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A Simple Three-Component Reaction for the Preparation of Silylated Primary Amines

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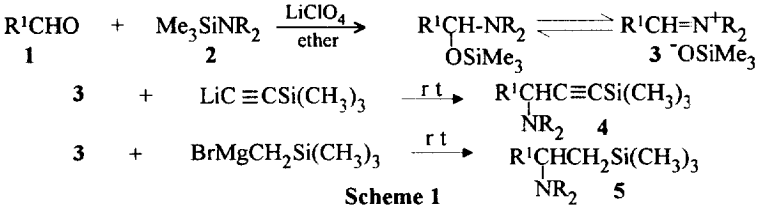
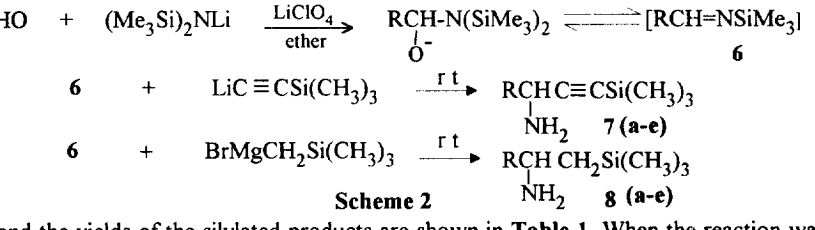
Abstract : In the presence of lithium perchlorate in diethyl ether, three-component reaction between aldehydes, hexamethyldisilazane, and silylated nucleophiles proceeded smoothly to afford trimethylsilylated primary amines in good yields. © 1997 Elsevier Science Ltd.

Recently, we reported the lithium perchlorate mediated one pot three-component aminosilylation of aldehydes, **1**, with (trimethylsilyl)dialkyl amines, **2**, and organosilicon nucleophiles, for the preparation of dialkyl-γ-trimethylsilyl-β-ynamines, **4**, and dialkyl-β-trimethylsilyl-amines, **5**, **Scheme 1**[1-5].



Scheme 1

Aldehyde, **1**, reacts with sodium or lithium hexamethyldisilazane in the presence of 5 M solution of lithium perchlorate in diethyl ether, at r.t. to produce imine, **6**, in *situ*, in about 30 min. Reaction of lithium (trimethylsilyl)acetylide or trimethylsilylmethylmagnesium chloride in diethyl ether with **6** at r.t. afforded the corresponding γ-trimethylsilyl-β-ynamines, **7**, and β-trimethylsilyl-amines, **8**, respectively, **Scheme 2.**



Scheme 2

The structure and the yields of the silylated products are shown in **Table 1**. When the reaction was carried out without using 5 M $LiClO_4$ diethyl ether solution, products **7** and **8** were produced in very low yields.

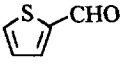
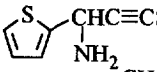
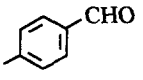
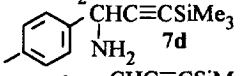
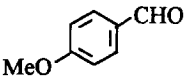
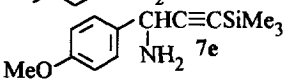
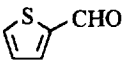
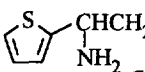
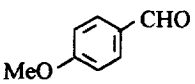
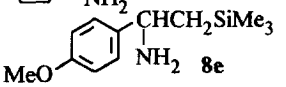
Experimental

$LiClO_4$ (Fluka) was dried at 160 °C and 10-1 Torr for 48 h.

Caution: Although we did not have any accident in using $LiClO_4$, the authors advise to dry lithium perchlorate in hood using suitable lab-sheild.

General Procedure for the Preparation of γ-trimethylsilyl-β-ynamines or β-trimethylsilyl-amines: Hexamethyldisilazane (3.3 mmol, 0.54g) was placed in two-necked flask fitted with a condenser, and a stirring bar under argon, and 3.5 mmol of sodium hydride (60-65%, after washing with light pet. ether) or 3.4 mmol of methyllithium in dry diethyl ether was added, and the mixture was stirred for for about 5 min. Then 3 mL solution of 5 M lithium perchlorate in diethyl ether and 2 mmol of aldehyde were added via syringe. After stirring for 30 min., lithium (trimethylsilyl)acetylide or trimethylsilylmethylmagnesium chloride (4 mmol) was added, and the mixture was stirred for additional 30 min. Water (10 mL) was added, and the product was extracted with ether (2x 10). The organic layer was separated and extracted with cold 0.5 M HCl solution. Neutralization with 2.0 M solution of KOH, gave the desired product. Further purification was done by preparative gas chromotography if needed. All products described had structures in accordance with their spectroscopic data.

Table 1

Entry	Aldehyde	Product	% Yield
1	C_6H_5CHO	$C_6H_5CH(NH_2)C{\equiv}CSiMe_3$ **7a**	70
2	$C_6H_5CH{=}CHCHO$	$C_6H_5CH{=}CHCH(NH_2)C{\equiv}CSiMe_3$ **7b**	75
3		 **7c**	72
4		 **7d**	68
5		 **7e**	73
6	C_6H_5CHO	$C_6H_5CH(NH_2)CH_2SiMe_3$ **8a**	75
7	$C_6H_5CH{=}CHCHO$	$C_6H_5CH{=}CHCH(NH_2)CH_2SiMe_3$ **8b**	69
8		 **8c**	60
9		 **8e**	60

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