

Properties of Quebrachite.—Purified quebrachite consists of colorless rhombs and six-sided and wedge-shaped forms which melt at 192–193° (corr.). Under reduced pressure the material readily sublimes, and in 5% aqueous solution it has a specific rotation of $[\alpha]_D^{20}$ -81.2° . Tanret² reported the melting point as 186–187° and α_D as -80° .

Calcd. for $C_7H_{14}O_6$: C, 43.28; H, 7.27; OCH_3 (1), 15.98. Found: C, 43.26; H, 7.25; OCH_3 , 15.94.

The optical crystallographic characteristics of the material were determined by George L. Keenan, of the Food and Drug Administration.

The rhomb-like and wedge-shaped forms predominate. In parallel polarized light (crossed nicols) the plates show low-order colors and extinguish in a hazy manner. In convergent polarized light (crossed nicols) most plates are sections perpendicular to the acute bisectrix, although the biaxial interference figures are only faintly shown. The refractive indices of the material, determined by the immersion method, are: η_α , 1.546; η_β , 1.552; η_γ , 1.572; all ± 0.003 .

The β - and γ -indices were found most frequently.

***l*-Inosite from the Hydrolysis of Quebrachite.**—One gram of quebrachite dissolved in 5 cc. of hydriodic acid, sp. gr. 1.7, was heated in a boiling water-bath for one and one-half hours. Eight volumes of boiling alcohol were added, and the mixture was placed in an ice-bath. Crystallization began at once and was soon completed. The yield was practically quantitative.

The inosite recrystallized by adding boiling alcohol to a hot, concentrated, clarified aqueous solution consisted of

heavy, colorless, irregular plates which began to sinter at 195° and melted and flowed at 242–243°. In 5% aqueous solution its specific rotation was $[\alpha]_D^{20}$ -64.7° . Tanret² reported the melting point as 238° and the specific rotation of the hydrate, $C_6H_{12}O_6 \cdot 2H_2O$, as $[\alpha]_D^{20}$ -55° . This calculated to the anhydrous form is -66° . Its optical crystallographic properties were as follows. In parallel polarized light (crossed nicols) first and second order polarization colors are usually shown. In convergent polarized light (crossed nicols) plates frequently occur showing biaxial interference figures characteristic of sections perpendicular to the acute bisectrix. The substance is optically negative, and therefore η_β and η_γ lie in the two positions at right angles to each other in the plane of the plates, and the η_α direction lies perpendicular to the plates and can only be measured by turning the plates on edge. The axial angle is not large. The refractive indices as determined by the immersion method are η_α , 1.553 (only approximate since it is difficult to orient the material to show this index); η_β , 1.562; η_γ , 1.566 (± 0.003).

The birefringence is moderate.

l-Inosite hexabenzate, prepared by the Schotten-Baumann method and recrystallized from *n*-butyl alcohol, melted at 247°. Tanret² gives 252°.

Summary

Quebrachite was found in the stems of *Haplophyton cimidum* to the extent of approximately 0.7%. A method for its preparation is given, and new and revised physical data are presented for quebrachite and *l*-inosite.

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(2) Tanret, *Compt. rend.*, **109**, 908 (1889).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

1-Chloro-2-methyl-2-propanol from 1,2-Dichloro-2-methylpropane¹

BY C. E. SPARKS AND R. E. NELSON

Introduction

Pogorshelski² reports that 2-methyl-1,2-propanediol is obtained on treating 1,2-dichloro-2-methylpropane with hot potassium carbonate solution.

The purpose of this investigation is to determine whether 1-chloro-2-methyl-2-propanol is formed in the liquid-phase hydrolysis of 1,2-dichloro-2-methylpropane. The 1,2-dichloro-2-methylpropane was prepared, unless otherwise specified, by converting 2-methyl-2-propanol into 2-chloro-2-methylpropane and chlorinating the latter.

(1) Based upon a portion of a thesis submitted by C. E. Sparks to the Faculty of Purdue University in partial fulfillment of the requirements for the Degree of Doctor of Philosophy, June, 1936.

(2) Pogorshelski, *Chem. Zentr.*, **76**, 1. 667 (1905).

Discussion

1-Chloro-2-methyl-2-propanol was the chief product isolated from the liquid-phase hydrolysis of 1,2-dichloro-2-methylpropane under neutral, slightly basic or slightly acidic conditions. That 1-chloro-2-methyl-2-propanol is formed is established by the boiling point of the product, the fact that it forms 1,2-dichloro-2-methylpropane when treated with concentrated hydrochloric acid and its conversion into 1,2-epoxy-2-methylpropane.

Table I shows, in general, decreased yields of 1-chloro-2-methyl-2-propanol when basic components were added to the hydrolysis mixtures.

Experimental

All of the hydrolysis experiments were performed in the same apparatus which consisted of a five-liter, three-necked

TABLE I
PERCENTAGE YIELD OF CRUDE 1-CHLORO-2-METHYL-2-PROPANOL

1,2-Dichloro-2-methylpropane, moles	Water, liters	Reagent	Time of refluxing, hrs.	Method	Yield, ^a %
1	4	Water	18.0	Distn. and ether extn.	48
1	4	52 g. CaCO ₃	4.5	Ether extn.	46
0.5	4	26 g. CaCO ₃	2.25	Distn. and ether extn.	42
1	4	Water	18.0	Ether extn.	41
1	4	52 g. CaCO ₃	4.5	Distn. and ether extn.	39
1 ^b	4	Water	17.5	Distn. and ether extn.	38
1	4	52 g. CaCO ₃	4.5	Distn., salting out and ether extn.	35 ^c
1	4	45 g. Ca(OH) ₂	5.0	Ether extn.	28
3	4	156 g. CaCO ₃	12.0	Distn. and ether extn.	28
1	4	95 g. NaHCO ₃	5.0	Ether extn.	20
1 ^b	4	52 g. CaCO ₃	4.75	Distn. and ether extn.	19
1	2	42 g. NaOH	4.25	Ether extn.	7.9
		2 l. water (added slowly)			
1	4	95 g. NaOH	10.0	Ether extn.	3.4

^a Based on amount of 1,2-dichloro-2-methylpropane reacting. ^b Prepared by chlorination of the monochlorides obtained from chlorinating 2-methylpropane. ^c Average of ten runs.

round-bottomed flask equipped with an electric motor, mercury-sealed stirrer, a reflux condenser and a thermometer. The source of heat was an electric heater and the temperatures of the refluxing liquids were from 70 to 80°.

The reaction mixtures, resulting from the hydrolysis runs were treated by one of three methods. The first method consisted of extracting the mixture with ether. The ether extract was dried over anhydrous sodium sulfate. The ether was distilled through a rectifying column and the resulting mixture fractionally distilled with a Vigreux column. This column is described in the literature.³ A constant pressure was maintained during the vacuum distillations by means of a regulator similar in principle to that described by Munch.⁴

The second method consisted of distilling under reduced pressure the constant boiling mixtures of water with the products and the unreacted 1,2-dichloro-2-methylpropane. The distillate was extracted with ether and treated by the first method. The pressure for this distillation should not exceed approximately 250 mm. since with higher pressures there is a slight decomposition of 1-chloro-2-methyl-2-propanol into 2-methylpropanal. It has been reported⁵ that 2-methylpropanal is formed when 1-chloro-2-methyl-2-propanol is boiled with water. This was confirmed.

In the third method the two layers of the above distillate were separated. The upper aqueous layer was saturated with sodium nitrate. This method proved unsatisfactory since a large amount of the 1-chloro-2-methyl-2-propanol remained in the water layer.

Three fractions were obtained during the fractional distillation of the reaction mixtures from the hydrolysis. The first fraction, 60-75°, consisted of two layers and contained additional products. The second fraction, 40-55° at 100 mm., was identified after purification as unreacted 1,2-dichloro-2-methylpropane. The third fraction, 55-72° at 100 mm., upon purification proved to be 1-chloro-2-methyl-2-propanol.

Identification of 1-Chloro-2-methyl-2-propanol

The crude 1-chloro-2-methyl-2-propanol was purified by fractional distillation. The column was packed with Penn-State spirals⁶ and is described in the literature.³

A pressure regulator was used with the column as previously mentioned. The fraction 71-71.5° at 100 mm. was the pure 1-chloro-2-methyl-2-propanol, b. p. 126-126.5° at 748.3 mm. The b. p. of this compound is reported⁷ as 126-127° at 736 mm.

1-Chloro-2-methyl-2-propanol forms 1,2-dichloro-2-methylpropane when treated with warm concentrated hydrochloric acid.⁸ The purified 1-chloro-2-methyl-2-propanol was converted into 1,2-dichloro-2-methylpropane by this method. This reaction also takes place at room temperature.

1-Chloro-2-methyl-2-propanol has been converted into 1,2-epoxy-2-methylpropane⁸ (p. 494). The 1-chloro-2-methyl-2-propanol obtained from 1,2-dichloro-2-methylpropane was converted into 1,2-epoxy-2-methylpropane by means of solid calcium hydroxide, solid calcium oxide and solid sodium hydroxide. A 95% yield of pure 1,2-epoxy-2-methylpropane was obtained with sodium hydroxide.

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Summary

1-Chloro-2-methyl-2-propanol was the chief product isolated in the liquid-phase hydrolysis of 1,2-dichloro-2-methylpropane under slightly basic, neutral or slightly acidic conditions.

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(3) Hass, McBee and Weber, *Ind. Eng. Chem.*, **27**, 1195 (1935).

(4) Munch, *J. Chem. Ed.*, **9**, 1275 (1932).

(5) Krassuski, *Chem. Zentr.*, **73**, II, 21 (1902).

(6) Wilson, Parker and Laughlin, *THIS JOURNAL*, **55**, 2795 (1932).

(7) Evans, *Z. physik. Chem.*, **7**, 337 (1891).

(8) Henry, *Compt. rend.*, **142**, 496 (1906).