N-*p*-tolylmaleamic acid.[6]

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(1) Present address: Department of Chemistry, University of Illinois, Urbana, Illinois.

(2) La Parola, *Gazz. chim. ital.*, **64**, 919 (1934); **65**, 624 (1935).

(3) Herz, THIS JOURNAL, **67**, 1854 (1945).

(4) Biedermann, *Ber.*, **19**, 636 (1886).

(5) Hantzsch and Witz, *ibid.*, **35**, 841 (1901).

(6) Dunlap and Phelps, *Am. Chem. J.*, **19**, 492 (1897).

UNIVERSITY OF COLORADO
BOULDER, COLORADO
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The Heat Capacity of Organic Vapors. VI. Acetone[1]

BY BEN T. COLLINS,[2] CHARLES F. COLEMAN AND THOMAS DE VRIES

The work reported in this paper is a continuation of a program for measuring the heat capacity of organic vapors. The heat capacity and heat of vaporization of acetone has been measured at 1 atm., at temperatures from near its boiling point to 150°.

Experimental and Results

Two sets of determinations are reported. Those of set I were made with a reverse-flow calorimeter and auxiliary equipment previously described[3]; those of set II, with the apparatus and by the procedure described in the preceding paper.[4]

The values obtained for the heat capacity are presented in Table I and Fig. 1. The latter also shows the value 22.5 cal./mole/degree at 137°, reported by Bennewitz and Rossner,[5] and a line drawn through the calculated values of C_p at 1 atm. by Dobratz.[6] Other values reported in the literature are 20.1 and 21.7 for the temperature

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(1) Abstracted from the Ph.D. thesis of C. F. Coleman.

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(3) De Vries and Collins, THIS JOURNAL, **63**, 1343 (1941).

(4) Coleman and De Vries, *ibid.*, **71**, 2839 (1949).

(5) Bennewitz and Rossner, *Z. physik. Chem.*, **B39**, 125 (1938).

(6) Dobratz, *Ind. Eng. Chem.*, **33**, 759 (1941).