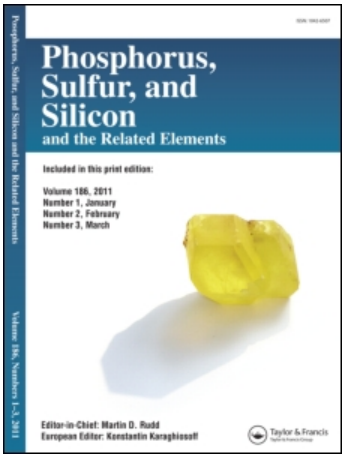


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# SYNTHESIS OF α, γ-DISILYLATED AMINES FROM ß-SILYLATED IMINES

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# SYNTHESIS OF α, γ-DISILYLATED AMINES FROM ß-SILYLATED IMINES

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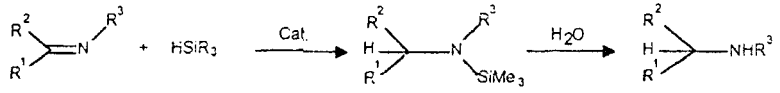
Lithium-promoted reductive coupling of β-silylated imines (1) with trimethylsilyl chloride (TMSCI, 2) in THF at 0–10°C gives the corresponding α, γ-disilylated amines in good yields.

*Keywords:* Disilylated Amines; β-Silylated Imines; Synthesis

Effective formation of a carbon-silicon bond is one of the most attractive subjects in organic synthesis due to the usefulness and importance of organosilicon compounds[1]. Silylated amines are important intermediates in organic synthesis. These compounds have been found interesting due to their biological activities and therapeutic effects[2,3]. One of the most frequent methods for the conversion of a C=N bond into the amine is the hydrosilylation reaction. In this reaction, the N-silylated product derived from imine can be readily hydrolysed. Therefore, the final product is equivalent to hydrogenation of a C=N bond[4] (Scheme 1).



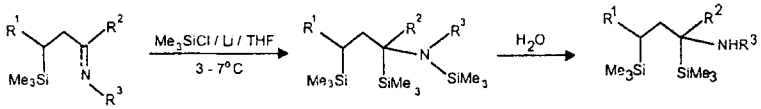

$R^1, R^2, R^3$ ; H, Alkyl, Aryl

SCHEME 1

* Corresponding Author.

Reductive silylation of imines is a facile synthetic method, for preparing the corresponding amines. In this process a carbon-silicon bond is formed at the α- position of amines[5,6]. One of the important features of this method is that the β-silylimines can be converted quantitatively into the α, γ-disilylated amines. It is well-known that many of these silylated compounds are biologically active and have been reported to have pharmaceutical effects with less toxicity[7].

In the previous works, we reported the synthesis of β- and γ-silylamines[8–11]. We now wish to report silylation reactions of β-silylated imines which result in facile reduction to the corresponding α, γ-disilylated amines. Both α, γ-disilylated amines, and β-silylated imines, (Scheme 2), are novel organosilicon compounds.




a $R^1$ = Ph , $R^2$ = $CH_3$ , $R^3$ = $CH_3CH\,CH_2CH_3$

b $R^1$ = Ph , $R^2$ = $CH_3$ , $R^3$ = $PhCH_2$

c $R^1$ = Ph , $R^2$ = $CH_3$ , $R^3$ = Cyclohexyl

d $R^1$, H = $CH_3$ , $CH_3$ , $R^2$ = $CH{=}C(CH_3)_2$ , $R^3$ = $PhCH_2$

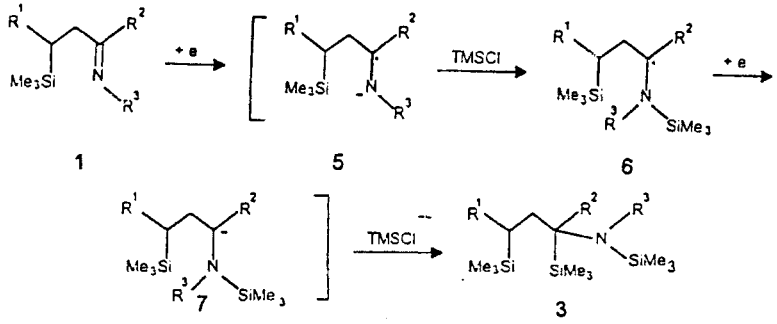
e $R^1$ =  , $R^2$ = $CH_3$ , $R^3$ = $PhCH_2$

Scheme 2

SCHEME 2

The mechanism of the reaction is depicted in Scheme 3. The reaction is initiated through an one electron transfer from Li metal to β-silylated imine **1** to give the corresponding radical anion **5.** The radical anion **5** is subjected to the electrophilic attack by TMSCI **2,** generating the radical species **6,** followed by the fast second electron transfer. Subsequently, the anionic intermediate **7** reacts with another TMSCI to produce N-trimethylsilyl α, γ- disilylated amine **3.** Hydrolysis of **3,** gives the corresponing α, γ-disilylated amine **4.**

In this reactions, three kinds of roles for TMSCI may be postulated; activation of imines as electrophiles by coordination to the nitrogen atom of




SCHEME 3



the C=N bond, stabilization of anion intermediates and activation of Li metal.

This procedure with mild conditions (0–10°C) gave good yields of the products. The prepared β-silylated imines and α, γ-disilylated amines are summarized in table I.

## EXPERIMENTAL

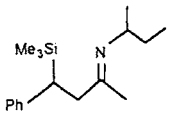
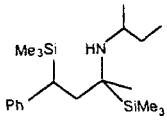
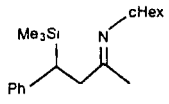
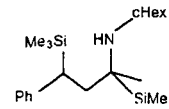
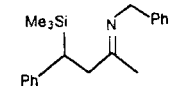
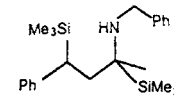
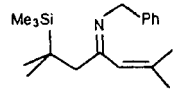
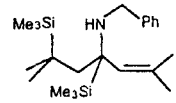
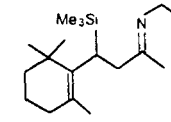
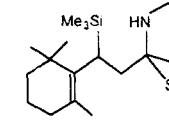
IR spectra were recorded on a Perkin Elmer model 883 and magna -IR 750 Nicolet FT-IR spectrometer. $^1H$ NMR spectra were recorded on a Bruker Ac 80 spectrometer in $CDCl_3$.

THF was distilled from Na/benzophenone under Ar, β-silylated ketones were easily prepared from the corresponding α, β-unsaturated ketones and $Me_3SiCl$/Mg/HMPA or $Me_3SiCl$/Li/THF according to the reported method[11]. Primary amines (Fluka and Merck) were distilled before they were used. All the reactions were carried out under an argon atmosphere.

### General procedure for the preparation of β-silylated imines

In a three-necked flask was placed 8 mmol of β-silylated ketone and 32 mmol of primary amine in 50 mL n-pentane under argon. The flask was placed in an ice-bath, and the temperature of the solution was kept under 0°C. A solution of $TiCl_4$ in $CH_2Cl_2$ (5 mmol/30 mL $CH_2Cl_2$) was added

TABLE I Product distribution data and the yield of the products

| Entry | β-Silylated Imine(1) | Yield(%) | α,γ-Disilylated Amine(4) | Yield(%) |
|---|---|---|---|---|
| a |  | 67 |  | 65 |
| b |  | 65 |  | 70 |
| c |  | 55 |  | 60 |
| d |  | 68 |  | 50 |
| e |  | 57 |  | 55 |

dropwise during 1.5 h. After 48 h stirring, the solid material was filtered off, and the filterate was dried over $Na_2SO_4$. The solvent was evaporated, and the crude material was distilled under reduced pressure. $^1H$ NMR and IR data for compounds 1a-1e are given below.

1a, (67%, 125°C, 10 mmHg), IR (film, $cm^{-1}$); 3226, 1665, 1251, 842 $^1H$ NMR ($CDCl_3$, δ); –0.2 (s, 9H), 0.2–1.5 (m.8H), 1.5 (s, 3H), 2.5–3.3 (m, 3H), 6.8–7.2 (m, 5H).

1b, (65%, 150°C, 10 mmHg), IR (film, $cm^{-1}$); 3228, 2960, 1662, 840 $^1H$ NMR ($CDCl_3$, δ); –0.0 (s, 9H), 0.9–1.9 (m.11H), 2.1 (s, 3H), 2.3–3.3 (m, 3H), 6.9–7.4 (m, 5H).

1c, (55%, 160°C, 10 mmHg), IR (film, $cm^{-1}$); 3263, 3229, 1670, 843 $^1H$ NMR ($CDCl_3$, δ); –0.2 (s, 9H), 1.5 (s.3H), 2.4–2.7 (m, 3H), 2.4 (s, 2H),

6.7–7.2 (m, 10H). 1d, (68%, 145°C, 10 mmHg), IR (film, $cm^{-1}$); 2952, 1685, 1627, 844 $^1H$ NMR ($CDCl_3$, δ); –0.2 (s, 9H), (s.6H), 1.6 (s, 2H), 1.8–2.4 (m, 6H), 4.5 (s, 2H), 5.6 (s, 1H), 7.1–7.4 (s, 5H).

1e, (57%, 170°C, 10 mmHg), IF (film, $cm^{-1}$), 3050, 2962, 1671, 1636, 1253, 844 $^1H$ NMR ($CDCl_3$, δ); –0.1 (s, 9H), 1.08 (s.6H), 1.5–1.6 (m, 6H), 1.74 (s, 3H), 1.86 (s, 3H), 2.2–2.5 (m, 3H), 4.5 (s, 2H), 7.39 (s, 5H).

**General procedure for the preparation of α, γ- disilylated amines**

In a three necked flask was placed 0.0525g (7.5 mmol) of Li pieces. TMS-CI (9mmol) in THF (40mL) was added. The flask was placed in an ice-bath, and the temperature of the solution was kept under 5°C. Then the β-silylated imine (3mmol) in THF (20mL) was added dropwise during 60 min under argon. The resulting solution was stirred with a mechanica stirrer for an additional 24h at 3–7°C. Then the mixture was poured into 20mL of cold water. Hydrolysis of the compounds was carried out with saturated $NaHCO_3$ solutions. The aqueous layer was extracted three times with ether. The etheral layer was dried over $Na_2SO_4$ and the solvent was evaporated. Then the curde product was purified by kugelrohr distillation (GKR-51 BÜCHI) to afford pure α,γ-disilylated amine. The isolated yield for each product is given in parentheses and the IR, $^1H$ NMR data for compounds 4a-4e are given below.

4a, (65%, 122–125°C, 10mmHg), IR (film, $cm^{-1}$); 3300–3400, 3030, 2962, 1254, 845 $^1H$ NMR ($CDCl_3$, δ); –0.067 (s, 9H), 0.237 (s, 9H), 0.8–1.8 (m, 9H), 1.8–2.4 (m, 4H), 2.6–3.1 (m, 2H), 7.2–7.4 (m, 5H).

4b, (70%, 160°C 10mmHg), IR (film, $cm^{-1}$); 3300–3400, 3029, 2960, 1256, 847 $^1H$ NMR ($CDCl_3$, δ); –0.075–0.4 (d, 18H), 0.8–2.0 (m, 11H), 2.1 (s, 3H), 2.3–3.2 (m, 3H), 6.9–7.4 (m, 5H).

4c, (60%, 130°C, 10mmHg), IR (film, $cm^{-1}$); 3300–3400, 3032, 2972, 1253, 847 $^1H$ NMR ($CDCl_3$, δ); –0.9 (s, 9H), 0.1 (s, 9H), 2.0 (s, 3H), 2.4–2.9 (m, 3H), 3.7 (s, 2H), 6.8–7.4 (m, 10H).

4d, (50%, 146–150°C, 10mmHg), IR (film, $cm^{-1}$); 3300–3400, 2952, 1627, 1253, 844 $^1H$ NMR ($CDCl_3$, δ); –0.1 (s, 18H), 0.9 (s, 6H), 1.6 (s, 2H), 1.8–2.5 (m, 6H), 3.9 (s, 2H), 6.1 (s, 1H), 7.1–7.4 (m, 5H).

4e, (55%, 180°C, 10mmHg), IR (film, $cm^{-1}$); 3300–3400, 3050, 2962, 1632, 845 $^1H$ NMR ($CDCl_3$, δ); –0.1 (s, 9H), 1.08 (s, 6H), 1.5–1.46 (m, 6H), 1.74 (s, 3H), 1.80 (s, 3H), 2.1–2.4 (m, 3H), 3.82 (s, 2H), 7.1 (s, 5H).

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