Flash Vacuum Thermolysis of α-Aminonitriles and Subsequent HCN Removal on Solid Base, a 'One Line' Multistep Sequence to Reactive *N*-Methyleneamines

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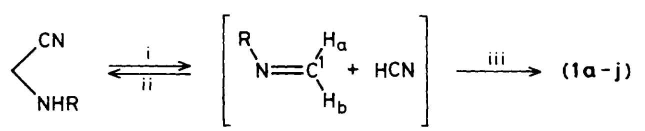
Reactive methyleneamines bearing alkyl or functional groups are isolated at low temperature in the condensate state by flash vacuum thermolysis of α-aminonitriles and subsequent vapour phase HCN removal on solid base.

Simple and reactive imines play an important role both as intermediates and as products in a wide variety of chemical reactions. The detailed molecular properties of many of them remained unstudied for a long time largely owing to the lack of an efficient synthesis for the monomeric form in the gas phase. Methanimine and its higher homologue ethanimine were first detected in the pyrolysis decomposition products from several alkylamines and alkylazides or from trimethyl-*s*-triazine.[1a,2] More recently, preparative syntheses of reactive aldimines[1b,3] and cyclic imines[4] were efficiently realized by two techniques: flash vacuum thermolysis (FVT) and gas–solid reaction (GSR).



(2a-i) (1a-j)

Scheme 1. *Reagents:* i, FVT, 240—300 °C, 10^{-3} Torr; ii, condensed state, 77 K; iii, KOH, 60 °C, vapour phase.

Considerable attention has been focused on the development of new synthetic equivalents of *N*-methyleneamines (**1**) but the reactive species themselves often postulated as intermediates[5] were rarely isolated in the condensed state.[1b,6] α-Aminonitriles were recognized as potential iminium salts,[7] precursors of stable imines,[8] and recently as *N*-methyleneamine equivalents,[5c] however their direct β-dehydrocyanation by FVT has rarely been studied.[9] This can be explained by the high reactivity of imine intermediates themselves or with respect to HCN.

We now report the synthesis of (**1**) by FVT of α-aminonitriles (**2**)† and subsequent vapour-phase removal of the

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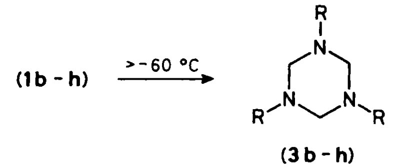
† α-Aminonitriles are easily obtained from cheap reagents in excellent yield by a Strecker reaction.

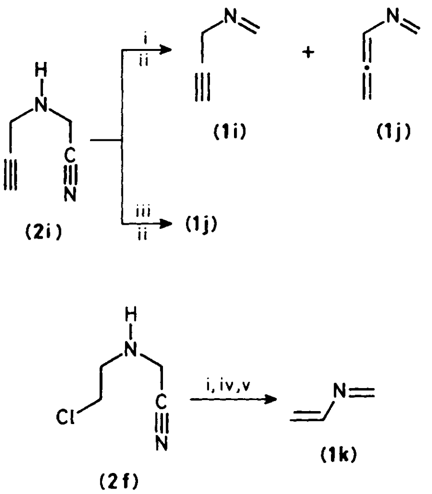
Table 1. *N*-Methyleneamines (**1a**—**k**): ^{1}H, ^{13}C n.m.r.[a] and i.r.[b] data.

Imines[c]	R	δ(H_a)	δ(H_b)	δ(C^1)	ν(C=N)/cm^{-1}
(**1a**)	H	7.70	7.58	164.6	1637
(**1b**)	Me	7.45	7.07	154.9	1653
(**1c**)	Et	7.45	7.04	152.5	1648
(**1d**)	Bu	7.43	7.05	153.0	1648
(**1e**)	CH_2=CH-CH_2	7.46	7.15	154.5	1645 [ν(C=C) 1601]
(**1f**)	$ClCH_2CH_2$	7.52	7.24	156.4	1648
(**1g**)	$ClCH_2CH_2CH_2$	7.54	7.16	154.9	1640
(**1h**)	$Me_3SiOCH_2CH_2$	7.39	7.06	154.9	1647
(**1i**)	HC≡C-CH_2	7.86	7.38	154.5	1605 [ν(C≡C) 2080]
(**1j**)	H_2C=C=CH	7.48	7.00	152.9	1610 [ν(C=C=C) 1900]
(**1k**)	H_2C=CH	7.48	7.15	153.4	1610 [ν(C=C) 1628]

[a] 10% solution in CD_2Cl_2 + CCl_3F at −100 °C with Me_4Si as internal reference. [b] NaCl window cooled with liquid nitrogen. [c] Compounds (**1a**—**e**) are synthesized in good yield (*ca.* 80%) on a preparative scale; (**1f**—**k**) are obtained in good yield only on an analytical scale.



Scheme 2



Scheme 3. *Reagents:* i, 240 °C, 10^{-3} Torr; ii, KOH, 60 °C; iii, 300 °C; iv, KOBu^t, 140 °C; v, cold trap (−90 °C, −HOBu^t).

resulting hydrogen cyanide on solid KOH (Scheme 1).‡ Owing to the high reactivity of HCN towards (**1**), recombination leads to the precursor (**2**) in the absence of solid base, even at low temperature (i.r., 77 K). *N*-Methyleneamines (**1**) are reactive species; (**1b**—**h**) trimerise rapidly to hexahydrotriazines in solution at a temperature higher than −60 °C (Scheme 2)§ and (**1a**), (**1i**—**k**) polymerise in the same conditions.

Pyrolysis of (**2i**) at 240 °C gives a mixture of imine (**1i**) (60%) and allenemethyleneamine (**1j**) (40%): when heated at 300 °C, only (**1j**) is observed.[10] 2-Azabutadiene (**1k**)[4a] is obtained by thermolysis of (**2f**), followed by basic HCN removal and HCl elimination on KOBu^t at 140 °C and trapping the resulting HOBu^t at −90 °C (Scheme 3).

Hence FVT–GSR is a versatile method for the synthesis of reactive methyleneamines, unknown up to now.

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‡ A Pyrex tube filled in half section with anhydrous pulverized KOH is fitted on the FVT apparatus. For a similar assembly see ref. 4b.

§ Hexahydrotriazines are identified by their spectral properties and comparison with those of authentic samples, ref. 5b.

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