millimicrons. The data were obtained by the Koppers Spectrographical Research Laboratory at Mellon Institute under the direction of Dr. J. J. McGovern.

Summary

1. Isoquinoline has been purified by fractional distillation and extensive recrystallization to a purity of over 99.5 mole per cent.

2. The following properties have been determined for the purified material: f. p., b. p., density, expansion coefficient and viscosity at frequent temperature intervals between 30 and 200°, refractive index at 5893 and 5461 Å. at 30°, the dipole moment, and the infrared and ultraviolet absorption spectra.

PITTSBURGH, PA. RECEIVED JULY 29, 1948

[CONTRIBUTION FROM PROJECT SQUID, PURDUE DEPARTMENT OF CHEMISTRY AND SCHOOL OF CHEMICAL ENGINEERING]

1,3-Dinitropropane

BY J. P. KISPERSKY, H. B. HASS AND D. E. HOLCOMB

Introduction

Keppler and Meyer[1] reported 1,3-dinitropropane, prepared by reaction between silver nitrite and 1,3-diiodopropane, to be a yellow, unstable, undistillable oil which changed after several days to a viscous, brown material. On the basis of our present knowledge there seemed to be no adequate reason for expecting 1,3-dinitropropane to be instable. The researches of Kornblum and students[2] in this Laboratory have shown that substantial amounts of organic nitrates are formed in the Victor Meyer reaction and can be removed from the nitro compounds by treatment with sulfuric and phosphoric acids.

3-Nitro-1-propyl nitrate and the corresponding nitrite would be expected to be instable because the primary nitro group tautomerizes to an acidic nitronic acid and neither nitrites nor nitrates are stable to acid.

It, therefore, seemed advisable to repeat the synthesis of 1,3-dinitropropane and to apply the recent purification procedures. As a result, 1,3-dinitropropane has been prepared for the first time in pure form. It is a stable, colorless liquid, distillable at low pressures, b. p. 103° at 1 mm., m. p. −21.4°, molal f. p. const. 4.5, ht. of fusion 27, cal./g., $n^{25}D$ 1.4638, density 1.353 g./ml. at 25.5°, n_D 20.0° − 1.4654; 21.6° − 1.4649; 30.0° − 1.4622.

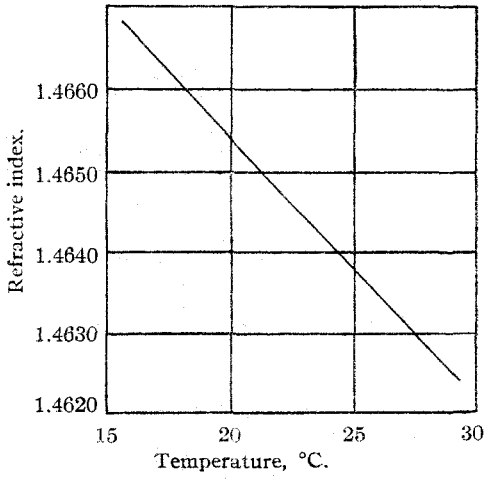

Fig. 1.—Change of refractive index with temperature.

Experimental

The silver nitrite was prepared according to the directions of McElroy.[3] A slurry was formed of five moles (770 g.) of silver nitrite in 1100 ml. of ether and two moles (592 g.) of 1,3-diiodopropane was added with stirring from a dropping funnel. The flask was cooled externally and the rate of addition regulated to cause gentle refluxing of the ether. After the addition was complete, stirring was continued at room temperature in the dark for twenty hours. Afterward the ether solution was removed by decantation and the residue extracted twice with 300 ml. portions of ether, filtered with suction and washed again with 300 ml. of ether. The ether was evaporated over a steam cone, washed with an equal volume of water and dried over Drierite. The orange-colored liquid residue from two such preparations weighed 300 g.

Distillation in a column resulted in decomposition but an ordinary vacuum distillation gave 90 g. of a fraction b. 100–110° at 1 mm. which gave a positive test with diphenylamine in sulfuric acid. Contrary to Mulliken[4] this color test is not given by pure, primary mononitro paraffins.

The material was then added to three times its volume of 96% sulfuric acid at 0°, stirred for several minutes, poured over ice, and the insoluble layer washed with water. After drying with Drierite the 18 g. remaining distilled at 103° at 1 mm. Qualitative tests showed the presence of nitrogen and absence of halogen. The diphenylamine test now showed the absence of nitrite or nitrate ester.

An estimate of the purity of the sample from the freezing point curve showed it to be 98.2 mole per cent. 1,3-dinitropropane. Nitromethane was added as the known impurity.

Analysis by Huffman Microanalytical Laboratories gave the following: Calcd.: H, 4.51; C, 26.87; N, 20.90. Found: H, 4.55, 4.53; C, 26.89, 26.95; N, 21.03, 20.95.

Molar refractivity calculated from Eisenlohr's values is 27.30. Calculated from observed data, 27.33.

Storage of 1,3-dinitropropane at room temperature from September, 1947, to July, 1948, produced no visible alteration.

Summary

1,3-Dinitropropane has been prepared for the first time in a state of high purity and the common physical constants determined.

RECEIVED AUGUST 6, 1948

(1) Keppler and Meyer, *Ber.*, **25**, 1710 (1892).

(2) Kornblum, Lichtin, Patton and Iffland, THIS JOURNAL, **69**, 307 (1947).

(3) W. R. McElroy, Ph.D. Thesis, Purdue University, 1943.

(4) Mulliken, "Identification of Pure Organic Compounds," Vol. II, 1916, p. 28.