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Nucleophilic alkynylation of *N*-bis(trimethylsilyl)methyl aldimines

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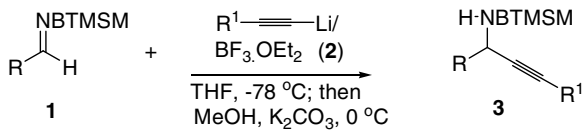
Abstract—*N*-Bis(trimethylsilyl)methyl aldimines undergo nucleophilic addition reaction with premixed lithium alkynides/$BF_3{\cdot}OEt_2$ to give moderate to good yields of *N*-bis(trimethylsilyl)methyl propargyl amines.

The 1-(1-amino-2-propynyl) moiety is a sub-structural feature found in various naturally occurring and medicinally important compounds.[1] Further, propargyl amines are useful intermediates[2] for the synthesis of other polyfuntionalized amines and heterocycles. There is a growing and sustained interest in devising methods[3] for the preparation of propargyl amines, and the most direct method is the nucleophilic addition of alkynylmetals to imines or activated imines; the imine reactants are either preformed or are generated in situ. The imine N-protecting group typically employed are the *N*-(arylsulfonyl[3c]), *N*-benzyl,[3d,e] *N*-phenyl,[3i,j] and *N*-(*o*-[3l] or *p*[3b,d,i,j]-anisyl) groups.

The use of the bis(trimethylsilyl)methyl (BTMSM[4]) group as an imine N-protecting group in nucleophilic addition reactions involving alkynylmetals have not yet been reported. The *N*-BTMSM group is attractive as an N-protecting group because it can readily be removed,[4,5] via oxidative cleavage, under mild reaction conditions. *N*-BTMSM imines have been used in a few synthetic manipulations such as preparation of N-alkyl *N*-BTMSM amines[4a] via hydride reduction, as a protecting group in [2+2] cycloaddition reaction with ketenes to form β-lactams,[4b,c] and in facilitating the formation of silicon-stabilized azaallyl carbanion wherein the bulky bis(trimethylsilyl) groups also functioned as regiocontrol elements in the subsequent reaction of the carbanion with electrophiles.[4d] Another study reported that *N*-BTMSM-1,3-azabutadienes underwent preferential 1,4-conjugate addition with organocuprates,[4e] and this outcome was attributed to the steric shielding from the BTMSM group, which suppressed the 1,2-addition pathway. However, it should be noted that 1,2-addition was also observed but only with heteroarylcuprate reagents.

In connection with an ongoing project on the Rh(II)-carbenoid mediated transformation of *N*-BTMSM diazoamides,[5] we required access to a trifunctionalized propargyl amine such as **3** ($R = CH_2OR$, Scheme 1). Compounds **3** can readily be accessed via the addition of alkynylmetals to *N*-BTMSM aldimines **1**. In light of the paucity of data on the nucleophilic addition reaction of *N*-BTMSM imines, we have investigated this alkynylation reaction and, herein, report our preliminary results.

N-BTMSM imines **1** were readily prepared in excellent yields by the condensation of BTMSM amine[4] with the appropriate aldehyde.[6] Initial studies showed that the direct reaction of *N*-BTMSM imines with lithium alkynides did not result in alkynylation of the imines. For example, treatment of imines **1** ($R = Me(CH_2)_6$) and **1f** with lithium 1-methoxy-2-propynide (THF, −78 °C) did not produce the corresponding propargyl amines. Further, reaction of **1f** with propynylmagnesium bromide was also unsuccessful. In all these cases, starting



Scheme 1. Nucleophilic addition to *N*-BTMSM aldimines.

Keywords: *N*-Bis(trimethylsilyl)methyl aldimine; *N*-BTMSM; Alkynylation.
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imine was recovered. We reasoned that the lack of reaction can be attributed to a combination of at least three factors; the well-known[3a] diminished reactivity of the imine group toward nucleophiles, the basicity of the organometallic reagent, which could favor 'α'-deprotonation of the imine[3a] to form the corresponding enamine over the desired nucleophilic addition, and steric shielding of the imine unit by the bulky *N*-BTMSM group.[4d,e] We, therefore, investigated the use of 'alkynylboranes' as nucleophilic reagents. It was shown[7] that treatment of alkynyl lithiums with $BF_3{\cdot}OEt_2$ generates the alkynyldifluoroboranes (or alkynyltrifluoroborates) in situ. The latter reagent has lower basicity which favored nucleophilic addition to the imine group.[7] Recent studies[8] on the nucleophilic addition reaction of premixed PhCCLi/$BF_3{\cdot}OEt_2$ to the unactivated *N*-cyclohexylmethylidenebutylamine (**4**) in THF at −85 °C suggested that the reactivity of the premixed reagent decreased dramatically with time. Thus, if imine **4** was added immediately after the PhCCLi/$BF_3{\cdot}OEt_2$ was premixed a 70% yield of the corresponding addition product was obtained. However, if the PhCCLi/$BF_3{\cdot}OEt_2$ mixture was allowed to age (>5 min, −85 °C) before addition of **4**, no product was formed. Further, speciation studies using IR and NMR techniques revealed that aged PhCCLi/$BF_3{\cdot}OEt_2$ produced a complex mixture of unreactive borate species, which had resulted from the condensation PhCCLi and $BF_3{\cdot}OEt_2$.

Our studies began with the determination of the optimal solvent for the reaction of premixed lithium alkynide/$BF_3{\cdot}OEt_2$ to representative imines **1c**–**e**.[9] The results are summarized in Table 1. Diethyl ether was found to be a poor reaction solvent; no product **3i** was detected for the reaction of **1e** (entry 4), and the reaction of **1c**,**d** with $MeOCH_2CCLi/BF_3{\cdot}OEt_2$ and PhCCLi/$BF_3{\cdot}OEt_2$, respectively, gave **3c**,**f** in low yields (entries 1 and 7). With toluene, the best yield (72%) was obtained for the reaction of **1e** and PhCCLi/$BF_3{\cdot}OEt_2$ (entry 8), but the nucleophilic alkynylation of **1c**,**d** with $MeOCH_2CCLi/BF_3{\cdot}OEt_2$ and PhCCLi/$BF_3{\cdot}OEt_2$, respectively, afforded much poorer yields (entries 2 and 5). Moderate to good yields of propargylamines **3c**,**f** and **i** were realized when THF was used as the reaction solvent (entries 3, 6, and 9). On the basis of these results, we further investigated the nucleophilic addition reaction of premixed lithium alkynides/$BF_3{\cdot}OEt_2$ with various *N*-BTMSM aldimines **1** in THF[9,10] and the results are collected in Table 2.

It is clear from Table 2 that conjugated imines such as **1a** (entry 1) do not undergo nucleophilic addition under the present reaction conditions. This was also observed for heteroaryl imines (**1**, R = 2-indolyl). For homologous imine **1b** (entry 2), the desired nucleophilic addition reaction occurred to afford propargyl amine **3b**. This result was encouraging, although a low yield (30%) of **1b** was realized. We attribute the low yield of **3b** to competing isomerization of **1b** to the corresponding conjugated enamine under the reaction conditions. When the phenyl group is two carbons away from the imine unit as in **1c**, a more respectable yield (53%) was obtained (entry 3). Alkyl imine **1d** and alkoxymethyl imines **1e**,**f** reacted well with **2** to afford moderate to good yields of product **3e**–**n** (entries 5–11, 13, 15, 17, and 18). In light of the higher yield (72%) obtained for the reaction of **1e** with PhCCLi/$BF_3{\cdot}OEt_2$ in toluene (Table 1, entry 8), we also repeated the reaction of **1e** with $MeOCH_2CCLi/BF_3{\cdot}OEt_2$, $Me_3SiCCLi/BF_3{\cdot}OEt_2$, and $4\text{-}ClC_6H_4CCLi/BF_3{\cdot}OEt_2$ in toluene (Table 2, entries 12, 14, and 16). The reaction of **1e** with $MeOCH_2CCLi/BF_3{\cdot}OEt_2$ led to a significant decrease in the yield of **3k** (entries 11 vs 12) and with $4\text{-}ClC_6H_4CCLi/BF_3{\cdot}OEt_2$ there was no improvement in yield (entries 15 vs 16). In the case of **1e** with $Me_3SiCCLi/BF_3{\cdot}OEt_2$, a slight improvement in the yield (from 67% to 73%) of **3l** was realized (entry 13 vs 14). From these composite results, it is clear that THF is the solvent of choice for the reaction and the use of toluene does not offer any advantage except in specific cases. Further, our results suggest that the premixed lithium alkynide/$BF_3{\cdot}OEt_2$[11] reagent in THF, unlike the literature results,[8] retains its chemical reactivity and successfully undergo nucleophilic addition to *N*-BTMSM imines **3**.

For the reactions involving ArCCLi/$BF_3{\cdot}OEt_2$ **2**, the parent PhCCLi/$BF_3{\cdot}OEt_2$ gave a higher yield of product than the (4-chlorophenyl)ethynyl one, which suggested that the electron-withdrawing chloro substituent lowered the reactivity of this reagent (Table 2: compare entries 6 and 7, and Table 1: entry 8 and Table 2: entry 16). In the (3-methoxyphenyl)ethynyl case, the yield of the propargyl amine product was comparable to that obtained for the parent reagent (Table 2: compare entries

Table 1. Nucleophilic alkynylation of aldimine **1c**–**e** in different solvents[a]

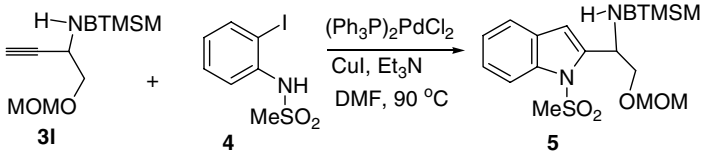
Entry	**1**; R	RCCLi/$BF_3{\cdot}OEt_2$ (**2**)[a]	Solvent	Yield[c] (%)	**3**; R	R[1]
1	**c**; $Ph(CH_2)_2$	$MeOCH_2CC$–	Et_2O	47	**c**; $Ph(CH_2)_2$	$MeOCH_2$
2	**c**; $Ph(CH_2)_2$	$MeOCH_2CC$–	Toluene	17	**c**; $Ph(CH_2)_2$	$MeOCH_2$
3	**c**; $Ph(CH_2)_2$	$MeOCH_2CC$–	THF	53	**c**; $Ph(CH_2)_2$	$MeOCH_2$
4	**d**; *n*-Pr	PhCC–	Et_2O	21	**f**; *n*-Pr	Ph
5	**d**; *n*-Pr	PhCC–	Toluene	33	**f**; *n*-Pr	Ph
6	**d**; *n*-Pr	PhCC–	THF	81	**f**; *n*-Pr	Ph
7	**e**; $MOMOCH_2$	PhCC–	Et_2O	0 (decomp.)[b]	**i**; $MOMCH_2$	Ph
8	**e**; $MOMOCH_2$	PhCC–	Toluene	72	**i**; $MOMCH_2$	Ph
9	**e**; $MOMOCH_2$	PhCC–	THF	61	**i**; $MOMCH_2$	Ph

[a] See Ref. 9 for experimental procedure.
[b] No product was detected and starting **1e** decomposed under the reaction conditions.
[c] Isolated yield of **3** over two steps.

Table 2. Alkynylation of *N*-BTMSM aldimines[a]

Entry	**1**; R	RCCLi/BF_3·OEt_2 (**2**)[a]	Solvent	Yield[c] (%)	**3**; R	R^1
1	**a**; Ph	$MeOCH_2CC$–	THF	0	**a**; Ph	$MeOCH_2$
2	**b**; $PhCH_2$	$MeOCH_2CC$–	THF	30	**b**; $PhCH_2$	$MeOCH_2$
3[b]	**c**; $Ph(CH_2)_2$	$MeOCH_2CC$–	THF	53	**c**; $Ph(CH_2)_2$	$MeOCH_2$
4	**c**; $Ph(CH_2)_2$	*n*-BuCC–	THF	85	**d**; $Ph(CH_2)_2$	*n*-Bu
5	**d**; *n*-Pr	$Me_2C(OSiMe_3)CC$–	THF	46	**e**; *n*-Pr	$Me_2C(OH)$
6[b]	**d**; *n*-Pr	PhCC–	THF	81	**f**; *n*-Pr	Ph
7	**d**; *n*-Pr	4-ClC_6H_4CC–	THF	43	**g**; *n*-Pr	4-ClC_6H_4
8	**d**; *n*-Pr	3-$MeOC_6H_4CC$–	THF	72	**h**; *n*-Pr	3-$MeOC_6H_4$
9[b]	**e**; $MOMOCH_2$	PhCC–	THF	61	**i**; $MOMCH_2$	Ph
10	**e**; $MOMOCH_2$	$Me(CH_2)_4CC$–	THF	83	**j**; $MOMCH_2$	$Me(CH_2)_4$
11	**e**; $MOMOCH_2$	$MeOCH_2CC$–	THF	47	**k**; $MOMOCH_2$	$MeOCH_2$
12	**e**; $MOMOCH_2$	$MeOCH_2CC$–	Toluene	25	**k**; $MOMOCH_2$	$MeOCH_2$
13	**e**; $MOMOCH_2$	Me_3SiCC–	THF	67	**l**; $MOMOCH_2$	H
14	**e**; $MOMOCH_2$	Me_3SiCC–	Toluene	73	**l**; $MOMOCH_2$	H
15	**e**; $MOMOCH_2$	4-ClC_6H_4CC–	THF	59	**m**; $MOMOCH_2$	4-ClC_6H_4
16	**e**; $MOMOCH_2$	4-ClC_6H_4CC–	Toluene	54	**m**; $MOMOCH_2$	4-ClC_6H_4
17	**f**; $BnOCH_2$	3-$MeOC_6H_4CC$–	THF	70	**n**; $BnOCH_2$	3-$MeOC_6H_4$
18	**f**; $BnOCH_2$	Me_3SiCC–	THF	54	**o**; $BnOCH_2$	H

[a] See Ref. 9 for experimental procedure.
[b] Results from Table 1; included here for comparison purposes.
[c] Isolated yield of **3** over two steps.



Scheme 2. Indole formation from propargyl amine **3l**.

6, 8, and 17). This indicated that the electron-withdrawing inductive effect of the *m*-methoxy group is insignificant compared to a *p*-chloro group. In the case of alicyclic reagents **2**, we found that the hexynylide and heptynylide reagents afforded higher yield of the product compared to the functionalized alkynylides (Table 2: compare entries 4 and 10 vs 3, 5, 11, 13, 18).

The versatility of the propargyl amines as synthetic intermediates[2] is demonstrated by the one-pot Sonogashira coupling/indolization[12] reaction of *N*-BTMSM propargyl amine **3k** and **4** to give the highly functionalized 2-substituted indole **5**[8] in a respectable 72% yield (Scheme 2). It is useful to note that the unmasked *N*-BTMSM moiety was tolerated under the reaction conditions.

In summary, we have developed conditions to effect nucleophilic addition of structurally varied lithium alkynides/BF_3·OEt_2 reagents **2** to *N*-BTMSM imines **1**. In spite of the lower reactivity of the imine unit and the presence of the sterically bulky *N*-BTMSM group, the success of our transformation should provide additional avenues for the use of *N*-BTMSM aldimines in synthesis. Further studies in this area are ongoing.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2007.03.171.

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6. The *N*-BTMSM imines are chromatographically stable compounds with the exception of **1b** wherein isomerization to the enamine was observed during chromatography. Aldehyde **1e** was prepared via ozonolysis of bis(MOM) ether of *cis*-2-butene-1,4-diol: Christine, S.; Anna-Maria, L.; Dominique, P.; Gerard, A.; Daniel, A.; Dieter, W.; Guenter, H. *Bull. Soc. Chim. Fr.* **1994**, *131*, 831.
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9. *Representative procedure*: To a solution of alkyne (0.5 mmol) in dry THF or toluene or ether (3 mL), *n*-butyllithium in hexane (2.5 M, 0.5 mmol) was slowly added at −78 °C under argon with stirring. After stirring for 1 h, $BF_3{\cdot}OEt_2$ (63 μL, 0.5 mmol) was added to the solution and the mixture was stirred for 30 min. The imine (0.2 mmol) in dry THF or toluene or ether (1 mL) was transferred under argon and the reaction mixture was stirred for 3 h at −78 °C and 1 h at room temperature. Most of the solvent was removed in vacuo. The residue was dissolved in dry MeOH (5 mL), and the solution was cooled to 0 °C in ice/water bath. K_2CO_3 (345 mg, 2.5 mmol) was added and the mixture was stirred at room temperature overnight. Methanol was removed in vacuo and water (2 mL) was added. The resulting aqueous mixture was extracted with CH_2Cl_2 (3 × 3 mL). The combined organic layers were dried over Na_2SO_4. After filtration, the solvent was evaporated in vacuo and the residue was purified by flash column chromatography.
10. All new compounds showed satisfactory spectroscopic and analytical data. Representative data: compound **3b**: ^{1}H NMR ($CDCl_3$, 300 MHz): δ −0.05 (s, 9H, $SiMe_3$), 0.05 (s, 9H, $SiMe_3$), 0.90–1.20 (br s, 1H, NH), 1.70–1.88 (br s, 1H, C*H*($SiMe_3$)$_2$), 2.78–3.00 (m, 2H, PhC*H*$_2$), 3.31 (s, 3H, OMe), 3.49–3.59 (m, 1H), 4.09 (d, 2H, J = 1.7 Hz, C*H*$_2$O), 7.26–7.29 (m, 5H, *PhH*); ^{13}C NMR ($CDCl_3$, 75 MHz): δ −0.1, 0.1, 36.9, 43.0, 54.7, 60.2, 79.4, 88.6, 126.8, 128.4, 130.0, 138.2. HRMS: calcd for $C_{18}H_{30}NOSi_2$ (M−15) 332.1866; found, 332.1864. Compound **3d**: ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.04 (s, 9H, $SiMe_3$), 0.06 (s, 9H, $SiMe_3$), 0.67–0.80 (br s, 1H, NH), 0.95 (t, 2H, J = 7.2 Hz, Me), 1.40–1.58 (m, 4H, $(CH_2)_2$), 1.80–1.95 (m, 3H, CH_2CC, C*H*($SiMe_3$)$_2$), 2.25 (ddd, 2H, J = 7.2, 7.2, 1.8 Hz, CH_2), 2.73–2.89 (m, 2H, $PhCH_2$), 3.17–3.25 (m, 1H, CHCC), 7.16–7.31 (m, 5H, PhH); ^{13}C NMR ($CDCl_3$, 75 MHz): δ −0.1, 0.1, 13.9, 18.5, 22.1, 31.5, 32.8, 37.0, 38.9, 53.5, 82.4, 84.0, 125.9, 128.5, 128.7, 142.4. HRMS: calcd for $C_{21}H_{36}NSi_2$ (M−15) 358.2386; found, 358.2379. Compound **3g**: ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.05 (s, 9H, $SiMe_3$), 0.15 (s, 9H, $SiMe_3$), 0.92–0.99 (m, 4H, Me, NH), 1.47–1.70 (m, 4H, $(CH_2)_2$), 1.85–1.90 (br s, 1H, C*H*($SiMe_3$)$_2$), 3.42–3.51 (m, 1H), 7.26–7.37 (m, 4H, PhH); ^{13}C NMR ($CDCl_3$, 75 MHz): δ −0.1, 0.1, 14.0, 19.8, 37.5, 39.0, 54.0, 82.2, 93.9, 122.5, 128.4, 133.0, 133.9. HRMS: calcd for $C_{18}H_{29}ClNSi_2$ (M−15) 350.1527; found, 350.1522. Compound **3k**: ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.05 (s, 9H, $SiMe_3$), 0.10 (s, 9H, $SiMe_3$), 1.08–1.22 (br s, 1H, NH), 1.72–1.80 (br s, 1H, C*H*($SiMe_3$)$_2$), 3.38 (s, 6H, 2OMe), 3.50–3.57 (br s, 1H, C*H*), 3.63 (d, 2H, J = 4.4 Hz, CH_2O), 4.10–4.17 (br s, 2H, OCH_2C), 4.67 (s, 2H, OCH_2O); ^{13}C NMR ($CDCl_3$, 75 MHz): δ −0.1, 0.1, 37.5, 53.9, 55.8, 58.0, 60.2, 71.0, 79.5, 87.0, 97.0. HRMS: calcd for $C_{14}H_{30}NO_3Si_2$ (M−15) 316.1764; found, 316.1768. Compound **3l**: ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.03 (s, 9H, $SiMe_3$), 0.05 (s, 9H, $SiMe_3$), 1.12–1.20 (br s, 1H, NH), 1.70 (s, 1H, C*H*($SiMe_3$)$_2$), 2.25 (d, 1H, J = 2.1 Hz, CCH), 3.37 (s, 3H, OMe), 3.47–3.58 (br s, 1H, CH), 3.64 (d, 2H, J = 4.8 Hz, OCH_2C), 4.67 (s, 2H, CH_2OMe); ^{13}C NMR ($CDCl_3$, 75 MHz): δ −0.1, 0.1, 36.8, 53.2, 55.7, 70.2, 72.0, 84.1, 96.5; HRMS: calcd for $C_{12}H_{26}NO_2Si_2$ (M−15) 272.1502; found, 272.1502. Indole **5**: IR (film) 3345.0 cm^{-1}, ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.05 (s, 9H, $SiMe_3$), 0.15 (s, 9H, $SiMe_3$), 1.55–1.65 (br s, 1H, NH), 1.70 (s, 1H, C*H*($SiMe_3$)$_2$), 3.04 (s, 3H, $MeSO_2$), 3.21 (s, 3H, OMe), 3.75 (dd, 1H, J = 5.9, 9.6 Hz, CC*H*′O), 4.54 (d, 1H, J = 6.2 Hz, OC*H*O), 4.58 (d, 1H, J = 6.2 Hz, OC*H*′O), 6.80 (s, 1H, H-3), 7.24–7.35 (m, 2H, H-5, H-6), 7.52–7.57 (m, 1H, H-4), 7.98–8.05 (m, 1H, H-7); ^{13}C NMR ($CDCl_3$, 75 MHz): δ −0.1, 0.1, 36.8, 40.3, 55.4, 58.0, 70.2, 96.5, 111.0, 114.8, 121.0, 124.0, 124.3, 129.9, 137.5, 143.8.
11. We also briefly examined the use of the $BF_3{\cdot}NBu_3$ complex as a substitute[8] for $BF_3{\cdot}OEt_2$ in the reaction (THF as solvent) of **1d** with PhCCLi and **1e** with 4-ClC_6H_4CCLi; the yields of the addition products for **1d** and **1e** were 60% and 51%, respectively. We conclude that there is no advantage to use $BF_3{\cdot}NBu_3$ in the present study.
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