NITRAMINE – A NEW ALKALOID FROM Nitraria schoberi

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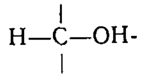
Continuing the separation of the mixture of alkaloids of N. schoberi L. [1], we have isolated a liquid optically active base (I). The alkaloid gave a crystalline nitrate and hydrochloride. The elementary analysis of (I) and of its salts established the composition $C_{10}H_{19}ON$ for it.

Compound (I) is transparent in the UV region. The IR spectrum shows absorption bands of active hydrogen at 3320 and 3365 cm^{-1} (in chloroform).

The acetylation of (I) gave a N-acetyl derivative (II) and an O,N-diacetyl derivative (III). The oxidation of (I) with chromium trioxide yielded a ketone (IV). Consequently, the base contains NH and  $\mathrm{H{-}\underset{|}{\overset{|}{C}}{-}OH}$- groups. Kuhn–Roth oxidation showed the presence of a $-C-CH_3$ group in it. Hence, it is possible to give the developed formula $C_9H_{14}(CH_3)$ (NH) (OH) for (I). Since the base is a new one, we have called it nitramine.

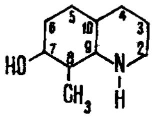
In the NMR spectrum of nitramine at 1.25 ppm there is a doublet with J = 6 Hz due to a $HC-CH_3$ group. A broadened two-proton single at 4.65 ppm, which undergoes a shift on the addition of deuteromethanol, is due to the protons of NH and OH groups.

In the mass spectrum of nitramine there is the peak of the molecular ion with m/e 169 (100%), confirming the composition of (I). In addition, there are strong peaks of ions with m/e 151 $(M-H_2O)$ (82%) 150 (34%), 123, 122 (41%), 96 (27%), 84 (71%), 57 (47%).

The dehydrogenation of (I) gave 8-methylquinoline, shown to be identical with an authentic sample by R_f values, by UV [2], mass, NMR [3], and IR spectra, and by a mixed melting point of the picrates. Consequently, nitramine is a hydroxy-8-methyldecahydroquinoline.

The presence in the mass spectrum of nitramine of a strong dehydration peak with m/e 151, and also a peak with m/e 96 formed as the result of the cleavage of the C_5-C_6 and C_8-C_9 bonds [corresponding peaks are found in all the derivatives of (I)] excludes positions at C_2, C_3, C_4, and C_5 for the hydroxy group [5]. Hence, nitramine is either 6-hydroxy-or 7-hydroxy-8-methyldecahydroquinoline.

Since substance (IV) condenses with only one molecule of benzaldehyde, its hydroxy group is most probably located at C_7. Thus, nitramine is 7-hydroxy-8-methyldecahydroquinoline (I).



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EXPERIMENTAL

The UV spectra were taken on a Hitachi instrument in ethanol, the mass spectra on an MKh-1303 spectrometer at 40 eV 0.5 mA, the NMR spectra on a JNM-4H-100/100 MHz instrument (the chemical shifts

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are given in the δ scale from the signal of HMDS taken as 0), and the IR spectra on a UR-10 instrument (in the form of a film and in chloroform solution). The molecular weights were determined by mass spectrometry. The individuality of the compounds obtained was confirmed by chromatography on a nonfixed layer of alumina in the chloroform–methanol–benzene (5 : 1 : 4) and chloroform–methanol (9 : 1) systems and also on a fixed layer of silica gel–gypsum (10 : 1) in the chloroform–ethanol (2 : 1) system, except where specially mentioned.

Isolation of Nitramine (I). The ethereal fraction of the combined extract from N. schoberi was separated by means of phosphate buffer solutions into ten fractions at unit pH intervals.

The fraction with pH 8 was dissolved in acetone, and the ice-cooled solution was treated with a 30% solution of HNO_3 in acetone. A crystalline nitrate with mp 187-190°C precipitated, and after several recrystallizations from ethanol it melted at 204-206°C.

The decomposition of the nitrate by the usual method gave substance (I) in the form of a colorless oil, $[\alpha]_D^{20}$ +16.5° (c 4.85; chloroform). The yield of the base was 0.003% of the weight of the dry plant. Nitramine is readily soluble in ether, chloroform, and acetone and less readily in petroleum ether.

Nitramine Hydrochloride. This compound was obtained by mixing an acetone solution of the base with an ethanolic solution of hydrogen chloride; mp 200-201°C (from ethanol).

N-Acetylnitramine (II). A mixture of 0.05 g of nitramine, 1 ml of pyridine, and 1 ml of acetic anhydride was left for two days. Then the solvents were evaporated off in vacuum, the residue was dissolved in water, and the solution was made alkaline with saturated Na_2CO_3 solution and was extracted with petroleum ether. After drying over potassium carbonate and the distillation of the solvent, substance (II) was obtained in the form of a colorless oil. Yield 0.03 g. IR spectrum, cm^{-1}: 1610 $(>N{-}\overset{|}{C}{=}O)$, 3680 (OH); mass spectrum: m/e 211 (M^+) (80%), 183 (30%), 168 (30%), 138 (15%), 126 (100%), 84 (41%).

O,N-Diacetylnitramine (III). A solution of 0.1 g of the base in 5 ml of acetic anhydride was treated with 0.15 g of p-toluenesulfonic acid. The mixture was heated at 100°C for 2 h (the course of the reaction being followed chromatographically). Then the reaction mixture was cooled with ice and was made alkaline with sodium carbonate, and the substance (III) was extracted with ether. Distillation of the solvent yielded 0.11 g of a colorless neutral oil.

IR spectrum of (III), cm^{-1}: 1610 (amide carbonyl), 1735 (ester carbonyl group). Mass spectrum: m/e 253 (9%), (M^+), 210 (11%), 168 (4%), 138 (5%), 61 (100%).

Oxidation of Nitramine. 8-Methyl-7-oxodecahydroquinoline. A mixture of 0.06 g of nitramine, 0.11 g of CrO_3, and 2.5 ml of acetic acid was left at room temperature for three days. The solvent was driven off in vacuum and the dry residue was treated with 2 ml of water and made alkaline with a 5% solution of NaOH. The reaction product was extracted with petroleum ether. This gave 0.04 g of the oily ketone (IV).

IR spectrum, cm^{-1}: 1700 (C=O); no absorption in the region of active hydrogen atoms; mass spectrum: m/e 167 (83%) (M^+), 150 (21%), 138 (11%), 110 (37%), 57 (100%).

N-Acetyl-8-methyl-7-oxodecahydroquinoline. A mixture of 0.03 g of the ketone, 1 ml of pyridine, and 1 ml of acetic anhydride was left at room temperature for five days (the course of the reaction being followed chromatographically). After the end of the reaction, the solvents were driven off in vacuum, and the residue was dissolved in water and made alkaline with 5% NaOH solution. The reaction products were extracted with petroleum ether, and the mixture obtained was separated preparatively on a fixed layer of alumina. The yield of N-acetyl-8-methyl-7-oxodecahydroquinoline was 0.01 g.

Mass spectrum: m/e 209 (M^+) (47%), 181 (100%), 166 (22%), 138 (14%), 82 (11%), 57 (24%).

Dehydrogenation of Nitramine. 8-Methylquinoline (V). The dehydrogenation of 0.31 g of nitramine was performed with 0.72 g of 40% Pd/C as catalyst (in three portions). The mixture was heated in a current of nitrogen at 225-250°C for 1 h. Then it was cooled and the products were extracted with boiling ethanol and chloroform. A very complex mixture (according to chromatography) was obtained. The combined ethanolic fraction from three experiments was separated on a column of silica gel (1 : 50) and was eluted with benzene, 50-ml fractions being collected. The residue after the distillation of the benzene (0.1 g) was separated preparatively on a fixed layer of silica gel–gypsum (10 : 1) in the chloroform–benzene–methanol (20 : 20 : 2.5) system. The yield of 8-methylquinoline was 0.026 g (3.3% of theoretical).

UV spectrum: λ_{max} 233, 235, 292, 304, 316 nm (log ε 4.51; 4.51; 3.55; 3.51; 3.39). Mass spectrum: peaks with m/e 143 (100%) (M^+), 142 (M−1). NMR spectrum: singlet (3H) at 2.72 ppm from a CH_3 group, multiplet (4H) with its center at 7.28 ppm, and two one-proton quartets at 7.88 and 8.76 ppm.

8-Methylquinoline Picrate. The substance was obtained by mixing ethanolic solutions of the base and of picric acid; mp 198-200°C. A mixture of the picrates of the product and of an authentic sample of 8-methylquinoline melted at 198-200°C.

SUMMARY

A new liquid base with the composition $C_{10}H_{19}ON$ has been isolated from the epigeal part of *N. schoberi* and has been called nitramine. The dehydrogenation of nitramine with Pd/C gave 8-methylquinoline. On the basis of a study of the UV, IR, NMR, and mass spectra of nitramine and its derivatives, the structure of 7-hydroxy-8-methyldecahydroquinoline has been established for it.

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