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AMINE-NITROIMIDES: A NEW FUNCTIONAL GROUP (1)

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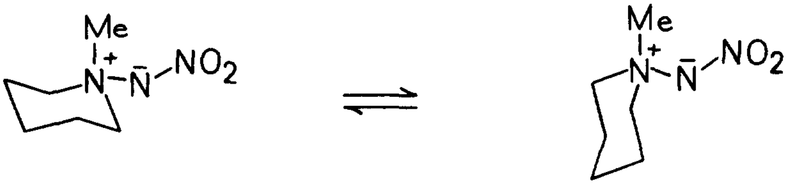
1, 1, 1-Trimethylhydrazinium nitrate (I) m. p. 77-78° (readily prepared from the corresponding iodide (3) by double decomposition with silver nitrate) is converted by acetic anhydride into trimethylamine nitroimide (II) which crystallises as colourless needles (4), m. p. 212-214°, from ethanol and sublimed at 190°/0. 3 mm. Compound II is the simplest member of a new class of compounds, the amine nitroimides, analogous to the known (5) acyl and sulphonyl derivatives $R_3N^+.N^-.COR$ and $R_3N^+.N^-.SO_2R$.

$$Me_3N^+.NH_2 \quad NO_3^- \quad \rightarrow \quad Me_3N^+.N^-.NO_2$$

(I) (II)

Trimethylamine nitroimide (II) is thermally stable, surviving temperatures up to 200° for several hours. It is very soluble in water, sparingly so in lower alcohols, and insoluble in non-polar solvents. It is unaffected by cold aqueous sodium hydroxide (except to be salted out of solution) and was also recovered unchanged after 2 hr refluxing with aqueous alkali. The compound dissolved in concentrated sulphuric acid: neutralisation of the diluted mixture, evaporation and extraction of the residue with ethanol recovered unchanged nitroimide.

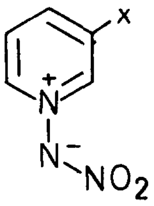
The nitroimide II is a weak base, its pK_a was determined as -4.2 ± 0.1 from the variation of the chemical shift of the methyl protons with the H_o of aqueous sulphuric acid solutions of the compound. The low basicity is noteworthy: compounds of type $RMe_2N^+.N^-.COR'$ and $RMe_2N^+.N^-.SO_2R'$ were reported (6) to have pK_a values of $+5.3$ and $+3.1$, respectively.



(a) (b)

(III)

The method of preparation illustrated by I → II appears to be general for nitroimides as was illustrated by the conversion of 1-amino-1-methylpiperidinium nitrate, m. p. 216 - 219° (decomp), into 1-methylpiperidine 1-nitroimide (III), which crystallised as needles, m. p. 181 - 182°, from ethanol. The nitroimide synthesis is equally applicable to heteroaromatic tertiary amines: pyridine 1-nitroimide (IV), needles (from ethanol), m. p. 149 - 150°, and its 3-methoxy derivative (V), plates (from ethanol), m. p. 141 - 142°, were readily prepared from the corresponding 1-aminopyridinium nitrates.



(IV), X=H

(V), X=OMe

Preliminary experiments indicate that the nitroimides III, IV and V have properties similar to the parent compound II. For example, analogous thermal stability is shown and the same lack of reaction on acid and base treatment.

The nitroimides show no bands in the NH-stretching region of the IR spectrum. The $N^{+}.N^{-}.NO_2$ group itself appears to be characterised in the IR region by a very strong band at 1300 - 1280 cm^{-1}; in addition a second strong band is found at <u>ca.</u> 1370 cm^{-1} for the aliphatic derivatives and <u>ca.</u> 1415 cm^{-1} for the heteroaromatic compounds. Trimethylamine nitroimide shows bands for methyl groups at 1440, 1465, and 1478 cm^{-1} and further absorption at 1408, 1380 and 1114 cm^{-1}. Pyridine 1-nitroimide (IV) shows the ν_{16} ring stretching mode at 1622 cm^{-1} and further sharp bands at 1189, 1150, 1053, 1002, 888, 782, 769, 727 and 677 cm^{-1} (nujol).

We have measured the resonance interaction of the $N^+.N^-.NO_2$ group with the aromatic ring in IV by means of the integrated intensity (7) of the band at 1619 cm^{-1} (in deuterium oxide): A = 1278, from which $\sigma_R^o = \pm 0.25$. This value may be compared for σ_R^o = -0.21 for the $N^+ - O^-$ group in pyridine 1-oxide (8), and indicates that considerable resonance interaction occurs between the nitroimide group and the pyridine ring. The sign is almost certainly negative, i.e. the nitroimide group is a resonance donor.

The NMR spectrum (9) of trimethylamine nitroimide (II) shows a singlet at τ 6.48 which may be compared with 7.82 for trimethylamine. 1-Methylpiperidine 1-nitroimide shows in the NMR spectrum the methyl signal as a singlet at τ 6.67, while the ring protons appear as two multiplets centred at ca. τ 6.48 (4H, α-CH_2 groups) and ca. τ 8.17 (6H, β- and γ-CH_2 groups).

The NMR spectra of the heteroaromatic nitroimides III and IV will be discussed elsewhere (10): they disclosed the expected A_2B_2C and ABCX pattern, respectively, and the chemical shifts and coupling constants show considerable resemblence to the corresponding N-oxides.

The obvious possibilities for thermal (cf. ref 11) and photochemical (cf. ref 12) reactions which these nitroimides possess are being investigated.

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