[Contribution from the Department of Chemistry, University of Colorado]

5-Amino-6-nitroacenaphthene

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5-Acetylacenaphthene on nitration yields 5-acetyl-6-nitroacenaphthene. This was converted to the oxime, rearranged, and hydrolyzed to 5-amino-6-nitroacenaphthene. A procedure for the purification of 5,6-dinitroacenaphthene is described.

In the course of some work on the chemistry of acenaphthene, the 5-amino-6-nitroacenaphthene was desired. Up to the present time only the 5-amino-4-nitro-, m.p. 224°,[1–3] the 3-amino-6-nitro-, m.p. 181°,[2] and the 3-amino-5-nitroacenaphthene, m.p. 199–200°[2] have been adequately described. The 3-amino-4-nitroacenaphthene, obtained as the formamido derivative, m.p. 193–196°, is also reported but its structure has not been firmly established.[2]

The nitration of 5-acetylacenaphthene is described by Mayer and Kaufmann,[4] but the position of the entering nitro group was not established. Dziewonski and Moszew[5] nitrated 5-propionylacenaphthene and assumed the formation of the 6-nitro derivative. If these derivatives were 6-nitroacenaphthenes, they could be readily converted into 5-amino-6-nitroacenaphthene and, at the same time, through this derivative the position of the entering nitro group could be established firmly.

In this work, 5-acetylacenaphthene was nitrated and the resulting nitro ketone was converted into the oxime. The oxime was rearranged to the nitroacetamidoacenaphthene with hydrogen chloride in acetic acid-acetic anhydride solution.[5] Hydrolysis of this product in dilute hydrochloric acid followed by neutralization yielded the amino nitro compound which was catalytically reduced, converted into the dibenzamide, and compared with the dibenzamide of the known 5,6-diaminoacenaphthene. A melting point of a mixture of the two dibenzamides showed no depression, thus establishing the structure of the nitration product as 5-acetyl-6-nitroacenaphthene and of the new 5-amino-6-nitroacenaphthene.

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EXPERIMENTAL

5-Acetyl-6-nitroacenaphthene. This compound was prepared essentially as described by Mayer and Kaufmann.[4] The temperature conditions given below were found desirable for consistent results. Crude 5-acetylacenaphthene[6] (5 g.) was dissolved in 30 ml. of warm glacial acetic acid and then was cooled to 25° and treated with 4 ml. of nitric acid (*d.* 1.42). The temperature was not allowed to rise above 32°. The product began to separate as yellow plates in about 20 minutes. The mixture was allowed to stand at room temperature for three hours, cooled, filtered, and the residue was washed with cold acetic acid and with water. There thus was obtained 2.6 g. (43%) of a crystalline product, m.p. 194–200° which after one recrystallization from glacial acetic acid formed golden plates, m.p. 202–204° (lit. 204°).[4]

4-Acetyl-5-nitronaphthalic anhydride. The 5-acetyl-6-nitroacenaphthene (0.5 g.) dissolved in 30 ml. of hot glacial acetic acid was treated slowly with 1 g. of chromic acid dissolved in the minimum amount of water. After the spontaneous reaction had subsided, the mixture was refluxed for 40 minutes. After cooling and filtration, there was obtained 0.38 g. of a light yellow crystalline product which discolored and sublimed but did not melt at 320° (bronze block). The product crystallized as fine pale yellow needles from glacial acetic acid.

Anal. Calc'd for $C_{14}H_7NO_6$: C, 58.94; H, 2.45. Found: C, 58.75; H, 2.53.

Methyl 6-nitro-5-acenaphthenyl ketoxime. 5-Acetyl-6-nitroacenaphthene (3 g.) dissolved in 40 ml. of dry pyridine was treated with 5 g. of hydroxylamine hydrochloride and was refluxed for two hours, filtered, and the oxime was precipitated by adding water. The precipitate was dissolved in ethanol (225 ml.), treated with decolorizing carbon, and crystallized by slow dilution with water. There was obtained 2.4 g. of product, m.p. 217–220° dec. Recrystallization from dilute alcohol gave material which after sintering and darkening melted at 220–221° with decomposition.

Anal. Calc'd for $C_{14}H_{12}N_2O_3$: N, 10.93. Found: N, 10.77.

Attempts to prepare the oxime by refluxing the nitro ketone and hydroxylamine hydrochloride in alcohol in the presence of sodium acetate or pyridine were not successful.

5-Acetamido-6-nitroacenaphthene. The oxime of 5-acetyl-6-nitroacenaphthene (2.4 g.) was dissolved in a mixture of 30 ml. acetic acid and 15 ml. of acetic anhydride, and dry hydrogen chloride was passed through the solution for 2 hours.[5] The mixture warmed up and crystals soon began to separate. After cooling, the product was filtered and washed with cold acetic acid. There thus was obtained 2 g. of crude rearranged material. The addition of water to the filtrate yielded an additional 0.3 g. The combined product was dissolved in glacial acetic acid, treated with decolorizing charcoal, and crystallized by the slow addition of water, m.p. 180–183°. Recrystallization from dilute acetic acid yielded light yellow flat needles m.p. 182–184°.

Anal. Calc'd for $C_{14}H_{12}N_2O_3$: N, 10.93. Found: N, 10.97.

5-Amino-6-nitroacenaphthene. 5-Acetamido-6-nitroacenaphthene (1.5 g.) suspended in 100 ml. of 10% hydrochloric acid was refluxed for 1.25 hours. The quite dark hot solution was filtered and the yellow-orange filtrate was cooled and made basic with sodium carbonate solution. The precipitated

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[1] Sachs and Mosebach, *Ber.*, **44**, 2852 (1911).

[2] Morgan and Harrison, *J. Soc. Chem. Ind.* (*London*), **49**, 413T (1930).

[3] Rowe and Davies, *J. Chem. Soc.*, **117**, 1344 (1920).

[4] Mayer and Kaufmann, *Ber.*, **53**, 295 (1920).

[5] Dziewonski and Moszew, *Bull. intern. acad. polonaise*, No. **2A**, 163 (1931).

[6] Nightingale, Ungnade, and French, *J. Am. Chem. Soc.*, **67**, 1263 (1945).

dark red 5-amino-6-nitroacenaphthene (1.1 g.) was crystallized from dilute ethanol to yield dark red lustrous plates, m.p. 140–141°.

Anal. Calc'd for $C_{12}H_{10}N_2O_2$: N, 13.08. Found: N, 12.91.

The *benzenesulfonamide* was obtained by treating the amine and benzenesulfonyl chloride in the presence of pyridine for 15 minutes at room temperature. Crystallization from dilute acetic acid gave light yellow crystals m.p. 193–194°.

Anal. Calc'd for $C_{18}H_{14}N_2O_4S$: N, 7.91. Found: N, 7.83.

5,6-Dinitroacenaphthene. Acenaphthene, 38.5 g. (0.25 mole) dispersed in 300 ml. of glacial acetic acid was nitrated with 155 ml. of concentrated nitric acid (*sp. gr.* 1.42) as described by Sachs and Mosebach.[1] Separation and purification was accomplished by cooling the reaction mixture to about 18° and the solid in the resulting thick mass was separated with the aid of a Büchner funnel, and washed three times with 25-ml. portions of cold glacial acetic acid followed by three washings with water. The yield of crude, yellow crystalline, air-dried product, m.p. 175–195°, was 38 g. (62%). This crude product was purified by boiling for 2–3 minutes with 200 ml. of toluene and the undissolved, purified residue was removed from the hot solution by filtration, washed twice with 25-ml. portions of toluene, and air-dried. The yield of golden-yellow product, m.p. 209–211°, was 22 g. (36%). The hot toluene filtrate was cooled to 30° and the separated product was removed by filtration. There thus was obtained 8 g. of crude product, m.p. 170–180°, which was extracted with 50 ml. of boiling toluene and filtered hot to yield an additional 4 g. of purified product, m.p. 210–212° (lit. m.p. 210–212°).[7] The total yield was 26 g. (42%).

Reduction of 5,6-dinitroacenaphthene and preparation of dibenzamide. A 1.5-g. sample of 5,6-dinitroacenaphthene was suspended in dry benzene with 150 mg. of 10% palladium on carbon and reduced with hydrogen at 2 atm. for 3 hours. The filtered yellow solution was treated with an excess of benzoyl chloride. After 12 hours the mixture was treated with 10% sodium hydroxide solution to hydrolyze the excess benzoyl chloride. It then was filtered to yield 1.6 g. of a light brown solid. This solid was dissolved in hot acetic acid, treated with decolorizing charcoal and with water to incipient cloudiness. On cooling, it deposited 0.9 g. of almost white crystals m.p. 261–263° (bronze block). An additional 0.6 g., m.p. 261–263°, was obtained by further dilution of the filtrate.

Anal. Calc'd for $C_{26}H_{20}N_2O_2$: N, 7.14. Found: N, 7.15.

Reduction of 5-amino-6-nitroacenaphthene. 5-Amino-6-nitroacenaphthene (0.9 g.) dissolved in 40 ml. of dry benzene was reduced and converted into the dibenzamide by the procedure described above, m.p. 261–262° (bronze block).

A melting point of a mixture of the dibenzamide prepared from the diamine resulting from reduction of the known 5,6-dinitroacenaphthene and the dibenzamide prepared from the diamine obtained by reduction of the new 5-amino-6-nitroacenaphthene showed no depression.

A sample of the 5-amino-6-nitroacenaphthene dissolved in absolute alcohol was reduced with 10% palladium on carbon as described above and water was added to crystallize the diamine. The crude, colored product melted at 153–156° (lit. 160°).[1] The material obtained by the catalytic reduction of the known 5,6-dinitroacenaphthene showed a similar melting point.

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(7) Monti, Martello, and Valente, *Gazz. chim. ital.*, **66**, 31 (1936).