

TABLE I

$\left. \begin{array}{c} \text{R} \\ \diagdown \\ \text{N}^+ \end{array} \right\}$	Yield, %	M. p., °C. <sup>a</sup>	Formula	Iodine, % <sup>b</sup>		Total halogen <sup>c</sup>	
				Calcd.	Found	Calcd.	Found
Pyridinium	73	87–89 <sup>e</sup>	C <sub>5</sub> H <sub>5</sub> Cl <sub>2</sub> IN	43.5	43.8	10.3	10.1
α-Picolinium	49	92–93	C <sub>7</sub> H <sub>10</sub> Cl <sub>2</sub> IN	41.5	41.0	9.82	9.67
Quinolinium	56	112–113 <sup>d</sup>	C <sub>10</sub> H <sub>10</sub> Cl <sub>2</sub> IN	37.2	36.9	8.77	8.63
Isoquinolinium	82	72–73	C <sub>10</sub> H <sub>10</sub> Cl <sub>2</sub> IN	37.2	36.7	8.77	8.53
Quinaldinium	64	109–110	C <sub>11</sub> H <sub>12</sub> Cl <sub>2</sub> IN	35.8	35.4	8.43	8.23

<sup>a</sup> Melting points are uncorrected. <sup>b</sup> Iodine was determined by titration with standard thiosulfate after addition of potassium iodide. The amount of iodine found was divided by two to obtain the iodine in the chloriodate(I) ion. <sup>c</sup> Bally, ref. 4, reports a m. p. of 90°. <sup>d</sup> Ostermayer, ref. 3, reports a m. p. of 112°. <sup>e</sup> The total halogen was determined by the Volhard method using dilute alcohol for a solvent. In the presence of alcohol all the halogen in the ion was readily converted to silver halide. The numbers in the table represent milliequivalents of halogen per gram of compound.

chloride,<sup>3</sup> by the reaction of chlorine with a quaternary ammonium iodide,<sup>4</sup> and by the reaction of a quaternary ammonium chloride with potassium iodate in concentrated hydrochloric acid.<sup>5</sup>

The general applicability of thionyl chloride for the preparation of compounds containing the chloriodate(I) ion was demonstrated by treating several quaternary iodides with this reagent. The compounds prepared, and their analyses, are summarized in the accompanying table. These substances are yellow or orange crystalline solids stable in air. They are slightly soluble in water first forming an oil which slowly enters solution. The resulting solutions liberate iodine color on standing. A drop of a saturated sodium bicarbonate when added to the chloriodate(I) solution caused the appearance of iodine color. Iodine color was also liberated by addition of potassium iodide, sodium thiosulfate or sodium bisulfite. An excess of the latter two reagents removed the iodine color.

#### Experimental

The following example describes the general method for carrying out the reaction.

**Methylpyridinium Chloriodate (I).**—Ten cc. of thionyl chloride, purified according to the method described by Fieser,<sup>6</sup> was added to 5 g. of dry methylpyridinium iodide. The reaction was vigorous and was accompanied by the initial formation of a dark tar which quickly entered solution. The excess thionyl chloride was removed by distillation *in vacuo*, the residue<sup>7</sup> was dissolved in 15 cc. of hot glacial acetic acid and the solution filtered to remove sulfur. After cooling the yellow crystalline product was separated, washed with cold acetic acid and finally with ether. The yield was 4.8 g. (73%) melting at 87–89°. The melting point was not depressed when the substance was mixed with a sample of authentic methylpyridinium chloriodate (I), prepared according to Bally.<sup>4</sup>

DEPARTMENT OF CHEMISTRY  
NORTHWESTERN UNIVERSITY  
EVANSTON, ILLINOIS

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(3) Ostermayer, *Ber.*, **18**, 591 (1885).

(4) Bally, *Ber.*, **21**, 1772 (1888).

(5) Zincke and Lawson, *Ann.*, **240**, 124 (1887).

(6) Fieser, "Experiments in Organic Chemistry," D. C. Heath and Co., New York, N. Y., 1941, p. 381.

(7) When this residue was shaken with benzene, sulfur separated from the crude oil.

#### L-Arabinose from Heartwood of Western Red Cedar (*Thuja plicata*)<sup>1</sup>

BY ARTHUR B. ANDERSON<sup>2</sup> AND H. ERDTMAN<sup>3</sup>

Free L-arabinose appears to be a common constituent of the heartwood of many conifers. It has been isolated from a great variety of pine heartwoods, especially from species belonging to the Diploxylon series (generally possessing leaves in bundles of three or two).<sup>4,5</sup> The amount present is generally small. The heartwood of pines belonging to the *Haploxyton* sub-group (generally having five leaves in a bundle) always appears to contain pinitol, sometimes in surprisingly large quantities, which renders the isolation of the sugars more difficult.

While investigating the extractives from the heartwood of western red cedar,<sup>6</sup> a yield of 1.29 g. of a sugar melting at 151–153° was obtained from 470 g. of wood. The material reduced Fehling solution and gave a strong pentose reaction with phloroglucinol and hydrochloric acid. This crude sugar has been identified as L-arabinose.

#### Experimental

Four hundred and seventy grams of western red cedar heartwood sawdust was extracted with acetone in a Soxhlet extractor for eight hours. The dark-red acetone extract was evaporated and the resulting residue extracted several times with ethyl ether. Several hundred ml. of water was added to the ether insoluble portion of the extract, heated on a steam-bath with stirring and charcoal (Darco) added. This was filtered and the resulting aqueous solution concentrated to a sirup under vacuum on a water-bath. The sirup was triturated with one volume of absolute ethanol and placed in a desiccator containing calcium chloride for about twenty-four hours or until the first crystals appeared and then placed in an ice-chest for several days to ensure complete crystallization. The solid was filtered and the precipitate washed with absolute ethanol and finally absolute ether. The resulting white

(1) The work by A. B. A. was carried on while on the staff of the Forest Products Laboratory, Madison, Wisconsin, and the authors wish to thank the U. S. Forest Products Laboratory for permission to publish this work.

(2) Present address: Oregon Lumber Co., Res. Lab., Portland, Ore.

(3) Royal Institute of Technology, Stockholm, Sweden.

(4) Erdtman, *Svensk Papperstidni*, **46**, 228 (1943).

(5) Lindstedt, unpublished observations.

(6) Anderson and Sherrard, *This Journal*, **55**, 3013 (1933).

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,<sup>1</sup> BETTY JANE ROBSON AND R. W. MOSHIER<sup>1</sup>

The preparation of the chlorides of several alkanolamines has been reported.<sup>2,3</sup> 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

$\beta$ -Hydroxyethylamine (ethanolamine) was obtained from the Eastman Kodak Co. N,N-Diethyl- $\beta$ -hydroxyethylamine, N,N-dimethyl- $\beta$ -hydroxyethylamine and N-methyl- $\beta$ -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.<sup>2,3,4,5</sup>

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  $-10^{\circ}$ . Crystals slowly formed, and after several hours at this temperature the supernatant liquid was decanted and the crystallization repeated.

TABLE I  
 $\beta$ -HYDROXYETHYLAMINE AND DERIVATIVES

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

<sup>a</sup> Corrected. <sup>b</sup> Two identical analyses.

(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).

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

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

CHEMISTRY DIVISION, RESEARCH DEPARTMENT  
NAVAL ORDNANCE TEST STATION

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### Oxidation in Decarboxylation of Acids with Copper Chromite

BY WILLIAM G. DAUBEN AND PETER COAD

It has been reported<sup>1</sup> that when phenylacetic acid labeled in the carboxyl group with C<sup>14</sup> 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<sup>2</sup> at pot temperatures of 170, 205 and 230°, the evolved carbon dioxide contained 0.07, 0.5 and 0.6%, respectively, of the C<sup>14</sup> which was originally present in the methylene carbon atom. When copper chromite prepared as described by Lazier<sup>3</sup> was used at 205°, only 0.3%<sup>4</sup> was found.

This oxidation of the toluene formed in the reaction is most likely due to the cupric oxide present in the catalyst<sup>5</sup> 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  $\beta$ -methylene-labeled- $\beta$ -phenylpropionic acid, prepared from methylene-labeled phenylacetic acid, was decarboxylated over copper chromite at 230°, 0.3% of the original C<sup>14</sup> was evolved. It is interesting to note that Fries and Calvin<sup>6</sup> 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

(1) Dauben, Reid, Yankwich and Calvin, *THIS JOURNAL*, **66**, 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).