Preparation and Reactivity of New β-Nitrogen-Functionalized Vinylic Organolithium Compounds from Secondary Aliphatic Allylamines

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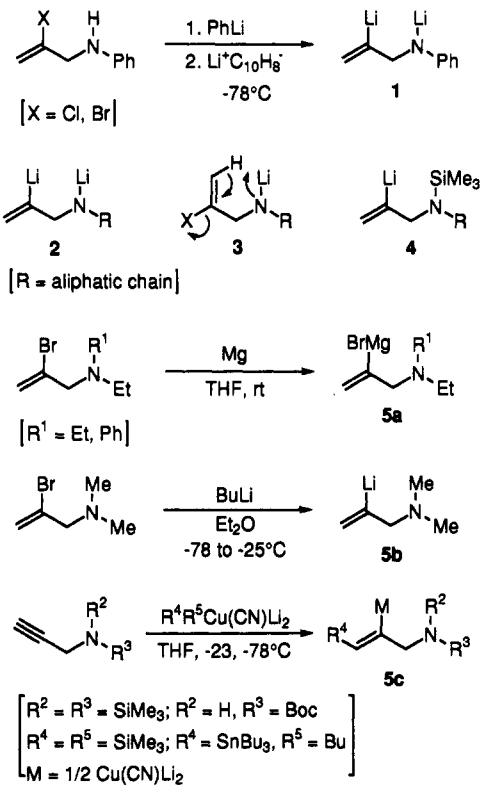
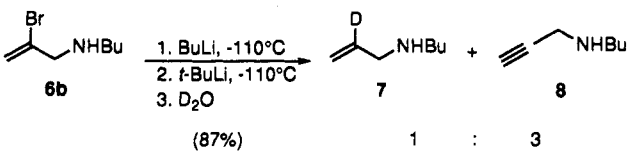
Two new types of β-nitrogen-functionalized vinylic organolithium compounds have been prepared from secondary aliphatic allylamines through the temporary silylation of the amino group. The monoanionic intermediates **4**, stable at −80 °C, are generated by a bromine–lithium exchange reaction and the dianionic derivatives **2**, stable at room temperature, by a tin–lithium transmetalation reaction. Both types of organolithium compounds react with different electrophiles giving functionalized allylamines **7** and **10–27**. Moreover, dianionic derivatives **30**, **33** can be prepared directly by bromine–lithium exchange when the β-elimination reaction of hydrogen bromide in the lithium 2-bromoallylamide is structurally hindered. Additionally, a novel type of anionic 1,3-rearrangement of a trimethylsilyl group from nitrogen to carbon is described.

The development of new functionalized organolithium reagents is an active area of research in synthetic organic chemistry, mainly because on reaction with electrophiles they afford directly polyfunctionalized molecules.[1] In a previous paper[2] we have described the preparation of intermediate **1** from (2-halogenoallyl)anilines by successive reaction with phenyllithium and lithium naphthalenide at −78 °C. This procedure did not allow the generation of analogous intermediate **2** from aliphatic 2-halogenoallylamines due to decomposition of the amide species **3** (X = Cl, Br), formed in the first step, by elimination of hydrogen halogenide. In addition, as shown in Scheme 2, the successive reaction of 2-bromoallylamine **6b** with butyllithium (1 equiv) and *tert*-butyllithium (2 equiv) in ether at −110 °C yielded, after quenching with D_2O at −110 °C, a mixture of deuterioallylamine **7** and propargylamine **8** in 1:3 ratio,[3] respectively. This experiment indicates that even at this very low temperature the elimination reaction of the corresponding amide intermediate of type **3** is the major reaction taking place. Herein we report a way to overcome this problem which has led to a general preparation and study of the reactivity of dianionic compounds **2** and at the same time to new related monoanionic derivatives **4**. Apart from the former report,[2] we are aware of only three examples of β-nitrogen-functionalized organometallics **5** (M = Mg,[4] Li,[5] Cu[6]), all monoanionic compounds and derived from tertiary allylamines in the two former cases **5a**,[4] **5b**[5] and from protected propargylamines in the later cases of intermediates **5c**[6] (Scheme 1).

Scheme 1



Scheme 2



Results and Discussion

The synthetic route to organolithium compounds **2** and **4** is outlined in Scheme 3. The goal was to replace the bromine atom of the starting materials **6** for an alternative functional moiety with reduced capacity to act as a leaving group and that could easily be transformed to an organolithium compound. This was accomplished by tem-

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(1) Recent reviews: (a) Barluenga, J. *Pure Appl. Chem.* **1990**, *62*, 595. (b) Nájera, C.; Yus, M. *Trends Org. Chem.* **1991**, *2*, 155.

(2) Barluenga, J.; Foubelo, F.; Fañanás, F. J.; Yus, M. *J. Chem. Soc., Perkin Trans. 1* **1989**, 553.

(3) Ratio of products was determined by gas chromatography analysis (HP-ULTRA 2 capillary column: 25 m × 0.2 mm i.d.; 0.33 μm film thickness).

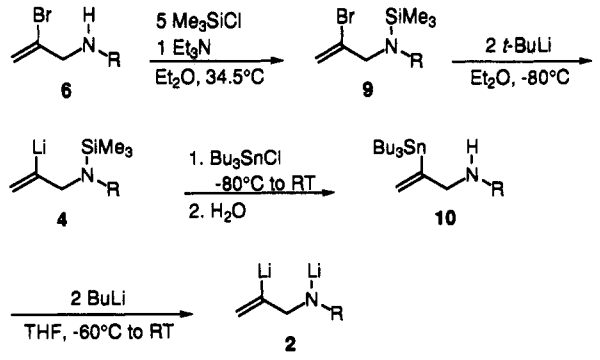
(4) Ficini, J.; Sarrade-Loucheur, G.; Normant, H. *Bull. Soc. Chim. Fr.* **1962**, 1219.

(5) Corey, E. J.; Cane, D. E.; Libit, L. *J. Am. Chem. Soc.* **1971**, *93*, 7016.

(6) (a) Capella, L.; Degl'Innocenti, A.; Reginato, G.; Ricci, A.; Taddei, M. *J. Org. Chem.* **1989**, *54*, 1473. (b) Capella, L.; Degl'Innocenti, A.; Mordini, A.; Reginato, G.; Ricci, A.; Seconi, G. *Synthesis* **1991**, 1201.

0022-3263/94/1959-0602$04.50/0

Scheme 3



a : R = CH_2=$CHCH_2$ **d** : R = $(CH_2)_5CH$
b : R = Bu **e** : R = $PhCH_2$
c : R = $CH_3(CH_2)_5$ **f** : R = $PhCH_2CH_2$

Table 1. Compounds 6 and 9 Prepared

product	R	yield (%)[a]	bp (°C)[b]
6a	CH_2=$CHCH_2$	70	55–57
6b	Bu	65	64–66[c]
6c	$CH_3(CH_2)_5$	80	89–90[d]
6d	$(CH_2)_5CH$	73	*e*
6e	$PhCH_2$	75	85–87[f]
6f	$PhCH_2CH_2$	70	94–95[f]
9a	CH_2=$CHCH_2$	98	*g*
9b	Bu	98	*g*
9c	$CH_3(CH_2)_5$	95	*g*
9d	$(CH_2)_5CH$	97	*g*
9e	$PhCH_2$	99	*g*
9f	$PhCH_2CH_2$	93	*g*

[a] Isolated yields based on the corresponding starting material (2,3-dibromopropene for compounds **6** and amines **6** for compounds **9**). [b] Determined at 0.1 mmHg. [c] Literature[10] bp 71–73 °C/10 mmHg. [d] Literature[11] bp 122–124 °C/24 mmHg. [e] See ref 2. [f] Literature[12] purified by column chromatography. [g] Obtained as pure compounds (over 95% by ^1H and ^{13}C NMR); used without further purification.

porary protection of the secondary amine group followed by conversion to the organotin reagents **10**.[7] Accordingly, treatment of *N*-alkyl-2-bromoallylamines **6**[8] with excess of chlorotrimethylsilane in the presence of triethylamine in refluxing diethyl ether cleanly provided the silylated amines **9**[9] (Table 1). The reaction of **9** with *t*-BuLi in ether at −80 °C afforded the monoanions **4** which on reaction with tributyltin chloride and after hydrolysis gave the stannylamines **10** (Table 2, entries 1–6). Finally, the reaction of **10** with BuLi in THF from −60 °C to room temperature led to the dianions **2**. Both intermediates **2** and **4** underwent reaction with several electrophiles, that were added to the cold reaction solutions before warming to room temperature and isolation of the products **7** and **11–27** summarized in Scheme 4 in the yields indicated in Table 2.

The reaction of monoanions **4** with other electrophiles is illustrated by using intermediate **4b**. Treatment of this monolithiated compound **4b** with deuterium oxide at −80 °C provided deuterated amine **7** (Table 2, entry 7), whereas this same treatment at room temperature led to C-silylated amine **11** (Table 2, entry 8). This result shows that the monoanionic compounds **4** are stable only at low temperatures; at higher temperatures they undergo a 1,3-migration of the trimethylsilyl group from nitrogen to carbon.[13] Additionally, the reaction of **4b** with MeI did not lead to the expected 2-methylallylamine; instead C-silylated tertiary amine **12** (Table 2, entry 9) was isolated. The formation of **12** clearly arises from reaction of lithium amide **28a** (Scheme 4) with MeI, indicating that the organolithium reagent **4b** does not react with MeI at −80 °C, and when the temperature is raised the probable intramolecular 1,3-anionic rearrangement of the Me_3Si group,[14] leading to compound **28a**, takes place preferentially. The reaction of **4b** with phenyl isocyanate and cyclohexanone furnished the α,β-unsaturated amide **13** (entry 10) and 1,3-amino alcohol **14** (entry 11), respectively. Addition of 2-cyclohexenone to **4b** gave 1,5-amino alcohol **15** (entry 12). This functionalized 1,3-diene is generated by 1,3-rearrangement of the tertiary allylic alcohol **28b** initially formed in the regioselective 1,2-addition reaction to the enone. This allylic transposition occurs in the workup when the reaction mixture is hydrolyzed with 2 N H_2SO_4 to cleave the nitrogen–silicon bond. This was proved by carrying out the hydrolysis with water. In these conditions *N*-silylated tertiary alcohol **28b** was isolated which by subsequent treatment with 2 N H_2SO_4 in the conditions of the acidic workup gave rise to secondary alcohol **15**. The reaction of **4b** with (*R*)-(−)-carvone led regio- and stereoselectively to the 1,2-addition product **16** as a single adduct (entry 13). The tentative stereochemistry of this compound most likely would be the axial alcohol corresponding to an equatorial attack, i.e., at the less-hindered side of the carbonyl group,[15] by the bulky nucleophile **4b**; but this has not been confirmed. In this reaction a minor amount (11%) of the secondary alcohol derived by allylic transposition of the hydroxy group in compound **16** was observed. The small amount of this isomer precluded their definitive assignment except by analogy to the above case. In a last example intermediate **4e** efficiently reacted with isobutyraldehyde giving amino alcohol **17** (entry 14).

Analogously, the reaction of dianions **2** with different electrophilic reagents provided the corresponding 2-substituted allylamines. In most cases, dilithiated compounds **2** were characterized by treatment with D_2O which afforded deuterated compounds **7**, **23–25**, and **27** (entries 16, 22–24, and 26). The stability of these dianionic compounds **2** was also studied by deuterolysis reactions. Thus, treatment of **2e** with D_2O at room temperature gave deuterated amine **25** (entry 24), but when D_2O was added

(7) (a) Pereyre, M.; Quintard, J. P.; Rahm, A. *Tin in Organic Synthesis*; Butterworths: London, 1987. For other β-nitrogen-functionalized vinylic tin compounds, see: (b) Mitchell, T. N.; Wickenkamp, R.; Amamria, A.; Dicke, R.; Schneider, U. *J. Org. Chem.* **1987**, *52*, 4868. (c) Ritter, K. *Synthesis* **1989**, 218 and refs cited therein. We thank one of the referees for reminding us of these two last references.

(8) Obtained from 2,3-dibromopropene and the corresponding amine by a slightly different experimental procedure from those reported in refs 10 and 12.

(9) Lalonde, M.; Chan, T. H. *Synthesis* **1985**, 817.

(10) Pollard, C. B.; Parcell, R. F. *J. Am. Chem. Soc.* **1951**, *73*, 2925.

(11) Bottini, A. T.; King, B. J.; Olsen, R. E. *J. Org. Chem.* **1963**, *28*, 3241.

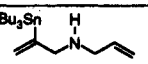
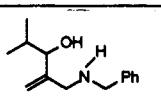
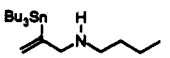
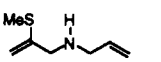
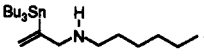
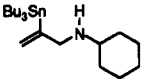
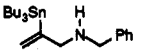
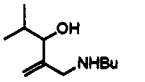
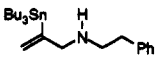
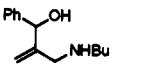
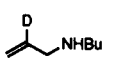
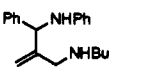
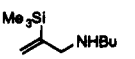
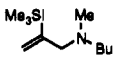
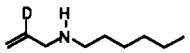
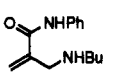
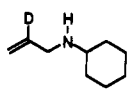
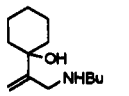
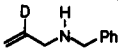
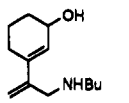
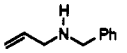
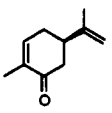
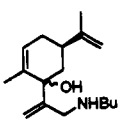
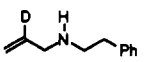
(12) Mori, M.; Chiba, K.; Okita, M.; Kayo, I.; Ban, Y. *Tetrahedron* **1985**, *41*, 375.

(13) (a) Brook, A. G.; Bassindale, A. R. Molecular Rearrangements of Organosilicon Compounds. In *Rearrangements in Ground and Excited States*; De Mayo, P., Ed.; Academic Press: New York, 1980; Vol. 2, p 149–227. (b) Colvin, E. *Silicon in Organic Synthesis*; Butterworths: London, 1981.

(14) For a closely related 1,4-silyl migration from N to C see: (a) Degl'Innocenti, A.; Mordini, A.; Pinzani, D.; Reginato, G.; Ricci, A. *Synlett* **1991**, 712. (b) Corriu, R. J. P.; Geng, B.; Moreau, J. J. E. *J. Org. Chem.* **1993**, *58*, 1443.

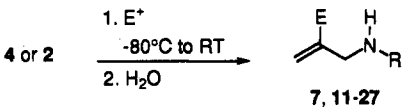
(15) For recent studies of stereoselectivities in nucleophilic additions to cyclohexanones and cyclohexenones see: (a) Trost, B. M.; Flórez, J.; Jebaratnam, D. J. *J. Am. Chem. Soc.* **1987**, *109*, 613. (b) Wu, Y.-D.; Houk, K. N.; Flórez, J.; Trost, B. M. *J. Org. Chem.* **1991**, *56*, 3656. (c) Frenking, G.; Köhler, K. F.; Reetz, M. T. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1146. (d) Wu, Y-D.; Houk, K. N.; Paddon-Row, M. N. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1019. (e) Reetz, M. T.; Stanchev, S. *J. Chem. Soc., Chem. Commun.* **1993**, 328 and refs cited therein.

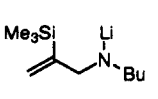
Table 2. Reaction of Intermediates 2 and 4 with Electrophiles

entry	intermediate	electrophile	product	yield (%)[a]	entry	intermediate	electrophile	product	yield (%)[a]
1	**4a**	Bu_3SnCl	 **10a**	88	14	**4e**	*i*-PrCHO	 **17**	96
2	**4b**	Bu_3SnCl	 **10b**	87	15	**2a**	Me_2S_2	 **18**	64
3	**4c**	Bu_3SnCl	 **10c**	85	16	**2b**	D_2O	**7**[c]	55
4	**4d**	Bu_3SnCl	 **10d**	89	17	**2b**	Me_2S_2	 **19**	90
5	**4e**	Bu_3SnCl	 **10e**	90	18	**2b**	*i*-PrCHO	 **20**	65
6	**4f**	Bu_3SnCl	 **10f**	71	19	**2b**	PhCHO	 **21**	70
7	**4b**	D_2O[b]	 **7**[c]	65	20	**2b**	PhCH=NPh	 **22**	70
8	**4b**	D_2O[d]	 **11**	99	21	**2b**	 **15**		72
9	**4b**	MeI	 **12**	88	22	**2c**	D_2O	 **23**[c]	75
10	**4b**	PhNCO	 **13**	68	23	**2d**	D_2O	 **24**[c]	86
11	**4b**		 **14**	92	24	**2e**	D_2O[d]	 **25**[e]	89
12	**4b**		 **15**	88	25	**2e**	D_2O[f]	 **26**	71
13	**4b**		 **16**	58	26	**2f**	D_2O	 **27**[c]	84

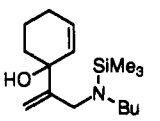
[a] Isolated yields based on the corresponding starting material **9** for monoanions **4** and **10** for dianions **2**. [b] Added at −80 °C. [c] Degree of deuteration >97%. [d] Added at room temperature. [e] 92–93% of deuterium incorporation. [f] Added at 65 °C.

Scheme 4





28a



28b

to a THF solution of **2e** after being heated at reflux for 2 h, compound **26** (entry 25) was obtained,[16] revealing that these dilithiated derivatives **2** are stable at rt but at higher temperatures they decompose by abstraction of a proton likely from the solvent.[17] Further reaction of intermediates **2a** and **2b** with other electrophiles such as dimethyl disulfide, carbonyl compounds, or *N*-benzylideneaniline produced the expected functionalized products **18–22** and **15** (entries 15 and 17–21).

When the β-elimination reaction of hydrogen bromide in the lithium 2-bromoallylamide structure is inhibited, the corresponding β-nitrogen-functionalized organolithium compounds can be prepared directly from the corresponding 2-bromoallylamine compounds by successive treatment with BuLi and *t*-BuLi at −80 °C in ether as solvent (Scheme 5). Thus, allylamine **29**, without hydrogen atoms in the position three, afforded organolithium **30** which on reaction with D_2O provided deuterated amine **31** (73% of deuterium incorporation). In a similar way, allylamine **32**, with the double bond inside a five-membered ring, furnished dilithiated compound **33** and by subsequent reaction with D_2O, deuterated amine **34** (degree of deuteration >97%).

(16) Under these same conditions other organolithium compounds **2** underwent a cyclodimerization reaction. These results will be reported separately.

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Scheme 5

29 X=Br, Y=H (42%)
30 X=Y=Li
31 X=D, Y=H (84%)

32 X=Br, Y=H (45%)
33 X=Y=Li
34 X=D, Y=H (74%)

In conclusion, two new types of vinylic carbanions, derived from secondary aliphatic allylamines, have been prepared. They react with electrophiles yielding different 2-substituted allylamines. The monoanionic derivatives are stable only at low temperatures (−80 °C), whereas the dianionic ones are stable at room temperature. While the monoanions are more accessible, the higher thermal stability of the dianions could justify their synthesis to be employed in reactions with more unreactive electrophiles which will need higher temperatures. The paper also describes a novel 1,3-silyl migration from N to C which could represent a useful route for intramolecular preparation of vinylsilanes from vinyl bromides.

Experimental Section

General. All reactions that involved organolithium compounds were conducted under an atmosphere of dry N_2 using oven-dried glassware and syringes. All solvents were freshly distilled from the appropriate drying agent before use;[18] THF and Et_2O were dried and distilled from sodium and benzophenone. Most of the reagents (BuLi, *t*-BuLi, primary amines, Et_3N, and electrophiles) were obtained from commercial sources and used without further purification. 1,2-Dibromo-3-methyl-2-butene was synthesized from 3-methyl-2-buten-1-ol by successive addition of Br_2, dehydrobromination,[19] and bromination of the allylic alcohol with CBr_4 and PPh_3.[12] 2,3-Dibromocyclopentene was prepared from 2-cyclopentenone by successive reaction with Br_2–Et_3N,[20] $NaBH_4$–$CeCl_3$,[21] and CBr_4–PPh_3.[12] *N*-Benzylideneaniline was prepared according to the literature.[22] Drying of all organic extracts was carried out with anhydrous Na_2SO_4. The term in vacuo refers to solvent removal in a rotatory evaporator.

TLC was performed on aluminum-backed plates coated with silica gel 60 with F_{254} indicator. Visualization was accomplished by iodine or/and UV light. Column chromatography was performed on silica gel 60, 230-400 mesh, or basic aluminum oxide, 70–290 mesh. GC analyses were carried out on a capillary column HP-ULTRA 2 (25 m × 0.2 mm i.d.; 0.33 μm film thickness). NMR spectra were recorded for $CDCl_3$ solutions, ^1H at 200 or 300 MHz and ^{13}C at 50.5 or 75.5 MHz, using tetramethylsilane (0.0 ppm, ^1H NMR) or chloroform-d_1 (77.0 ppm, ^{13}C NMR) as internal standard; δ values are given in ppm and the coupling constants and Δν values are recorded in hertz. Carbon multiplicities were obtained from DEPT experiments. Low-resolution electron impact mass spectra (EI-LRMS) were obtained at 70 eV and are reported as percent relative intensity to the base peak after the corresponding *m/z* value. Optical rotation data are reported as follows: $[\alpha]^{20}_D$ (concentration g/100 mL of solvent). Melting points were obtained using open capillary tubes and are uncorrected. The degree of deuteration was determined by NMR. The level of purity of compounds is indicated by the inclusion of copies of NMR spectra presented in the supplementary material.

(18) Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*, 3rd ed.; Pergamon Press: Oxford, 1988.
(19) Schlosser, M.; Hammer, E. *Helv. Chim. Acta* **1974**, *57*, 2547.
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(21) Ziegler, F. E.; Nangia, A. Schulte, G. *J. Am. Chem. Soc.* **1987**, *109*, 3987.
(22) (a) Layer, R. W. *Chem. Rev.* **1963**, *63*, 498. (b) Sandler, S. R.; Karo, W. *Organic Functional Group Preparations*; Academic Press: New York, 1971; Vol. 12–II, p 255.

The preparation of 2-bromoallylamines **6**, **29**, **32** (by a slightly different experimental procedure from those reported[10,12]), and silylated amines **9** and data for these compounds are provided as supplementary material.

General Procedure for the Preparation of Organolithium Compounds 4 and Reaction with Electrophiles. A solution of the corresponding *N*-silylamine **9** (5 mmol) in Et_2O (30 mL) was cooled to −80 °C and treated with *t*-BuLi (1.7M in pentane, 10 mmol) dropwise. The solution was stirred for 3 h at −80 °C and then treated with the corresponding electrophile (5 mmol). The mixture was slowly warmed to rt overnight and then hydrolyzed with 2 N H_2SO_4 for 10–15 min, neutralized with 2 N NaOH, and extracted with ether. When Bu_3SnCl was used as electrophile, the reaction mixture was hydrolyzed with water with some drops of 2 N H_2SO_4 solution for 1–2 d and then neutralized. The organic phase was dried and concentrated in vacuo and the resulting crude material purified by distillation (in this case, bp is given at the corresponding pressure) or flash column chromatography on silica gel (in this case, R_f is reported with the eluent solvent used in the column). Compound **16** was first purified by distillation and then by flash column chromatography. Yields are listed in Table 2. This method was used to prepare the following compounds.

***N*-Allyl-2-(Tributylstannyl)allylamine (10a)**: yellow oil, crude material; ^1H NMR δ 0.8–1.0 (m, 15H), 1.2–1.7 (m, 13H), 3.2 (d, *J* = 6.0, 2H), 3.4 (s, 2H), 5.0–5.2 (m, 3H), 5.8–6.0 (m, 2H); ^{13}C NMR δ 9.4, 13.5, 27.3, 29.0, 41.6, 58.2, 115.3, 124.2, 136.8, 154.5.

***N*-Butyl-2-(tributylstannyl)allylamine (10b)**: colorless oil, R_f 0.25 (hexane); ^1H NMR δ 0.9–1.05 (m, 18H), 1.3–1.7 (m, 17H), 2.6 (t, *J* = 7.0, 2H), 3.4 (apparent t, *J* = 1.5, 2H), 5.2 (dt, *J* = 2.6, 1.4, 1H), 5.85 (dt, *J* = 2.6, 1.7, 1H); ^{13}C NMR δ 9.4, 13.5, 13.9, 20.4, 27.3, 29.0, 32.2, 49.0, 58.9, 123.8, 154.7.

***N*-Hexyl-2-(tributylstannyl)allylamine (10c)**: colorless oil, R_f 0.34 (hexane:Et_2O, 10:1); ^1H NMR δ 0.8–0.95 (m, 18H), 1.2–1.65 (m, 21H), 2.55 (t, *J* = 6.8, 2H), 3.35 (m, 2H), 5.15, 5.8 (2m, 2H); ^{13}C NMR δ 9.5, 13.6, 13.9, 22.6, 27.0, 27.3, 29.1, 30.2, 31.8, 49.5, 59.2, 123.7, 155.2.

***N*-Cyclohexyl-2-(tributylstannyl)allylamine (10d)**: colorless oil, R_f 0.34 (hexane:AcOEt, 10:1); ^1H NMR δ 0.85–1.95 (m, 38H), 2.4 (m, 1H), 3.4 (m, 2H), 5.2 (dt, *J* = 2.6, 1.4, 1H), 5.8 (dt, *J* = 2.6, 1.7, 1H); ^{13}C NMR δ 9.6, 13.5, 24.9, 26.2, 27.3, 29.1, 33.6, 56.0, 56.2, 126.6, 155.4.

***N*-Benzyl-2-(tributylstannyl)allylamine (10e)**: yellow oil, crude material; ^1H NMR δ 0.8–1.0 (m, 15H), 1.15–1.7 (m, 13H), 3.4 (m, 2H), 3.75 (s, 2H), 5.2, 5.85 (2m, 2H), 7.2–7.4 (m, 5H); ^{13}C NMR δ 9.5, 13.6, 27.3, 29.2, 53.3, 58.6, 124.5, 126.6, 127.9, 128.1, 140.4, 154.6.

***N*-(2-Phenylethyl)-2-(tributylstannyl)allylamine (10f)**: colorless oil, R_f 0.3 (hexane:Et_2O, 20:1); ^1H NMR δ 0.8–1.0 (m, 15H), 1.2–1.7 (m, 13H), 2.8 (m, 4H), 3.35 (m, 2H), 5.15, 5.75 (2m, 2H), 7.1–7.35 (m, 5H); ^{13}C NMR δ 9.5, 13.6, 27.3, 29.2, 36.4, 50.5, 58.9, 123.9, 125.9, 128.2, 128.6, 140.1, 154.8.

***N*-Butyl-2-deuterioallylamine (7)**: clear oil; bulb-to-bulb distillation rt, 0.1 mmHg; ^1H NMR δ 0.9 (t, *J* = 7.0, 3H), 1.2–1.55 (m, 4H), 1.6 (br s, 1H), 2.6 (t, *J* = 7.0, 2H), 3.25 (s, 2H), 5.05, 5.15 (2m, 2H); ^{13}C NMR δ 13.6, 20.1, 31.9, 48.8, 52.1, 115.2, 136.3 (t, *J* = 23.5); MS *m/z* 114 (M^+, 0.7), 72 (5), 71 (100), 42 (20).

***N*-Butyl-2-(trimethylsilyl)allylamine (11)**: colorless oil; bulb-to-bulb distillation rt, 0.1 mmHg; ^1H NMR δ 0.1 (s, 9H), 0.9 (t, *J* = 7.0, 3H), 1.2 (br s, 1H), 1.25–1.6 (m, 4H), 2.6 (t, *J* = 7.0, 2H), 3.35 (t, *J* = 1.4, 2H), 5.4, 5.7 (2m, 2H); ^{13}C NMR δ −2.0, 13.5, 20.0, 31.8, 48.7, 54.8, 122.9, 150.2; MS *m/z* 185 (M^+, 3), 86 (92), 73 (100), 44 (61).

***N*-Butyl-*N*-methyl-2-(trimethylsilyl)allylamine (12)**: colorless oil, R_f 0.42 (hexane); ^1H NMR δ 0.05 (s, 9H), 0.8 (t, *J* = 7.0, 3H), 1.1–1.4 (m, 4H), 1.95 (s, 3H), 2.15 (t, *J* = 7.0, 2H), 2.9 (s, 2H), 5.25, 5.6 (2m, 2H); ^{13}C NMR δ −1.4, 14.0, 20.5, 29.6, 41.4, 57.8, 65.9, 125.4, 150.8; MS *m/z* 199 (M^+, 8), 100 (100), 73 (77), 58 (76).

***N*-Phenyl-2-[(butylamino)methyl]-2-propenamide (13)**: yellow oil, R_f 0.19 (AcOEt); ^1H NMR δ 0.8 (t, *J* = 7.0, 3H), 1.1–1.6 (m, 5H), 2.5 (t, *J* = 6.8, 2H), 3.4 (s, 2H), 5.35 (s, 1H), 6.15 (m, 1H), 6.95, 7.2, 7.5 (3m, 5H), 11.6 (s, 1H); ^{13}C NMR δ 13.5, 20.0, 31.5, 47.8, 52.2, 119.4, 123.2, 124.9, 128.4, 138.4, 139.2, 164.9; MS *m/z* 232 (M^+, 7), 140 (100), 96 (67), 69 (70); IR (film) ν 3307, 3121, 1673, 1629, 1598 cm^{-1}.

1-[1-[(Butylamino)methyl]ethenyl]cyclohexanol (14): colorless oil, bp 75–76 °C/0.001 mmHg; ^{1}H NMR δ 0.9 (t, J = 7.0, 3H), 1.1–1.8 (m, 14H), 2.55 (t, J = 6.8, 2H), 3.4 (s, 2H), 3.5–4.0 (br s, 2H), 4.95, 5.0 (2s, 2H); ^{13}C NMR δ 13.2, 19.7, 21.3, 25.3, 31.2, 37.5, 48.0, 53.2, 72.5, 110.9, 151.9; MS m/z 211 (M^+, 14), 150 (100), 86 (51), 41 (93).

3-[1-[(Butylamino)methyl]ethenyl]-2-cyclohexen-1-ol (15): colorless oil; bp 97–99 °C/0.001 mmHg; ^{1}H NMR δ 0.9 (t, J = 7.0, 3H), 1.2–2.05 (2m, 10H), 2.2 (br s, 2H), 2.6 (t, J = 7.0, 2H), 3.4 (s, 2H), 4.3 (m, 1H), 5.1, 5.15 (2s, 2H), 5.9 (m, 1H); ^{13}C NMR δ 13.8, 19.2, 20.3, 25.8, 31.6, 31.8, 49.1, 51.9, 65.8, 112.1, 126.8, 137.1, 145.3; MS m/z 209 (M^+, 14), 91 (28), 86 (100), 44 (35).

(5*R*)-1-[1-[(Butylamino)methyl]ethenyl]-2-methyl-5-(1-methylethenyl)-2-cyclohexen-1-ol (16): yellow oil, R_f 0.28 (AcOEt); bp 105–106 °C/0.001 mmHg; $[\alpha]_D$ −76° (c 0.57, CH_2Cl_2); ^{1}H NMR δ 0.85 (t, J = 7.1, 3H), 1.2–1.45 (m, 4H), 1.55, 1.6 (2s, 6H), 1.65–2.2 (m with d at 1.7, J = 12.7, 5H), 2.45–2.7 (2m, 2H), 3.35 (AB q, Δν = 109.2, J = 11.5, 2H), 4.6 (m, 2H), 4.85 (m, 1H), 4.95 (s, 1H), 5.5 (m, 1H);[23] ^{13}C NMR δ 13.7, 17.6, 20.1, 20.3, 30.8, 31.5, 38.0, 40.6, 48.1, 52.6, 78.2, 108.4, 116.1, 123.9, 137.0, 146.8, 148.9; MS m/z 263 (M^+, 1), 43 (37), 41 (100), 39 (54).

2-[(Benzylamino)methyl]-4-methyl-1-penten-3-ol (17): yellow solid, R_f 0.35 (hexane:AcOEt, 1:1); mp 78–80 °C; ^{1}H NMR δ 0.75 (d, J = 6.7, 3H), 1.0 (d, J = 6.7, 3H), 1.7 (m, 1H), 3.2–3.7 (br s, 2H), 3.35 (AB q, Δν = 36.3, J = 12.7, 2H), 3.65–3.85 (m, 3H), 5.0 (s, 2H), 7.3 (m, 5H); ^{13}C NMR δ 18.6, 19.1, 32.6, 52.0, 52.9, 82.4, 115.1, 127.0, 128.0, 128.2, 139.0, 146.2; MS m/z 186 (2), 91 (100), 43 (35), 41 (37).

General Procedure for the Preparation of Organolithium Compounds 2 and Reaction with Electrophiles. A solution of the corresponding stannylated amine **10** (4 mmol) in THF (30 mL) was cooled to −60 °C and treated with BuLi (2.5 M in hexane, 8 mmol) dropwise. The solution was stirred for 2 h at −60 °C and then 2 h at rt. After cooling again to −60 °C, the appropriate electrophile (4 mmol) was added. The mixture was slowly warmed to rt and stirred overnight and then hydrolyzed with 2 N H_2SO_4 and extracted with ether to remove Bu_4Sn. The aqueous layer was neutralized with 2 N NaOH and extracted with ether. The organic phase was dried and concentrated in vacuo and the resulting crude material purified by distillation (in this case, bp is given at the corresponding pressure) of flash column chromatography on silica gel (in this case, R_f is reported with the eluent solvent used in the column), unless otherwise indicated. In the thermal stability tests, the reaction mixture obtained after stirring for 2 h at rt was treated at this same temperature with the electrophile (excess of D_2O) or was refluxed for 2 h before adding D_2O, and then worked up as indicated. Yields are listed in Table 2. This method was used to prepare **7** and **15**, described above, and the following compounds.

***N*-Allyl-2-(methylthio)allylamine (18)**: yellow oil; bulb-to-bulb distillation rt, 0.1 mmHg; ^{1}H NMR δ 2.1 (br s, 1H), 2.25 (s, 3H), 3.25 (d, J = 6.0, 2H), 3.4 (s, 2H), 4.75 (s, 1H), 5.05–5.25 (m, 3H), 5.9–6.0 (m, 1H); ^{13}C NMR δ 14.2, 50.7, 54.0, 105.6, 116.1, 136.3, 145.4; MS m/z 143 (M^+, 2), 70 (100), 56 (70), 41 (44).

***N*-Butyl-2-(methylthio)allylamine (19)**: yellow oil, R_f 0.26 (basic aluminum oxide, hexane:ether, 1:1); ^{1}H NMR δ 0.9 (t, J = 7.0, 3H), 1.2–1.5 (m, 5H), 2.25 (s, 3H), 2.55 (t, J = 7.0, 2H), 3.4 (s, 2H), 4.7, 5.2 (2s, 2H); ^{13}C NMR δ 13.8, 14.1, 20.2, 31.9, 48.1, 54.9, 105.1, 145.8; MS m/z 159 (M^+, 4), 116 (82), 88 (91), 86 (100).

2-[(Butylamino)methyl]-4-methyl-1-penten-3-ol (20): yellow oil, R_f 0.2 (AcOEt); ^{1}H NMR δ 0.8 (d, J = 6.5, 3H), 0.9 (t, J = 7.0, 3H), 1.05 (d, J = 6.5, 3H), 1.2–1.6 (m, 4H), 1.6–1.85 (m, 1H), 2.45–2.75 (m, 2H), 3.1–3.8 (br s, 2H), 3.35 (AB q, Δν = 37.1, J = 12.5, 2H), 3.75 (d, J = 8.3, 1H), 5.0 (s, 2H); ^{13}C NMR δ 13.7, 18.6, 19.1, 20.1, 31.6, 32.7, 48.6, 52.8, 82.4, 114.6, 146.3; MS m/z 185 (M^+, <1), 142 (100), 124 (65), 86 (48).

2-[(Butylamino)methyl]-1-phenyl-2-propen-1-ol (21): yellow oil, bp 115–117 °C/0.001 mmHg; ^{1}H NMR δ 0.9 (t, J = 6.9, 3H), 1.15–1.55 (m, 4H), 2.4–2.7 (m, 2H), 3.15 (AB q, Δν = 17.0, J = 12.8, 2H), 3.2–4.2 (br s, 2H), 5.0, 5.1, 5.3 (3s, 3H), 7.15–7.45 (m, 5H); ^{13}C NMR δ 13.6, 20.0, 31.4, 48.4, 52.2, 77.9, 114.4, 125.6, 126.5, 127.6, 143.2, 147.2; MS m/z 219 (M^+, 6), 158 (32), 131 (26), 129 (100).

(23) OH and NH hydrogens were not observed in $CDCl_3$, but in C_6D_6 solution they were observed at 3.15–3.7 as br s.

3-Methylene-1,2-diphenyl-1,5-diazanonane (22): yellow oil, R_f 0.28 (hexane:AcOEt, 1:1); ^{1}H NMR δ 0.9 (t, J = 7.0, 3H), 1.25–1.55 (m, 6H), 2.55 (td, J = 7.0, 2.0, 2H), 3.15 (AB q, Δν = 12.5, J = 13.5, 2H), 5.0, 5.1, 5.2 (3s, 3H), 6.5–7.45 (m, 10H); ^{13}C NMR δ 13.8, 20.3, 32.0, 48.9, 52.5, 62.9, 112.9, 114.0, 116.7, 127.0, 127.1, 128.3, 128.8, 141.5, 146.9, 147.3; MS m/z 294 (M^+, 3), 221 (70), 220 (100), 200 (47).

***N*-Hexyl-2-deuterioallylamine (23)**: clear oil, R_f 0.38 (AcOEt); ^{1}H NMR δ 0.8 (t, J = 6.2, 3H), 1.2 (m, 6H), 1.3–1.5 (m, 2H), 2.5 (td, J = 7.3, 1.3, 2H), 2.55 (s, 1H), 3.15 (s, 2H), 5.0, 5.05 (2s, 2H); ^{13}C NMR δ 13.7, 22.3, 26.7, 29.4, 31.4, 48.9, 51.9, 115.6, 135.8 (t, J = 23.5); MS m/z 142 (M^+, 32), 127 (43), 100 (37), 72 (100).

***N*-Cyclohexyl-2-deuterioallylamine (24)**: clear oil, R_f 0.37 (AcOEt); ^{1}H NMR δ 0.9–1.4 (m, 5H), 1.55–1.95 (m, 6H), 2.35–2.55 (m, 1H), 3.25 (s, 2H), 5.05, 5.15 (2m, 2H); ^{13}C NMR δ 24.6, 25.7, 33.1, 49.0, 55.7, 115.0, 136.5 (t, J = 23.5); MS m/z 140 (M^+, 13), 98 (8), 97 (100), 84 (8).

***N*-Benzyl-2-deuterioallylamine (25)**: clear oil, bp 40–41 °C/0.1 mm Hg; ^{1}H NMR δ 1.65 (s, 1H), 3.25 (s, 2H), 3.8 (s, 2H), 5.1, 5.15 (2s, 2H), 7.3 (m, 5H); ^{13}C NMR δ 50.9, 52.5, 115.1, 126.2, 127.5, 127.7, 135.9 (t, J = 23.5), 139.6; MS m/z 148 (M^+, 10), 147 (29), 92 (14), 91 (100).

***N*-Benzylallylamine (26)**: clear oil; bp 40–41 °C/0.1 mmHg; ^{1}H NMR δ 1.6 (br s, 1H), 3.2 (dt, J = 6.0, 1.3, 2H), 3.7 (s, 2H), 5.05 (dq, J = 10.3, 1.3, 1H), 5.1 (dq, J = 17.2, 1.7, 1H), 5.85 (ddt, J = 17.2, 10.3, 6.0, 1H), 7.1–7.25 (m, 5H); ^{13}C NMR δ 51.6, 53.1, 115.9, 126.8, 128.0, 128.2, 136.6, 140.0; MS m/z 147 (M^+, 10), 91 (100), 41 (31), 39 (30).

***N*-(2-Phenylethyl)-2-deuterioallylamine (27)**: clear oil, R_f 0.25 (hexane:AcOEt, 1:1); ^{1}H NMR δ 1.35 (br s, 1H), 2.8 (m, 4H), 3.2 (s, 2H), 5.05, 5.1 (2m, 2H), 7.15–7.35 (m, 5H); ^{13}C NMR δ 36.0, 50.1, 51.8, 115.3, 125.7, 128.0, 128.3, 136.0 (t, J = 23.5), 139.6; MS m/z 162 (M^+, <1), 91 (16), 71 (100), 42 (26).

General Procedure for the Preparation of Organolithium Compounds 30 and 33 and Reaction with D_2O. A solution of the amine **29** or **32** (4 mmol) in Et_2O (30 mL) was cooled to −80 °C and treated with BuLi (2.5 M in hexane, 4 mmol) dropwise. The resulting solution was stirred for 30 min at −80 °C, and then t-BuLi (1.7 M in pentane, 8 mmol) was added dropwise and stirring was continued for 3 h at −80 °C. The resulting mixture was treated with an excess of D_2O and allowed to warm to rt for 1 h and then was diluted with H_2O and extracted with ether. The organic layer was dried and concentrated in vacuo and the residue was purified by flash column chromatography on silica gel in the case of compound **31** and by distillation in the case of **34**. Yields are reported in the text. This method was used to prepare the following two compounds.

***N*-Cyclohexyl-2-deuterio-3-methyl-2-butenylamine (31)**: clear oil, R_f 0.26 (AcOEt); ^{1}H NMR δ 0.95–1.3 (m, 5H), 1.5–1.9 (m with 2 s at 1.6 and 1.7, 12H), 2.4 (m, 1H), 3.15 (s, 2H); ^{13}C NMR δ 17.2, 24.5, 25.1, 25.7, 33.1, 43.7, 55.9, 123.0 (t, J = 22.0), 132.9; MS m/z 168 (M^+, 23), 125 (73), 70 (63), 56 (100).

***N*-Butyl-2-deuterio-2-cyclopentenylamine (34)**: clear oil; bp 37–38 °C/0.1 mmHg; ^{1}H NMR δ 0.85 (t, J = 7.2, 3H), 1.15–1.55 (m, 6H), 2.05–2.45 (m, 3H), 2.55 (t, J = 7.2, 2H), 3.75 (m, 1H), 5.8 (m, 1H); ^{13}C NMR δ 13.5, 20.1, 30.2, 30.6, 32.1, 46.9, 63.8, 131.9, 132.2 (t, J = 25.1); MS m/z 140 (M^+, 12), 97 (84), 83 (37), 68 (100).

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Supplementary Material Available: Experimental procedures, physical and spectral data for **6**, **29**, **32**, and **9** and copies of ^{1}H and ^{13}C NMR spectra of **6a**, **29**, **32**, **9**, **7**, **10–27**, **31**, and **34** (38 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.