A Straightforward Synthesis of Silylated and Stannylated Ynamines and Ynehydrazines

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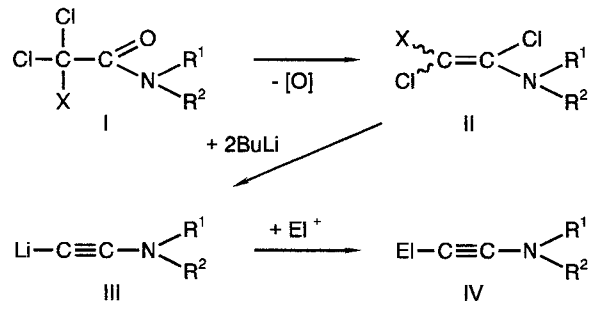
Metallated ynamines **5a–f** and ynehydrazines **5g,h** were prepared in a very short reaction sequence by consecutive treatment of trichloroethylene (**1**) with the lithium salt of secondary amines or of trimethylhydrazine, 2 equivalents of butyllithium and chlorotriorganosilanes or -stannanes.

The ynamines **IV** have been prepared by us up to now using the method of Ficini et al.[1] (Scheme 1). Thus, dichloro- or mainly trichlorovinylamines **II** are converted by treatment with butyllithium into the lithium acetylides **III**, which can be substituted at the acetylenic position by various electrophiles to furnish differently substituted ynamines **IV**. The enamines **II** normally are obtained by deoxygenation of the corresponding chloroacetamides **I** with trivalent phosphorus compounds.[2] As our interest turned to the chemistry of (alk-1-ynyl)hydrazines,[3–5] we tried to transfer the analogous steps to their synthesis. But because in our hands the deoxygenation of the trichloroacethydrazide **I** (R^1 = NMe_2, R^2 = Me, X = Cl) failed, we had to look for another access to the chlorinated hydrazine derivatives **II**, while we wanted to retain the remaining part of Ficini's methodology.

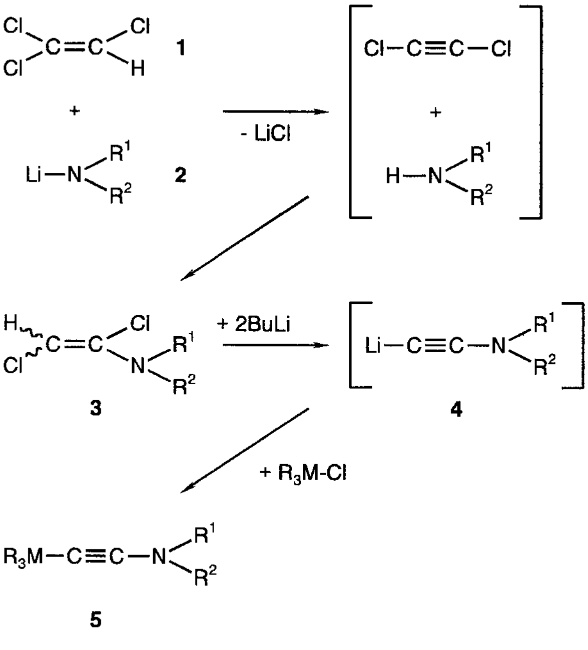


(X = H,Cl; R^1,R^2 = alkyl,aryl; El = H,Me,MR_3..)

Scheme 1

In analogy to the synthesis of 1-(ethynyl)pyrrole,[6,7] we developed a very simple, almost one-pot synthesis of silylated and stannylated ynehydrazines and ynamines. Individual steps for this synthesis of ynamines are known one by one, but never have been put together in this way.

Trichloroethylene (**1**) is treated with lithium salts **2** of secondary amines and of trimethylhydrazine. In analogy to published results,[8] the 1,2-dichlorovinyl compounds **3** should be formed by dehydrohalogenation of trichloroethylene to dichloroacetylene[8,9] which easily adds amines to furnish the enamine derivatives of **3**.[10,11] Similarly, trimethylhydrazine should equally add to dichloroacetylene to form the dichlorovinyl compound **3e**. The very unstable dichlorovinyl compounds **3a–e** are not isolated, neither is their stereochemistry (*E*/*Z*) ascertained; they are directly reacted with two equivalents of butyllithium to form the lithium acetylides **4**. After treatment with chlorotrimethylsilane, chlorotrimethylstannane or chlorotributylstannane these acetylides furnish the easily isolable metallated ynamines **5a–f** and ynehydrazines **5g, h**.



2-4	R^1	R^2	5	R^1	R^2	MR_3
a	Et	Et	**a**	Et	Et	$SiMe_3$
b	$-(CH_2)_4-$		**b**	$-(CH_2)_4-$		$SiMe_3$
c	$-(CH_2)_5-$		**c**	$-(CH_2)_5-$		$SiMe_3$
d	$-(CH_2)_2O(CH_2)_2-$		**d**	$-(CH_2)_2O(CH_2)_2-$		$SiMe_3$
e	NMe_2	Me	**e**	Et	Et	$SnBu_3$
			f	$-(CH_2)_5-$		$SnMe_3$
			g	NMe_2	Me	$SiMe_3$
			h	NMe_2	Me	$SnMe_3$

Scheme 2

The structure of **5** is proved by the existence of intensive IR absorptions of the C≡C bond, in the case of the ynamines for the most part by comparison with the spectra of authentic examples and in the case of the ynamine **5c** and of the novel ynehydrazines **5g** and **5h** by the existence of two singlets in the ^{13}C NMR spectra for the acetylenic C atoms.

The method of synthesis of trimethylhydrazine and the used analytical and spectral instruments have been listed in Ref.5.

Ynamines 5a–f, Ynehydrazines 5g,h; General Procedure:
To a magnetically stirred solution of the secondary amine (50 mmol), or of the trimethylhydrazine (3.7 g, 50 mmol) in Et_2O (25 mL) was added BuLi (1.1 equiv, 1.6 M solution in hexane) at −40 °C. The cooling bath was removed and stirring was continued for 1 h at r.t. The resulting mixture was added to a magnetically stirred solution of trichloroethylene (6.57 g, 50 mmol) in Et_2O (50 mL) at −70 °C. After removing the cooling bath stirring was continued at r.t. for 1.5 h or at reflux for 1 h. After recooling to −40 °C BuLi (2.2 equiv, 1.6 M solution in hexane) was added dropwise to the reaction mixture. The mixture was stirred for 1 h at r.t., then recooled to −40 °C and treated dropwise with a solution of Me_3SiCl, Bu_3SnCl or Me_3SnCl (50 mmol, each) in Et_2O (40 mL). After stirring at r.t. for 2 h the solid components were removed by centrifugation and the solvents by distillation. The metallated ynamines and ynehydrazines **4** were isolated by distillation under reduced pressure.

N-Diethyl-N-(trimethylsilylethynyl)amine (**5a**); yield: 63 %, bp 25–30 °C/0.2 Torr (bulb to bulb distillation) (Lit.[14] yield: 65 %, bp 63 °C/13 Torr; Lit.[15] yield: 63 % or 44 %; bp 73–75 °C/23 Torr).

IR (film): $\nu = 2130\ cm^{-1}$ (vs), (Lit.[14] $\nu = 2150\ cm^{-1}$, Lit.[15] $\nu = 2160\ cm^{-1}$).

N-(Trimethylsilylethynyl)pyrrolidine (**5b**); yield: 73 %, bp 45–47 °C/0.25 Torr (Lit.[15] yield: 49 %; bp 95–98 °C/19 Torr)

IR (neat): $\nu = 2140\ cm^{-1}$ (vs), (Lit.[15] $\nu = 2160\ cm^{-1}$).

N-(Trimethylsilylethynyl)piperidine (**5c**); yield: 50 %; bp 50–52 °C/0.2 Torr (bulb to bulb distillation).

IR (film): $\nu = 2140\ cm^{-1}$ (vs).

^{1}H NMR ($CDCl_3$): $\delta = 0.12$ [s, 9 H, $Si(CH_3)_3$], 1.45 (m, 6 H, $CH_2CH_2NCH_2CH_2CH_2$), 2.96 (m, 4 H, CH_2NCH_2).

^{13}C NMR ($CDCl_3$): $\delta = 0.83$ [q, $Si(CH_3)_3$], 23.42, 24.83 (2 q, CH_2), 52.70 (t, $J = 137$ Hz, NCH_2), 61.11, 110.51 (2 s, C≡C).

$C_{10}N_{19}NSi$	calc.	C 66.23	H 10.56	N 7.72
(181.4)	found	66.20	10.70	7.40

N-(Trimethylsilylethynyl)morpholine (**5d**); yield: 55 %; bp 45–50 °C/0.25 Torr (bulb to bulb distillation) (Lit.[15] yield 55 %; bp 88–90 °C/9 Torr).

IR (neat): $\nu = 2140\ cm^{-1}$ (vs) (Lit.[15] $\nu = 2160\ cm^{-1}$).

N,N-Diethyl-N-(tributylstannylethynyl)amine (**5e**); yield: 78 %; bp 90–110 °C/0.3 Torr (bulb to bulb distillation) (Lit.[16] yield: 58–69 %; bp 110–115 %/0.1 Torr).

IR (neat): $\nu = 2110\ cm^{-1}$ (vs) (Lit.[16] $\nu = 2130\ cm^{-1}$).

N-(Trimethylstannylethynyl)piperidine (**5f**): yield: 34 %; colourless oil; bp 24–30 °C/0.1 Torr (bulb to bulb distillation) (Lit.[17] yield: 57–79 %; bp 65–70 °C/0.25 Torr).

IR (neat): $\nu = 2122\ cm^{-1}$ (vs) (Lit.[17] $\nu = 2133\ cm^{-1}$).

^{13}C NMR ($CDCl_3$): $\delta = -7.18$ [q, $Sn(CH_3)_3$], 23.35, 24.80 (2 t, CH_2), 53.01 (t, $J = 138$ Hz, NCH_2), 57.71, 114.18 (2 s, C≡C).

N-(Trimethylsilylethynyl)trimethylhydrazine (**5g**); yield: 58 %; colourless oil; bp 68–70 °C/24 Torr.

IR (neat): $\nu = 2120\ cm^{-1}$ (vs).

^{1}H NMR ($CDCl_3$): $\delta = 0.16$ [s, 9 H, $Si(CH_3)_3$], 2.42 [s, 6 H, $N(CH_3)_2$], 2.84 (s, 3 H, NCH_3).

^{13}C NMR ($CDCl_3$): $\delta = 0.70$ [q, $J = 119$ Hz, $Si(CH_3)_3$], 41.56 (q, $J = 135$ Hz, NCH_3), 41.93 [q, $J = 139$ Hz, $N(CH_3)_2$], 73.41, 101.93 (2 s, C≡C).

$C_8H_{18}N_2Si$[18]	calc.	C 56.39	H 10.67	N 16.45
(170.4)	found	55.60	10.50	15.10

N-(Trimethylstannylethynyl)trimethylhydrazine (**5h**); yield: 6.8 g (52 %); colourless oil; bp 64–66 °C/0.375 Torr.

IR (neat): $\nu = 2106\ cm^{-1}$ (vs).

^{1}H NMR ($CDCl_3$): $\delta = 0.25$ [s, 9 H, $Sn(CH_3)_3$], 2.43 [s, 6 H, $N(CH_3)_2$], 2.83 (s, 3 H, NCH_3).

^{13}C NMR ($CDCl_3$): $\delta = -7.27$ [q, $J = 129.6$ Hz, $Sn(CH_3)_3$], 41.68 [q, $J = 134.4$ Hz, $(CH_3)_2N{-}NCH_3$], 70.08, 105.15 (2 s, C≡C).

$C_8H_{18}N_2Sn$[18]	calc.	C 36.83	H 6.95	N 10.74
(261.0)	found	35.80	6.40	8.10

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