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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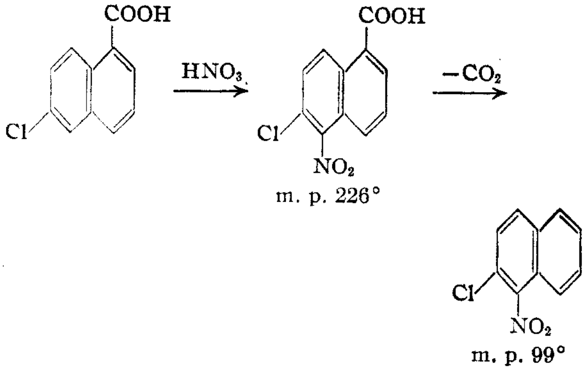
The Nitration of 6-Chloro-1-naphthoic Acid

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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[1] Present address: Department of Chemistry, Swarthmore College, Swarthmore, Pa.

[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).

literature are somewhat divergent (Vesely,[5] Colerdi and Moe,[6] Hodgson and Leigh[7]) we synthesized this compound from β-naphthylamine following for the Sandmeyer step the directions of Hodgson and Walker.[8] The 2-chloro-1-nitronaphthalene so obtained had a melting point of 99-99.5°. The mixed melting point with the sample obtained by the decarboxylation of the 6-chloro-nitro-1-naphthoic acid was 98.5-99°. Accordingly our nitro product must be 6-chloro-5-nitro-1-naphthoic acid.

Nitration of Methyl 6-Chloro-1-naphthoate.—A 9.0-g. sample (0.041 mole) of pure methyl 6-chloro-1-naphthoate (m. p. 66°) was treated with 15 cc. of fuming nitric acid (d. 1.49-1.50) and warmed for five minutes on a water-bath. After cooling, a crystalline mass deposited which was collected on a glass filter and washed with a small portion of cold nitromethane. The crystal mass was already almost white, and after one recrystallization from aqueous methanol, pure methyl 6-chloro-5-nitro-1-naphthoate was obtained: yield, 3.3 g. (30%), m. p. 143.5-144°.

Anal. Calcd. for $C_{12}H_8O_4NCl$: C, 54.23; H, 3.03; N, 5.27; Cl, 13.36. Found: C, 54.52; H, 3.23; N, 5.07; Cl, 13.34.

Hydrolysis of the Nitro Ester.—A solution of 0.5 g. of the ester was refluxed in 30 cc. of 20% aqueous potassium hydroxide, to which 4 g. of salt was added. The substance dissolved after one-half hour of vigorous boiling. In acidification, a dark brown precipitate was obtained. This was filtered and twice recrystallized from nitromethane. Greenish-yellow crystals were obtained which melted at 226.5°. A mixed melting point with 6-chloro-5-nitro-1-naphthoic acid above gave 226-226.5°, showing the identity of the two compounds.

Anilide from the Nitro Acid.—A mixture of 0.2 g. of 6-chloro-5-nitro-1-naphthoic acid and 0.5 cc. of thionyl chloride was refluxed for one-half hour. The reaction mixture was treated with 1 cc. of redistilled aniline and dissolved in 15 cc. of benzene. The yellow suspension was washed with water, with dilute hydrochloric acid, with water and with sodium carbonate solution. After evaporation of the benzene, the residue was recrystallized from aqueous ethanol, using charcoal. The slightly greenish crystalline substance had a melting point of 193-193.5°.

Anal. Calcd. for $C_{17}H_{11}O_3N_2Cl$: C, 62.46; H, 3.40; N, 8.57; Cl, 10.85. Found: C, 62.71; H, 3.30; N, 8.68; Cl, 11.10.

Anilide from the Nitro Ester.—(a) A 0.28-g. sample of the ester was treated with three to four-fold excess of anilinomagnesium bromide for ten minutes on the water-bath. (The anilinomagnesium bromide was prepared by addition of 8 g. of aniline to ethylmagnesium bromide, prepared from 2 g. of magnesium and 10 g. of ethyl bromide in 60 cc. of ether, until the very vigorous evolution of ethane ceased.) Ten cc. of dilute hydrochloric acid was added to the mixture and the ether evaporated at room temperature. The dark brown solid residue from the ether layer was separated from the acidic solution by filtration, and it was recrystallized from aqueous ethanol, yielding 0.12 g. of anilide (34%), m. p. 190-191°. This was recrystallized twice (first with charcoal) to give almost colorless crystals, m. p. 193.5-194°, identical with the anilide obtained from the acid.

(b) When 0.3 g. of the ester was heated with 0.2 g. of aniline at 160-170° for twenty minutes, the ester was recovered unchanged, m. p. 143.5-144°.

Amide from the Nitro Acid.—A 0.22-g. sample of 6-chloro-5-nitro-1-naphthoic acid was heated with 1 cc. of thionyl chloride for twenty minutes. The mixture was poured into 10 cc. of ice-cooled 33% ammonium hydroxide. It was cautiously heated on the water-bath for five minutes, then cooled, filtered and recrystallized from aqueous ethanol, m. p. 207-208°.

Anal. Calcd. for $C_{11}H_7O_3N_2Cl$: N, 11.17. Found: N, 10.70.

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(5) Vesely, *Ber.*, **38**, 137 (1905).

(6) Colerdi and Moe, *Rend. Int. Lomb.*, **57**, 646 (1924).

(7) Hodgson and Leigh, *J. Chem. Soc.*, 1352 (1937).

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9,9-Dibromofluorene and Formation of a Dangerous Skin Irritant

BY JOHN R. SAMPEY AND SCOTT J. CHILDRESS

The preparation of 9-bromofluorene by direct photobromination[1] suggested the preparation of 9,9-dibromofluorene by the addition of a second mole of bromine under strong irradiation.

A solution of 16 g. of fluorene in 150 ml. of carbon tetrachloride was placed in a 250 ml. Vitreosil Erlenmeyer flask equipped with reflux condenser. By the use of a six-inch mercury arc close to the flask, the contents were heated to reflux while a solution of 2 moles of bromine in 50 ml. more solvent was added dropwise through the condenser in thirty minutes. Anhydrous conditions were assumed by a calcium chloride tube and irradiation continued thirty minutes after the addition. Evaporation of the solvent yielded a light gray crystalline product recrystallized from acetic acid, *n*-heptane or absolute alcohol. The yield was 45% of material melting at 115° (uncor.). The literature value for 9,9-dibromofluorene is 114°.[2]

Experiments to further identify the 9,9-dibromofluorene were discontinued when two additional workers to those reported previously,[3] were stricken with a severe dermatitis which has spread over large areas of the body, and which is responding slowly to medical treatment. Intense itching, pus formation, and considerable swelling of the hands, arms and face accompany the irritation.

The authors acknowledge with pleasure the interest of Dr. E. Emmet Reid.

(1) J. R. Sampey and E. E. Reid, THIS JOURNAL, **69**, 234-235 (1947).

(2) H. Staudinger and A. Gaule, *Ber.*, **49**, 1951 (1916).

(3) J. R. Sampey, A. B. King, T. A. Roe, Jr., and S. J. Childress, *Science*, **105**, 621 (1947).

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Nuclear Substituted 9-(4'-Diethylamino-1'-methylbutylamino)-acridines[1]

BY E. R. SHEPARD AND H. A. SHONLE[2]

At the suggestion of the Committee on Medical Research of the OSRD several years ago, the preparation of a series of nuclear substituted acridines was undertaken. They were prepared in order to study clinically the absorption, excretion and metabolic changes which these materials undergo. In addition, it was of interest to inquire further

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(1) Presented before the Division of Medicinal Chemistry at the 109th meeting of the American Chemical Society, Atlantic City, New Jersey, April, 1946.

(2) Deceased, February 24, 1947.