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Metastable Isomers of Acetonitrile: Syntheses of Vinylideneamine and Δ^1 -Azirine

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The flash vacuum thermolysis and/or gas-solid phase multistep sequences allow the synthesis of vinylideneamine and a safe, preparative-scale synthesis of Δ^1 -azirine.

Methyl cyanide is an important interstellar molecule and its metastable isomers vinylideneamine and ethynylamine, though not yet detected, are also likely cosmic species;¹ Δ^{1} -azirine, but not methyl isocyanide, should be formed from the dissociative recombination of the protonated precursor $C_2H_4N^{+,1}$ Experimental reports, dealing with these three possible cosmic isomers of methyl cyanide, are limited to the analytical microwave characterization of Δ^{1} -azirine² and evidence for the transient formation of vinylideneamine in the matrix interaction of excited argon atoms with methyl cyanide.³

We have made use of the flash vacuum thermolysis (FVT) and/or gas-solid phase multistep sequences (Figure 1) (see ref. 4 for a description of the technique) and now report different ways of obtaining vinylideneamine (1) and a safe, preparative-scale synthesis of Δ^1 -azirine (2) (Scheme 1).



Figure 1. Schematic representation of the FVT technique.

Flash vacuum thermolysis of the imino-Diels-Alder adducts (3) or (4), obtained from the corresponding ketones and ammonia (tetrahydrofuran, room temp., 3 Å molecular sieve,



Scheme 1. i, FVT, 10⁻⁶ Torr, 850 °C; ii, KOBu^t, 80 °C, 0.1 Torr; iii, 400 °C, 0.1 Torr.



(+ cyclopentadiene)

Scheme 2

5 days) leads, not only to the corresponding diene and variable amounts of methyl cyanide, but also to (1) characterized by its i.r. spectrum at 77 K [v(C=C=N) 2035 cm⁻¹, in good agreement with ref. 3]; the high reactivity of (1) precludes the measurement of its n.m.r. spectrum as well as any purification or trapping experiments. A similar mixture of (1), methyl cyanide, and cyclopentadiene is obtained in the gas phase sequence (Scheme 2) starting from 2-aminonorborn-5-ene (5) and avoiding any isolation of the unstable intermediary imine (6).

The gas phase dehydrochlorination of β -chloroethyl azide (7) over solid KOBu^t affords vinyl azide (8) which is directly thermolysed to give Δ^1 -azirine (2), accompanied by some methyl cyanide [(2); $\delta({}^{1}\text{H})(\text{CDCl}_3, -50 \,^{\circ}\text{C})$ 1.26 (d, 2H, J 2.05 Hz) and 9.93 (t, 1H); $\delta({}^{13}\text{C})(\text{CDCl}_3, -50 \,^{\circ}\text{C})$ 14.4 (J C-3-H 180 Hz, J C-3-C-2-H 8.5 Hz), 162.4 (J C-2-H 244.1

Hz, J C-2-C-3-H 2.5 Hz) p.p.m.; $\dagger \nu_{max}$ (solid film, 77 K) 3060, 2978, 1648, and 965 cm⁻¹; λ_{max} (pentane) 229 nm]. Since (8) is not condensed, this avoids any hazard due to its manipulation, allowing a preparative scale synthesis of (2).[‡] The stability of the azirine (2) is greater than previously reported:² its polymerization is slow at -10 °C and becomes fast only at +10 °C. A very small amount of (1) was also detected in the thermolysis of azide (8).

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[‡] Starting from 0.17 moles of (7) and 1 mole of KOBu^t, 0.1 moles of (2) are obtained [59%] overall yield from (7), low temperature ¹H n.m.r. analysis].

 $[\]dagger$ ^{13}C Values are in good agreement with those previously predicted (ref. 5).