Tetrahedron Letters,Vol.30,No.45,pp 6147-6150,1989 0040-4039/89 $3.00 + .00
Printed in Great Britain Pergamon Press plc

N,N-BIS(TRIMETHYLSILYL)YNAMINES

Reinhard H. Weigmann and Ernst-Ulrich Würthwein*
Institut für Organische Chemie der Universität Münster,
Orléansring 23, D-4400 Münster

Abstract: A simple three step procedure for the synthesis of N,N-bis(trimethylsilyl)ynamines 1 is described. The substances 1 are valuable synthetic equivalents for the preparatively inaccessible primary ynamines, as shown by a new synthesis of N-methyleneynamines from 1a and aldehydes.

Ynamines, more precisely N-alkinyl-N,N-dialkyl-amines ("tertiary ynamines"), are very useful starting materials in organic synthesis¹⁾. Examination of the reported applications of ynamines clearly shows, that most of these reactions take place at the CC-triple bond; simple reactions at the amino function are rare, but often intermediate attack of electrophiles at the nitrogen atom (protons, Lewis acids etc.) initiates further C-C bond forming processes.

From the point of amine chemistry it would be highly desirable to have also derivatives of secondary or even primary ynamines, especially for the synthesis of novel N-alkinyl compounds. In these reactions, the CC triple bond should be preserved.

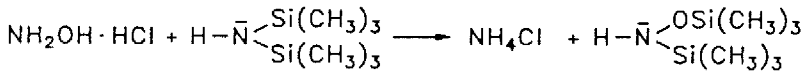
However, in condensed phase such NH-compounds are thermodynamically not stable, because of rapid isomerization yielding the more favourable keten-imines (in the case of secondary ynamines) or acetonitrile derivatives (from primary ynamines) by intermolecular hydrogen migration²⁾. Quantum chemical model calculations clearly support these experimental findings: $HC{\equiv}C{-}NH_2$ is predicted to be 52 kcal/mol and $H_2C{=}C{=}NH$ ca. 36 kcal/mol less favourable than acetonitrile (table 1, *ab initio* MP2/6-31G*//6-31G*³⁾).

Table 1: *ab initio* Results for C_2H_3N isomers (MP2/6-31G*//6-31G*)

	CH_3CN	$H_2C{=}C{=}NH$	$H{-}C{-}C{-}NH_2$
Symmetry	C_{3v}	C_s	C_s
E_{tot} [au]	-132.33372	-132.27641	-132.25115
E_{rel} [kcal/mol]	0.00	35.96	51.81

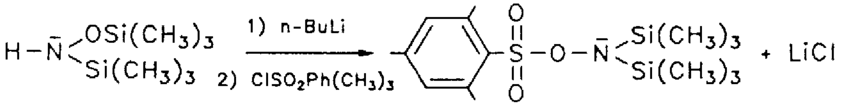
N-Silyl amines[4] and imines[5] are valuable synthetic equivalents for the corresponding NH compounds. For the synthesis of a large number of N-functionalized ynamines (N-methyleneynamines, alkinyl diazonium salts, alkinyl isocyanides etc.) it is therefore very worthwhile to investigate the synthetic access to N,N-bis(trimethylsilyl)ynamines 1. In this communication we report a versatile method for the preparation of these hitherto unknown synthetic building blocks. To our knowledge, the only reported example is substance 1c, which was obtained by Gornowicz and West[6] in a mixture with the corresponding ketenimine from the silylation of acetonitrile.

As it is often the case in ynamine chemistry[7], here also the main synthetic problem for the synthesis of the substances 1 lies in the C-N bond formation between the alkinyl and the amine moiety. For example, the direct coupling of halogeno acetylenes with N-lithio-hexamethyldisilazane is not successful[6,8]. However, with regard to our positive experiences with oxime sulfonates[9] (electrophilic imination) we have chosen the silylated hydroxylamine sulfonate 2 for this umpolung reaction (electrophilic amination[10]). The compound 2 is easily accessible by a two step literature procedure[11,12]:



$$\mathrm{NH_2OH\cdot HCl} + \mathrm{H{-}\bar{N}}\Big\langle{}^{\mathrm{Si(CH_3)_3}}_{\mathrm{Si(CH_3)_3}} \longrightarrow \mathrm{NH_4Cl} + \mathrm{H{-}\bar{N}}\Big\langle{}^{\mathrm{OSi(CH_3)_3}}_{\mathrm{Si(CH_3)_3}}$$

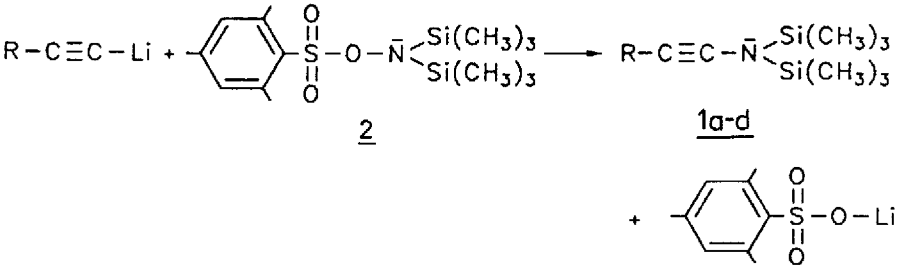
(Ref.11)



2

(Ref.12)

In contrast to the corresponding tosylate, which is oily, the mesitylenesulfonate 2 is crystalline and shows sufficient stablility.



The key step in this synthesis is the reaction 2 with lithium acetylides; the starting materials are mixed at room temperature in dry diethylether and stirred for several hours (table 2); after filtration and evaporation of the solvent the substances 1 are purified by distillation. In our experience, cuprates are not superior to simple lithium compounds in this reaction. We did not observe rearrangement reactions of 1a and 1b as long as the temperature was kept below 100°C; however, 1c and 1d should not be warmed above room temperature to avoid rearrangement to the corresponding ketenimines. The substances 1 are sensitive towards moisture and hydrolyse slowly in wet air. Final hydrolysis products are the corresponding nitriles.

Table 2: N,N-Bissilylynamines 1:

	R	Reaction time [h]	Bp [°C/Torr]	Yield [%]	IR ((C-C)) [cm^{-1}]	^{13}C NMR [ppm] β-C	α-C
1a	Ph	48	69/0.01	63	2210	62.77	81.32
1b	tBu	72	57/0.01	35	2220	56.47	94.36
1c	SiMe$_3$	72	35/0.01	12	2140	62.77	81.32
1d	CH$_3$	72	41/0.01	18	2220	48.35	81.12

The IR spectra of the substances 1 indicate high sensitivity of the CC-stretching vibration depending on the alkinyl substituent: The phenyl-derivate 1a shows this absorbance at 2210 cm^{-1}, the alkyl molecules 1b,d at 2220 cm^{-1} and the silyl derivative 1c at 2140 cm^{-1}. Similary, the ^{13}C NMR shifts of the alkinyl carbon atoms vary very significantly: the α-carbon atom, next to the amino group, is - as expected - electron poor (range: 81.12 - 107.70 ppm, table 2); the β-carbon atoms on the other hand show high electron density (range from 48.35 - 62.77 ppm). These data indicate, that in these N,N-bissilylated ynamines the electron distribution and the reactivity is not very different from other ynamines, inspite of the electronic effects of the trimethylsilyl substituents.

Some preliminary results support the postulated synthetic utility of the compounds 1: With simple aldehydes (benzaldehyde, pivalaldehyde) 1a reacts under fluoride catalysis to yield novel examples of N-methyleneynamines[8,9] (Ph-C≡C-N=CHR (R = Ph yield: 44%; R = tBu: yield = 39%), which were otherwise not accessible; this condensation reaction is similar to the reaction of N,N-bissilyl-enamines with aldehydes, which results in novel 2-azabutadiene derivatives[13]. Further investigations are in progress.

We thank the Fonds der Chemischen Industrie for financial support.

Dedicated to Professor Paul von Ragué Schleyer on the occasion of his 60th birthday.

References

1) H.G.Viehe, "The Chemistry of Acetylenes", Marcel Dekker, N.Y., 1969; J.Ficini, Tetrahedron **32** (1976) 1449; G.Pitacco, E.Valentin, in Patai, Suppl. F "The Chemistry of Amino, Nitroso and Nitro Compounds and their Derivatives", part 1, p.623 Wiley, N.Y. 1982.

2) C.Wentrup, H.Briehl, P.Lorenčak, U.J.Vogelbacher, H.-W.Winter, A.Maquestiau, R.Flemming, J.Am.Chem.Soc. **110** (1988) 1337 and references therein.

3) J.S.Binkley, R.A.Whiteside, K.Raghavachari, R.Seeger, D.J.De Frees, H.B.Schlegel, M.J.Frisch, J.A.Pople, L.A.Khan, Carnegie-Mellon University 1982.

4) S.Pawlenko, in "Methoden der Organischen Chemie (Houben-Weyl)", Vol. XIII/5, Chap. A.VIII, 226, Thieme, Stuttgart, 1980.

5) For example: R.Kupfer, S.Meier, E.-U.Würthwein, Synthesis **1984**, 688.

6) G.A.Gornowicz, R.West, J.Am.Chem.Soc. **93** (1971) 1714.

7) J.Collard-Motte, Z.Janousek, Top.Curr.Chem. **130** (1986) 89.

8) R.H.Weigmann, Dissertation, Universität Erlangen 1989.

9) E.-U.Würthwein, R.Weigmann, Angew.Chem. **99** (1987) 918; Angew.Chem. Int.Ed. Engl. **26** (1987) 923.

10) G.Boche, M.Bernheim, M.Nießner, Angew.Chem. **95** (1983) 48; Angew.Chem. Int.Ed.Engl. **22** (1983) 53.

11) J.P.Llonch, F.Duboudin, G.Vincon, F.Dabescat, E.Frainett, J.Organomet. Chem. **52** (1973) C24.

12) F.D.King, D.R.M.Walton, Synthesis **1975**, 788.

13) R.J.P.Corriu, V.Huynh, J.J.E.Moreau, M.Pataud-Sat, Tetrahedron Lett. **23** (1982) 3257; J.Organomet.Chem. **255** (1983) 359.

(Received in Germany 26 July 1989)