Synthesis of Allylic and Propargylic Primary Amines by Reaction of Organometallic Reagents with α-Amidoalkyl Sulfones

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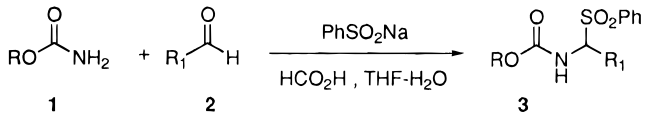
Introduction

Allylic and propargylic amines play a prominent role in organic synthesis, and their importance continues to grow with time.[1] A plethora of synthetic methods have been devised for the preparation of allylic amines, including substitution reactions with nucleophilic nitrogen,[2] use of azallylic anions,[3] coupling reactions,[4] and palladium-catalyzed reactions.[5] Similar approaches can also be used for the synthesis of propargylamines,[6] but the most reliable and efficient method for the preparation of allylic and propargylic amines still remains the addition of an appropriate organometallic reagent to imino derivatives.[7] The reaction of strongly basic organometallic reagents to *N*-alkyl imines rarely produces synthetically useful results because α deprotonation of the imine often competes with the addition reaction.[8] This unwanted side reaction can be partially suppressed by using organometallic reagents with low basicity, whose preparation is not always straightforward.[9] These reagents sometimes give unexpected results, as in the case of vinylcerium dichloride, which reacts with imines to give a regio- and stereoisomeric mixture of homoallylic amines.[10]

The utilization of more electrophilic *N*-acyl or *N*-tosyl imines considerably improves the efficiency of the process even though the preparation of these derivatives is rather difficult.[11] Furthermore, the cleavage of the acyl moiety to give the free amino group frequently requires harsh conditions.[12] In this context, nitrones present an enhanced reactivity as electrophiles and can be treated with vinyl and ethynyl organometallic reagents to give the relative hydroxylamines, which can be further reduced to the parent amino compounds.[13] Finally, the use of metalloalkyne complexes with *N*-metallo imines represents a valid option to the above cited methods for the synthesis of primary unsaturated amines.[8c,14]

Scheme 1



1 **2** **3**

1a R = Bn

1b R = *t*-Bu

The troubles associated with the preparation of *N*-acyl imines have spurred the search for some synthetic analogues of these substrates that would behave as reactive imines but are endowed by easy access and stability. 1-(α-Amidoalkyl)benzotriazoles partially exist as benzotriazolide−iminium ion pair in solution and, therefore, may react with organometallic reagents to give the corresponding amino derivatives.[15] This method permits the synthesis of tertiary propargylamines through the use of alkynyllithium reagents generated from 1-alkynes.

Results and Discussion

We have found that a similar behavior is displayed by α-amidoalkyl sulfones **3**, which can be easily prepared by reaction of a carbamate **1** with a suitable aldehyde **2** and sodium benzenesulfinate, in the presence of formic acid[16] (Scheme 1, Table 1). The utilization of sulfones **3** as *N*-acyl imine equivalents is particularly advantageous because these derivatives are mostly stable solids and can be recovered from the reaction mixture by simple filtration and purified by crystallization. α-Amidoalkyl sulfones **3** are known to react with stabilized carbanions, giving a product that arises from a formal substitution of the phenylsulfonyl anion with the nucleophile.[17] Vinylmagnesium bromide **4** is able to react with sulfones **3** at −20 °C in THF affording in good yields the corre-

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Table 1. Synthesis of α-Amidoalkyl Sulfones 3

entry	carbamate 1	aldehyde 2	sulfone 3	yield[a] %
1	**1a**	*n*-$C_7H_{15}CHO$	**3a**	90
2	**1a**	$C_5H_{11}CH{=}CHCH_2CH_2CHO$	**3b**	84
3	**1a**	$PhCH_2CH_2CHO$	**3c**	82
4	**1b**	$BnOCH_2CH_2CH_2CH_2CHO$	**3d**	75
5	**1b**	PhCHO	**3e**	70
6	**1b**	$(CH_3)_2CHCH_2CHO$	**3f**	89
7	**1b**	*c*-$C_6H_{11}CHO$	**3g**	83
8	**1b**	$PhCH_2CH_2CHO$	**3h**	77
9	**1a**	$(CH_3)_2CHCH_2CHO$	**3i**	88

[a] Yields of pure, isolated products.

Scheme 2

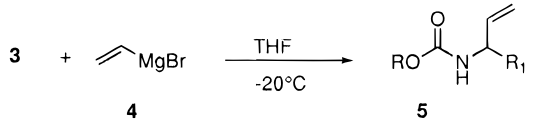


Table 2. Synthesis of Allylamines 5 by Reaction of Vinylmagnesium Bromide 4 with Sulfones 3

entry	sulfone 3	allylamine 5	yield[a] %
1	**3a**	**5a**	80
2	**3b**	**5b**	92
3	**3c**	**5c**	90
4	**3d**	**5d**	85
5	**3e**	**5e**	93

[a] Yields of pure, isolated products.

Scheme 3

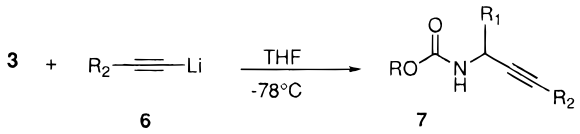


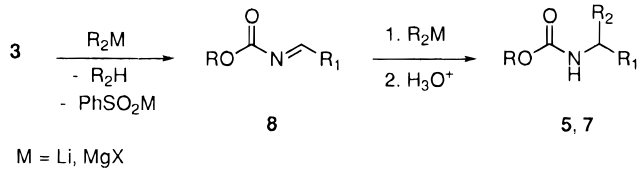
Table 3. Synthesis of Propargylamines 7 by Reaction of 1-Alkynyllithiums 6 with Sulfones 3

entry	sulfone 3	alkynyllithium 6 R_2	propargylamine 7	yield[a] %
1	**3a**	Ph	**7a**	78
2	**3a**	CO_2Me	**7b**	75
3	**3c**	$MOMOCH_2$	**7c**	70
4	**3d**	Ph	**7d**	68
5	**3e**	Ph	**7e**	78
6	**3f**	Ph	**7f**	81
7	**3g**	Ph	**7g**	88
8	**3h**	*n*-Bu	**7h**	89
9	**3h**	Me_3Si	**7i**	77
10	**3h**	Ph	**7j**	88

[a] Yields of pure, isolated products.

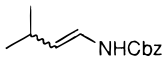
sponding *N*-protected allylamines **5** (Scheme 2, Table 2). It is worth noting that this reaction also shows an interesting chemoselectivity as the carbamoyl group is not affected by the organomagnesium reagent used. Analogously, simple or functionalized 1-alkynyllithium reagents **6** react at −78 °C in THF with sulfones **3** to give *N*-protected propargylamines **7** in satisfactory yields[18] (Scheme 3, Table 3). The use of carbamates **1** as nitrogeneous derivatives for the synthesis of sulfones **3** is particularly beneficial because, unlike other *N*-substituents such as alkyl, acyl, and tosyl groups, they are

Scheme 4



efficiently removed when the free primary amine is required. 1-Alkynyllithium **6** can be opportunely generated from the corresponding alkynes using *n*-butyllithium as a base and presents a better synthetic flexibility than vinyl organomagnesium reagents. Indeed, the inclusion of several extra functions into the lithium derivatives **6** as alkoxy, ester, and trimethylsilyl groups allows a supplementary synthetic manipulation of the propargylamines **7** obtained.[19]

α-Amidoaryl sulfone **3e**, prepared from benzaldehyde, is known to undergo a base-assisted elimination of phenylsulfinate anion, giving the corresponding *N*-acyl imine.[16a] This eliminative process is, however, less efficient when attempted on sulfones **3** coming from aliphatic aldehydes. Indeed, when sulfone **3f** is treated with 1 equiv of DBU in THF at room temperature, a diastereomeric mixture of enamines **9f** is recovered in



9f

55% yield. In light of these facts, the proposed mechanism for the synthesis of *N*-protected allylic and propargylic amines is portrayed in Scheme 4. The organometallic reagent initially acts as a base, converting the sulfone **3** into the imine **8**, which immediately reacts with another molecule of the reagent to give the addition product **5** or **7**. As a matter of fact, 2 equiv of the organometallic reagent are needed to obtain the primary amine in satisfactory yields. When 1 equiv of the reagent is used all of the sulfone **3** is consumed; however, the yield of the *N*-protected amine is low, and it is possible to observe the presence of a certain amount of the corresponding enamine coming from a tautomerization of the unreacted imine **8**.

In conclusion we have demonstrated that α-amidoalkyl sulfones **3** can be used as synthetic equivalents of *N*-acyl imines, a class of reactive substrates hardly achievable through a direct reaction from aldehydes.[11a] Addition of a suitable organometallic reagent to sulfones **3** allows in a straighforward fashion the synthesis of allylic and propargylic *N*-protected primary amines that are amenable for useful synthetic transformations.

Experimental Section

^1H NMR were performed at 300 MHz in $CDCl_3$ as solvent. THF was dried by refluxing it over sodium wire. All chemicals used are commercial. Vinylmagnesium bromide **4** was prepared from vinyl bromide and magnesium turnings using standard conditions. 4-(Benzyloxy)pentanal,[20] 3-(methoxymethoxy)prop-1-yne,[21] and *tert*-butyl phenylsulfonylphenylmethylcarbamate **3e**[16a] were prepared following literature methods.

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General Procedure for the Preparation of α-Amidoalkyl Sulfones 3. Carbamate **1** (5 mmol) was dissolved in THF (2 mL), and then water (5 mL), sodium phenylsulfinate (5 mmol), and the appropriate aldehyde (5.4 mmol) were sequentially added at room temperature. Formic acid (1.2 mL) was added, and the mixture was stirred for 12 h. The resulting white precipitate was filtered and purified by crystallization (hexanes−ethyl acetate (4:1)).

Benzyl 1-phenysulfonyloctylcarbamate (3a): yield 90%; mp 90 °C; IR (cm^{-1}, KBr) 3340, 1698, 1310, 1140; ^1H NMR δ ppm 0.87 (t, 3H, J = 6.3 Hz), 1.19−1.53 (m, 9H), 1.60−1.81 (m, 1H), 2.18−2.32 (m, 1H), 2.40−2.65 (m, 1H), 4.78−4.95 (m, 3H), 5.25 (d, 1H, J = 10.4 Hz), 7.15−7.53 (m, 7H), 7.55−7.70 (m, 1H), 7.83−7.94 (m, 2H). Anal. Calcd for $C_{22}H_{29}NO_4S$ (403.53): C, 65.48; H, 7.24; N, 3.47. Found: C, 65.57; H, 7.17; N, 3.52.

***tert*-Butyl 5-(benzyloxy)-1-phenylsulfonylpentylcarbamate (3d):** yield 75%; waxy solid; IR (cm^{-1}, neat) 3337, 1719, 1308, 1143; ^1H NMR δ ppm 1.20 (s, 9H), 1.41−1.90 (m, 5H), 2.21−2.38 (m, 1H), 3.48 (t, 2H, J = 5.6 Hz), 4.48 (s, 2H), 4.81−4.98 (m, 1H), 5.18 (d, 1H, J = 11.5 Hz), 7.29−7.38 (m, 4H), 7.45−7.68 (m, 4H), 7.90−7.99 (m, 2H). Anal. Calcd for $C_{23}H_{31}NO_5S$ (433.56): C, 63.72; H, 7.21; N, 3.23. Found: C, 63.81; H, 7.26; N, 3.29.

***tert*-Butyl cyclohexylphenylsulfonylmethylcarbamate (3g):** yield 83%; mp 134 °C; IR (cm^{-1}, KBr) 3345, 1710, 1325, 1150; ^1H NMR δ ppm 1.05−1.48 (m, 12H), 1.61−1.82 (m, 6H), 2.05−2.18 (m, 1H), 2.40−2.53 (m 1H), 4.69 (dd, 1H, J = 11.3, 3.3 Hz), 5.14 (d, 1H, J = 11.3 Hz), 7.45−7.70 (m, 3H), 7.85−7.93 (m, 2H). Anal. Calcd for $C_{18}H_{27}NO_4S$ (353.47): C, 61.16; H, 7.70; N, 3.96. Found: C, 61.09; H, 7.75; N, 4.03.

General Procedure for the Preparation of Allylamines 5. Sulfone **3** was dissolved in dry THF (15 mL), and the solution was cooled at −20 °C. Vinylmagnesium bromide **4** (4.1 mmol, 0.8 M in THF) was then added dropwise over 15 min, and after 30 min at −20 °C the temperature was slowly raised to 0 °C. The reaction mixture was then quenched with saturated aqueous NH_4Cl (3 mL), and after exctraction with CH_2Cl_2 the organic phase was dried over $MgSO_4$. Removal of the solvent afforded the crude *N*-protected allylamine **5**, which was purified by column chromatography (hexanes−ethyl acetate (7:3)).

Benzyl 1-heptylallylcarbamate (5a): yield 80%; mp 44 °C; IR (cm^{-1}, KBr) 3330, 1700, 1650; ^1H NMR δ ppm 0.88 (t, 3H, J = 6.8 Hz), 1.15−1.42 (m, 10H), 1.45−1.62 (m, 2H), 4.05−4.25 (m, 1H), 4.62−4.80 (m, 1H), 5.07 (d, 1H, J = 1.3 Hz), 5.11 (s, 2H), 5.21 (d, 1H, J = 1.3 Hz), 5.67−5.81 (m, 1H), 7.29−7.40 (m, 5H). Anal. Calcd for $C_{18}H_{27}NO_2$ (289.41): C, 74.70; H, 9.40; N, 4.84. Found: C, 74.61; H, 9.46; N, 4.78.

***tert*-Butyl 1-[4-(benzyloxy)butyl]allylcarbamate (5d):** yield 85%; oil; IR (cm^{-1}, neat) 3320, 1710, 1650; ^1H NMR δ ppm 1.40−1.55 (m, 13H), 1.60−1.77 (m, 2H), 3.47 (t, 2H, J = 6.4 Hz), 4.05−4.15 (m, 1H), 4.35−4.45 (m, 1H), 4.50 (s, 2H), 5.05−5.20 (m, 2H), 5.65−5.85 (m, 1H), 7.30−7.42 (m, 5H). Anal. Calcd for $C_{19}H_{29}NO_3$ (319.44): C, 71.44; H, 9.15; N, 4.38. Found: C, 71.56; H, 9.09; N, 4.41.

General Procedure for the Preparation of Propargylamines 7. 1-Alkyne (4 mmol) was dissolved in dry THF (15 mL), and the solution was cooled to −20 °C. BuLi (4.1 mmol, 2.7 mL, 1.5 M in hexane) was added dropwise, and after 30 min at −20 °C the temperature was lowered to −78 °C. Sulfone **3** (2 mmol) dissolved in dry THF (5 mL) was added, and the temperature was kept at −78 °C for 1 h. Quenching was made at −78 °C by rapid addition of saturated aqueous NH_4Cl (4 mL), and the mixture was allowed to reach room temperature. The mixture was extracted with CH_2Cl_2, and the organic phase was dried over $MgSO_4$. After removal of the solvent the *N*-protected propargylamine **7** obtained was purified by column chromatography (hexanes−ethyl acetate (8:2)).

Benzyl 1-heptyl-3-phenylprop-2-ynylcarbamate (7a): yield 78%; mp 57 °C; IR (cm^{-1}, KBr) 3340, 2230, 1700; ^1H NMR δ ppm 0.89 (t, 3H, J = 6.8 Hz), 1.16−1.62 (m, 10H), 1.68−1.80 (m, 2H), 4.55−4.79 (m, 1H), 4.93−5.05 (m, 1H), 5.14 (s, 2H), 7.29−7.45 (m, 10H). Anal. Calcd for $C_{24}H_{29}NO_2$ (363.49): C, 79.39; H, 8.04; N, 3.85. Found: C, 79.31; H, 7.99; N, 3.91.

Methyl 4-[(benzyloxycarbonyl)amino]undec-2-ynoate (7b): yield 75%; mp 79 °C; IR (cm^{-1}, KBr) 3330, 1690; ^1H NMR δ ppm 0.86 (t, 3H, J = 6.5 Hz), 1.12−1.40 (m, 10H), 1.50−1.78 (m, 2H), 3.36 (s, 3H), 4.78−4.93 (m, 1H), 4.95−5.10 (m, 1H), 5.13 (s, 2H), 7.29−7.42 (m, 5H). Anal. Calcd for $C_{20}H_{27}NO_4$ (345.43): C, 69.54; H, 7.88; N, 4.05. Found: C, 69.48; H, 7.97; N, 4.00.

Benzyl 4-(methoxymethoxy)-1-phenethylbut-2ynylcarbamate (7c): yield 70%; oil; IR (cm^{-1}, neat) 3350, 2180, 1705; ^1H NMR δ ppm 1.95−2.10 (m, 2H), 2.76 (t, 2H, J = 8.1 Hz), 3.38 (s, 3H), 4.24 (s, 2H), 4.50−4.67 (m, 1H), 4.71 (s, 2H), 4.93−5.05 (m, 1H), 5.11 (s, 2H), 7.12−7.41 (m, 10H). Anal. Calcd for $C_{22}H_{25}NO_4$ (367.44): C, 71.91; H, 6.86; N, 3.81. Found: C, 71.83; H, 6.95; N, 3.76.

***tert*-Butyl 1-phenethyl −3-trimethylsilylprop-2-ynylcarbamate (7i):** yield 77%; oil; IR (cm^{-1}, neat) 3322, 2200, 1715; ^1H NMR δ ppm 0.18 (s, 9H), 1.45 (s, 9H), 1.85−2.05 (m, 2H), 2.76 (t, 2H, J = 7.3 Hz), 4.32−4.51 (m, 1H), 4.63−4.70 (m, 1H), 7.15−7.40 (m, 5H). Anal. Calcd for $C_{19}H_{29}NO_2Si$ (331.53): C, 68.84; H, 8.82; N, 4.22. Found: C, 68.93; H, 8.77; N, 4.30.

***tert*-Butyl 1-phenethyl-3-phenylprop-2-ynylcarbamate (7j):** yield 88%; mp 96 °C; IR (cm^{-1}, KBr) 3330, 2205, 1720; ^1H NMR δ ppm 1.45 (s, 9H), 2.00−2.15 (m, 2H), 2.81 (t, 2H, J = 8.1 Hz), 4.60−4.75 (m, 1H), 4.80−4.95 (m, 1H), 7.15−7.50 (m, 10H). Anal. Calcd for $C_{22}H_{25}NO_2$ (335.44): C, 72.77; H, 7.51; N, 4.18. Found: C, 72.88; H, 7.52, N, 4.25.

Benzyl 3-methylbut-3-enylcarbamate (9f). Sulfone **3f** (0.33 g, 1 mmol) was dissolved in dry THF (8 mL), and DBU (0.18 g, 1.2 mmol) was added at room temperature. After the mixture strirred for 1 h at room temperature, the solvent was evaporated, and the crude product was purified by column chromatography (hexanes−ethyl acetate (95:5)), giving 0.12 g (55% yield) of a colorless oil: IR (cm^{-1}, neat) 3325, 1708. ^1H NMR δ ppm *(E)*-isomer: 0.99 (d, 6H, J = 6.8 Hz), 2.29 (sextet, 1H, J = 6.5 Hz), 4.98 (dd, 1H, J = 14.2, 7.0 Hz), 5.14 (s, 2H), 6.20−6.35 (m, 1H), 6.44 (dd, 1H J = 14.2, 10.8 Hz), 7.30−7.48 (m, 5H); *(Z)* -isomer: 0.98 (d, 6H, J = 6.6 Hz), 2.25−2.45 (m, 1H), 4.45−4.60 (m, 1H), 5.15 (s, 1H), 6.25−6.45 (m, 2H), 7.30−7.45 (m, 5H). Anal. Calcd for $C_{13}H_{17}NO_2$ (219.28): C, 71.21; H, 7.81; N, 6.34. Found: C, 71.33; H, 7.89; N, 6.30.

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Supporting Information Available: Spectral and physical data for compounds not included in the Experimental Section. This material is available free of charge via the Internet at http://pubs.acs.org.

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