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Preliminary Communication

N-alkylydene[bis(trimethylsilyl)methyl]-amines: a new series of stable imines

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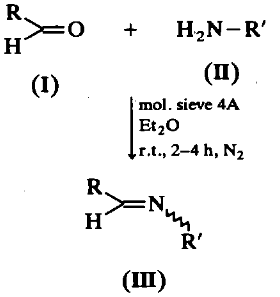
Abstract

Reaction of [bis(trimethylsilyl)methyl]amine with aldehydes, leads to Schiff bases with unexpected remarkable stability.

Extensive studies of the synthesis of imines of carbonyl derivatives have attracted a great deal of attention because these derivatives are versatile building blocks in many synthetic processes [1], for example, as heterodienophilic components of 2 + 2 cycloaddition reactions in the construction of *β*-lactams [2]. A continuous synthetic challenge is the search for new synthetic methods for the preparation of imino derivatives of formaldehyde. Their high reactivity [3] and their use as synthons in aminomethylation [4] or methylene transfer [5] reactions also suffer from severe limitations. For example, some *N*-methylene amines prepared from a suitable amine and HCHO, in which the N atom is attached to a tertiary C atom, are reported [6] to be stable and distallable. In contrast a lower degree of substitution at the carbon bearing the nitrogen, results in *N*-methyleneamines having a very low stability, which is common also to a large number of aldimines [7] with the exception of *N*-methylene cyclohexylamine [8]. In general low temperatures are necessary to keep these compounds monomeric.



Entry	R	R′	III (yield %) [a]	
a	Me_3C	Me_3C	30	vu [b]
b	Me_3C	$(Me_3Si)_2CH$	78	s [c]
c	Me	MeCHEt	30	vu [b]
d	Me	$(Me_3Si)_2CH$	75	s [c]
e	H	$(Me_3Si)_2CH$	80	s [c]

[a] Isolated yield not optimized; [b] vu = very unstable; [c] s = stable.

Scheme 1.

Trialkylsilyl groups can be considered as 'bulky protons' and have been widely used for stabilizing otherwise unstable systems. We report here the ability of [bis(trimethylsilyl)methyl]amine [9] (BSMA) to confer stability on imino derivatives formed by condensation with representative aldehydes, which, by contrast, give rise to poorly stable Schiff bases, even when condensed with rather sterically hindered amines which do not bear R_3Si moieties.

Although Schiff bases derived from BSMA have already been employed in the synthesis of 2-aza-1,3-dienes [10], these preparations have so far been limited to a small range of carbonyl derivatives. Scheme 1 summarizes the results of the reaction under study [11*]. The aldimines **IIIb,d** and, most surprisingly, **IIIe**, appear to be stable for hours at room temperature and can be kept for months at 0°C without noticeable decomposition, a behaviour which has no counterpart in the case of **IIIa** which has to be stored at −30°C since it otherwise easily dimerises [12]. In addition,

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* Reference number with asterisk indicates a note in the list of references.

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N-ethylydenamines have been reported [8,13] to undergo decomposition so fast as to prevent characterization in some cases.

A representative procedure is the preparation of *N*-methylene[bis(trimethylsilyl)methyl]amine (**IIIe**). Formaldehyde, obtained by depolymerization of 1 g of paraformaldehyde at 180°C, was bubbled under a stream of Ar, through a solution of BSMA (2.5 g, 0.014 mol) in dry ether (20 ml), in the presence of 6 g of activated molecular sieves (4A) [14]. The progress of the reaction was monitored by GC. Upon completion (5 h at r.t.) the sieve was filtered off under argon and removal of the solvent led to 2.1 g (80%) of the crude imine **IIIe**.

The stabilizing effects exerted by the BSMA moiety which are probably due to steric as well as to electronic effects [15*], emphasize the synthetic potential of this bis(silylated) amine, in which the synthetic equivalence to a H_2NCH^{2-} dianionic synthon, is coupled with possible easy access to otherwise inaccessible Schiff bases. A most featuring result is the preparation of *N*-methylene[bis(trimethylsilyl)methyl]amine (**IIIe**), a new member of the rare class of methylenimines, and a remarkably stable masked form of the Schiff base $H_2C{=}N{-}CH_3$, whose reactivity is now being actively investigated in our laboratory.

Acknowledgements

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11 Spectroscopic data for imines: **IIIb:** ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = -0.073$ (s, 18H), 0.975 (d, 9H), 2.38 (s, 1H), 7.21 (s, 1H); IR (neat): ν (cm^{-1}) = 2950, 2860, 2790, 2720, 1640 (C=N), 1460, 1360, 1250, 1050, 980, 960, 840. **IIId**: ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = -0.058$ (s, 18 H), 1.84 (d, 3H, $J = 4.8$ Hz), 2.42 (s, 1H), 7.34 (q, 1H, $J = 4.8$ Hz); IR (neat): ν (cm^{-1}) = 2940, 2880, 2820, 2720, 1645 (C=N) 1470, 1340, 1250, 1060, 1020, 840. **IIIe**: ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 0.04$ (s, 18 H), 2.63 (s, 1 H), 6.99 (d, 1H, $J = 17.1$ Hz, A part of an AB system), 7.16 (d, 1H, $J = 17.1$ Hz, B part of n AB system; ^{13}C NMR (300 MHz, $CDCl_3$): $\delta = -1.4$, 62.1, 148.2; IR ($CDCl_3$): ν (cm^{-1}) 1618 (C=N); GC/MS: m/z (%) = 187 (M^+, 0.9, 186 (5), 173 (19), 172 (100), 128 (17), 117 (15), 115 (29), 114 (99), 98 (14), 86 (46), 85 (42), 75 (35), 72 (98), 58 (99), 45 (98), 43 (95).

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15 To clarify this problem, *ab initio* calculations and photoelectron spectroscopy (PES) studies are currently underway on a wide series of BSMA and *N,N*-dialkyl imino derivatives.