

SYNTHESIS OF DOUBLE ^{15}N -LABELED NITRAMINES: N-NITROPIPERIDINE AND N-NITRO-DIMETHYLAMINE

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SUMMARY

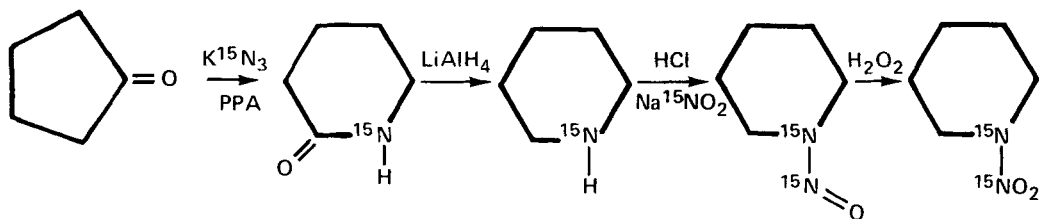
Double ^{15}N -labeled N-nitropiperidine and N-nitrodimethylamine have been conveniently prepared by oxidation of the corresponding nitrosamines. Dimethylamine- ^{15}N was commercially available while the required piperidine- ^{15}N was synthesized from cyclopentanone via the Schmidt ring-expansion procedure using potassium azide- ^{15}N , followed by hydride reduction of the resulting 2-piperidinone- ^{15}N .

Key Words: Nitramines, Nitrogen-15, N-Nitropiperidine, N-Nitrodimethylamine, Dimethylnitramine, Mass Spectra.

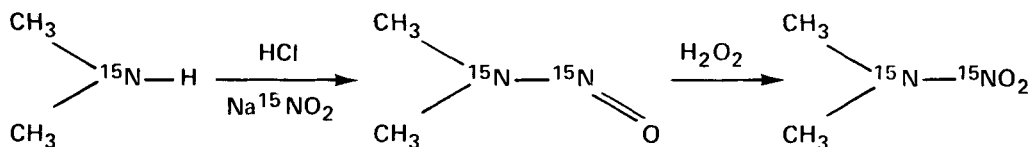
INTRODUCTION

The properties of secondary nitramines are of great interest to this laboratory because they are important energetic materials. As model compounds in the study of the decomposition mechanism of compounds containing more than one nitramine moiety (1), and to investigate the structural parameters that influence the spin-coupling between directly bonded ^{15}N - ^{15}N nuclei (2), several double ^{15}N -labeled nitramines were required in these laboratories. The preparation of two ^{15}N -labeled secondary nitramines, 1,3,5-trinitro-1,3,5-triazacyclohexane and 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane by nitrolysis (3) of hexamine with ammonium nitrate and nitric acid is the subject of a separate report (4). This report describes the details of another method, namely, the oxidation (5) of the corresponding nitrosamines, used to obtain the nitramines, N-nitropiperidine and N-nitrodimethylamine.

SCHEME I



SCHEME II



The reaction sequence outlined in Scheme I was used to synthesize the ^{15}N -labeled piperidine and is patterned after the procedure previously used (6) to prepare 2- ^{14}C -N-nitroso hexamethyleneimine. The last step in this sequence representing the H_2O_2 oxidation was also common to the oxidation of the ^{15}N -labeled dimethylnitrosamine indicated in Scheme II.

EXPERIMENTAL

The ^{15}N -labeled materials used in these procedures were obtained from Stoehler Isotope Chemicals and contained the following nitrogen-15 abundances: K^{15}N_3 (50% N-1), $\text{Na}^{15}\text{NO}_2$ (99%) and $(\text{CH}_3)_2^{15}\text{NH}_2^+ \text{Cl}^-$ (99%). ^1H -NMR spectra were obtained using a Varian Associates T-60 spectrometer. Mass spectra were obtained using a DuPont 21-492 double focusing mass spectrometer. Melting points are uncorrected.

N -[nitro- ^{15}N]-piperidine- ^{15}N

To a stirred solution of 1.04 g of cyclopentanone in 20.0 g of polyphosphoric acid at room temperature was added in small portions over 1 h, 0.99 g of potassium azide-1- ^{15}N (99%). The temperature of the reaction mixture was raised to 55°C and stirring was continued for 12 h. The reaction was quenched by the addition of

of crushed ice (10 g) and after adjusting the pH to 9 by the dropwise addition of 50% NaOH the mixture was extracted with 7 x 25 mL portions of chloroform. The combined extracts were dried over Na_2SO_4 and after removal of the solvent by distillation through a 30 cm Vigreux column there was obtained 1.2 g (99%) of crude 2-piperidinone- ^{15}N (50% enriched) as oil. A mass spectrum of the sample showed the molecular ions at m/e 99 and m/e 100 (^{15}N) in approximately 1:1 ratio.

To a cooled solution of the crude 2-piperidinone- ^{15}N (1.2 g) in 32 mL of anhydrous ether was added 0.684 g of lithium aluminum hydride. The resulting suspension was heated under reflux for 5 h and allowed to stand at room temperature for 12 h. Dropwise addition of 0.7 mL of water and stirring for 0.5 h gave a granular precipitate from which the ethereal solution was easily filtered. Removal of the ether gave 0.45 g (44%) of piperidine- ^{15}N (50% enriched; molecular ions in the mass spectrum at m/e 85 and 86 in 1:1 ratio.)

A solution of 0.45 g of sodium nitrite- ^{15}N (99% ^{15}N) in 0.5 mL of water was added dropwise over 1 h to a pH 1 solution of 0.37 g of piperidine- ^{15}N in 0.5 mL of 0.1N HCl. The mixture was heated at 55°C for 1 h, cooled and made basic by the addition of about 10 mg of potassium carbonate. The nitroso derivative was isolated by extracting seven times with 5 mL portions of ether and the combined ether extracts were dried over sodium sulfate. Removal of the ether gave 0.48 g (78%) of the N-[nitroso- ^{15}N] -piperidine- ^{15}N as an oil, whose mass spectrum confirmed the ^{15}N abundance as 50% and 99% in the nitroso and amino groups respectively.

To a stirred solution of 0.18 g of nitrosopiperidine in 0.5 mL of trifluoroacetic acid was added 0.30 mL of 30% hydrogen peroxide at 0°C. The reaction mixture was slowly heated and maintained at 40°C for 3 h. The product was isolated by the addition of crushed ice (20 g), careful neutralization with 5% sodium carbonate, followed by extracting three times with 10-mL portions of ether. The ethereal solution was dried over sodium sulfate and after removal of the solvent there was obtained 0.20 g (97%) of N-Nitropiperidine- $^{15}\text{N}_2$ (99% enriched in the NO_2 and 50% in the ring nitrogen). The mass spectrum shows corresponding molecular ions at m/e 131 and 132, in 1:1 ratio. The ^1H -NMR spectrum (CDCl_3) exhibited two multiplets centered at δ 1.72 and δ 3.86, respectively. These properties were essentially the

same as those observed for unlabeled material prepared on a larger scale and having bp 86°C at 7 mm.

N-[Nitro-¹⁵N]-dimethylamine-¹⁵N

A solution of 0.83 g of sodium nitrite-¹⁵N (99%¹⁵N) in 1.0 mL of water was added dropwise over 1 h to a solution of 1.08 g of dimethylamine-¹⁵N (99%¹⁵N) hydrochloride dissolved in 0.5 mL of water and adjusted to pH 1.5 by the addition of a trace of hydrochloric acid. The resulting dimethylnitrosamine was extracted with three 5-mL aliquots of methylene chloride. The combined extracts were dried over Na₂SO₄ and removal of the solvent gave 0.67 g (76%) of an oil which was dissolved in 2.5 mL of trifluoroacetic acid and treated with 2.0 mL of 30% H₂O₂. After stirring at room temperature for 1.5 h the mixture was poured on crushed ice and extracted three times with 5.0 mL portions of methylene chloride. The combined extracts were washed with 5% sodium carbonate followed by water and finally dried over Na₂SO₄. Removal of the solvent and recrystallization of the crude solid from hexane-chloroform gave 0.35 g (43%) of dimethylnitramine-¹⁵N, mp 54-55°C. The mass spectrum (1) of the product shows the molecular ion at m/e 92 corresponding to (CH₃)₂¹⁵N-¹⁵NO₂.

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