Thermal Cyclodimerization of Aliphatic Secondary *C,N*-Dilithioallylamine Derivatives

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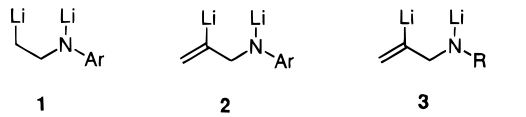
β-Nitrogen-functionalized vinylic organolithium compounds derived from secondary aliphatic allylamines have been found to undergo upon heating (reflux of THF) either a dimerization or a regio- and stereoselective cyclodimerization reaction affording diamino 1,4-dienes or *cis*-2,3-disubstituted 4-methylenepyrrolidines, respectively, according to reaction time. In contrast, the corresponding dianions derived from aromatic allylamines underwent protonation by the solvent under analogous thermal treatment. A mechanism accounting for all these results has been proposed, which involves a spontaneous β-elimination of lithium hydride and an intramolecular nucleophilic cyclization by addition of a lithium amide to an alkene group as critical steps. In addition, experimental evidence is provided about the formation of 3-lithio-1-aza 1,3-dienes as intermediates in these unusual thermal transformations.

Recently, we described the preparation and reactivity of β-nitrogen-functionalized vinylic organolithium compounds derived from aliphatic secondary allylamines[1] and allylamine itself.[2] In the course of this study, we observed that some of these dilithio derivatives underwent a cyclodimerization reaction on heating at reflux of tetrahydrofuran. The results of this unexpected behavior are reported in the present paper.

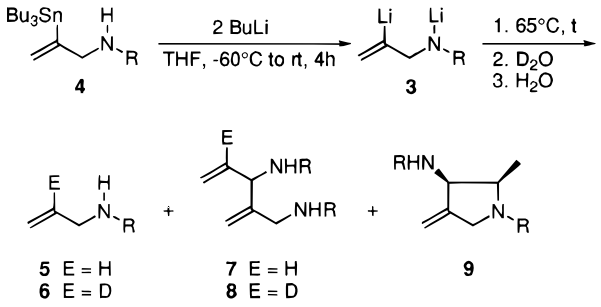
It is known that the stability of functionalized organolithium compounds is highly dependent on the nature of the functional group and the hybridization of the carbon atom attached to the metal and very sensitive to the relative position of both functionalities.[3] In the case of β-nitrogen-functionalized organolithium compounds, the sp^3 dianionic derivatives **1**[4] (Scheme 1) are very unstable species which have to be kept at low temperatures (−78 °C) owing to their tendency to undergo at higher temperatures either a β-elimination of $ArNLi_2$ or proton abstraction from the solvent. On the other hand, the sp^2 dianionic compounds **2**[5] and **3**[1] are generally stable at room temperature, although they show different reactivity when they are heated at reflux of THF. As we describe herein, the aromatic derivatives **2** decompose by abstraction of a proton from the solvent whereas the aliphatic intermediates **3** undergo a β-elimination of lithium hydride which represents a very unusual process in the chemistry of organolithium compounds containing β-hydrogens.[6]

Scheme 1



1 [Ar=Ph, PhCO] **2** [Ar=aromatic group] **3** [R=aliphatic group]

Scheme 2



4 **3**

5 E = H
6 E = D

7 E = H
8 E = D

9

a R = Bu
b R = $CH_3(CH_2)_5$
c R = $(CH_2)_5CH$
d R = $(EtO)_2CH(CH_2)_3$
e R = $PhCH_2$
f R = $PhCH_2CH_2$

Results and Discussion

In order to examine the thermal stability of organolithium compounds **3**, which were prepared from the appropriate 2-(tributylstannyl)allylamine **4** as previously described,[1] a THF solution of the corresponding dianionic derivative **3** was heated at reflux for 2−4 h and then successively treated with D_2O and H_2O. After workup, we unexpectedly noted the formation either of the dimerization products **7** or the cyclodimerization compounds **9** in addition to different amounts of the initially expected protonation derivatives **5** (Scheme 2). The ratio of these compounds depends on the nature of the dianion **3** (R group) and on the reflux time. Under these conditions (THF, 65 °C), incorporation of deuterium was not observed in any reaction product, indicating that organolithium intermediates are not stable at 65 °C and react with the ethereal solvent via proton abstraction. The detailed results from this investigation are provided in Table 1.

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Table 1. Thermal Stability of Organolithiums 3. Results from the Heating of 3 at Reflux of THF

entry	dianion	R	*T* (°C)	*t*[a] (h)	products	yield[b] (%)
1	**3**a	Bu	65	2	**7**a	18
2	**3**a	Bu	65	3	**7**a	30[c]
3	**3**a	Bu	65	4	**9**a	15
4	**3**b	$CH_3(CH_2)_5$	65	3	**9**b	17
5	**3**c	$(CH_2)_5CH$	20	2[d]	**6c**[e]	37
					8c[e]	37
6	**3**c	$(CH_2)_5CH$	65	3	**9**c	15
					5c	12
7	**3**d	$(EtO)_2CH(CH_2)_3$	65	2	**9**d	20
					5d	15
8	**3**e	$PhCH_2$	65	2	**5**e	73
9	**3**f	$PhCH_2CH_2$	65	2	**7**f	50
					5f	38
10	**3**f	$PhCH_2CH_2$	65	4	**9**f	10
					7f	16
					5f	14

[a] Reaction time at reflux. [b] Isolated yields based on the corresponding 2-(tributylstannyl)allylamine **4**. [c] A mixture of ether: THF 1.5:1 was used as solvent. [d] Reaction time; the organolithium **3c** was kept at room temperature before adding D_2O. [e] Degree of deuteration was 97% for **6c** and 95% for **8c**.

In the case of organolithium **3a**, the 1,4-diene **7a** was isolated as the only reaction product after 2 h at reflux of THF or 3 h at reflux of a 1.5:1 mixture of Et_2O:THF (Table 1, entries 1 and 2, respectively). In contrast, after 4 h at reflux pyrrolidine **9a** was obtained as a single diastereoisomer (Table 1, entry 3). This same result was observed with dianions **3b** and **3c** which led to the corresponding 3-methylenepyrrolidines **9b** and **9c** after heating for 3 h (Table 1, entries 4 and 6, respectively), although in the last case allylamine **5c** was also isolated. An analogous behavior was observed with intermediate **3d** which afforded a mixture of **9d** and **5d** (Table 1, entry 7). However, thermal treatment of organolithium **3e** derived from *N*-benzylallylamine gave rise exclusively to the corresponding allylamine **5e** (Table 1, entry 8). Additionally, dianion **3f** afforded amino diene **7f** after heating for 2 h and a mixture of this diene **7f** and *cis*-2,3-disubstituted pyrrolidine **9f** when the reaction mixture was heated for 4 h. In both experiments different amounts of allylamine **5f** were present (Table 1, entries 9 and 10). In general, short reaction times seem to favor the formation of dimeric compounds **7**, while longer times led to cyclodimeric products **9** (Table 1, entries 1 and 9 vs 3 and 10, respectively), which appears to mean that dienic derivatives are intermediates in the transformation of dianions **3** to pyrrolidines **9**. As indicated above, in the reactions with organolithiums **3a** and **3b** the corresponding allylamines **5a** and **5b** have not been isolated, which could be a consequence of the volatility and high polarity of these compounds; indeed, these allylamines were detected in the ^{13}C NMR spectra of the crude products. It is worthy of note that organolithium **3c** derived from *N*-cyclohexylallylamine is even partially unstable at room temperature. Thus, treatment of **3c** with D_2O at rt provided deuterated allylamine **6c** accompanied by an equimolecular amount of the monodeuterated dimeric compound **8c** (Table 1, entry 5), which means that at rt the organolithium intermediates do not undergo proton abstraction from the medium. Despite the fact that no other products were detected in the initial product mixtures, the isolated yields of the dimeric compounds **7** and **9** are low to modest. These poor recoveries could be in part originated by the polar nature of these products or by the formation of polymeric materials, given that a large amount of mass is lost during the silica gel flash column chromatography purification. The structure and stereochemistry of pyrrolidines **9** were established for compound **9a** on the basis of ^1H and ^{13}C NMR spectra, including 2D ^1H to ^{13}C correlation through $^1J_{CH}$ and NOE difference experiments (Figure 1). The enhancements observed between the methine ring protons indicate a *cis* orientation between both atoms. In all other products this stereochemistry has been assumed by analogy.

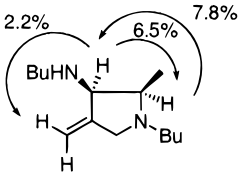
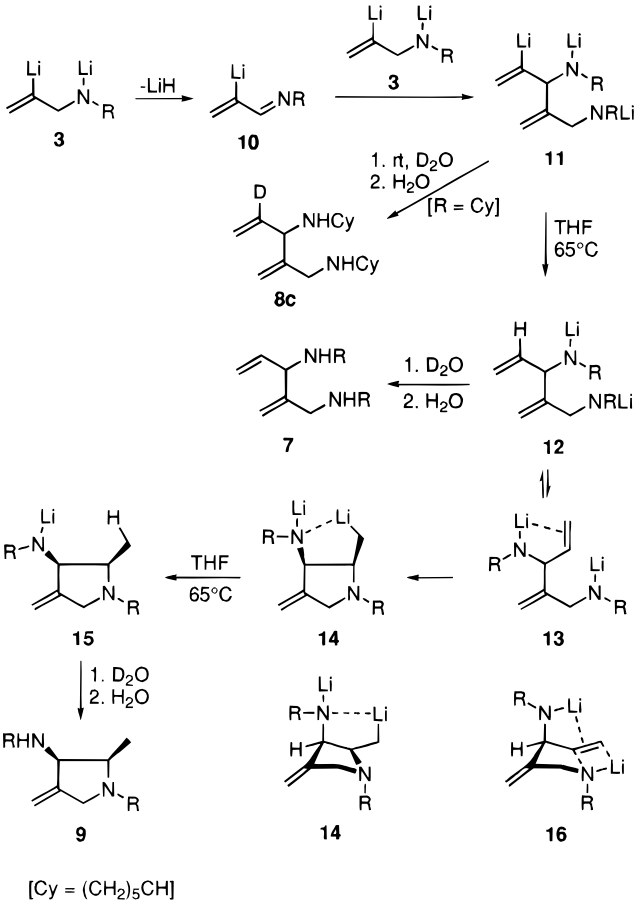


Figure 1. Observed NOEs for pyrrolidine **9a** measured at 300.13 MHz in $CDCl_3$.

Scheme 3



A mechanism which is consistent with the results presented here is proposed in Scheme 3. In light of the connectivity of dienes **7** and **8**, it would appear that on warming organolithium compounds **3** undergo an initial β-elimination of LiH,[7] affording 3-lithio-1-aza dienes **10** which subsequently are trapped by another molecule of

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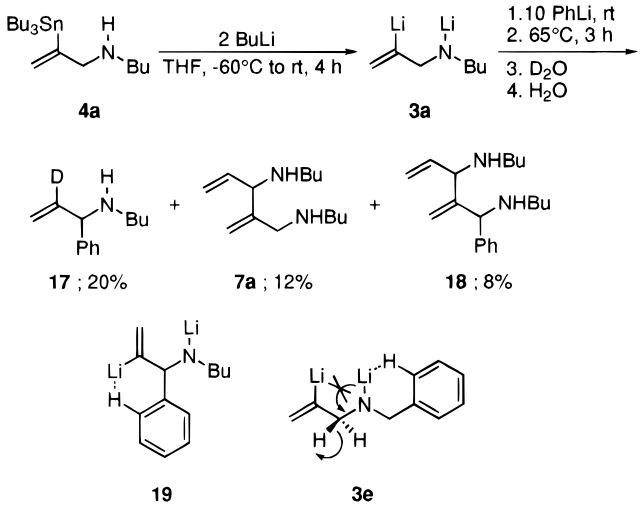
dianion **3** to give intermediate **11.**[8,9] At reflux of THF these trianions **11** are unstable and suffer protonation by the solvent to give bis(lithium amides) **12**, which after hydrolysis yield amino dienes **7.** But, at rt trianions **11** are stable which explains the isolation of deuterated diene **8c** in the case of organolithium **3c**. On longer reaction times unsaturated lithium amides **12** undergo, most likely through conformation **13**, a regio- and diastereoselective cyclization affording primary organolithiums **14**, which analogously decompose by proton abstraction from the solvent and upon hydrolysis lead to *cis*-2,3-disubstituted 4-methylenepyrrolidines **9**.[10] The selective formation of the *cis* diastereoisomer in the present intramolecular anionic addition of N−Li bond to an alkene group[11] can be explained in terms of a cyclic four-center transition state **16** similar to the one reported by Bailey et al. for the intramolecular addition of a C−Li bond to an unactivated alkene that resembles a chair cyclohexane in which substituents preferentially occupy pseudoequatorial positions.[12] In our case the lithium (bonded to the other amide group present in the structure)−alkene π-stabilizing interaction presumably serves to establish the pseudoaxial orientation of the lithium amide substituent which leads to the *cis* isomer; furthermore, this orientation enhances the stability of **14** by intramolecular heteroatom coordination.

The unusual thermal β-elimination of LiH observed in 1,3-dilithio derivatives **3** could be favored by the 1,3 relationship of both lithium atoms which simultaneously stabilize the transition state of this reaction by $\sigma-\pi$ conjugation as concluded in previous studies.[13] In an effort to provide additional evidence for this lithium hydride elimination, we attempted to trap the lithiated azadiene **10** with an external nucleophile which would be added to the reaction mixture after the generation of organolithium compound **3**. Accordingly, a THF solution of dianion **3a** at rt was treated with an excess (10 equiv) of an Et_2O solution of phenyllithium before the reaction mixture was warmed to reflux temperature (Scheme 4). In this reaction, the expected phenyl-substituted allylamine **17** was obtained as the major product accompanied by the formation of dienes **7a** and **18**. The isolation of **17**, which surprisingly incorporates a deuterium atom (97%) in its structure, proves the formation of 3-lithio-1-aza dienes **10** as intermediates in these thermal dimerization reactions. The unexpected stability of organolithium **19** under these reaction conditions (reflux of a mixture THF:Et_2O 1.5:1 as solvent; see on a comparative basis Table 1, entry 2) can be apparently due to an stabilizing agostic interaction between the vinylic lithium atom and the *ortho* hydrogen−carbon bond of the adequately positioned phenyl group.[14] The dianion **19** was even able to react with aza diene intermediate **10a** (R = Bu) to give **18**. An analogous Li−H agostic interaction between the nitrogen-bound lithium and the aromatic *ortho* hydrogen atoms, as depicted in Scheme 4 for **3e**, could account for the above-mentioned lack of LiH elimination observed with this dianion.

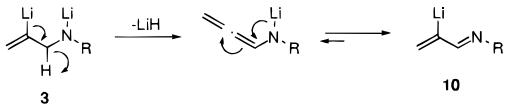
Scheme 4



The nature of the R group has great influence on the thermal behavior of vinylic β-nitrogen-functionalized organolithium compounds **3**. Thus, dianion **2a**, which was directly prepared from the corresponding aromatic 2-bromoallylamine **20** by successive treatment with BuLi and *t*-BuLi, was also unstable at 65 °C, but it decomposed by abstraction of a proton from the solvent to afford **21** without undergoing LiH elimination, probably due to the enhanced stability of the aromatic lithium amide (Scheme 5).

In conclusion, we have observed that when vinylic organolithium compounds derived from secondary aliphatic allylamines are heated at reflux of THF, they

(8) An alternative path for the β-elimination of LiH, which can not be ruled out, would involve the vinylic lithium atom and lead to an allenic intermediate which subsequently would undergo isomerization to **10**:



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(11) For intramolecular additions of NLi to olefins see: (a) Evans, B. E.; Anderson, P. S.; Christy, M. E.; Colton, C. D.; Remy, D. C.; Rittle, K. E.; Engelhardt, E. L. *J. Org. Chem* **1979**, *44*, 3127. (b) Tokuda, M.; Yamada, Y.; Takagi, T.; Suginome, H. *Tetrahedron* **1987**, *43*, 281. (c) Tokuda, M.; Miyamoto, T.; Fujita, H.; Suginome, H. *Tetrahedron* **1991**, *47*, 747. (d) Fujita, H.; Tokuda, M.; Nitta, M.; Suginome, H. *Tetrahedron Lett.* **1992**, *33*, 6359. (e) Luo, F.-T.; Wang, R.-T. *Tetrahedron Lett.* **1992**, *33*, 6835.

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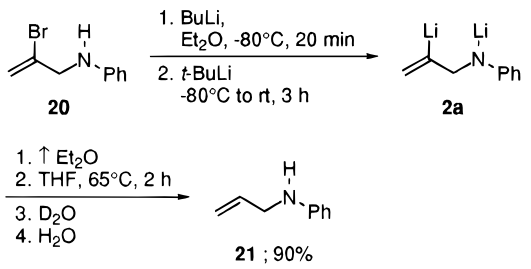
Scheme 5



mainly decomposed by initial LiH elimination which finally resulted in the formation, although with low yields, of dimeric or cyclodimeric products depending on the reaction time. In contrast, the similar 1,3-dilithio derivatives prepared from aromatic allylamines decomposed by proton abstraction from the solvent upon warming to 65 °C.

Experimental Section

General Procedures. General experimental techniques and analytical measurements were applied as previously described.[1] 2-(Tributylstannyl)allylamines **4** were synthesized as previously reported.[1] *N*-(2-Bromoallyl)aniline **20**[15] and PhLi[16] were prepared according to literature procedures. The level of purity of compounds is indicated by the inclusion of copies of NMR spectra presented in the supporting information.

General Procedure for the Thermal Treatment of Organolithiums 3. To a solution of the corresponding 2-(tributylstannyl)allylamine **4** (5 mmol) in THF (30 mL) cooled at −60 °C was added BuLi (2.5 M in hexane, 10 mmol) dropwise. The resulting solution was stirred for 2 h at −60 °C and 2 h at rt and then was refluxed for 2−4 h (the reaction time for each case is indicated in Table 1). The reaction mixture was quenched with D_2O (3 mL) and, after being stirred for 10−15 min, was treated 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 was purified either by flash column chromatography on silica gel (in this case, R_f is reported with the eluent solvent used in the column in each case) or by distillation (in this case, bp is given at the corresponding pressure). Yields are listed in Table 1. Compounds **5e** and **6c** have been previously described.[1] Compounds **5c**,**d**,**f** are known as their 2-deuterioallyl derivatives and were compared with those samples.[1,17] The analytical data of products **7**−**9** are as follows.

6-Ethenyl-7-methylene-5,9-diazatridecane (7a): yellow oil; R_f 0.20 (AcOEt:THF, 2:1); ^{1}H NMR δ 0.90, 0.91 (2t, J = 7.3 Hz, 6H), 1.25−1.50 (m, 10H), 2.55 (m, 4H), 3.22 (AB q, $\Delta\upsilon$ = 17.0, J = 14.8 Hz, 2H), 3.64 (d, J = 7.3 Hz, 1H), 5.05−5.20 (m, 4H), 5.75 (m, 1H); ^{13}C NMR δ 13.9, 20.3, 31.8, 32.1, 47.0, 48.9, 51.9, 65.8, 111.9, 115.5, 139.5, 147.4; MS m/z 223 (M^+ − 1, <1), 109 (24), 108 (100), 79 (29), 41 (24).

4-Ethenyl-5-methylene-1,9-diphenyl-3,7-diazanonane (7f): yellow oil; R_f 0.43 (AcOEt:THF, 5:1); ^{1}H NMR δ 1.12−1.61 (broad signal, 2H), 2.71 (m, 8H), 3.09 (AB q, $\Delta\upsilon$ = 13.85, J = 14.4 Hz, 2H), 3.52 (d, J = 7.3 Hz, 1H), 4.90−5.10 (m, 4H), 5.61 (m, 1H), 7.00−7.20 (m, 10H); ^{13}C NMR δ 36.2, 48.4, 50.4, 51.6, 65.3, 111.6, 115.6, 125.9, 128.3, 128.6, 139.4, 139.9, 147.5.

1,5-Dicyclohexyl-2-(1-deuterioethenyl)-3-methylene-1,5-diazapentane (8c): colorless oil; R_f 0.36 (THF); ^{1}H NMR δ 1.00−1.90 (m, 22H), 2.35 (m, 2H), 3.18 (AB q, $\Delta\upsilon$ = 20.8, J = 14.6 Hz, 2H), 3.75 (s, 1H), 5.00 (m, 4H); ^{13}C NMR δ 24.8, 24.9, 26.0, 33.3, 33.4, 33.5, 33.6, 48.9, 53.0, 55.9, 61.6, 111.1, 114.6, 139.8 (t, J = 23.5 Hz), 148.8; MS m/z 277 (M^+, <1), 135 (76), 96 (85), 95 (67).

(2*R,3*R**)-1-Butyl-3-(butylamino)-2-methyl-4-methylenepyrrolidine (9a):** yellow oil; R_f 0.11 (AcOEt); ^{1}H NMR δ 0.82, 0.83 (2t, J = 7 Hz, 6H), 0.86 (d, J = 6.4 Hz, 3H), 1.25−1.50 (m, 9H), 2.15 (m, 1H), 2.45 (m, 1H), 2.60 (m, 2H), 2.84 (m, 1H), 3.08 (d, J = 14 Hz, 1H), 3.36 (d, J = 14 Hz, 1H), 3.40 (d, J = 5.6 Hz, 1H), 4.92 (m, 2H); ^{13}C NMR δ 9.5, 13.9, 20.4, 20.6, 30.2, 32.3, 47.0, 52.5, 55.8, 60.8, 63.8, 105.8, 149.1; MS m/z 224 (M^+, 3), 125 (85), 100 (100), 82 (77).

(2*R,3*R**)-1-Hexyl-3-(hexylamino)-2-methyl-4-methylenepyrrolidine (9b):** yellow oil; R_f 0.5 (hexane:AcOEt, 1:1); ^{1}H NMR δ 0.88 (m, 6H), 0.93 (d, J = 6.4 Hz, 3H), 1.20−1.55 (m, 17H), 2.23 (m, 1H), 2.48−2.72 (m, 3H), 2.91 (m, 1H), 3.13 (dt, J = 14.2, 2.1 Hz, 1H), 3.40 (d, J = 14 Hz, 1H), 3.47 (d, J = 5.2 Hz, 1H), 4.98 (m, 2H); ^{13}C NMR δ 9.4, 13.9, 22.5, 26.9, 27.2, 28.0, 30.1, 31.7, 47.4, 52.8, 55.8, 60.8, 63.8, 105.7, 149.1; MS m/z 280 (M^+, 3), 128 (100), 82 (78), 43 (60).

(2*R,3*R**)-1-Cyclohexyl-3-(cyclohexylamino)-2-methyl-4-methylenepyrrolidine (9c):** yellow oil; R_f 0.2 (AcOEt); ^{1}H NMR δ 0.68 (d, 3H), 1.00−2.00 (m, 20H), 2.20−2.70 (broad signal with 2m at 2.30 and 2.43, 3H), 3.02 (m, 1H), 3.45 (m, 1H), 3.64 (m, 1H), 3.80 (m, 1H), 4.88, 4.95 (2m, 2H); ^{13}C NMR δ 6.3, 24.7, 24.9, 25.9, 26.0, 30.0, 31.3, 33.0, 34.3, 51.6, 54.5, 55.3, 57.8, 60.5, 104.6, 149.7; MS m/z 276 (M^+, <1), 126 (35), 55 (81), 41 (100).

(2*R,3*R**)-1-(4,4-Diethoxybutyl)-3-[(4,4-diethoxybutyl)amino]-2-methyl-4-methylenepyrrolidine (9d):** yellow oil; R_f 0.31 (AcOEt:THF, 10:1); ^{1}H NMR δ 0.89 (d, 3H), 1.13 (t, J = 7 Hz, 12H), 1.45−1.65 (m, 9H), 2.21 (m, 1H), 2.49 (m, 1H), 2.63 (m, 2H), 2.84 (m, 1H), 3.05 (d, J = 14.5 Hz, 1H), 3.42, 3.57 (2m, 10H), 4.43 (t, J = 5.1 Hz, 2H), 4.90 (m, 2H); ^{13}C NMR δ 9.7, 15.2, 23.2, 25.3, 31.3, 31.4, 46.8, 52.4, 55.7, 60.9, 61.0, 63.7, 102.6, 102.7, 106.0, 148.6; MS m/z 400 (M^+, 1), 98 (64), 71 (62), 47 (76).

(2*R,3*R**)-1-(2-Phenylethyl)-3-[(2-phenylethyl)amino]-2-methyl-4-methylenepyrrolidine (9f):** yellow oil; R_f 0.33 (hexane:AcOEt, 1:1); ^{1}H NMR δ 0.85 (d, 3H), 1.30−1.70 (broad signal, 1H), 2.50 (m, 1H), 2.75−2.95 (m, 8H), 3.11 (d, J = 14.6 Hz, 1H), 3.39 (m, 2H), 4.89 (s, 2H), 7.25 (m, 5H); ^{13}C NMR δ 9.6, 34.7, 36.5, 48.8, 54.7, 55.8, 60.9, 63.8, 106.3, 125.9, 126.0, 128.2, 128.5, 128.6, 140.1, 140.4, 148.6; MS m/z 320 (M^+, <1), 173 (66), 148 (72), 82 (100).

Reaction of Organolithium 3a with PhLi. To a solution of *N*-butyl-2-(tributylstannyl)allylamine (**4a**, 2.0 g, 5 mmol) in THF (30 mL) cooled at −60 °C was added BuLi (2.5 M in hexane, 4 mL, 10 mmol) dropwise. The resulting solution was stirred for 2 h at −60 °C and then 2 h at rt. To this was added phenyllithium (1.25 M in ether, 40 mL, 50 mmol) at rt. The mixture was heated under reflux for 3 h and then treated with D_2O (3 mL). After being stirred for 10−15 min, the reaction mixture was treated 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 was purified by flash column chromatography on silica gel (R_f is reported with the eluent solvent used in the column). This reaction yielded **7a**, described above, and the following compounds. Yields are reported in Scheme 4.

***N*-Butyl-2-deuterio-1-phenylallylamine (17):** clear oil; R_f 0.59 (hexane:THF, 10:1); ^{1}H NMR δ 0.90 (t, J = 7.2 Hz, 3H), 1.30−1.70 (m, 5H), 2.45−2.65 (m, 2H), 4.18 (s, 1H), 5.10−5.20 (2s, 2H), 7.20−7.40 (m, 5H); ^{13}C NMR δ 13.7, 20.2, 32.0, 47.0, 66.0, 114.4, 126.7, 126.9, 128.1, 140.7 (t, J = 23.5 Hz), 142.8; MS m/z 190 (M^+, 2), 147 (16), 118 (100), 116 (21).

6-Ethenyl-8-phenyl-7-methylene-5,9-diazatridecane (18): yellow oil; R_f 0.29 (hexane:THF, 10:1); ^{1}H NMR δ 0.93 (m, 6H), 1.21−1.52 (m, 8H), 2.21−2.52 (m, 6H), 3.53 (d, J = 7.1 Hz, 1H), 4.30 (s, 1H), 5.05−5.25 (m, 4H), 5.72 (m, 1H), 7.20−7.51 (m, 5H); ^{13}C NMR δ 13.9, 20.3, 20.4, 31.9, 32.2, 46.8, 47.5, 63.6, 65.8, 112.5, 114.8, 126.8, 128.0, 128.2, 140.0, 142.3, 151.8; MS m/z 300 (M^+, <1), 227 (77), 226 (45), 184 (100), 170 (45).

Thermal Treatment of Organolithium 2a. To a solution of *N*-(2-bromoallyl)aniline (**20**, 1.06 g, 5 mmol) in ether (25 mL) was added BuLi (2.5 M in hexane, 2 mL, 5 mmol) at −80

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(17) For **5d** see the supporting information.

°C. After being stirred for 20 min at this temperature, the reaction mixture was treated with *t*-BuLi (1.7 M in pentane, 5.9 mL, 10 mmol) dropwise. The resulting solution was stirred for 1.5 h at −80 °C and then 1.5 h at rt. Solvents were removed under reduced pressure (0.1 mmHg), and the residue was dissolved in 25 mL of dry THF. This reaction mixture was refluxed for 2 h and then treated with D_2O (3 mL) with stirring for 10−15 min. The reaction was hydrolyzed with H_2O and extracted with ether. The organic phase was dried and concentrated in vacuo, and the resulting crude material was purified by distillation (0.1 mmHg) to give 0.59 g (90%) of *N*-allylaniline (**21**).[18]

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Supporting Information Available: Analytical data of the 2-deuterioallyl derivative of **5d**. Copies of ^1H and ^{13}C NMR spectra of **7a**,**f**, **8c**, **9a**−**d**,**f**, **17**, and **18** (11 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.

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