Critical Temperature and Pressure of Diborane[1]

By Arthur E. Newkirk

In connection with studies of the boron hydrides the critical temperature and pressure of diborane have been measured experimentally by observing the temperature and pressure at which the meniscus between liquid and vapor disappeared on warming. The apparatus was patterned after that of Kay.[2] The temperature was estimated to 0.01° and the pressure to one p.s.i. The sample of diborane was taken from a cylinder and analyzed by low temperature fractional distillation yielding 0.2% of non-condensable gas and 99.8% diborane. The gas used for measurement was therefore vaporized from the cylinder, frozen in a thin layer on the walls of a glass bulb, pumped to remove non-condensable gas and distilled to the capillary. The remainder of the capillary was filled with mercury, attached to the apparatus, and the capillary, its holder and the mercury reservoir placed in a bath at 14°. The bath warmed at the rate of 2° per hour. Several cycles of warming and cooling were made with each run to avoid accidental errors. The results are given in Table I.

Table I

	Crit. temp., °C.	Crit. pressure, p. s. i. a.
Run 1	16.94	582
Run 2	16.69	582
Run 2 after 20 hr. at *ca.* 21.5°	17.1	586
Run 2 extrapolated to zero time	16.63	581
Average corrected value	16.7 ± 0.2	581 ± 5

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(1) This work was performed under U. S. Army Ordnance Contract TUI-2000.

(2) W. B. Kay, *Ind. Eng. Chem.*, **28**, 1014 (1936).

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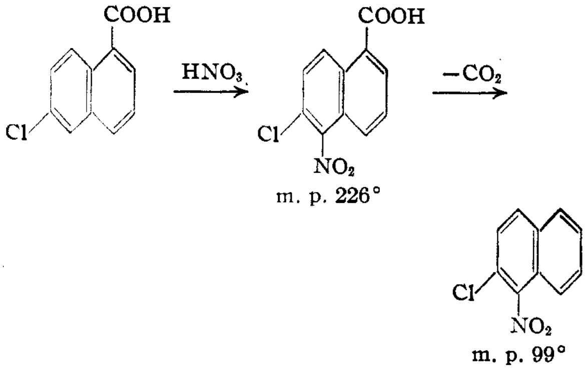
The Nitration of 6-Chloro-1-naphthoic Acid

By Charles C. Price, Thomas J. Bardos and Herman I. Enos[1]

In an exploration of possible routes to a heterocyclic ring system analogous to that in morphine[2] but based on the naphthalene rather than the phenanthrene nucleus, we have investigated the nitration of 6-chloro-1-naphthoic acid with the hope that it might produce the 3-nitro derivative. Nitration of the acid, or preferably of its ester, proceeded satisfactorily to give only one product which could be isolated in pure crystalline condition. This material was shown to be the 5-nitro derivative by decarboxylation to 1-nitro-2-chloronaphthalene, identified by mixing melting point with an authentic sample.



Experimental

Preparation of 6-Chloro-1-naphthoic Acid.—The method of Price and Huber[3] was followed in its original form. The ester fraction obtained was hydrolyzed with 15% aqueous sodium hydroxide solution until it dissolved and the acid was precipitated with dilute hydrochloric acid. The total yield of *crude* 6-chloro- and 7-chloro-1-naphthoic acid mixture was 66% (40% from the straight acid fraction and 26% from the ester fraction; the melting points were 183–185° and 171°, respectively). The 6- and 7-chloro isomers were separated through their acid chlorides, following the procedure of Jacobs, Winstein, Seymour and Linden.[4] Methyl 6-chloro-1-naphthoate was obtained (35%, m. p. 66°) and only 8% of the 7-chloro-1-naphthoyl chloride (m. p. 100–104°). The methyl 6-chloro-1-naphthoate was saponified with 20% aqueous sodium hydroxide, and the acid (m. p. 215.5–216°) precipitated.

Nitration of 6-Chloro-1-naphthoic Acid.—An 11-g. sample (0.053 mole) of the pure 6-chloro-1-naphthoic acid was treated with 18 cc. of fuming nitric acid (d. 1.49–1.50). The substance dissolved partly under vigorous evolution of nitrous oxides and of heat. The reaction mixture was warmed for five to ten minutes on the water-bath. After cooling, fine crystals deposited which were collected on a glass filter, washed with some cold nitromethane, and recrystallized from nitromethane. After this first recrystallization, 8.2 g. (62%) of the greenish yellow nitration product was obtained melting in the range of 198–215°. Five more recrystallizations from nitromethane raised the melting point to 224.8–225.5°. The yield of this pure mono-nitro derivative was 3.7 g. (27.5%) obtained as white needles with a greenish tint; neutralization equivalent, 246 (calcd., 251).

Anal. Calcd. for $C_{11}H_6O_4NCl$: C, 52.48; H, 2.41; N, 5.56; Cl, 14.05. Found: C, 52.70; H, 2.21; N, 5.48; Cl, 14.48.

Decarboxylation of the Nitro Acid.—A sample of 0.48 g. of the 6-chloro-nitro-1-naphthoic acid in 1 cc. of redistilled quinoline was heated in an oil-bath to 220–230° until a homogeneous solution was obtained. Then 0.1 g. of hydrogen-reduced copper powder was added. Immediately vigorous carbon dioxide evolution was observed. The temperature was raised to 240° for five minutes and then the mixture was cooled. It was extracted with ether, the ether extract filtered, washed with dilute hydrochloric acid, with 10% aqueous sodium bicarbonate solution and with water. Finally it was treated with some charcoal, filtered and the ether evaporated: large, pale yellow crystals were obtained. This substance was again recrystallized from aqueous ethanol, with charcoal, to yield pale yellow crystals, m. p. 96.5°. After a further recrystallization almost colorless crystals were obtained, m. p. 98.5–99°.

This corresponds closely to the melting point reported for 1-nitro-2-chloronaphthalene. Since the data in the

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(2) Barltrop, *J. Chem. Soc.*, 399 (1947).

(3) Price and Huber, This Journal, **64**, 2136 (1942).

(4) Jacobs, Winstein, Seymour and Linden, *J. Org. Chem.*, **11**, 292 (1946).