# Generation of 1-Azapentadienyl Anion from *N*-(*tert*-Butyldimethylsilyl)-3-buten-1-amine

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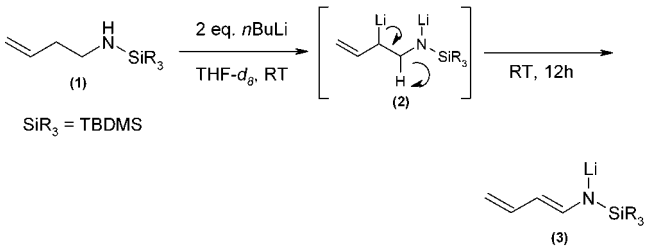
**Abstract:** *N*-(*tert*-Butyldimethylsilyl)-3-buten-1-amine undergoes allylic deprotonation at the 2-position when exposed to 2 equiv of *n*BuLi in THF. This allylic anion undergoes lithium hydride elimination to generate a 1-azapentadienyl anion. The anion is generated cleanly and completely.

Much work has been done on pentadienyl anions.[1] They have been shown to be useful reagents in the preparation of interesting acyclic complexes.[2] Pentadienyl anions are also valuable precursors for pentadienylsilanes and stannanes, through which aldehydes or ketones can be converted to dienyl alcohols.[3] Silylated and tin pentadienyl complexes are useful intermediates in synthetic organic synthesis, either as reagents for selective transformations or as intermediates for the creation of carbon−carbon bonds. The high selectivity of the tin−carbon bond cleavage in transmetalations, transition-metal catalyzed couplings, and direct reactions is well established.[4] As an extension of the wealth of pentadienyl anion chemistry that abounds, azapentadienyl anions have attracted attention in both organic and inorganic chemistry. Azapentadienyl derivatives from silicon,[5] germanium and tin,[2c,6] and related compounds[7] have been made and studied to investigate the related chemistry of these species, and to explore their use in transmetalation reactions. Würthwein and co-workers have carried out extensive studies on the experimental and theoretical chemistry of lithium azapentadienyl species,[8] and Pearson et. al. have, among other things, synthesized pyrrolidines, 1-pyrrolines, and pyrroles by the [4$\pi$s + 2$\pi$s] cycloaddition of nonstabilized 2-azaallyl anions with alkenes.[9]

1-Azapentadienyl anions, upon which this report focuses, are useful ambident nucleophiles in organic synthesis.[5a,7a,10] Würthwein has generated 1-azapentadienylanions from *N*-(*tert*-butyl)crotanaldimine, using LDA in THF at −15 °C.[8c] These anions are synthetically useful and add to $\alpha,\beta$-unsaturated carbonyls in a Michael fashion to generate, after hydrolysis, the corresponding aldehydes and ketones.

In this work, we have discovered that *N*-(*tert*-butyldimethylsilyl)-3-buten-1-amine (**1**) unexpectedly generates the 1-azapentadienyl anion (**3**) when exposed to 2 equiv of *n*BuLi in THF, as depicted in Scheme 1. The anion is generated cleanly and completely.

**Scheme 1**




(1) (a) Yasuda, H.; Nakamura, A. *J. Organomet. Chem.* **1985**, *285*, 15 and references therein. (b) Powell, P. *Adv. Organomet. Chem.* **1986**, *26*, 125 and references therein. (c) Wilson, D. R.; Stahl, L.; Ernst, R. D. *Organometallic Synthesis*; King, R. B., Eisch, J. J., Eds.; Elsevier Science: Amsterdam, 1986, *3*, 136.

(2) For examples of open metallocenes, see: (a) Ernst, R. D. *Chem. Rev.* **1988**, *88*, 1255. (b) Ernst, R. D.; Freeman, J. W.; Swepston, P. N.; Wilson, D. R. *J. Organomet. Chem.* **1991**, *402*, 17. (c) Newbound, T. D.; Rheingold, A. L.; Ernst, R. D. *Organometallics* **1992**, *11*, 1693. (d) Kralik, M. S.; Stahl, L.; Arif, A. M.; Strouse, C. E.; Ernst, R. D. *Organometallics* **1992**, *11*, 3617. (e) Waldman, T. E.; Stahl, L.; Wilson, D. R.; Arif, A. M.; Hutchinson, J. P.; Ernst, R. D. *Organometallics* **1993**, *12*, 1543. (f) Waldman, T. E.; Waltermire, B.; Rheingold, A. L.; Ernst, R. D. *Organometallics* **1993**, *12*, 4161. (g) Weng, W.; Arif, A. M.; Ernst, R. D. *Organometallics* **1993**, *12*, 1537. (h) Trakarnpruk, W.; Arif, A. M.; Ernst, R. D. *J. Organomet. Chem.* **1995**, *485*, 25. For examples of half-open-metallocenes, see: (i) Kralik, M. S.; Stahl, L.; Arif, A. M.; Strouse, C. E.; Ernst, R. D. *Organometallics* **1992**, *11*, 3617. (j) Trakarnpruk, W.; Arif, A. M.; Ernst, R. D. *Organometallics* **1992**, *11*, 1686. (k) Gedridge, R. W.; Hutchinson, J. P.; Rheingold, A. L.; Ernst, R. D. *Organometallics* **1993**, *12*, 1553. (l) Hyla-Kryspin, I.; Waldman, T. E.; Melendez, E.; Trakarnpruk, W.; Arif, A. M.; Ziegler, M. L.; Ernst, R. D.; Gleiter, R. *Organometallics* **1995**, *14*, 5030. For other half-sandwich transition metal complexes, see: (m) Bleeke, J. R.; Hays, M. K.; Wittenbrink, R. J. *Organometallics* **1988**, *7*, 1417 and references therein. (n) Bleeke, J. R.; Wittenbrink, R. J. *J. Organomet. Chem.* **1991**, *405*, 121. (o) Schumann, H.; Dietrich, A. *J. Organomet. Chem.* **1991**, *401*, C33. (p) Newbound, T. D.; Arif, A. M.; Wilson, D. R.; Rheingold, A. L.; Ernst, R. D. *J. Organomet. Chem.* **1992**, *435*, 73. (q) Kunze, K.; Arif, A. M.; Ernst, R. D. *Bull. Soc. Chim. Fr.* **1993**, *130*, 708. (r) Bleeke, J. R.; Luaders, S. T.; Robinson, K. D. *Organometallics* **1994**, *13*, 1592. (s) Arif, A. M.; Ernst, R. D.; Melendez, E.; Rheingold, A. L.; Waldman, T. E. *Organometallics* **1995**, *14*, 1761. (t) Bleeke, J. R.; Luaders, S. T. *Organometallics* **1995**, *14*, 1667. (u) Gutierrez, J. A.; Navarro Clemente, Ma. E.; Paz-Sandoval, M. A.; Arif, A. M.; Ernst, R. D. *Organometallics* **1999**, *18*, 1068.

(3) (a) Seyferth, D.; Pornet, J. *J. Org. Chem.* **1980**, *45*, 1721. (b) Hosomi, A.; Saito, M.; Sakurai, H. *Tetrahedron Lett.* **1980**, *26*, 3783.

(4) Pereyre, M.; Quintard, J.-P.; Rahm, A. *Tin in Organic Synthesis*; Butterworth: London, 1987.

(5) (a) Takabe, K.; Fukiwara, H.; Katagiri, T.; Tanaka, J. *Tetrahedron Lett.* **1975**, *16*, 1273. (b) Bellassoued, M.; Salemkour, M. *Tetrahedron Lett.* **1993**, *34*, 5281. (c) Bellassoued, M.; Majidi, A. *J. Organomet. Chem.* **1993**, *444*, C7. (d) Bellassoued, M.; Salemkour, M. *Tetrahedron* **1996**, *52*, 4607.

(6) (a) Pearson, W. H.; Barta, N. S.; Kampf, J. W. *Tetrahedron Lett.* **1997**, *38*, 3369. (b) Gutierrez, J. A.; Paz-Sandoval, M. A.; Robles, J. *J. Organomet. Chem.* **2000**, *599*, 147.

(7) (a) Ahlbrecht, H.; Liesching, D. *Synthesis* **1976**, 746. (b) Ahlbrecht, H.; Düber, E.-O. *Synthesis* **1980**, 630. (c) Ahlbrecht, H.; Düber, E.-O. *Synthesis* **1982**, 273. (d) Barluenga, J.; Joglar, J.; Fustero, S.; Gotor, V. *J. Chem. Soc., Chem. Commun.* **1986**, 361. (e) Armstrong, D. R.; Clegg, W.; Dunbar, L.; Liddle, S. T.; MacGregor, M.; Mulvey, R. E.; Reed, D.; Quinn, S. A. *J. Chem. Soc., Dalton Trans.* **1998**, *20* 3431.

(8) (a) Würthwein, E.-U.; Wilhelm, E.; Seitz, B. *Tetrahedron Lett.* **1983**, *24*, 581. (b) Wolf, G.; Würthwein, E.-U. *Tetrahedron Lett.* **1988**, *29*, 3647 (c) Baumann, F.; Würthwein, E.-U. *Tetrahedron Lett.* **1991**, *32*, 4683. (d) Wolf, G.; Würthwein, E.-U. *Chem. Ber.* **1991**, *124*, 889. (e) Wegmann, S.; Würthwein, E.-U. *Tetrahedron Lett.* **1993**, *34*, 307. (f) Schulte, N.; Fröhlich, R.; Hecht, J.; Würthwein, E.-U. *Liebigs Annal. Chem.* **1996**, 371. (g) Stakemeier, H.; Würthwein, E.-U. *Liebigs Annal. Chem.* **1996**, 1833. (h) Könemann, M.; Erker, G.; Fröhlich, R.; Würthwein, E.-U. *J. Am. Chem. Soc.* **1997**, *119*, 11155 and references therein.

(9) (a) Pearson, W. H.; Szura, D. P.; Harter, W. G. *Tetrahedron Lett.* **1988**, *29*, 761. (b) Pearson, W. H.; Szura, D. P.; Postich, M. J. *J. Am. Chem. Soc.* **1992**, *114*, 1329. (c) Pearson, W. H.; Postich, M. J. *J. Org. Chem.* **1992**, *57*, 6354. (d) Pearson, W. H.; Stevens, E. P. *Tetrahedron Lett.* **1994**, *35*, 2641. (e) Pearson, W. H.; Postich, M. J. *J. Org. Chem.* **1994**, *59*, 5662. (f) Pearson, W. H.; Lovering, F. E. *Tetrahedron Lett.* **1994**, *35*, 9173. (g) Pearson, W. H.; Lovering, F. E. *J. Am. Chem. Soc.* **1995**, *117*, 12336.

(10) (a) Stork, G.; Benaim, J. *J. Am. Chem. Soc.* **1971**, *93*, 5938. (b) Oppolzer, W.; Fröstl, W. *Helv. Chim. Acta* **1975**, *58*, 587. (c) Kieczykowski, G. R.; Schlessinger, R. H.; Sulsky, R. B. *Tetrahedron Lett.* **1976**, *17*, 597 (d) Corey, E. J.; Enders, D. *Chem. Ber.* **1978**, *111*, 1337, 1362. (e) Vedejs, E.; Gapinski, D. M. *Tetrahedron Lett.* **1981**, *22*, 4913.

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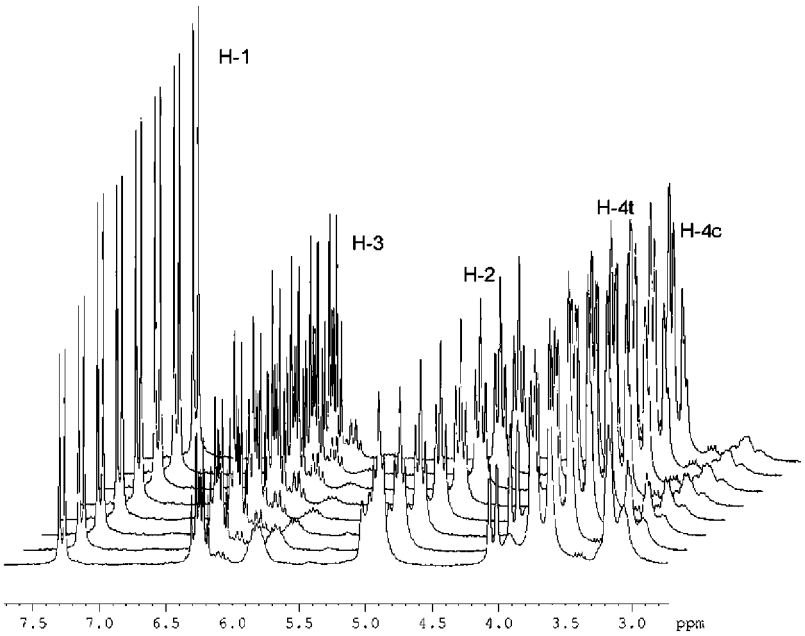



**Figure 1.** $^1$H NMR (stacked plots) showing the conversion of **1** into **3**, in THF-$d_8$ at room temperature. Unlabeled peaks correspond to starting material, **1**. Labeled peaks correspond to **3**.

Our interest in the dilithiation of silyl-protected allylamines and related compounds[11] led us to investigate the reactivity of *N*-(*tert*-butyldimethylsilyl)-3-buten-1-amine **1**. This compound has previously been reported to form the bis-silyl-3-buten-1-amine upon reaction with 2 equiv of *n*BuLi in diethyl ether, followed by quench with TMSCl.[12] The investigators did not report any products resulting from allylic or vinylic deprotonation of the starting material.

Contrary to these results, we note the formation of 1-azapentadienyl anions when **1** is exposed to 2 equiv of $^n$BuLi in THF, as depicted in Scheme 1. The initial anion, (**2**), is formed by allylic deprotonation at the 2-position of the amine by *n*BuLi. This allylic anion then immediately undergoes lithium hydride elimination[8h,13] at room temperature, to form the azapentadienyl anion **3**, and in fact, **2** cannot be detected. The overall reaction, however, can be followed by $^1$H NMR, as shown in Figure 1. The conversion is clean and the 1-azapentadienyl anion is fully generated within 12 h (Figure 2). The anion has been fully characterized by 1- and 2D NMR,[14] and the structure was further confirmed by comparison with literature data for *N*-(*tert*-butyl)-1-azapentadienyllithium,

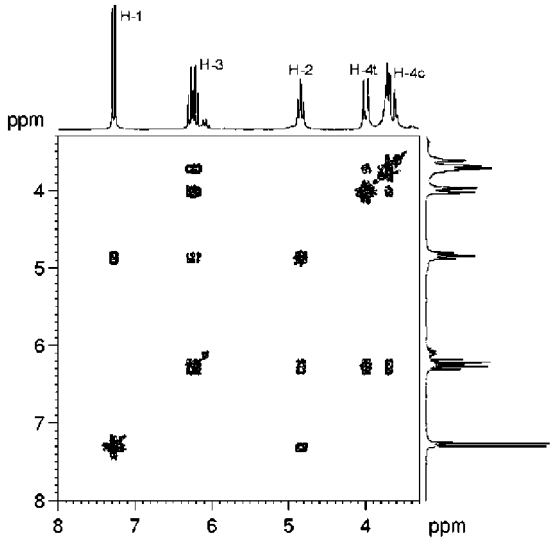



**Figure 2.** COSY of **3**, in THF-$d_8$ at room temperature.

which was generated from the *tert*-butyl protected crotonaldimine, using LDA as the base.[8d] Analogy to the same literature data also suggested that the carbon backbone of **3** adopts a "W" conformation in solution. The aggregation state of **3** was not determined.

However, when the reaction is carried out at lower temperatures, LiH elimination is slower than dianion formation and thus samples containing high concentrations of **2** could be prepared.[15] Careful NMR analysis of a sample containing an approximately 1:1 mixture of **2** and **3** at −90 °C in THF-$d_8$ confirmed the structure of **2** as an allylic dianion. The $^1$H and $^{13}$C chemical shifts of **2**

(11) (a) Williard, P. G.; Jacobson, M. A. *Org. Lett.* **2000**, *2*, 2753. (b) Jacobson, M. A.; Williard, P. G. *J. Org. Chem.* **2002**, *67*, 32.

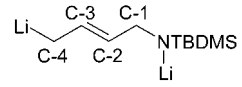
(12) Burns, S. A.; Corriu, R. J. P.; Huynh, V.; Moreau, J. J. E. *J. Organomet. Chem.* **1987**, *333*, 281.

(13) For lithium hydride elimination in lithium amides, see: (a) Ziegler, Von K.; Gellert, H.-G. *Liebigs Annal. Chem.* **1950**, *567*, 179. (b) Wittig, G.; Schmidt, H.-J.; Renner, H. *Chem. Ber.* **1962**, *95*, 2377. (c) Bach, R. D.; Bair, K. W.; Willis, C. L. *J. Organomet. Chem.* **1974**, *77*, 31. (d) Kowalski, C.; Creary, X.; Rollin, A. J.; Burke, M. C. *J. Org. Chem.* **1978**, *43*, 2601. (e) Melamed, U.; Feit, B.-A.; *J. Chem. Soc., Perkin Trans. 1* **1980**, 1267. (f) Richey, H. G., Jr.; Erickson, W. F. *J. Org. Chem.* **1983**, *48*, 4349. (g) Li, M.-Y.; San Fillipo, J., Jr. *Organometallics* **1983**, *2*, 554. (h) Newcomb, M.; Burchill, M. T. *J. Am. Chem. Soc.* **1984**, *106*, 8276. (i) Majewski, M. *Tetrahedron Lett.* **1988**, *29*, 4057 and references therein. (j) Barluenga, J.; Canteli, R.-M.; Florez, J. *J. Org. Chem.* **1996**, *61*, 3753.

(14) $^1$H NMR (THF-$d_8$) data for compound **3**: $\delta$ 7.27 (dm, 1H, $J$ = 12.0 Hz), 6.23 (dddd, 1H, $J$ = 16.4 Hz, 10.6 Hz, 9.9 Hz, 0.6 Hz), 4.85 (ddm, 1H, $J$ = 12.0 Hz, 10.6 Hz), 3.99 (ddm, 1H, $J$ = 16.4 Hz, 2.9 Hz), 3.70 (ddm, 1H, $J$ = 9.9 Hz, 3.0 Hz), 0.86 (s, 9H), −0.06 (s, 6H). Multiplicities and coupling constants were extracted using resolution enhancement (unshifted sine bell multiplication).

(15) A sample containing *n*BuLi (2 equiv) and **1** (1 equiv) was prepared at −78 °C. No reaction could be observed at this temperature over several hours. The temperature was gradually raised to 0 °C, where after about 6 h a very small amount of deprotonation could be observed. The sample was stored at −20 °C for 48 h, and at this point most of the starting material had been converted to the allylic anion **2** which was then observed at −90 °C.

**Table 1. $^1$H- and $^{13}$C NMR Data for 2 in THF-$d_8$ at −90 °C**




| atom | $^{13}$C NMR[a] | atom | $^1$H NMR |
|---|---|---|---|
| C-1 | 45.3 | H-1a | 3.37 |
| | | H-1b | 3.72 |
| C-2 | 91.4 | H-2 | 3.98 |
| C-3 | 145.3 | H-3 | 6.24 |
| C-4 | 28.9 | H-4c | 1.17 |
| | | H-4t | 0.88[b] |

[a] Determined from 2D HMQC. [b] Determined from 2D COSY.

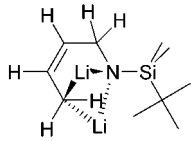


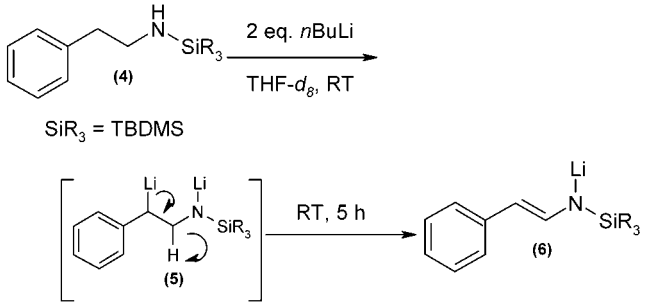

**Figure 3.** Proposed structural unit of dianion **2**.

could be fully assigned based on 2D COSY and HMQC experiments. The aggregation state of **2** was not determined. We found that the methylene protons of **2** are chemically nonequivalent suggesting that the dianion exists in a rigid conformation. $^{13}$C chemical shifts are consistent with a localized allylic anion with the lithium atom situated at the terminal position[16] (Table 1). Based on these results, and drawing analogy to our previous work on the solid-state structure of related dianions,[11a] we propose that the fundamental structural unit of dianion **2** is cyclic with the two lithium atoms bridging between the nitrogen and the terminal carbon atom (Figure 3). This structure is fully consistent with the NMR spectra and was found to be a minimum on the potential energy surface by PM3 semiempirical calculations.[17]

Silylation has been shown to occur in different positions of azapentadienyl anions.[5a,18] Silylation of **3** with TMSCl (2 equiv) resulted in the exclusive formation of *N*-(*tri*-methylsilyl)(*tert*-butyldimethylsilyl))-1,3-dibuten-1-amine, as confirmed by GC/MS and NOESY experiments.

*N*-(*tert*-Butyldimethylsilyl)phenethylamine (**4**) generates a 3-phenyl-1-azaallyl anion, (**6**), when exposed to 2 equiv of *n*BuLi in THF at room temperature.[19] As with **1**, the azaallyl anion is formed from lithium hydride elimination of a stabilized dianion, in this case the benzylic anion (**5**) (Scheme 2). However, the reaction of **4**, in contrast to that of **1**, does not go to completion. The base (*n*BuLi) appears to deprotonate the solvent faster than it deprotonates **4**, and only 25% of the starting material **4** goes on to form product, *N*-(*tert*-butyldimethylsilyl)styrylamine (**6**), with 2 equiv of *n*BuLi. With a large excess of base the reaction could be pushed to completion, but this would generate large amounts of side products from decomposition of the solvent under the influence of the base.

**Scheme 2**




It is also interesting to note the different reactivity of *N*-allyl-2,2-dimethylpropionamide (**7**), where **1** and **7** differ only in the nature of the protecting group. When **7** is exposed to similar conditions (2 equiv of *n*BuLi, THF, 20 °C), no identifiable products are recovered. However, if less than 2 equiv of *n*BuLi is used, a different reactivity is observed. In this reaction lithium hydride is not eliminated following the allylic deprotonation. Instead, one molecule of **9** presumably deprotonates one molecule of the mono-lithium amide of **8**, to give **10** and regenerate **9**. This is then repeated until the reaction reaches its thermodynamic sink, 2,2-dimethyl-*N*-(lithiopent-1-enyl)-propionamide (**12**) (Scheme 3). The overall reaction is not clean, but **12** can be identified as one of the components of the mixture at the end of the experiment, by 1D and 2D NMR.

It is apparent that the nature of the protecting group plays a great role in the reactivity of 3-buten-1-amines. When the amine is protected as an amide, and exposed to alkyllithium base, several products are formed. One of the major products can be identified as the rearranged product **12**. On the other hand, if a trialkylsilyl-protected amine is used, allylic deprotonation is followed by lithium hydride elimination, generating the 1-azapentadienyl anion **3**. In this communication we have demonstrated a new and simple method of generating these synthetically useful 1-azapentadienyl anions. Future work will focus on applying these dianions to significant synthetic targets. The reactivity of related amines and their derivatives will also be explored.

## Experimental Section

**General Methods.** Diethyl ether and THF were distilled from sodium/benzophenone under a nitrogen atmosphere. *n*-Buthyllithium was obtained from Aldrich Chemical Co. (2.5 M in hexanes), and the exact concentration of the solution was determined by direct titration with 2,5-dimethoxybenzyl alcohol in THF. All chemicals were purchased from Aldrich Chemical Co. and distilled prior to use when appropriate. Deuterated NMR solvents were dried over 3 Å Linde sieves prior to use. All reactions and NMR studies were carried out under argon atmosphere, using flame-dried glassware. GC analyses were performed using a mass selective detector. IR spectra were recorded on a FTIR instrument. NMR spectra were collected on spectrometers operating at 400 and 300 MHz for $^1$H and 100 and 75 MHz for $^{13}$C observation. The chemical shifts were referenced to $CDCl_3$ ($^1$H 7.27 ppm and $^{13}$C 77.23 ppm), $CD_3OD$ ($^1$H 3.31 ppm and $^{13}$C 49.15 ppm) or THF-$d_8$ ($^1$H 1.73 ppm and $^{13}$C 25.37 ppm) as internal standards. HRMS were performed at the Brown University Mass Spectrometry laboratory.

***N*-(*tert*-Butyldimethylsilyl)-3-buten-1-amine (1).** $LiAlH_4$ (1.7 g, 45 mmol) was weighed into a flask, and 70 mL of dry diethyl ether was added. The flask was placed in a 0 °C icebath,

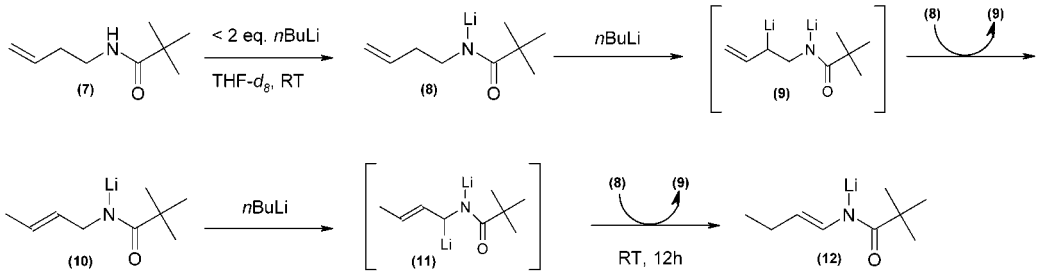
(16) (a) Fraenkel, G.; Duncan, J. H.; Wang, J. *J. Am. Chem. Soc.* **1999**, *121*, 432. (b) Fraenkel, G.; Cabral, J.; Lanter, C.; Wang, J. *J. Org. Chem.* **1999**, *64*, 1302.

(17) PM3: Stewart, J. J P. *J. Comput. Chem.* **1989**, *10*, 209. Li parameters: Anders, E.; Koch, R.; Freunscht, P. *J. Comput. Chem.* **1993**, 14, 1301. The calulations were performed with PC Spartan Pro, Wave function Inc. 18401 Von Karman Ave., Suite 370, Irvine, CA 92715.

(18) Addition of acylating agents as electrophiles, will yield thermodynamically stable dienamides: See footnote 10b.

(19) As observed by $^1$H and COSY NMR experiments.

**Scheme 3**




and $AlCl_3$ (6.0 g, 45 mmol) was added in small portions over 10 min. The resulting slurry was stirred for 5 min. Allyl cyanide (3.6 mL, 45 mmol) was placed in a flask with 20 mL of dry diethyl ether. The mixture was added to the $LiAlH_4/AlCl_3$ slurry over 10 min. Effervescence was observed upon addition. The reaction mixture was stirred at 0 °C for 2 h, after which the reaction was quenched by careful addition of 10% NaOH, also at 0 °C. NaOH was added until the reaction mixture tested basic on pH paper and effervescence was no longer observed. The aqueous layer was extracted with diethyl ether (4 × 40 mL) and dried over NaOH pellets.[20] $^1$H NMR confirmed the presence of 3-butene-1-amine, which was silylated directly, without further workup.

Triethylamine (6.0 mL, 43 mmol), followed by *tert*-butyldimethylsilyl chloride (6.4 g, 42.8 mmol) dissolved in 20 mL of diethyl ether, was added to the ether layer containing the amine, and the reaction mixture was stirred at room temperature for 72 h. The presence of **1** was confirmed by GC/MS. The reaction mixture was filtered through florisil and the filtrate stirred with $CaH_2$ for 20 h. Filtration, removal of the ether and low-boiling impurities by distillation, followed by Kugelrohr distillation (bp125 °C, 0.25 mmHg) of the remaining liquid, resulted in 0.39 g (22% yield) of **1**. Despite repeated efforts, **1** was isolated with 12% 1,3-di-*tert*-butyl-1,1,3,3-tetramethyldisiloxane and 10% *tert*-butyldimethylsilyl hydroxide. FTIR (neat): $\nu$ ($cm^{-1}$) 3401, 3078, 2953, 2855, 1640. $^1$H NMR ($CDCl_3$): $\delta$ 5.77 (m, 1H). 5.05 (m, 2H), 2.82 (q, 2H), 2.16 (m, 2H), 0.88 (s, 9H), 0.05 (s, 6H). $^{13}$C NMR ($CDCl_3$): $\delta$ −4.6, 26.1, 26.8, 39.6, 42.1, 116.5, 137.2. HRMS calculated for $C_{10}H_{23}NSi$: 185.1599. Found: 185.1597.

***N*-(*tert*-Butyldimethylsilyl)phenethylamine (4).** Triethylamine (11.1 mL, 0.080 mol) and phenethylamine (10 mL, 0.080 mol) was added to 240 mL of diethyl ether. *tert*-Butyldimethylsilyl chloride (12.0 g, 0.080 mol), in 100 mL of diethyl ether, was added to the amine/triethylamine mixture. Within a few minutes white solid precipitated out. The reaction mixture was stirred at room temperature for 6 days, and the presence of **4** was confirmed by GC/MS. The reaction mixture was filtered through florisil, and the filtrate was stirred with $CaH_2$ for 3 h. Filtration, followed by removal of the solvent in vacuo, resulted in 15.3 g (82% yield) of **4**. FTIR (neat): $\nu$ ($cm^{-1}$) 3401, 3027, 2951, 2853, 1603. $^1$H NMR ($CD_3OD$): $\delta$ 7.36 (m, 2H). 7.27 (m, 3H), 2.95 (m, 2H), 2.82 (m, 2H), 1.02 (s, 9H), 0.02 (s, 6H). $^{13}$C NMR ($CD_3OD$): $\delta$ −4.04, 18.3, 25.6, 39.0, 43.2 126.4, 128.7, 128.9, 139.8.

***N*-Allyl-2,2,-dimethylpropionamide (7).** 3-Butene-1-amine was prepared in the same fashion as described for compound **1**, except all amounts were doubled. $^1$H NMR confirmed the presence of 3-butene-1-amine, which was pivaloyl protected directly, without further workup. Triethylamine (11.3 mL, 81 mmol) was added to the ether layer containing the 3-buten-1-amine. Trimethylacetyl chloride (10 mL, 81 mmol) was placed in an addition funnel and added dropwise to the reaction mixture, at 0 °C. Immediately upon addition of the trimethylacetyl chloride, fumes developed and a white solid precipitated. The reaction mixture was stirred at room temperature for 12 h, and the presence of **7** was confirmed by GC/MS. The reaction mixture was filtered through florisil, and the ether was removed in vacuo, resulting in 1.7 g (12% yield) of **7**. FTIR (neat): $\nu$ ($cm^{-1}$) 3351, 3078, 2966, 1634. $^1$H NMR ($CDCl_3$): $\delta$ 5.83 (bs, 1H), 5.66 (m, 1H), 4.97 (m, 2H), 3.18 (m, 2H), 2.15 (m, 2H), 1.07 (s, 9H). $^{13}$C NMR ($CDCl_3$): $\delta$ 27.4, 33.6, 38.0, 38.4, 116.9, 135.3, 178.1. HRMS calculated for $C_9H_{17}NONa$: 178.1208. Found: 178.1213.

**General Procedure for the Preparation of NMR Samples To Follow the Reaction of 1, 4, and 7 with *n*BuLi.** A 0.13 mmol amount of *n*-butyllithium in hexanes was placed in a flame-dried NMR tube under argon atmosphere. The hexanes were removed in vacuo, and 0.6 mL of THF-$d_8$ was added. To this clear and colorless solution **1** or **4** ($6.6 \times 10^{-5}$ mol), or **7** (9 mg, $6.0 \times 10^{-5}$ mol), was added.

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**Supporting Information Available:** $^1$H and $^{13}$C NMR for compounds **1**, **4**, and **7**. $^1$H NMR for compound **2** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(20) Procedure adapted from Sato, T.; Nakamura, N.; Ikeda, K.; Okada, M.; Ishibashi, H.; Ikeda, M. *J. Chem. Soc., Perkin Trans. 1* **1992**, 2399.