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-azirine[2] 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).

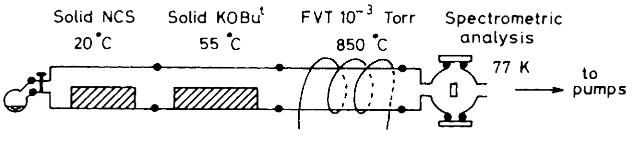
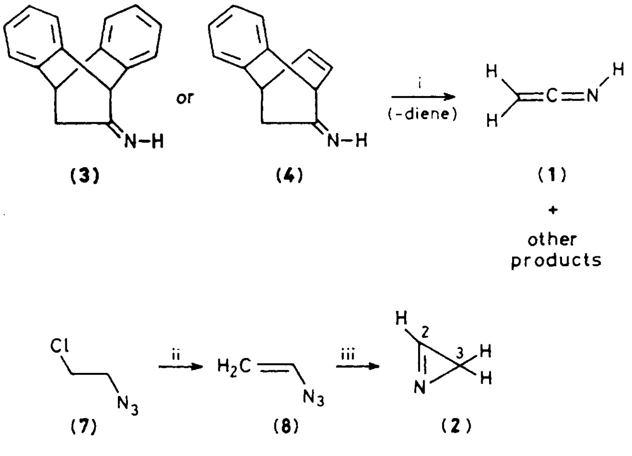
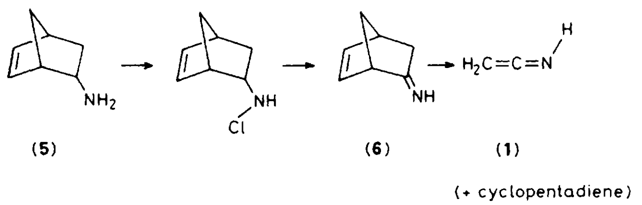


Figure 1. Schematic representation of the FVT technique.

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.



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 [ν(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**); δ(^{1}H)(CDCl$_3$, −50 °C) 1.26 (d, 2H, *J* 2.05 Hz) and 9.93 (t, 1H); δ(^{13}C)(CDCl$_3$, −50 °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.;[†] ν_{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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[†] ^{13}C Values are in good agreement with those previously predicted (ref. 5).

[‡] 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 ^{1}H n.m.r. analysis].