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Preliminary communication

USES OF Si—N BONDS IN SYNTHESIS: EASY ROUTES TO FUNCTIONAL PROTECTED PRIMARY AMINES FROM PROPARGYLIC SILYLAMINES

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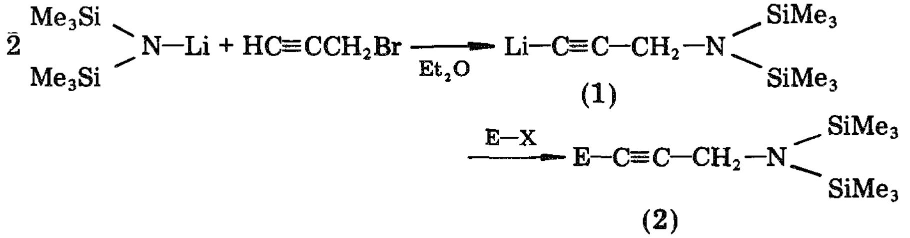
Summary

The readily obtained *N,N*-bis(trimethylsilyl)-propargylic amines are shown to be useful precursors of various functional protected primary amines. It readily gives rise to *N,N*-bis(trimethylsilyl)dienamines, 2-aza-1,3,5-hexatrienes, α-allenic amines, substituted allylamines and lactams.

We recently reported a simple synthesis of silyl-protected α-acetylenic amines by use of lithium *N,N*-bis(trimethylsilyl)aminomethylacetylide I (eq. 1) [1].



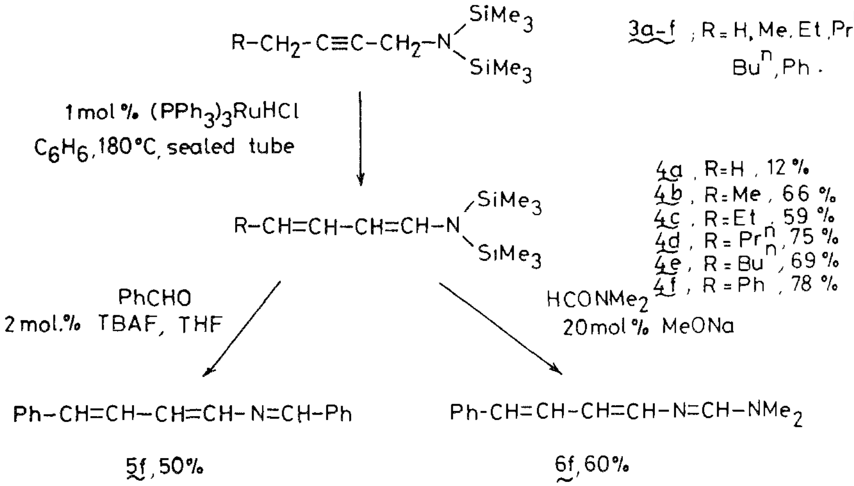
$$2\,(Me_3Si)_2N{-}Li + HC{\equiv}CCH_2Br \xrightarrow[Et_2O]{} \underset{(1)}{Li{-}C{\equiv}C{-}CH_2{-}N(SiMe_3)_2} \xrightarrow{E-X} \underset{(2)}{E{-}C{\equiv}C{-}CH_2{-}N(SiMe_3)_2} \qquad (1)$$

(E—X = R—X, aldehyde, ketone, enone...)

The functional α-acetylenic amines 2 obtained can be used to provide easy access to various functional protected amines, and we report below easy routes to the new bis(silyl)dienamines and to allenic, allylic amines and lactams.

Isomerisation to N,N-bis(trimethylsilyl)dienamines

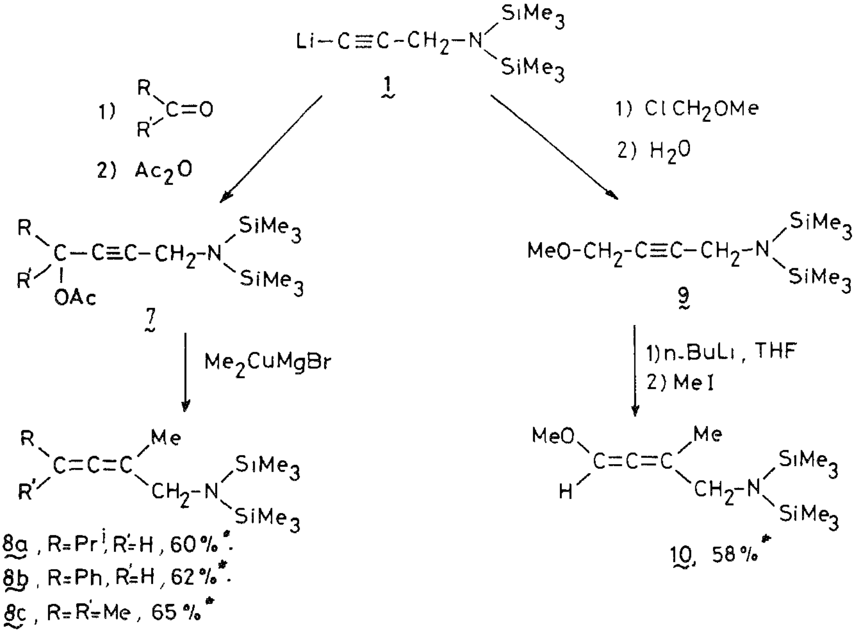
We found that the ruthenium complex $(PPh_3)_3RuHCl$, which is known to isomerize propargylic silyl ether [2], was also effective for the isomerization of α-acetylenic silylamines. As shown in Scheme 1, the amines 3 (readily obtained



SCHEME 1. Isomerisation of *N,N*-bis(trimethylsilyl)-α-acetylenic amines catalysed by $(PPh_3)_3RuHCl$.

by alkylation of the lithium acetylide **1** [1]) were converted into conjugated dienamines by heating in benzene solution at 180°C in sealed tubes in the presence of 1 mole percent of $(PPh_3)_3RuHCl$.

Good yields of the isomerized product were obtained in most cases, except for but-2-ynylamine **3a**, for which 80% of the starting material was recovered after prolonged heating. The dienamines **4a—4f** were formed as a mixture of *Z* and *E* isomers which were not separated. They are very stable and are similar in reactivity to *N,N*-bis(silyl)enamines [3]. Nucleophilic activation of the silicon—



SCHEME 2. Access to silyl protected α-allenic amines (*, non-optimized yields calculated from $HC{\equiv}CCH_2N(SiMe_3)_2$).

nitrogen bond by fluoride ion or sodium methoxide allowed reaction of benzaldehyde or dimethylformamide. In this case 2-aza-1,3,5-hexatrienes **5f**—**6f** were formed.

Conversion to α-allenic amines

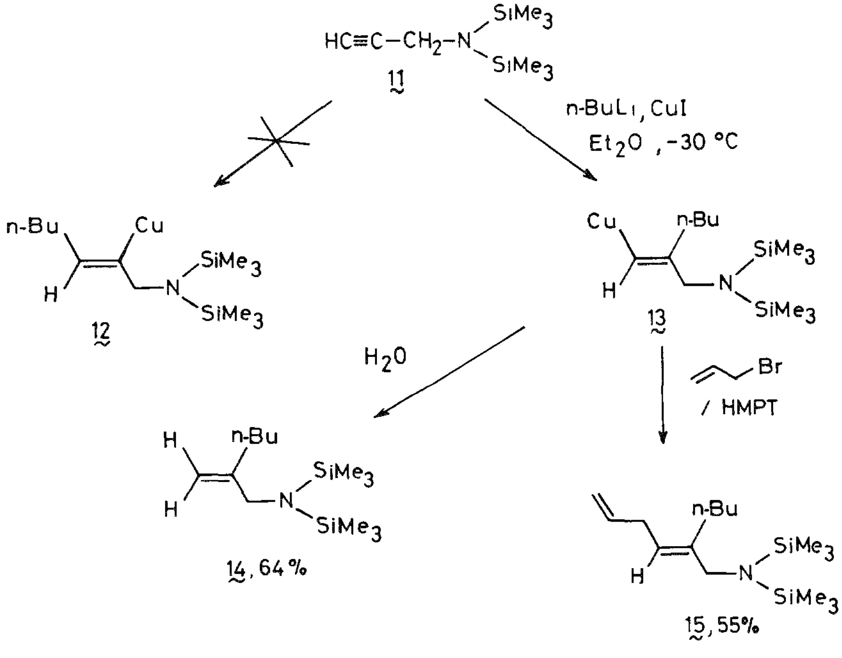
As shown in Scheme 2, α-allenic amines [4], are readily obtained from functional α-acetylenic amines.

The reaction of methyl-cuprate with the propargylic acetates [5] **7** obtained by condensation of carbonyl compounds with the lithium acetylide **1** gave the substituted α-allenic amines **8a**—**8c** in 60 to 65% yield based on the lithium reagent **1**. The α-aminoallenic ether **10** was also readily prepared in 58% from **1** via the metallation α to the oxygen atom [6] and alkylation of the acetylenic amino ether **9**.

Addition of organocopper reagents

We also examined the reaction of organocopper reagents with the propargylamine **11** and the acetylenic amino ester **16** which were prepared respectively in 80 and 60% yields in one-pot reactions from propargyl bromide according to eq. 1. As shown in Scheme 3, substituted allylamines [7,8] have been readily obtained.

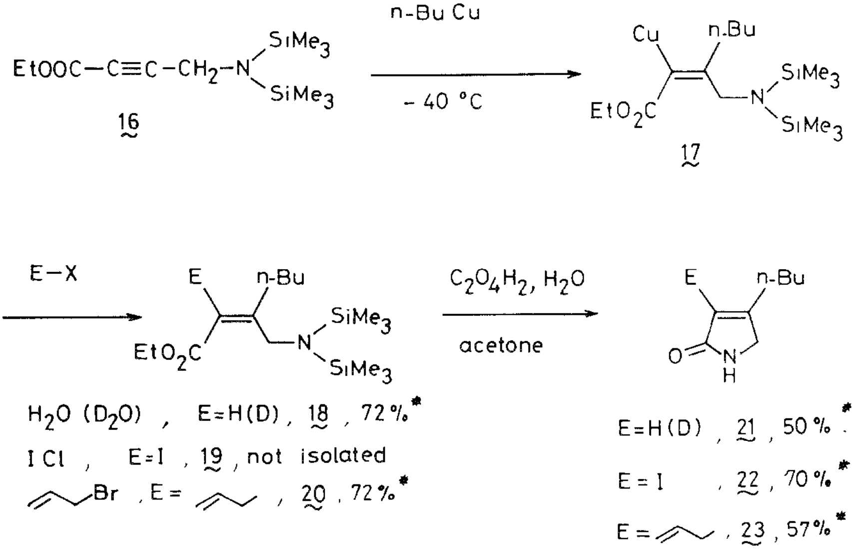
The regioselectivity of the addition of reagents to propargylic dialkylamines was reported to result in formation of the linear or branched adduct depending on the solvent (Et_2O or THF) used [9]. In contrast to the reaction with the dialkyl analogues, addition to *N,N*-bis(silyl)propargylamine **11** gave exclusively the branched adduct, and allowed isolation of allylic amines **14** and **15**. Under the same reaction conditions the reverse regioselectivity was observed in the case



SCHEME 3. Preparation of substituted allylamines.

of *N,N*-dialkylpropargylamines. In agreement with the previous interpretation [9] the low nucleophilicity of the $(Me_3Si)_2N$ group may account for a lack of intramolecular stabilisation of the linear adduct **12**.

Addition of butylcopper to the acetylenic ester **16** was also carried out (Scheme 4). Quenching of the intermediate **17** with electrophiles (H_2O, D_2O, ICl or $CH_2{=}CHCH_2Br$) led to the expected *cis*-adducts [10] **18**—**20**. These underwent cyclization to lactams **21**—**23** upon desilylation by oxalic acid; yields were 50 to 70% based on the starting ester **16**.



SCHEME 4. Preparation of substituted 3-pyrrolin-2-ones.(*, non optimized yields calculated from **16**).

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