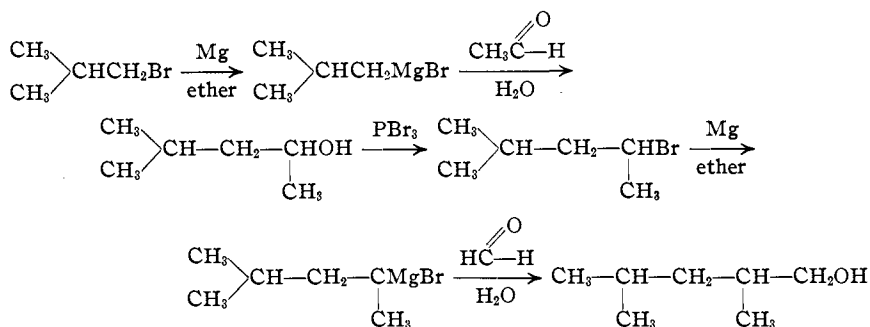


NOTES

Synthesis and Characterization of 2,4-Dimethylpentanol-1.—Several new higher alcohols have been isolated from the products formed by the reduction of carbon monoxide by hydrogen.¹ One of these, 2,4-dimethylpentanol-1, has now been synthesized and characterized. The synthesis was accomplished by the following series of reactions



All of these preparations were carried out according to the usual methods, so no details of the preparations will be given except to mention the yields and the physical properties of the compounds.

From 274 g. of isobutyl bromide, 50 g. of magnesium and 90 g. of acetaldehyde there was obtained 100 g. (49% of the theoretical amount) of 4-methylpentanol-2 boiling at 129–131°. The bromide was prepared from 102 g. of this alcohol and 100 g. of phosphorus tribromide. The yield was 101 g. (61% of the theoretical amount) of a product which boiled at 130–132°. The 2,4-dimethylpentanol-1 was prepared from 101 g. of this bromide, 18 g. of magnesium and an excess of formaldehyde. The new alcohol boiled at 160–162° at ordinary pressure or at 65–67° (18 mm.). The yield was 22 g. (30% of the theoretical amount), d_4^{20} 0.793; n_D^{20} 1.427.

To characterize the new alcohol the 3-nitrophthalate was prepared according to the method of Nicolet and Sacks.² This derivative melted at 154–155° and titration gave a neutral equivalent of 311, whereas the theoretical value is 309.

Anal. (Micro Dumas). Calcd. for $\text{C}_{15}\text{H}_{19}\text{O}_6\text{N}$: N, 4.53. Found: N, 4.3.

CONTRIBUTION FROM THE
CHEMICAL LABORATORY OF THE
UNIVERSITY OF ILLINOIS

URBANA, ILLINOIS

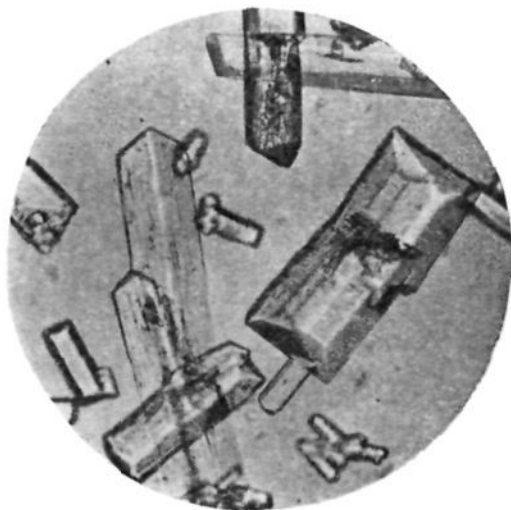
RECEIVED JULY 13, 1931
PUBLISHED DECEMBER 10, 1931

TSE-TSING CHU
C. S. MARVEL

¹ Graves, *Ind. Eng. Chem.*, **23**, 1381 (1931).

² Nicolet and Sacks, *THIS JOURNAL*, **47**, 2348 (1925).

Rotenone. XVII. Note on the Dimorphic Forms of Dihydrorotenone.—In the first article¹ of this series dihydrorotenone was reported as melting at 164°. A number of different preparations were made, but in no case was a product obtained which melted at 216°, the melting point observed by several other investigators. However, the various derivatives obtained from the material melting at 164° agreed in their physical properties with those reported by others as having been made from the material melting at 216°. After an interval of several months we again had occasion to prepare dihydrorotenone, and this time it melted at 216°. On examination of several old preparations it was found that



Dihydrorotenone, m. p. 164° (×50).

they had changed to the higher melting form, and since that time we have obtained only the product melting at 216°. The crystallographic data obtained on the old form were quite different from those observed on the new form. This is a very striking case of dimorphism. **Dihydrorotenone, m. p. 164°.**—When examined under the microscope in ordinary light dihydrorotenone melting at 164° was seen to consist of well-formed rectangular and six-sided prisms. In parallel polarized light with crossed nicols, the extinction was straight and the elongation negative. In convergent polarized light with crossed nicols, fragments occasionally were found which showed a biaxial interference figure with the optic axis inclined. The refractive indices, determined in solutions of potassium mercuric iodide in glycerol and water, were as follows: n_{α} , 1.550 (common on irregular fragments and lengthwise on elongated forms); n_{β} , indet.; n_{γ} , 1.682 (frequently crosswise on elongated forms); both ± 0.003 . (It is not to be assumed that the crystal forms remained intact when the optical constants were being obtained. They were determined on the finely powdered material) (Fig. 1).

Dihydrorotenone, m. p. 216°.—When examined in ordinary light the sample of dihydrorotenone which melts at 216° was seen to be composed

of irregular fragments of the higher melting form, and since that time we have obtained only the product melting at 216°.

The crystallographic data obtained on the old form were quite different from those observed on the new form. This is a very striking case of dimorphism.

Dihydrorotenone, m. p. 216°.—When examined under the microscope in ordinary light dihydrorotenone melting at 216° was seen to consist of irregular fragments of the higher melting form. In parallel polarized light with crossed nicols, the extinction was straight and the elongation negative. In convergent polarized light with crossed nicols, fragments occasionally were found which showed a biaxial interference figure with the optic axis inclined. The refractive indices, determined in solutions of potassium mercuric iodide in glycerol and water, were as follows: n_{α} , 1.550 (common on irregular fragments and lengthwise on elongated forms); n_{β} , indet.; n_{γ} , 1.682 (frequently crosswise on elongated forms); both ± 0.003 . (It is not to be assumed that the crystal forms remained intact when the optical constants were being obtained. They were determined on the finely powdered material) (Fig. 1).



Dihydrorotenone, m. p. 216° (×50).

¹ LaForge and Smith, *THIS JOURNAL*, 51, 2574 (1929).

of wedge-shaped forms and short, stout prisms differing markedly in habit from the material melting at 164° . In parallel polarized light with crossed nicols, the material was characterized by not extinguishing sharply when the microscope stage was rotated. In convergent polarized light with crossed nicols, biaxial interference figures showing one optic axis in the center of the field or in the eccentric position were common. The material was not soluble in the ordinary organic liquids. The refractive indices were as follows: n_{α} , 1.600; n_{β} , 1.625; n_{γ} , 1.680; all ± 0.003 (Fig. 2).

Dihydrorotenone exists in dimorphic forms, the one melting at 164° , the other at 216° . The high melting form is the more stable.

CONTRIBUTION FROM THE
INSECTICIDE DIVISION
BUREAU OF CHEMISTRY AND SOILS, AND
THE MICROANALYTICAL LABORATORY
FOOD AND DRUG ADMINISTRATION
WASHINGTON, D. C.

F. B. LAForge
G. L. KEENAN

RECEIVED AUGUST 11, 1931
PUBLISHED DECEMBER 10, 1931

Composition of Copper Xanthate.¹—Much confusion exists concerning the formula of the yellow precipitate formed on adding a cupric salt to a xanthate solution. From the time of its first analysis² until recently, the discoverer's claim that it is a cuprous salt was generally accepted. Then Johnson,³ assuming that all the xanthate is precipitated—whereas half of it is oxidized to dixanthogen—believed it to be a cupric salt. This view has been accepted by recent workers,^{4,5,6,7,8} with a few exceptions.^{9,10}

The writer has analyzed three samples of the precipitate made by adding excess copper sulfate solution to fresh solutions of potassium xanthate. After filtering, washing with water, triturating with alcohol to remove the dixanthogen, filtering again, washing with alcohol and drying overnight, the copper in a known weight of precipitate was determined by dissolving with saturated bromine water, boiling off the excess oxidant, evaporating to a small volume, adding 1 g. of potassium iodide and titrating with thio-sulfate. From these data, assuming one atom of copper to each molecule,

¹ Published by permission of the Director, U. S. Bureau of Mines. (Not subject to copyright.)

² Zeise, *Ann. Physik. Chem. (Poggendorff)*, **35**, 487-514 (1835).

³ Johnson, *THIS JOURNAL*, **28**, 1210-1214 (1906).

⁴ Harding and Doran, *ibid.*, **29**, 1476-1482 (1907).

⁵ Calcott, English and Downing, *Eng. Mining J.-Press*, **118**, 980-981 (1924).

⁶ Hallett and Ryder, *ibid.*, **119**, 690 (1925).

⁷ Huff, *THIS JOURNAL*, **48**, 81-87 (1926).

⁸ Holtz, "Dissertation," Johns Hopkins University, 1930, pp. 23-24.

⁹ Spielmann and Jones, *J. Soc. Chem. Ind.*, **38**, 185-187T (1919).

¹⁰ Duncan, Ott and Reid, *Ind. Eng. Chem.*, **23**, 382 (1931).

the molecular weight of the precipitate was calculated. The values so obtained, 190.8, 190.4 and 188.2, differ from the theoretical for cuprous xanthate ($\text{CuSCSOC}_2\text{H}_5$), 184.7, by only two or three per cent., the discrepancy being attributed to occlusion of dixanthogen. As the molecular weight of cupric xanthate ($\text{Cu}(\text{SCSOC}_2\text{H}_5)_2$), 305.9, is very much larger, the precipitate is undoubtedly the cuprous salt.

CONTRIBUTION FROM THE
PHYSICAL CHEMISTRY SECTION
PITTSBURGH EXPERIMENT STATION
U. S. BUREAU OF MINES

PITTSBURGH, PENNSYLVANIA

RECEIVED AUGUST 22, 1931
PUBLISHED DECEMBER 10, 1931

MARYAN P. MATUSZAK

The Melting Point of Normal Butyl Ether.—Incidental to some other research the melting point of normal butyl ether has been determined, we believe, for the first time.

Eastman Kodak Company pure normal butyl ether was further purified by distillation in a small laboratory column, the middle third being used.

The apparatus used in this measurement consisted of a copper calorimeter wound with a heater and supplied with a copper-constantan thermocouple. This was hung by threads within a heavy copper cylinder, which was also provided with heater and thermocouple. The whole was suspended in a silvered glass tube connected to a mercury vapor pump to provide thermal insulation.

The apparatus was cooled below the melting point of the normal butyl ether and evacuated. The calorimeter was then warmed gradually by means of the heating coil. The ether melted very sharply at $177.8 \pm 0.2^\circ\text{K}$., the sharpness of the melting point being sufficient evidence of the purity of the sample.

CONTRIBUTION FROM THE
CHEMICAL LABORATORY OF THE
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA

RECEIVED SEPTEMBER 18, 1931
PUBLISHED DECEMBER 10, 1931

R. C. ARCHIBALD