**Methyl α-diazo-2-nitrophenylacetate (18)** was obtained by adding tosyl azide (400 mg, 2.05 mmol) to a mixture of methyl 2-nitrophenylacetate (400 mg, 2.05 mmol) and $KF-Al_2O_3$[40] (420 mg, 2.05 mmol) in MeCN (6 mL), followed by usual workup, as an orange solid (350 mg, 77.2%): mp 69-72 °C; $^1H$ NMR ($CCl_4$) δ 3.78 (s, 3 H), 7.30-7.62 (m, 3 H), 7.96 (d, $J$ = 8.1 Hz, 1 H); IR (KBr disc) 2110, 1715, 1690, 1530, 1370 $cm^{-1}$.

**3-(2-Nitrophenyl)-3-chlorodiazirine (20).** A mixture of 2-nitrobenzonitrile (2.22 g, 15.0 mmol), $AlCl_3$ (2.0 g, 15.0 mmol), and urea (14.4 g) was heated at 200 °C for 2 h. To the cooled mixture, hot water (20 mL) was poured, and the solution was then poured onto 5 N NaOH aqueous solution (40 mL), which was extracted with $CHCl_3$. Evaporation of the solvent left brown residue, which was dissolved in EtOH. Addition of picric acid to the solution, followed by cooling for 3 days produced 2-nitrobenzamidine picrate[41] as a yellow solid (0.51 g, 8.6%). To a solution of picrate (300 mg) and NaLi (185 mg) in DMSO (3.1 mL)-$n$-hexane (2.4 mL) was added NaOCl aqueous solution (3 mL) containing NaCl (525 mg) under cooling and vigorous stirring. After stirring for 30 min at 10 °C, the mixture was extracted with hexane. Preparative TLC (silica gel) with $CHCl_3$-$n$-hexane (1:20) of the extract provided the desired diazirine (11 mg, 8.0%); $^1H$ NMR ($CCl_4$) δ 7.52-7.70 (m, 3 H), 7.98-8.12 (m, 1 H); IR (NaCl neat) 1570, 1530, 1350 $cm^{-1}$.

**2-(1-Nitronaphthyl)diazomethane (22)** was prepared by stirring NaH and tosylhydrazone of 1-nitro-2-naphthaldehyde[42] in anhydrous THF for 15 min at room temperature followed by usual workup and TLC as an orange solid in 39% yield; mp 73.0 °C (dec); $^1H$ NMR ($CDCl_3$) δ 5.52 (s, 1 H), 7.00-8.00 (m, 6 H); IR (KBr) 2070, 1502, 1405, 1341, 1320, 808, 741 $cm^{-1}$.

**o-Nitrosobenzaldehyde (3)** was prepared by heating *trans*-2,2'-diformylazobenzene dioxide.[9] **2,1-Benzisoxazolone (4)** was obtained by the treatment of (*o*-hydroxylamino)-*N*,*N*-dimethylbenzamide with aqueous alkaline solution.[15] **Carbonylcyclopentadiene imine (5)** was generated by the photolysis of benzotriazole.[16] **o-Azidobenzoic acid (8)** was obtained by treatment of antranilic acid with $HCl/NaNO_2$ followed by $NaN_3$.[43] *N*-Hydroxyisatin was prepared[44] by the reaction of 2-nitrobenzoyl chloride with $CH_2N_2$. All other chemicals were used as received or distilled before use as specified.

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# Highly Stereoselective Tandem Cyclizations of 5-Hexenyllithiums: Preparation of Endo-2-Substituted Bicyclo[2.2.1]heptanes and 3-Substituted *trans*-Bicyclo[3.3.0]octanes

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*Contribution from the Department of Chemistry, The University of Connecticut, Storrs, Connecticut 06269-3060.* *Received May 1, 1992*

**Abstract:** Tandem cyclization of diolefinic alkyllithiums, derived from acyclic diolefinic alkyl iodides by low-temperature lithium-iodine exchange, proceeds via two highly stereoselective and totally regiospecific 5-*exo-trig* ring closures to deliver bicyclic alkyllithiums. Trapping of the organolithium product by addition of an electrophile cleanly affords functionalized bicyclic molecules in good yield. In this way both endo-2-substituted bicyclo[2.2.1]heptanes and 3-substituted *trans*-bicyclo[3.3.0]octanes have been prepared in isolated yields of 65-80% from the readily available 3-(2-iodoethyl)-1,5-hexadiene (**5**) and 7-iodo-4-ethenyl-1-heptene (**9**), respectively. Attempts to effect tandem cyclization of 5,10-undecadienyllithium (**11**), which would be mediated by a secondary alkyllithium species, were unsuccessful. The results suggest that tandem anionic cyclization provides a convenient route to a variety of bicyclic systems not readily available by other approaches.

The isomerization of 5-hexenyllithiums has attracted the attention of a number of groups as a route to functionalized cyclopentylmethyl-containing products.[1,2] We have recently demonstrated that such cyclizations involving monosubstituted 5-hexenyllithiums are highly stereoselective and totally regiospecific 5-*exo-trig* processes.[3] Molecular orbital calculations indicate that the high degree of stereocontrol inherent in these cyclizations is a consequence of an energetically favorable coordination of the lithium atom at C(1) with the carbon-carbon π-bond leading to a fairly rigid transition-state structure, shown below, resembling


a chair cyclohexane in which a substituent preferentially occupies a pseudoequatorial position.

This recently acquired ability to predict the stereochemical outcome of isomerization of a substituted 5-hexenyllithium,

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(3) Bailey, W. F.; Khanolkar, A. D.; Gavaskar, K.; Ovaska, T. V.; Rossi, K.; Thiel, Y.; Wiberg, K. B. *J. Am. Chem. Soc.* **1991**, *113*, 5720.

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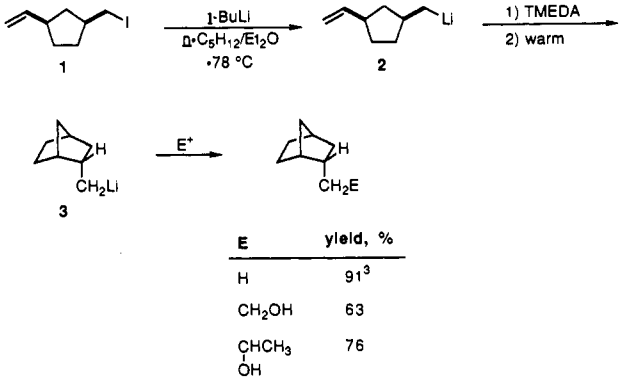
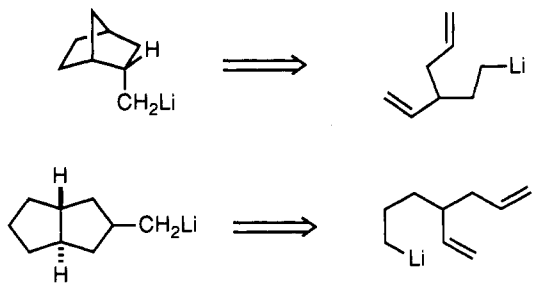
**Scheme I**




| E | yield, % |
|---|---|
| H | 91[3] |
| $CH_2OH$ | 63 |
| $CHCH_3$ (OH) | 76 |

coupled with the ease with which the cyclic organolithium product may be functionalized, offers the possibility of designing approaches to rather complex polycyclic ring systems via stereoselective tandem cyclizations. Our preliminary account describing sequential tandem cyclization of diolefinic alkyllithiums was restricted to model systems which did not address this stereochemical issue.[4] Herein we report the results of a study of tandem cyclization of simple acyclic diolefinic alkyllithiums that demonstrates the utility of this stereoselective anionic approach to bicyclic molecules. As detailed below, both endo-2-substituted bicyclo-



[2.2.1]heptanes and 3-substituted *trans*-bicyclo[3.3.0]octanes may be readily prepared by functionalization of the bicyclic organolithiums generated upon stereoselective tandem cyclization of (3-ethenyl-5-hexenyl)lithium and (4-ethenyl-6-heptenyl)lithium, respectively. Attempts to effect tandem cyclization using substrates in which the initial cyclization generates a transient secondary alkyllithium en route to the final product were unsuccessful.

## Results and Discussion

**Endo-2-Substituted Bicyclo[2.2.1]heptanes.** At the inception of this study it was not clear that it would be possible to stereoselectively generate and successfully trap the sterically hindered *endo*-2-$CH_2Li$ functionality. Indeed, isomerization and trapping compete with reactions that consume anions such as proton abstraction and oxidation with adventitious oxygen. Preliminary experiments using the hexenyllithium prepared from *cis*-1-ethenyl-3-(iodomethyl)cyclopentane (**1**) demonstrated that reasonable yields of endo-2-substituted bicyclo[2.2.1]heptanes could be produced by simple monocyclization. Thus, as illustrated in Scheme I,[5] low-temperature lithium–iodine exchange between **1** and 2.2 equiv of *tert*-butyllithium (*t*-BuLi) in a solution of *n*-pentane–diethyl ether (3:2 by volume) following our general protocol[6] serves to cleanly generate [(*cis*-3-ethenylcyclopentyl)-methyl]lithium (**2**). This cyclic 5-hexenyllithium is stable at −78 °C as evidenced by the fact that low-temperature quench of the reaction mixture affords *cis*-1-ethenyl-3-methylcyclopentane in virtually quantitative yield. Upon warming in the presence of *N,N,N′,N′*-tetramethylethylenediamine (TMEDA), **2** undergoes

**Scheme II**

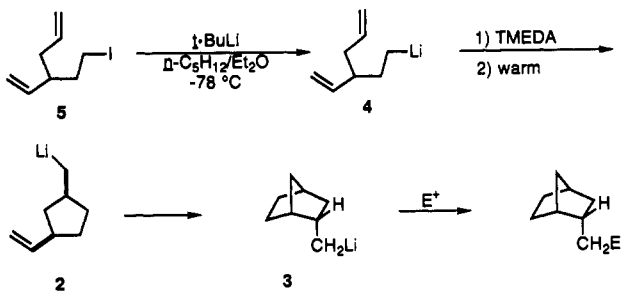
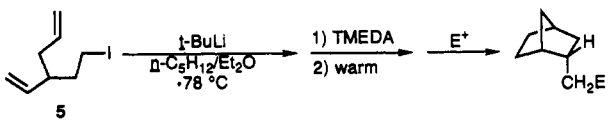



**Table I.** Preparation of *endo*-2-Substituted Bicyclo[2.2.1]heptanes[a]




| entry | $E^+$ | E | yield,[b] % |
|---|---|---|---|
| 1 | $CH_3OH$ | H | 89[c] |
| 2 | $CH_3OD$ | D | 75[c] |
| 3 | $CO_2$ | $CO_2H$ | 65 |
| 4 | $(CH_2O)_n$ | $CH_2OH$ | 74 |
| 5 | $(CH_3)_2NCHO$ | CHO | 72 |
| 6 | $(CH_3)_3CCHO$ | $(CH_3)_3CCH(OH)$ | 80 |
| 7 | $Br(CH_2)_2Br$ | Br | 75 |
| 8 | $(CH_3)_3SiCl$ | $Si(CH_3)_3$ | 81 |
| 9 | $(n\text{-}Bu)_3SnCl$ | $Sn(n\text{-}Bu)_3$ | 71 |

[a] Diolefinic alkyllithium **4** was generated at −78 °C by addition of 2.2 equiv of *t*-BuLi to a solution of **5** in *n*-pentane–diethyl ether (3:2 by volume). TMEDA (2.2 equiv) was then added, the cooling bath was removed, and the mixture was allowed to warm to 0 °C and stand at this temperature for 4 min before the addition of an excess of the electrophile. [b] Isolated yields of chromatographically pure product unless otherwise noted. [c] Determined by GC/MS analysis of the crude product.

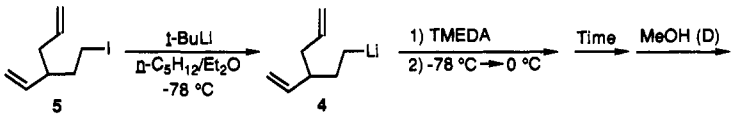
a highly endo-selective cyclization (*endo*/*exo* ≈ 50/1) to give [(*endo*-2-bicyclo[2.2.1]heptyl)methyl]lithium (**3**). As indicated in Scheme I, **3** may be trapped by reaction with an electrophile to deliver functionalized product. While this approach provides a viable route to endo-2-substituted bicyclo[2.2.1]heptanes, the preparation of multigram quantities of stereoisomerically pure precursor iodide **1** is not a trivial task. For this reason we turned our attention to the construction of the bicyclic organolithium by tandem cyclization of a diolefinic alkyllithium.

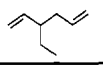
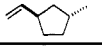
Consideration of the chairlike transition state for isomerization of a 3-substituted 5-hexenyllithium suggests that the cis product **2** should be formed with a high degree of stereocontrol upon monocyclization of (3-ethenyl-5-hexenyl)lithium (**4**). This organolithium could, in turn, be derived from readily available 3-(2-iodoethyl)-1,5-hexadiene (**5**) by lithium–iodine exchange. On the basis of this analysis, tandem cyclization of **4** would be expected to proceed via two highly stereoselective steps to give **3**. This one-pot preparation of functionalized endo-2-substituted bicyclo[2.2.1]heptanes, which is summarized in Scheme II, was found to provide a convenient route to such materials.

Addition of 2.2 equiv of *t*-BuLi to an approximately 0.1 M solution of **5** in *n*-pentane–diethyl ether (3:2 by volume) at −78 °C cleanly gave the diolefinic alkyllithium **4** as demonstrated by the fact that quench of such a reaction mixture with methanol afforded 3-ethyl-1,5-hexadiene in essentially quantitative yield. Tandem cyclization of **4** was effected as illustrated in Scheme II (**4** → **2** → **3**) by addition of 2.2 equiv of TMEDA and removal of the cooling bath. The reaction mixture was allowed to warm to 0 °C under an atmosphere of argon, and it was held at this temperature for 4 min to complete the isomerization. As indicated by the results presented in Table I, the [(*endo*-2-bicyclo[2.2.1]-heptyl)methyl]lithium (**3**) may be trapped by addition of any of a variety of electrophiles to afford functionalized endo-2-substituted bicyclo[2.2.1]heptanes in isolated yields of 65–80%. It should be noted that the precise conditions used for the tandem

(4) Bailey, W. F.; Rossi, K. *J. Am. Chem. Soc.* **1989**, *111*, 765.
(5) Organolithiums are depicted as monomeric for the sake of pictorial clarity. The actual aggregation of the olefinic alkyllithiums under the reaction conditions is unknown.
(6) Bailey, W. F.; Punzalan, E. R. *J. Org. Chem.* **1990**, *55*, 5404.

**Table II.** Exploratory Cyclizations of Diolefinic Organolithium **4**[a]




| time,[c] min | products, % yield (%d)[b] | | | | |
|---|---|---|---|---|---|
| |  |  |  |  |  |
| 10 | 4.2 | <0.2 | 10.0 (~100) | 1.7 | 84.1 (89) |
| 15 | 5.8 | | 9.8 | 1.7 | 82.7 (88) |
| 20 | 3.8 | | 9.7 | 1.8 | 84.7 (86) |
| 30 | 3.4 | | 8.9 | 1.8 | 85.6 (82) |
| 60 | 3.1 | | 5.7 | 1.8 | 89.3 (61) |

[a] TMEDA (2.2 equiv) was added at −78 °C to a solution of diolefinic alkyllithium **4**, generated as described in footnote a of Table I. The mixture was stirred for 5 min at −78 °C, the cooling bath was removed, and after reaching 0 °C (ca. 6 min) the mixture was immersed in an ice bath for a period of time before addition of MeOH (or MeOD). Yields were determined by GC analysis. [b] Percent incorporation of deuterium upon quench with MeOD. [c] Time from removal of the cooling bath.

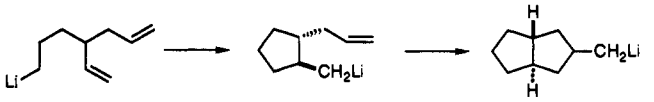
cyclization of **4** to **3** are not crucial to the success of the method: longer reaction times or temperatures higher than 0 °C afford functionalized product in only slightly diminished yield (vide infra) provided that both water and oxygen are excluded from the reaction flask.

The efficiency of the tandem cyclization of **4** to **3** was probed and optimal conditions for the preparation of functionalized product were established in a series of experiments, summarized in Table II, that involved quenching the reaction mixture at various times with dry, deoxygenated methanol (or MeOD). The data presented in Table II indicate that [(*endo*-2-bicyclo[2.2.1]-heptyl)methyl]lithium (**3**) is a rather persistent organolithium: deuterium incorporation studies demonstrate that reaction mixtures may be held at 0 °C for extended periods with little loss of activity. These exploratory isomerizations also illustrate that the conversion of **4** to **3** is a remarkably clean process and that the two-step sequence (**4** → **2** → **3**) is more rapid than potentially troublesome reactions that consume anions such as proton abstraction from solvent. Indeed, the only side products generated in the two-step isomerization are ~10% of the trans isomer of **2** (assayed as *trans*-1-ethenyl-3-methylcyclopentane) and an almost negligible amount (<2%) of the exo isomer of **3** (assayed as *exo*-2-methylbicyclo[2.2.1]heptane). The cyclization of intermediate **2** to the product organolithium **3** is complete within a few minutes at 0 °C as evidenced by the fact that no *cis*-1-ethenyl-3-methylcyclopentane was detected in the reaction mixtures. Thus, the conversion of **4** to **2** is cis-selective to the extent of ca. 9:1, and the cyclization of **2** to **3** is endo-selective to the extent of almost 50:1. The low and variable quantities of 3-ethyl-1,5-hexadiene found in the reaction mixtures are a byproduct of the initial lithium–iodine exchange to give **4**; as noted elsewhere,[6] the diene is produced by proton abstraction from the cogenerated *t*-BuI. As a practical matter, isolation of pure, functionalized endo-substituted product (Table I) is normally a fairly simple matter since the major byproducts are the unfunctionalized diene and ca. 10% of the isomeric alkene derived from trapping of the trans isomer of **2**.

It is of some interest to compare the behavior of diolefinic alkyllithium **4** with that of the analogous 3-ethenyl-5-hexenyl radical. The radical, which has been studied by Beckwith and co-workers,[7] also undergoes two successive 5-*exo*-*trig* ring closures. However, in contrast to the highly stereoselective isomerizations which characterize the two-step conversion of **4** to **3**, tandem cyclization of the 3-ethenyl-5-hexenyl radical is a less selective process that affords a mixture of hydrocarbons including *exo*- and *endo*-2-methylbicyclo[2.2.1]heptanes as well as the isomeric monocyclic alkenes.

The selectivity of the anionic tandem cyclization approach to endo-2-substituted bicyclo[2.2.1]heptanes rivals that of the classical Diels–Alder route to such systems.[8] Moreover, the two approaches are complementary: whereas the powerful Diels–Alder methodology is most efficient when the dienophile bears an electron-withdrawing substituent, the anionic cyclization methodology allows for preparation of derivatives bearing an *endo*-2-$CH_2X$ moiety that are not readily available by cycloaddition of a diene and a dienophile.

**3-Substituted *trans*-Bicyclo[3.3.0]octanes.** The major product of isomerization of (4-methyl-5-hexenyl)lithium is [(*trans*-2-methylcyclopentyl)methyl]lithium.[3] On this basis it was expected that cyclization of a (4-allyl-5-hexenyl)lithium such as **6** would proceed via a chairlike transition state to afford a cyclopentane incorporating a trans-disposed 5-hexenyllithium moiety (**7**). It




**6** **7** **8**

was, however, not at all obvious that subsequent cyclization of such a species would ensue to deliver a trans-fused bicyclo-[3.3.0]octane skeleton. Indeed, the trans ring fusion in a molecule such as **8** engenders considerable ring strain in the bicyclo-[3.3.0]octane skeleton as evidenced by the fact that the parent trans-fused hydrocarbon is some 6.1–6.4 kcal/mol less stable than its cis isomer.[9] This particular system was, in fact, chosen for study in an effort to assess the potential utility of the tandem cyclization methodology for the preparation of relatively unstable molecular frameworks.[10] Clearly, **8** will be the major product of the two-step cyclization only to the extent that the activation energy for the closure of **7** to **8** is less than the activation energy for the reverse of the first step, i.e., **7** → **6**, since equilibration of the 5-hexenyllithiums and (cyclopentylmethyl)lithiums would invariably lead to a product mixture rich in the cis-fused isomer of **8**.

The preparation of 7-iodo-4-ethenyl-1-heptene (**9**) needed for the generation of **6** was easily accomplished in three steps from α-allyl-δ-valerolactone by reduction to the lactol followed by Wittig olefination and conversion of the resulting alcohol to the iodide. The diolefinic alkyllithium **6** was cleanly generated in the normal way by addition of 2.2 equiv of *t*-BuLi to a solution of **9** in *n*-pentane–diethyl ether (3:2 by volume) at −78 °C. TMEDA (2.2 equiv) was then added to the cold solution, and the cooling bath was removed. The mixture was allowed to warm and stand

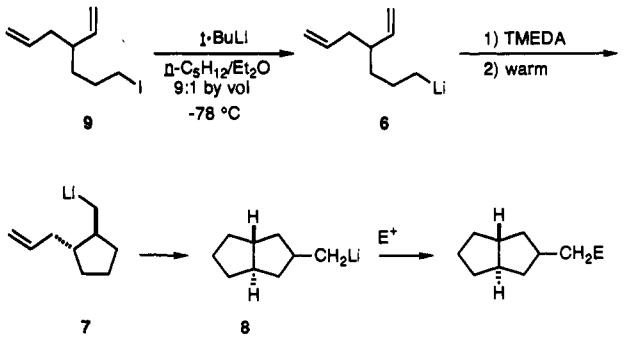
(7) Beckwith, A. L. J.; Lawrence, T.; Serelis, A. K. *J. Chem. Soc., Chem. Commun.* **1980**, 484.

(8) Carruthers, W. *Cycloaddition Reactions in Organic Synthesis*; Pergamon Press: New York, 1990.

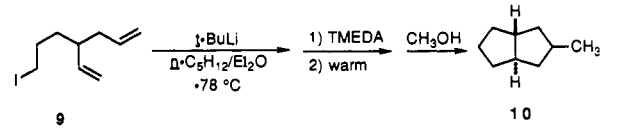
(9) (a) Chang, S.; McNally, D.; Shary-Tehrany, S.; Hickey, M. J.; Boyd, R. H. *J. Am. Chem. Soc.* **1970**, *92*, 3190. (b) Allinger, N. L.; Tribble, M. T.; Miller, M. A.; Wertz, D. H. *J. Am. Chem. Soc.* **1971**, *93*, 1673. (c) Lii, J.-H.; Allinger, N. L. *J. Am. Chem. Soc.* **1989**, *111*, 8566.

(10) A preliminary account of the tandem cyclization of (4-ethenyl-6-heptenyl)lithium (**6**) has been published: Bailey, W. F.; Khanolkar, A. D. *Tetrahedron Lett.* **1990**, *31*, 5993.

**Scheme III**




at room temperature under an atmosphere of dry argon for 1 h prior to the addition of deoxygenated methanol. Analysis of the

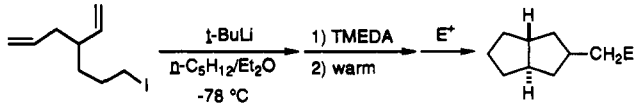



reaction mixture by capillary GC revealed that a single 3-methylbicyclo[3.3.0]octane, identified as the trans-fused isomer **10** (vide infra), had been produced in 87% yield. The balance of the product mixture consisted of uncyclized diene (7%), isomeric 1-allyl-2-methylcyclopentanes (3%), and a small amount (~3%) of cis-fused 3-methylbicyclo[3.3.0]octane. The major product of the reaction was easily isolated by washing the reaction mixture with cold, concentrated sulfuric acid to remove the olefinic impurities. The observation of exactly nine separate resonances in the $^{13}C$ NMR spectrum of the material (two of which are nearly isochronous; see Experimental Section) is consonant with the $C_s$ symmetry of the *trans*-bicyclo[3.3.0]octane skeleton, and this served to unambiguously establish the structure as **10**.

Encouraged by this result, we turned our attention to the preparation of functionalized derivatives of 3-methyl-*trans*-bicyclo[3.3.0]octane.[11,12] This seemingly simple exercise was not trivial, and a discussion of the difficulties encountered is instructive for the practical utilization of the anionic cyclization approach to functionalized products.

Preliminary experiments using MeOD to quench reaction mixtures revealed that the conversion of **6** to **8** is, as might be expected, much slower than the tandem cyclization of **4** to **3** (Scheme II). This became a potentially serious problem. From the low deuterium incorporation obtained in the bicyclic product when the reaction mixture was allowed to stand at room temperature for extended periods of time to complete the cyclization, it was obvious that organolithium **8** was being protonated either by the diethyl ether solvent or the TMEDA additive or both of these potentially acidic molecules.[13] Fortunately, the extent of unwanted protonation could be reduced by reducing the amount of diethyl ether in the solvent system used for the preparation of **6**. Apparently it is the ether rather than the (presumably) complexed TMEDA that is responsible for the protonation of the organolithium. Since, as noted elsewhere,[6] it is necessary to conduct the exchange between an iodide and *t*-BuLi in a solvent mixture that contains diethyl ether, it is not possible to prepare

Table III. Preparation of 3-Substituted *trans*-Bicyclo[3.3.0]octanes[a]




| entry | $E^+$ | E | yield,[b] % |
|---|---|---|---|
| 1 | $CH_3OH$ | H | 87[c] |
| 2 | $CH_3OD$ | D | 73[c] |
| 3 | $CO_2$ | $CO_2H$ | 71 |
| 4 | $(CH_2O)_n$ | $CH_2OH$ | 72 |
| 5 | $(CH_3)_2NCHO$ | CHO | 79 |
| 6 | $(CH_3)_3CCHO$ | $(CH_3)_3CCH(OH)$ | 81 |
| 7 | $CH_3CHO$ | $CH_3CH(OH)$ | 73 |
| 8 | $(CH_3)_3SiCl$ | $Si(CH_3)_3$ | 78 |
| 9 | $I_2$ | I | 65 |

[a] Diolefinic alkyllithium **6** was generated at −78 °C by addition of 2.2 equiv of *t*-BuLi to a 0.1 M solution of **9** in *n*-pentane–diethyl ether (9:1 by volume). TMEDA (2.2 equiv) was then added, and the cooling bath was removed. The mixture was allowed to warm to 0 °C (~6 min) and then immersed in an ice bath for 24 min (total time from removal of cooling bath ~30 min) before the addition of an excess of the electrophile. [b] Isolated yields of chromatographically pure products unless otherwise noted. [c] Determined by GC/MS analysis of the crude product.

**6** in pure pentane. The use of a 9:1 (vol/vol) mixture of *n*-pentane–diethyl ether was a compromise; it allowed the rapid generation of **6** at −78 °C and also served to minimize quench of the reactive organolithium intermediates during the tandem cyclization of **6** → **8**.

Conditions for the preparation of functionalized 3-methyl-*trans*-bicyclo[3.3.0]octanes via tandem cyclization of **6** (Scheme III) were optimized in a series of experiments, involving quench of reaction mixtures with MeOD, analogous to those described above (Table II) for the synthesis of endo-2-substituted bicyclo[2.2.1]heptanes. The objective of the exercise was to establish the minimum time required for the complete conversion of **6** to **8** under conditions that maximize the yield of deuterated bicyclic product. Higher reaction temperatures lead to a more rapid tandem cyclization, but they also result in a loss of alkyllithium product due to relatively more rapid proton abstraction from the solvent. For the conversion of **6** to **8**, the minimum temperature at which a reasonable rate of cyclization was observed was ~0 °C, and preparative scale reactions were conducted at this temperature. Thus, the diolefinic alkyllithium **6** was prepared virtually instantaneously at −78 °C by addition of 2.1–2.2 equiv of *t*-BuLi in *n*-pentane to a solution of iodide **9** in *n*-pentane–diethyl ether (9:1 by volume). Tandem cyclization (Scheme III, **6** → **7** → **8**) was effected by addition of 2.1–2.2 equiv of TMEDA and removal of the cooling bath. The mixture was allowed to warm to 0 °C (~6 min) and was held at this temperature for 24 min to complete the two-step isomerization (~30 min total time from removal of the cooling bath). Addition of an electrophile delivered functionalized product in isolated yields of 65–80% (Table III). These preparations shared a hallmark of the tandem anionic-cyclization methodology: virtually the only contaminants present in the product mixture were unfunctionalized hydrocarbons. Simple chromatography or short-path distillation served to give pure material.

The ease with which the relatively inaccessible *trans*-bicyclo[3.3.0]octane skeleton may be prepared by tandem cyclization of a diolefinic alkyllithium is noteworthy in several respects. The initial stereoselective isomerization of **6** to **7** is apparently operationally irreversible and kinetically controlled since a trans-fused bicyclo[3.3.0]octane is produced in the subsequent cyclization. The facility of this second cyclization (Scheme III, **7** → **8**) is an indication of the favorable thermodynamics associated with such isomerizations: ring closure of a 5-hexenyllithium to a (cyclopentylmethyl)lithium generates a σ-bond (bond energy ca. 88 kcal/mol) at the expense of a π-bond (bond energy ca. 60 kcal/mol). On this basis, it seems reasonable to anticipate that

(11) (a) Paquette, L. A. *Top. Curr. Chem.* **1979**, *79*, 41–165. (b) Paquette, L. A. *Top. Curr. Chem.* **1984**, *119*, 1–160.

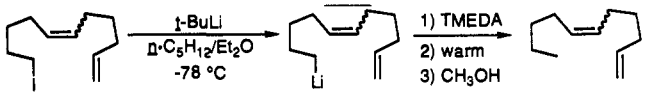
(12) Very few 3-substituted *trans*-bicyclo[3.3.0]octanes have been reported in the literature. See, for example: (a) Linstead, R. P.; Meade, E. M. *J. Chem. Soc.* **1934**, 935. (b) Barret, J. W.; Linstead, R. P. *J. Chem. Soc.* **1935**, 1069. (c) Granger, R.; Nau, P. F. G.; Nau, J. *Bull. Soc. Chim. Fr.* **1960**, 1350 and references therein. (d) Knotnerus, J.; Bickel, A. F. *Recl. Trav. Chim. Pays-Bas* **1964**, *83*, 400. (e) Bourn, P. M.; Klyne, W. *J. Chem. Soc.* **1960**, 611. (f) Rousset, C. J.; Swanson, D. R.; Lamaty, F.; Negishi, E. *Tetrahedron Lett.* **1989**, *30*, 5105.

(13) At elevated temperatures, organolithiums readily abstract protons from both diethyl ether (Wakefield, B. J. *The Chemistry of Organolithium Compounds*; Pergamon Press: New York, 1974) and TMEDA (Kohler, F. H.; Hertkorn, N.; Blumel, J. *Chem. Ber.* **1987**, *120*, 2081).

other relatively unstable molecular frameworks should be accessible by stereoselective tandem anionic cyclization of suitably constituted diolefinic alkyllithiums.

Consideration of the thermodynamically favorable conversion of **6** to **8** suggests the possibility of conducting a tandem cyclization in which a primary diolefinic alkyllithium is transformed into a primary bicyclic alkyllithium via the intermediacy of a less stable secondary olefinic alkyllithium. Such a two-step process, if reduced to practice, would considerably extend the utility of the methodology. Previous work had, however, shown that 5-hexenyllithiums bearing an alkyl group at the terminal olefinic carbon do not cyclize; presumably, the isomerization of a primary alkyllithium to an unstabilized secondary species is energetically too costly.[14] Nevertheless, it seemed worthwhile to explore the feasibility of constructing a bicyclic system by tandem cyclization involving a transient secondary alkyllithium since the secondary species, if generated, would undoubtedly isomerize rapidly by 5-*exo-trig* cyclization to give a more stable primary alkyllithium product.

To this end, 5,10-undecadienyllithium (**11**) was prepared in the usual way, as shown below, by low-temperature exchange between *t*-BuLi and 11-iodo-1,6-undecadiene (**12**; $Z/E$ = 78/22). A series of experiments in which solutions of **11** were allowed to stand at room temperature in the presence of TMEDA (or other Lewis bases known to facilitate cyclization such as PMDTA and THF)[3] for periods of 1–3 h revealed no evidence of cyclization. Moreover,




**12** **11**

the relative proportions of (*E*)- and (*Z*)-**11** do not change during the course of these experiments; the 1,6-undecadiene recovered after the quench of such reaction mixtures was found to have the same cis-rich isomeric composition ($Z/E \approx 80/20$) as the precursor iodide. These observations indicate that tandem cyclization of diolefinic alkyllithiums may be confined to situations involving primary organolithium intermediates. We are, however, currently exploring the possibility of effecting tandem isomerizations of substrates in which an intermediate secondary alkyllithium is stabilized by a moderately electron-withdrawing substituent.[14]

## Conclusions

The results described above demonstrate that the stereocontrol inherent in the totally regiospecific 5-*exo-trig* isomerizations of substituted 5-hexenyllithiums may be exploited for the stereoselective synthesis of bicyclic systems by tandem cyclization of acyclic diolefinic alkyllithiums. Four features of the methodology are worthy of note. (1) The initial C–Li bond may be easily and cleanly generated at low temperature by lithium–iodine exchange between *t*-BuLi and a readily available diolefinic alkyl iodide. (2) The favorable thermodynamics associated with the ring closures allows preparation of relatively unstable molecular frameworks in a highly stereoselective fashion. (3) The tandem cyclizations are clean and highly efficient processes; the bicyclic organolithiums are readily functionalized by reaction with an electrophile, and pure product may be easily isolated in good yield by simple chromatography or short-path distillation. (4) The unsuccessful attempt to effect tandem cyclization mediated by a secondary alkyllithium underscores the often complementary utility of anionic and radical based approaches to cyclic systems.

In summary, the results presented above and those contained in our preliminary communication[4] indicate that tandem anionic cyclization provides a convenient and selective route to a variety of molecular frameworks that are not readily available by more traditional approaches.

## Experimental Section

**General Procedures.** Instrumental and chromatographic procedures, methods used for the purification of solvents, and precautions regarding the preparation and manipulation of organolithiums have been previously reported.[3]

Literature procedures were followed for the preparation of *cis*-1-ethenyl-3-methylcyclopentane,[3] *cis*-1-ethenyl-3-(iodomethyl)cyclopentane[3] (**1**), and authentic samples of *endo*- and *exo*-2-methylbicyclo[2.2.1]heptane.[15]

**3-Ethenylhex-5-en-1-ol.** A suspension of 1.40 g (35.2 mmol) of oil-free potassium hydride in 20.0 mL of dry THF was stirred at room temperature, and 7.50 mL (35.2 mmol) of dry 1,1,1,3,3,3-hexamethyldisilazane was added slowly over a period of 15 min. The resulting turbid solution was stirred at room temperature until evolution of hydrogen ceased. In a separate three-necked flask, 12.6 g (35.3 mmol) of methyltriphenylphosphonium bromide and 100 mL of dry THF were placed under an atmosphere of nitrogen. The flask was cooled to 0 °C in an ice bath, and the solution of potassium hexamethyldisilazide (KHMDS) in THF was added dropwise using a Teflon-brand cannula. The resulting yellow suspension was stirred at 0 °C for 15 min and at room temperature for 1 h. The mixture was then recooled to 0 °C, and a solution of 1.40 g (11.0 mmol) of 3-(2-propenyl)-2,3,4,5-tetrahydrofuran-2-ol,[16] prepared by reduction of α-allyl-γ-butyrolactone[17] with diisobutylaluminum hydride in toluene, in 10 mL of dry THF was added slowly over a period of 1.5 h. The reaction mixture was stirred for an additional hour at 0 °C and then poured into 75 mL of 10% aqueous hydrochloric acid. The organic layer was separated, and the aqueous layer was extracted with two 50-mL portions of fresh diethyl ether. The combined organic extracts were washed with saturated aqueous sodium bicarbonate solution and brine and then dried ($MgSO_4$). Solvents were removed under reduced pressure to give an oil to which pentane (ca. 50 mL) was added, and the flask was left in the refrigerator overnight. The mixture was filtered to remove the triphenylphosphine oxide, and the filtrate was concentrated by rotary evaporation. The residue was purified by flash chromatography on silica gel (25% ethyl acetate–hexanes as eluent) to give 1.20 g (65%) of the title alcohol: $R_f$ 0.12 (25% ethyl acetate–hexanes); $^1$H NMR δ 5.88–5.54 (m, 2 H), 5.12–4.94 (m, 4 H), 3.59 (m, 2 H), 2.33–1.42 (complex pattern, 6 H); $^{13}$C NMR δ 142.04 (*C*H=CH$_2$ or C(5)), 136.48 (C(5) or *C*H=CH$_2$), 115.99 (CH=*C*H$_2$ or C(6)), 114.83 (C(6) or CH=*C*H$_2$), 60.86 (C(1)), 40.56 (C(3)), 39.55 (C(2)), 36.83 (C(4)). Mass spectroscopic molecular weight calcd for $C_8H_{12}$ ($M^+ - H_2O$) 108.0939, found 108.0940.

**3-(2-Iodoethyl)-1,5-hexadiene (5).** Following the general procedure of Crossland and Servis,[18] 1.35 g (10.8 mmol) of 3-ethenylhex-5-en-1-ol was converted to its mesylate. The crude mesylate was added to a solution of 3.30 g (22.0 mmol) of dry sodium iodide in 33.0 mL of anhydrous acetone, and the mixture was stirred at room temperature under an atmosphere of nitrogen for 16 h. Inorganic salts were then removed by filtration, and the filtrate was concentrated by rotary evaporation. The residue was taken up in 50 mL of pentane, and the solution was washed successively with 10% aqueous sodium thiosulfate, water, and brine. After the solution was dried ($MgSO_4$) pentane was removed, and the residue was purified by flash chromatography using hexanes as eluent to afford 1.85 g (73%) of the title iodide: $R_f$ 0.43 (hexanes); $^1$H NMR δ 5.83–5.45 (m, 2 H), 5.16–4.94 (m, 4 H), 3.29–3.00 (m, 2 H), 2.29–1.58 (complex pattern, 5 H); $^{13}$C NMR δ 140.47 (C(2) or C(5)), 136.19 (C(5) or C(2)), 116.56 (C(1) or C(6)), 116.19 (C(6) or C(1)), 44.50 (C(4)), 39.16 (C(3)), 37.71 (*C*H$_2$CH$_2$I), 5.05 (CH$_2$I). Mass spectroscopic molecular weight calcd for $C_5H_8I$ ($M^+ - C_3H_5$) 194.9671, found 194.9668.

**4-Ethenyl-6-hepten-1-ol.** A solution of KHMDS in THF, prepared as described above from 11.1 mL (52.8 mmol) of dry 1,1,1,3,3,3-hexamethyldisilazane, 2.12 g (52.8 mmol) of oil-free potassium hydride, and 33.0 mL of dry THF, was added dropwise via a Teflon brand cannula

(14) For a discussion of this point, see ref 3 and references contained therein. More recently, we have found that attachment of a moderately activating group such as phenyl, trimethylsilyl, cyclopropyl, or vinyl to the terminal C(6) carbon of a 5-hexenyllithium serves to facilitate the cyclization. Thus, for example, [6-(trimethylsilyl)-5-hexenyl]lithium readily isomerizes to [(trimethylsilyl)cyclopentylmethyl]lithium at temperatures well below ambient. The ease with which such terminally substituted 5-hexenyllithiums undergo cyclization is undoubtedly a consequence of the ability of the substituents to stabilize the resulting organometallic. It remains to be seen whether such substituents can be used to advantage in tandem cyclization strategies. It might be noted in this connection that highly stabilized organometallics, such as those produced in Michael-type ring closures of 5-hexenyllithiums bearing a strongly electron-withdrawing group at C(6), have little or no propensity for further cyclization. See, for example: ref 1c and Cooke, M. P., Jr.; Widener, R. K. *J. Org. Chem.* **1987**, *52*, 1381.

(15) Holder, R. W.; Matturro, M. G. *J. Org. Chem.* **1977**, *42*, 2166.

(16) (a) Jalali, M.; Boussac, G.; Lallemand, J. Y. *Tetrahedron Lett.* **1983**, *24*, 4307. (b) Jalali-Naini, M.; Lallemand, J. Y. *Tetrahedron Lett.* **1986**, *27*, 497.

(17) Posner, G. H.; Loomis, G. L. *J. Chem. Soc., Chem. Commun.* **1972**, 892.

(18) Crossland, R. K.; Servis, K. L. *J. Org. Chem.* **1970**, *35*, 3195.

to 18.8 g (52.8 mmol) of methyltriphenylphosphonium bromide in 150 mL of dry THF. The yellow suspension was stirred at room temperature for 0.5 h and then recooled to 0 °C, and a solution of 3.00 g (21.1 mmol) of 3-(2-propenyl)-2,3,4,5,6-pentahydropyran-2-ol,[16] prepared by diisobutylaluminum hydride reduction of α-allyl-δ-valerolactone,[19] in 10 mL of dry THF was added. The light yellow slurry was stirred overnight at room temperature and then poured into 75 mL of cold, 10% aqueous hydrochloric acid and worked up as described above. The residue was purified by flash chromatography on silica gel (20% ethyl acetate–hexanes as eluent) to give 2.10 g (69%) of the pure title alcohol: $R_f$ 0.14 (20% ethyl acetate–hexanes); IR (neat) 3331, 3076, 1641, 1420, 1058, 995, 912 cm$^{-1}$; $^1$H NMR δ 5.82–5.50 (m, 2 H), 5.03–4.93 (m, 4 H), 3.61 (t, $J$ = 6.40 Hz, 2 H), 2.18–1.99 (m, 3 H), 1.68–1.17 [overlapping patterns, i.e., 1.68–1.17 (m, 4 H) and 1.30 (br s, 1 H, exchanges with $D_2O$)]; $^{13}$C NMR δ 142.28 ($CH_2$=*C*H or C(7)), 136.84 (C(7) or $CH_2$=*C*H), 115.80 (*C*$H_2$=CH or C(6)), 114.62 (C(6) or *C*$H_2$=CH), 62.94 (C(1)), 43.52 (C(4)), 39.52 (C(3)), 30.30 (C(5)), 30.18 (C(2)). Anal. Calcd for $C_9H_{16}O$: C, 77.09; H, 11.50. Found: C, 76.71; H, 11.84.

**7-Iodo-4-ethenyl-1-heptene (9).** The crude mesylate prepared from 2.50 g (17.8 mmol) of 4-ethenylhept-6-en-1-ol was added to a solution of 5.30 g (35.4 mmol) of dry sodium iodide in 50 mL of dry acetone, and the mixture was stirred at room temperature under a nitrogen atmosphere for 9 h followed by heating at gentle reflux for 1 h. The reaction mixture was cooled, inorganic salts were removed by filtration, and the filtrate was concentrated by rotary evaporation. The residue was taken up in 50 mL of *n*-pentane and washed successively with 10% aqueous sodium thiosulfate solution and brine. After the solution was dried ($MgSO_4$), the solvent was evaporated to afford an oil which was purified by flash chromatography on silica gel (pentane as eluent) to yield 3.40 g (76%) of the title iodide: $R_f$ 0.37 (*n*-pentane); IR (neat) 3076, 1641, 1424, 1175, 994, 914 cm$^{-1}$; $^1$H NMR δ 5.82–5.49 (m, 2 H), 5.09–4.91 (m, 4 H), 3.22–3.09 (m, 12 lines, 2 H), 2.17–2.00 (m, 3 H), 1.94–1.24 (m, 4 H); $^{13}$C NMR δ 141.77 ($CH_2$=*C*H or C(2)), 136.44 (C(2) or $CH_2$=*C*H), 115.97 (*C*$H_2$=CH or C(1)), 114.88 (*C*$H_2$=CH or C(1)), 42.83 (C(4)), 39.39 (C(3)), 34.86 (C(6)), 31.12 (C(5)), 6.93 (C(7)). Anal. Calcd for $C_9H_{15}I$: C, 43.22; H, 6.05. Found: C, 43.38; H, 6.23.

**General Procedure for Tandem Cyclization of Diolefinic Alkyllithiums.** An approximately 0.1 M solution of the appropriate iodide in *n*-pentane–diethyl ether (3:2 by volume for iodides **5** and **12** and 9:1 by volume for iodide **9**) was cooled to −78 °C under an atmosphere of dry, oxygen-free argon, and 2.2 equiv of a solution of *t*-BuLi in pentane (Aldrich) was added dropwise over a period of 5 min. The reaction mixture was stirred at −78 °C for 5 min, and 2.2 equiv of dry, deoxygenated TMEDA was then added dropwise via syringe. The addition of TMEDA resulted in the formation of a thick, pale yellow precipitate. After the mixture was stirred for 5 min at −78 °C, the cooling bath was removed and the reaction mixture was allowed to warm. When the internal temperature of the reaction mixture reached 0 °C (~6 min for a 0.5–2-mmol scale reaction), the flask was immersed in an ice bath for a further period of time [4 min in the case of organolithium **4** (Scheme II) and 24 min in the case of **6** (Scheme III)] to complete the isomerization. Functionalization of the resulting bicyclic alkyllithium was accomplished by recooling the reaction mixture to −78 °C, adding an excess (typically 2 equiv) of the appropriate electrophile (Tables I and III), and allowing the mixture to warm to room temperature. The reaction mixtures were worked up in the usual manner,[20] and the products were purified by flash chromatography or short-path distillation. Exploratory cyclizations (Table II) were conducted in the same manner, and product mixtures were analyzed by capillary GC on a 25-m × 0.2-mm cross-linked methyl silicone column.

***endo*-2-Methylbicyclo[2.2.1]heptane.** A solution of **3**, prepared from 40.8 mg (0.17 mmol) of **5** as described above, was quenched with 1 mL of dry, deoxygenated methanol. The product mixture was washed with water and dried ($MgSO_4$). Analysis of the reaction mixture by capillary GC and GC/MS revealed that the title hydrocarbon, which was identified by coinjection with an authentic sample[9] as well as by comparison of MS fragmentation patterns, had been formed in 89% yield. The methyl-*d* compound, prepared in 84% yield by quench of **3** with MeOD, was found by GC/MS to have a *d* content of 89%.

***endo*-2-Bicyclo[2.2.1]heptylacetic Acid.** A solution of **3**, prepared as described above from 117.9 mg (0.50 mmol) of **5**, was recooled to −78 °C and added via a Teflon-brand cannula to a flask containing excess powdered dry ice covered with dry diethyl ether. The reaction mixture was warmed to room temperature with stirring and then poured into 2.5 mL of aqueous hydrochloric acid. The organic layer was separated, washed once with water, dried ($MgSO_4$), and concentrated by rotary evaporation to give 50.0 mg (65%) of the known[21,22] title acid as an oil: IR (neat) 3431–2764, 1708, 1413, 1298, 943 cm$^{-1}$; $^1$H NMR δ 2.41–2.14 (m, 4 H), 1.91–1.77 (m, 1 H), 1.60–1.04 (m, 7 H), 0.73–0.63 (m, 1 H); $^{13}$C NMR δ 180.29, 40.11, 39.75, 37.33, 37.09, 36.62, 36.17, 29.96, 22.58.

**2-(*endo*-2-Bicyclo[2.2.1]heptyl)ethanol.** A solution of **3**, prepared as described above from 146.0 mg (0.62 mmol) of **5**, was recooled to −78 °C, and a suspension of 70.0 mg (2.33 mmol) of dry paraformaldehyde in 0.5 mL of dry diethyl ether was added. The cooling bath was removed, and the reaction mixture was allowed to warm to room temperature over a period of 0.5 h and then poured into 2.5 mL of saturated, aqueous ammonium chloride. The organic layer was separated, washed with water, and dried ($MgSO_4$). Evaporation of the volatile components at reduced pressure gave the crude alcohol which was purified by flash chromatography on silica gel (15% ethyl acetate–hexanes as eluent) to afford 64.1 mg (74%) of the known[23,24] alcohol: $R_f$ 0.15 (15% ethyl acetate–hexanes); IR (neat) 3353, 1452, 1045, 1018 cm$^{-1}$; $^1$H NMR δ 3.62 (t, $J$ = 6.98 Hz, 2 H), 2.23–1.02 (series of m, 13 H), 0.72–0.58 (m, 1 H); $^{13}$C NMR δ 62.61, 40.02, 39.91, 37.04, 36.95, 36.36, 36.05, 30.15, 22.51.

***endo*-2-Bicyclo[2.2.1]heptylacetaldehyde.** A solution of **3**, prepared from 200.1 mg (0.85 mmol) of **5** as described above, was recooled to −78 °C, and 0.13 mL (1.70 mmol) of dry dimethylformamide was added via syringe. The reaction mixture was allowed to warm to room temperature, and it was then added to 5 mL of saturated, aqueous ammonium chloride. The organic layer was separated and dried ($MgSO_4$), and the solvents were removed by rotary evaporation to afford an oil. Purification by flash chromatography on silica gel (15% ethyl acetate–hexanes) gave 84.5 mg (72%) of the known[21] aldehyde: $R_f$ 0.33 (15% ethyl acetate–hexanes); IR (neat) 2870, 1725, 1453 cm$^{-1}$; $^1$H NMR δ 9.74 (t, $J$ = 2.11 Hz, 1 H), 2.61–1.02 (series of m, 12 H), 0.72–0.59 (m, 1 H); $^{13}$C NMR δ 202.80, 47.33, 40.09, 39.72, 36.96, 36.65, 34.01, 29.90, 22.63.

**1-(*endo*-2-Bicyclo[2.2.1]heptyl)-3,3-dimethylbutan-2-ol.** A solution of **3**, prepared as described above from 245.0 mg (1.04 mmol) of **5**, was recooled to −78 °C, and 0.23 mL (2.08 mmol) of freshly distilled trimethylacetaldehyde was added dropwise via syringe. The reaction mixture was then allowed to warm to room temperature with stirring and poured into 5.0 mL of saturated, aqueous ammonium chloride. The organic layer was separated and dried ($MgSO_4$), and the solvents were removed by evaporation. The residue was purified by flash chromatography on silica gel (15% ethyl acetate–hexanes as eluent) to afford 162.9 mg (80%) of the title alcohol as an approximately 1:1 mixture of diastereomers: $R_f$ 0.35 (15% ethyl acetate–hexanes); IR 3385, 1364, 1464, 1077, 1005 cm$^{-1}$; $^1$H NMR (two diastereomers) δ 3.20–3.14 (m, 8 lines, 2 H); 2.24–1.00 (series of m, 26 H), 0.88 (s, 9 H), 0.89 (s, 9 H), 0.67–0.50 (m, 2 H); $^{13}$C NMR (two diastereomers; several of the resonances are common to both diastereomers) δ 79.17, 79.02, 41.31, 40.17, 39.81, 38.91, 37.60, 37.17, 36.82, 36.62, 34.93, 34.09, 30.30, 25.71, 22.85, 22.35. Anal. Calcd for $C_{13}H_{24}O$: C, 79.53; H, 12.32. Found: C, 79.95; H, 12.69.

***endo*-2-(Bromomethyl)bicyclo[2.2.1]heptane.** A solution of **3**, prepared as described above from 237.8 mg (1.01 mmol) of **5**, was added slowly, dropwise via a Teflon-brand cannula to a −78 °C solution of 0.17 mL (2.00 mmol) of dry 1,2-dibromoethane in 4.00 mL of dry *n*-pentane. The reaction mixture was allowed to warm slowly to room temperature and then poured into 5.0 mL of saturated, aqueous ammonium chloride. The organic phase was separated and dried ($MgSO_4$), and the solvents were removed by rotary evaporation to afford an oil. Purification by flash chromatography on silica gel (*n*-pentane as eluent) gave 143.1 mg (75%) of the known bromide:[25] $R_f$ 0.45 (*n*-pentane); $^1$H NMR δ 3.49–3.28 (m, 2 H), 2.37–2.20 (m, 3 H), 1.87–1.04 (m, 7 H), 0.74–0.63 (m, 1 H); $^{13}$C NMR δ 42.93, 39.81, 39.85, 37.51, 36.83, 36.69, 29.84, 21.92.

***endo*-2-[(Trimethylsilyl)methyl]bicyclo[2.2.1]heptane.** A solution of **3**, prepared as described above from 224.4 mg (0.95 mmol) of **5**, was recooled to −78 °C, and 0.24 mL (1.90 mmol) of freshly distilled chlorotrimethylsilane was added dropwise via syringe. The reaction mixture was allowed to warm to room temperature and then poured into 5.0 mL of saturated, aqueous sodium bicarbonate. The organic layer was separated and dried ($MgSO_4$), and the solvents were carefully removed by rotary evaporation. The crude organosilane was purified by flash chro-

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matography on silica gel (*n*-pentane as eluent) to give 140.4 mg (81%) of the pure title compound: $R_f$ 0.58 (*n*-pentane); IR 1248, 861, 841, 690 $cm^{-1}$; $^1H$ NMR $\delta$ 2.14–1.01 (series of m, 10 H), 0.46–0.57 [overlapping patterns, i.e., 0.56 (d, $J$ = 7.20 Hz, 2 H) and 0.60–0.46 (m, 1 H)], –0.03 (s, 9 H); $^{13}C$ NMR $\delta$ 42.87, 39.98, 39.78, 37.66, 36.08, 30.46, 22.11, 20.56, –0.83. Mass spectroscopic molecular weight calcd for $C_{11}H_{22}Si$ 182.1491, found 182.1489.

***endo*-2-[(Tributylstannyl)methyl]bicyclo[2.2.1]heptane.** A solution of **3**, prepared from 127.4 mg (0.54 mmol) of **5**, was recooled to –78 °C, and 0.29 mL (1.08 mmol) of freshly distilled tributyltin chloride was added dropwise. The reaction mixture was allowed to warm to room temperature with stirring and then poured into 5.0 mL of saturated, aqueous sodium bicarbonate. The organic layer was separated and dried ($MgSO_4$), and the solvents were removed by rotary evaporation to afford an oil. It did not prove possible to purify the organotin compound by flash chromatography, and for this reason the entire reaction product was purified by preparative GC (9 ft, 15% SE-30 on Chromosorb W; 190 °C isothermal) to give 152.6 mg (71%) of the pure title compound: $^1H$ NMR $\delta$ 2.13–0.66 [overlapping patterns, i.e., 2.13–0.66 (series of m, 30 H), 0.88 (t, $J$ = 7.19 Hz, 9 H)], 0.51–0.41 (m, 1 H); $^{13}C$ NMR $\delta$ 43.47, 40.73, 40.42, 38.55, 38.03, 30.56, 29.36, 27.53, 21.83, 13.77, 13.18, 9.14. Mass spectroscopic molecular weight calcd for $C_{16}H_{31}Sn$ ($M^+ - C_4H_9$) 343.1448, found 343.1440.

**3-Ethyl-1,5-hexadiene.** A solution of 239.3 mg (1.01 mmol) of 3-(2-iodoethyl)-1,5-hexadiene (**5**) in a mixture of 6.0 mL of *n*-pentane and 4.0 mL of diethyl ether was cooled to –78 °C, and 0.81 mL of a 2.75 M solution of *t*-BuLi (2.23 mmol) in *n*-pentane was added dropwise over a period of 5 min. The reaction mixture was stirred at –78 °C for 5 min and then quenched at –78 °C by addition of 1 mL of deoxygenated methanol. GC analysis of the reaction mixture revealed that the title diene had been produced in virtually quantitative yield. The product mixture was washed with water, dried ($MgSO_4$), and carefully concentrated on a rotary evaporator. A sample of the previously reported diene[26] was collected by preparative GC (10 ft, 15% SE-30 on Chromosorb W; 60 °C isothermal): $^1H$ NMR $\delta$ 5.88–5.50 (m, 2 H), 5.13–4.88 (m, 4 H), 2.21–1.92 (m, 3 H), 1.63–1.17 (m, 2 H), 0.86 (t, $J$ = 7.38 Hz, 3 H); $^{13}C$ NMR $\delta$ 142.45 (C(2) or C(5)), 137.18 (C(5) or C(2)), 115.50 (C(1) or C(6)), 114.30 (C(6) or C(1)), 45.38 (C(3)), 39.11 (C(4)), 26.94 ($CH_2CH_3$), 11.49 ($CH_2CH_3$).

**3-Methyl-*trans*-bicyclo[3.3.0]octane (10).** A solution of **8**, prepared from 256.1 mg (1.024 mmol) of **9** as described above, was recooled to –78 °C, and 1 mL of dry, deoxygenated methanol was added. The reaction mixture was allowed to warm to room temperature, and then the product mixture was washed with water, dried ($MgSO_4$), and analyzed by gas–liquid chromatography. Analysis revealed that the title hydrocarbon had been formed in 87% yield. An analytical sample of 3-methyl-*trans*-bicyclo[3.3.0]octane was obtained by washing the crude reaction mixture with several portions of concentrated sulfuric acid to remove alkene and diethyl ether, followed by sequential washing of the pentane extract with saturated, aqueous sodium bicarbonate solution and water. The organic extract was dried ($MgSO_4$), and the solvent was carefully removed by rotary evaporation to give pure title hydrocarbon: $^1H$ NMR $\delta$ 2.62–2.44 (m, 1 H), 2.08–0.60 [overlapping patterns, i.e., 2.08–0.60 (m, 12 H), 1.02 (d, $J$ = 7.05 Hz, 3 H)]; $^{13}C$ NMR (500 MHz) $\delta$ 54.96 (CH), 52.73 (CH), 39.26 (CH), 36.87 ($CH_2$), 34.80 ($CH_2$), 29.59 ($CH_2$), 26.47 ($CH_2$), 26.45 ($CH_2$), 23.59 ($CH_3$). Mass spectroscopic molecular weight calcd for $C_9H_{16}$ 124.1252, found 124.1255. The methyl-*d* compound, prepared in an analogous manner using MeOD to quench the reaction mixture, was found by GC/MS analysis to have *d* content of 88%.

***trans*-3-Bicyclo[3.3.0]octylacetic Acid.** A solution of **8**, prepared from 261.2 mg (1.04 mmol) of **9**, was recooled to –78 °C, and dry carbon dioxide gas was bubbled through the solution for 10 min using a Teflon-brand cannula. The solution was allowed to warm to room temperature over a period of 0.5 h and then poured into 10 mL of 10% aqueous hydrochloric acid. The organic phase was separated, washed with water, and dried ($MgSO_4$), and solvent was removed to give almost pure title carboxylic acid as a white solid. Purification by flash chromatography on silica gel (25% diethyl ether–hexanes) afforded 124.1 mg (71%) of pure acid: $R_f$ 0.32 (25% diethyl ether–hexanes); mp 78–80 °C; IR (KBr pellet) 3333–2453, 1702, 1429, 1406, 1216, 920 $cm^{-1}$; $^1H$ NMR $\delta$ 2.96–2.78 (m, 1 H), 2.41 (d, $J$ = 7.79 Hz, 2 H), 2.14–1.86 (m, 3 H), 1.72–0.72 (series of m, 9 H); $^{13}C$ NMR $\delta$ 179.69, 54.23, 52.81, 42.08, 40.83, 34.54, 32.58, 29.46, 26.28 (two carbons). Mass spectroscopic molecular weight calcd for $C_{10}H_{16}O_2$ 168.1150, found 168.1142.

***trans*-3-Bicyclo[3.3.0]octylacetaldehyde.** A solution of **8**, prepared from 240.6 mg (0.96 mmol) of **9**, was recooled to –78 °C, and 0.15 mL (1.92 mmol) of dry, freshly distilled dimethylformamide was added via syringe. The cooling bath was removed, and the reaction mixture was stirred as it warmed to room temperature. The mixture was poured into 5 mL of saturated, aqueous ammonium chloride and worked up in the usual manner to give, after purification by flash chromatography on silica gel (15% ethyl acetate–hexanes), 115.5 mg (79%) of the pure aldehyde: $R_f$ 0.46 (25% ethyl acetate–hexanes; IR (neat) 2862, 1686, 1398, 920 $cm^{-1}$; $^1H$ NMR $\delta$ 9.72 (t, $J$ = 2.12 Hz, 1 H), 3.00–2.88 (m, 1 H), 2.53 and 2.50 (AB portion of ABX pattern, $J_{AX} = J_{BX}$ = 2.12 Hz, $J_{AB}$ = 7.48 Hz, 2 H), 2.11–1.89 (m, 3 H), 1.72–0.72 (series of m, 9 H); $^{13}C$ NMR $\delta$ 202.59, 54.27, 52.85, 52.09, 38.55, 34.68, 32.59, 29.42, 26.19 (two carbons). Mass spectroscopic molecular weight calcd for $C_{10}H_{16}O$ 152.1201, found 152.1199.

**2-(*trans*-3-Bicyclo[3.3.0]octyl)ethanol.** A solution of **8**, prepared from 348.8 mg (1.39 mmol) of **9**, was recooled to –78 °C, and a suspension of ca. 83 mg (~2.80 mmol) of dry paraformaldehyde in 1 mL of dry *n*-pentane was added via syringe. The cooling bath was removed, and the reaction mixture was allowed to warm to room temperature. After being stirred at room temperature for 1 h, the reaction mixture was poured into 5 mL of saturated, aqueous ammonium chloride. The organic phase was separated, washed with water, and dried ($MgSO_4$), and the solvents were removed by rotary evaporation. The residue was purified by flash chromatography on silica gel (25% ethyl acetate–hexanes as eluent) to afford 154.2 mg (72%) of the title alcohol: $R_f$ 0.18 (25% ethyl acetate–hexanes); IR (neat) 3333, 1451, 1049, 731 $cm^{-1}$; $^1H$ NMR $\delta$ 3.56 (t, $J$ = 6.98 Hz, 2 H), 2.57–2.40 (m, 1 H), 2.29 (br s, 1 H), 2.07–1.91 (m, 2 H), 1.89–1.76 (m, 1 H), 1.68–1.43 (complex m, 6 H), 1.37–1.19 (m, 2 H), 1.11–0.91 (m, 2 H), 0.78–0.64 (m, 1 H); $^{13}C$ NMR $\delta$ 61.73, 54.16, 52.83, 41.18 (two carbons), 34.95, 32.64, 29.44, 26.36, 26.32. Mass spectroscopic molecular weight calcd for $C_{10}H_{16}$ ($M^+ - H_2O$) 136.1252, found 136.1251.

**1-(3-*trans*-Bicyclo[3.3.0]octyl)-3,3-dimethylbutan-2-ol.** A solution of **8**, prepared from 237.9 mg (0.95 mmol) of **9**, was recooled to –78 °C, and 0.21 mL (1.90 mmol) of freshly distilled trimethylacetaldehyde was added via syringe. The reaction mixture was then warmed to room temperature, with stirring, over a period of 0.5 h and poured into 5 mL of saturated, aqueous ammonium chloride. The organic layer was separated, washed with water, and dried ($MgSO_4$), and the solvents were removed by rotary evaporation. The residue was purified by flash chromatography on silica gel (10% ethyl acetate–hexanes as eluent) to afford 161.8 mg (81%) of the title alcohol as a mixture of diastereomers: $R_f$ 0.38 (10% ethyl acetate–hexanes); mp 59–61 °C; IR (KBr pellet) 3325, 1461, 1360, 1074, 1004 $cm^{-1}$; $^1H$ NMR $\delta$ 3.26–3.15 (m, 1 H), 2.79–2.58 (m, 1 H), 2.06–1.84 (m, 3 H), 1.70–1.22 (m, 9 H), 1.14–0.61 [overlapping patterns, i.e., 1.14–0.61 (m, 3 H), 0.88 (s, 9 H)]; $^{13}C$ NMR (two diastereomers) $\delta$ 78.81, 78.07, 54.33, 54.03, 52.89, 52.81, 41.96, 41.82, 40.41, 39.98, 35.89, 34.82, 34.66, 33.81, 31.81, 29.48, 26.47, 25.70. Mass spectroscopic molecular weight calcd for $C_{10}H_{17}O$ ($M^+ - C_4H_9$) 153.1279, found 153.1276.

**1-(*trans*-3-Bicyclo[3.3.0]octyl)propan-2-ol.** A solution of **8**, prepared from 264.8 mg (1.06 mmol) of **9**, was cooled to –78 °C, and 0.12 mL (2.12 mmol) of freshly distilled acetaldehyde was added via syringe. The reaction mixture was then warmed to room temperature and poured into 5 mL of saturated, aqueous ammonium chloride. The organic layer was separated, washed with water, and dried ($MgSO_4$), and the solvents were removed by rotary evaporation. The residue was purified by flash chromatography on silica gel (10% ethyl acetate–hexanes as eluent) to afford 130.5 mg (73%) of the title alcohol as a mixture of diastereomers: $R_f$ 0.14 (10% ethyl acetate–hexanes); IR (neat) 3340, 1451, 1368, 1118, 1049, 936 $cm^{-1}$; $^1H$ NMR $\delta$ 3.82–3.71 (m, 1 H), 2.64–2.46 (m, 1 H), 2.04–0.92 [overlapping patterns, i.e., 2.04–0.92 (m, 14 H), 1.15 (d, $J$ = 6.19 Hz, 3 H)], 0.78–0.65 (m, 1 H); $^{13}C$ NMR (two diastereomers) $\delta$ 66.95, 66.84, 54.15, 52.90, 52.81, 48.09, 48.01, 41.53, 41.48, 35.28, 35.04, 33.01, 32.56, 29.46, 26.41, 26.37, 23.89, 23.69. Mass spectroscopic molecular weight calcd for $C_{11}H_{18}$ ($M^+ - H_2O$) 150.1409, found 150.1406.

**3-[(Trimethylsilyl)methyl]-*trans*-bicyclo[3.3.0]octane.** A solution of **8**, prepared from 273.1 mg (1.10 mmol) of **9**, was recooled to –78 °C, and 0.28 mL (2.20 mmol) of freshly distilled chlorotrimethylsilane was added via syringe. The reaction mixture was allowed to warm to room temperature and then poured into 5 mL of saturated, aqueous sodium bicarbonate. The organic phase was separated, washed with water, and dried ($MgSO_4$), and the solvents were removed by rotary evaporation to afford a virtually pure TMS derivative. Purification by column chromatography on silica gel (hexanes as eluent) gave 168.2 mg (78%) of the title organosilane: $R_f$ 0.57 (hexanes); $^1H$ NMR $\delta$ 2.62–2.46 (m, 1 H), 2.05–0.94 (complex m, 12 H), 0.74 (d, $J$ = 7.71 Hz, 2 H), –0.022 (s, 9 H); $^{13}C$ NMR $\delta$ 54.75, 52.96, 41.12, 38.83, 36.57, 29.40, 27.44, 26.66, 26.55, –0.68. Mass spectroscopic molecular weight calcd for $C_{12}H_{24}Si$ 196.1647, found 196.1638.

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**3-(Iodomethyl)-*trans*-bicyclo[3.3.0]octane.** A solution of **8** was prepared from 130.6 mg (0.52 mmol) of **9** as described above. In another flask, a solution of 0.26 g (1.00 mmol) of iodine in 5 mL of dry diethyl ether was cooled to −78 °C under an atmosphere of argon. The solution of **6** was then added dropwise to the iodine solution via a Teflon-brand cannula. The reaction mixture was stirred at −78 °C for 0.5 h and then warmed to room temperature and poured into 5 mL of 10% aqueous sodium thiosulfate. The organic phase was separated, washed with water, and dried ($MgSO_4$), and the solvents were removed by rotary evaporation. The residue was purified by column chromatography on silica gel using hexanes as eluent to obtain 84.9 mg (65%) of the pure iodide: $R_f$ 0.45 (hexanes); $^1$H NMR δ 3.24 (d, $J$ = 7.12 Hz, 2 H), 2.87–2.71 (m, 1 H), 2.13–1.90 (m, 3 H), 1.73–0.74 (m, 9 H); $^{13}$C NMR δ 54.47, 52.64, 47.79, 36.22, 33.93, 29.22, 26.34, 26.31, 16.43. Mass spectroscopic molecular weight calcd for $C_9H_{15}I$ 250.0221, found 250.0202.

**Cyclization and Trapping of [(*cis*-3-Ethenylcyclopentyl)methyl]lithium (2) (Scheme I).** An approximately 0.1 M solution of *cis*-1-ethenyl-3-(iodomethyl)cyclopentane (**1**) in *n*-pentane–diethyl ether (3:2 by volume) was prepared at −78 °C by lithium–iodine exchange following the procedure described above. TMEDA (2.2 equiv) was then added, the mixture was stirred for 5 min at −78 °C, and the cooling bath was removed. The reaction mixture was allowed to warm to approximately 10 °C to complete the isomerization of **2** (Scheme I), and functionalization of **3** was accomplished as described above for the case of tandem cyclizations.

Quench of such a reaction mixture with methanol gave *endo*-2-methylbicyclo[2.2.1]heptane in 91% yield (Scheme I and ref 3). Trapping of **3** with dry paraformaldehyde gave 2-(*endo*-2-bicyclo[2.2.1]-heptyl)ethanol in 63% isolated yield (Scheme I): the material was identical in all respects to the sample described above which was prepared by tandem cyclization of **4**.

**1-(*endo*-2-Bicyclo[2.2.1]heptyl)propan-2-ol.** A solution of **2**, prepared as described above from 216.0 mg (0.91 mmol) of **1**, was recooled to −78 °C, and 1 mL of freshly distilled acetaldehyde was added via syringe. The reaction mixture was allowed to warm to room temperature over a period of 0.5 h and then poured into 10 mL of saturated, aqueous ammonium chloride. The organic layer was separated and dried ($MgSO_4$), and the solvents were removed by rotary evaporation to afford a light yellow oil. Purification by flash chromatography on silica gel (15% ethyl acetate–hexanes) gave 106.1 mg (76%) of the pure title alcohol as an approximately 1:1 mixture of diastereomers: $R_f$ 0.21 (15% ethyl acetate–hexanes); $^1$H NMR (two diastereomers) δ 3.78 (m, 7 lines, 2 H), 2.20–1.00 [overlapping patterns, i.e., 2.20–1.00 (complex pattern, 28 H), 1.19 (d, $J$ = 6.00 Hz, 3 H), 1.18 (d, $J$ = 6.43 Hz, 3 H)], 0.65 (m, 2 H); $^{13}$C NMR (two diastereomers; several of the resonances are common to both diastereomers) δ 67.55, 67.47, 42.69, 42.38, 40.35, 39.99, 39.89, 39.76, 37.07, 37.02, 36.97, 36.46, 30.11, 23.78, 23.75, 22.53, 22.46. Mass spectroscopic molecular weight calcd for $C_{10}H_{16}$ ($M^+ - H_2O$) 136.1252, found 136.1247.

**(*Z*)- and (*E*)-5,10-Undecadien-1-ol.** To a dark red solution of 5-hexenyltriphenylphosphonium ylide, made by dropwise addition of 16.0 mL (45.0 mmol) of a 2.85 M solution of *n*-BuLi in hexanes to a suspension of 17.70 g (41.60 mmol) of 5-hexenyltriphenylphosphonium bromide (mp 164–166 °C; lit.[27] mp 165–168 °C) in 100 mL of anhydrous diethyl ether, was added 4.25 g (41.6 mmol) of 2-hydroxytetrahydropyran[28] in 10 mL of anhydrous diethyl ether. The resultant solution was stirred overnight at room temperature and then poured into 100 mL of an ice-water mixture. Solids were removed by filtration, the solution was extracted with four 50-mL portions of pentane, and the organic extracts were washed with two 50-mL portions of water. The organic phase was dried ($MgSO_4$) and concentrated to give an oil which was distilled (Kugelrohr) to give 2.58 g (37%) of a mixture of *cis*- and *trans*-5,10-undecadien-1-ols in a ratio of 80/20 as adjudged by GC analysis: bp (bath temperature) 90–95 °C (0.5-0.6 mm); IR (neat) 3335, 2997, 2934, 2867, 1654, 1442, 1065, 966, 719 cm$^{-1}$; $^1$H NMR (two isomers) δ 5.53–5.32 (m, 4 H), 3.63 (t, $J$ = 6.50 Hz, 2 H), 2.78–2.67 (m, 1 H), 2.09–1.32 (m, 12 H), 0.99–0.92 (m, 1 H); $^{13}$C NMR (two isomers; several of the resonances are common to both diastereoisomers) δ 132.35, 130.37, 129.84, 129.56, 128.14, 127.18, 125.01, 62.74, 32.59, 32.28, 32.19, 30.34, 27.29, 26.89, 26.76, 25.75, 25.71, 17.82, 13.76. Mass spectroscopic molecular weight calcd for $C_{11}H_{20}O$ ($M^+ - H_2O$) 150.1409, found 150.1406.

**(*Z*)- and (*E*)-11-Iodo-1,6-undecadiene (12).** The mesylate of an 80/20 mixture of *Z*- and *E*-isomers of 5,10-undecadien-1-ol, prepared from 1.50 g (8.90 mmol) of the alcohols, was treated in the usual way with 2.80 g (18.0 mmol) of sodium iodide in 30 mL of dry acetone to give 1.80 g (73% from the alcohols) of a 78/22 mixture of the *Z*- and *E*-isomers of the title iodide: IR (neat) 2932, 1651, 1450, 965, 724 cm$^{-1}$; $^1$H NMR (two isomers) δ 5.43–5.35 (m, 4 H), 3.18 (t, $J$ = 6.95 Hz, 2 H), 2.85–2.55 (m, 1 H), 2.09–0.93 (m, 12 H); $^{13}$C NMR (two isomers; several of the resonances are common to both diastereoisomers) δ 132.48, 130.82, 129.99, 129.33, 129.24, 128.57, 127.09, 125.13, 33.05, 32.61, 31.39, 30.45, 30.39, 27.35, 26.10, 25.95, 25.53, 17.90, 13.82, 6.82. Mass spectroscopic molecular weight calcd for $C_{11}H_{19}I$ 278.0534, found 278.0521.

**Attempted Cyclization of 5,10-Undecadienyllithium (11).** Solutions of **11** in *n*-pentane–diethyl ether were generated from **12** ($Z/E \approx 80/20$) at −78 °C following the general procedure outlined above. Various Lewis base additives, including TMEDA, PMDTA, and THF, were added to the solutions, and the mixtures were allowed to warm and stand at ambient temperature for extended periods of time before being quenched with deoxygenated methanol. No evidence for cyclization was observed, and GC analysis revealed the presence of the previously reported[29] (*E*)- and (*Z*)-1,6-undecadiene.

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