8.2 Hz, 2 H), 2.356 (s, 3 H), 2.349 (s, 3 H); IR (Ar = p-$CH_3C_6H_4$) (CH_2Cl_2) $\nu_{C=O}$ 1800 cm^{-1}. In a separate experiment, heating a sample of mesylate **14b** in trifluoroacetic acid for 2 h at 55 °C gave only p-methylacetophenone, **16**.

In a separate experiment, 8.5 mg of trifluoroacetate **15**, isolated as described above, was dissolved in 0.5 mL of trifluoroacetic acid containing 0.2 M sodium trifluoroacetate in an NMR tube. The conversion of **15** to p-methylacetophenone, **16**, was monitored by 300-MHz NMR at 25 °C by observing the appearance of the two methyl signals of **16**, which appear downfield from the methyl signals of **15**. The first-order rate constant for this process is 3.05×10^{-5} s^{-1}. After completion of the reaction an authentic sample of p-methylacetophenone was added to the NMR tube to confirm its presence.

Solvolysis of Mesylate 14b in Acetic Acid. A solution of 74 mg of **14b** in 10 mL of HOAc containing 0.05 M NaOAc and 1% acetic anhydride was heated at 70 °C for 4 h. The mixture was then taken up into ether, the solution was washed with dilute NaOH solution and saturated NaCl solution, and the organic phase was dried over $MgSO_4$. The solvent was removed on a rotary evaporator, leaving 46 mg of a clear oil. Analysis by 300-MHz NMR showed the presence of acetate **17** (Ar = p-$CH_3C_6H_4$), the elimination product **18** (Ar = p-$CH_3C_6H_4$), and p-methylacetophenone, **16**, in a 25:15:60 ratio, respectively. Hexane was added to the oil which was cooled in a freezer. A solid crystallized, and the hexanes were decanted leaving 10 mg of acetate **17** (Ar = p-$CH_3C_6H_4$): IR (Ar = p-$CH_3C_6H_4$) (CH_2Cl_2) $\nu_{C=O}$ 1760 cm^{-1}; ^1H NMR (Ar = p-$CH_3C_6H_4$) ($CDCl_3$) δ 7.71-7.62 (m, 3 H), 7.466 (t, J = 7.8 Hz, 2 H), 7.13-7.02 (AA'BB' quartet, 4 H), 2.334 (s, 3 H), 2.277 (s, 3 H), 2.139 (s, 3 H). **18**: ^1H NMR (Ar = p-$CH_3C_6H_4$) ($CDCl_3$) δ 7.695 (d, 2 H), 7.526 (t, 1 H), 7.403 (t, 2 H), 7.212 (d, 2 H), 7.069 (d, 2 H), 6.596 (s, 1 H), 5.932 (s, 1 H), 2.315 (s, 3 H). p-Methylacetophenone, **16**, formed in the acetolysis was identified by NMR spectral comparison with an authentic sample.

Solvolysis of Mesylate 14b in Trifluoroethanol. A solution of 43 mg of **14b** in 6 mL of TFE containing 40 mg of Et_3N was kept at 25 °C for 7.5 h. The solvent was then removed on a rotary evaporator, and the residue was taken up into ether. The mixture was then washed with water, dilute KOH, and saturated NaCl and dried over $MgSO_4$. The ether was removed on a rotary evaporator to give 32 mg of a mixture of ketal **19a** (96%) and the elimination product **18** (4%). **19a**: ^1H NMR (Ar = p-$CH_3C_6H_4$) ($CDCl_3$) δ 7.43-7.35 (d, 2 H), 7.24-7.16 (d, 2 H), 3.90-3.66 (m, 4 H), 2.362 (s, 3 H), 1.666 (s, 3 H).

Solvolysis of Bromide 35b in Formic Acid. A solution of 258 mg of **35b** in **17** mL of formic acid containing 0.05 M sodium formate was heated at 55 °C for 5 h. The mixture was taken up into ether, washed with water, dilute Na_2CO_3, and saturated NaCl, and dried over $MgSO_4$. The solvent was removed on a rotary evaporator, and the residue was chromatographed on 6 g of silica gel and eluted with 5% ether in hexanes. Diphenyl disulfide, **36**, eluted first (41 mg) followed by p-methylacetophenone (75 mg, 70%), and finally the thiosulfonate **37**[25] (32 mg) eluted. These products were all identified by spectral comparison with authentic samples.

In a separate experiment, the reaction of 10 mg of **35b** in 0.7 mL of formic acid containing 0.05 M sodium formate was monitored directly by 300-MHz NMR at 45 °C. p-Methylacetophenone, **16**, was observed to form at the same rate that **35b** disappeared. No buildup of an intermediate could be observed. The two diastereomers of **35b** disappeared at rates which were identical within the limits of NMR determination.

Solvolysis of Bromide 35b in Trifluoroethanol. A solution of 170 mg of **35b** in 8 mL of TFE containing 0.075 M 2,6-lutidine was heated for 5 h at 60 °C. The solvent was removed on a rotary evaporator, and the residue was taken up into ether, washed with water and saturated NaCl, and dried over $MgSO_4$. NMR analysis showed the presence of ketal **19a** and p-methylacetophenone, **16**, along with the elimination product **38** in a 2.3:1.3:1 ratio, respectively. Also present were diphenyl disulfide, **36**, and the thiosulfonate **37**. The residue was chromatographed on 7 g of silica gel and eluted with 5% ether in hexanes. The initial fraction (61 mg) contained a mixture of ketal **19a** and diphenyl disulfide, **36**, which were identified by spectral methods and by comparison of gas chromatographic retention times with those of authentic samples. p-Methylacetophenone, **16** (32 mg, 45%), eluted next, followed by **37** (22 mg). The solvent polarity was then changed to 100% ether, and the elimination product **38** (28 mg, 22%) eluted: ^1H NMR (Ar = p-$CH_3C_6H_4$) ($CDCl_3$) δ 7.47-7.27 (m, 5 H), 7.09 (s, 4 H), 6.21 (s, 1 H), 5.88 (s, 1 H), 2.31 (s, 3 H).

Solvolysis of Bromide 35b in 70% Aqueous Acetone. A solution of 144 mg of **35b** in 5 mL of 70% aqueous acetone (by volume) containing 55 mg of Et_3N was heated at 70 °C for 46 h and at 80 °C for 16 h. The solvent was removed on a rotary evaporator, and the residue was taken up into ether, washed with water, dilute HCl, and saturated NaCl solution, and dried over $MgSO_4$. After solvent removal on a rotary evaporator, the residue (102 mg) was analyzed by NMR and gas chromatography, which showed p-methylacetophenone, **16**, and the elimination product **38** in a 86 to 14 ratio, along with diphenyl disulfide, **36**.

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Preparation and Regiospecific Cyclization of Alkenyllithiums[1]

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Abstract: A two-step, one-pot sequence has been developed that provides an anionic route to functionalized carbocycles containing five- or six-membered rings. Primary alkenyllithiums, which are prepared in excellent yield by metal-halogen interchange between the appropriate iodide and t-BuLi at -78 °C, are stable at low temperature. These species have been found to undergo regiospecific, and in several instances totally stereoselective, isomerization at elevated temperature to give a five- or six-membered ring bearing a CH_2Li moiety that may be functionalized with electrophiles. The more complex behavior of secondary alkenyllithiums is discussed.

The construction of C-C bonds is arguably the most important operation in organic synthesis. It is therefore not surprising that much recent interest has focused on the synthetic utility[2] of the highly regiospecific isomerization of 5-hexen-1-yl radicals to cyclopentylmethyl-containing products.[3] A major disadvantage of this otherwise powerful methodology is the fact that the product radical is difficult to trap in a controlled, intermolecular reaction to give a functionalized product.[2,4] A conceptually simple solution to this limitation of radical cyclizations would seem to be provided by the well-established tendency of various organometallic de-

[†] On leave from the University of Turku, Turku, Finland.

(1) Presented in part at the 190th National Meeting of the American Chemical Society, Chicago, IL, Sept 1985; ORGN 121.

(2) Representative examples may be found in: (a) Hart, D. J. *Science (Washington, D. C.)* **1984**, *223*, 883. (b) Curran, D. P.; Rakiewicz, D. M. *Tetetrahedron* **1985**, *19*, 3943. (c) Curran, D. P.; Kuo, S.-C. *J. Am. Chem. Soc.* **1986**, *108*, 1106. (d) Stork, G.; Sher, P. M. *J. Am. Chem. Soc.* **1983**, *105*, 6765. (e) Tsang, R.; Fraser-Reid, B. *J. Am. Chem. Soc.* **1986**, *108*, 2116. (f) Meijs, G. F.; Beckwith, A. L. J. *J. Am. Chem. Soc.* **1986**, *108*, 5890. (g) Beckwith, A. L. J.; Roberts, D. H. *J. Am. Chem. Soc.* **1986**, *108*, 5893.

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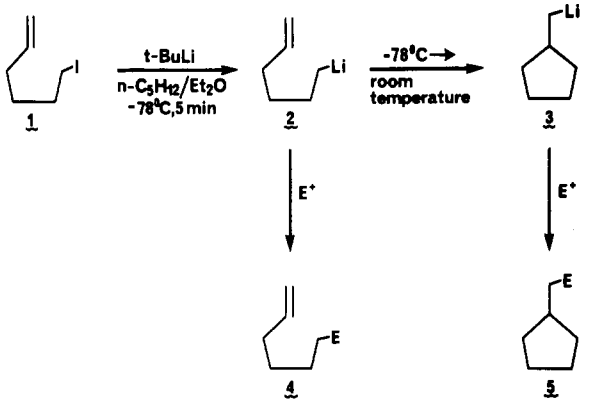
rivatives of the 5-hexenyl system to cyclize to cyclopentylmethyl organometallics.[5-9] There are however two rather stringent prerequisites to the exploitation of such anionic cyclizations for the construction of functionalized carbocycles: (1) the organometallic must be produced in high yield with a minimum of side-product formation from readily available precursors; (2) the organometallic must undergo clean, rapid cyclization in a regiospecific and highly stereoselective manner. Herein we report the results of experiments designed to probe the utility of alkenyllithium cyclization as a route to functionalized carbocycles containing five- or six-membered rings. As shown below, this approach provides a synthetically useful counterpart to radical-based strategies for the construction of carbocyclic products.

Results and Discussion

Preparation of Alkenyllithiums. Development of alkenyllithium cyclization as a viable alternative to radical-mediated methods requires that the organolithium be produced conveniently and in good yield. In the course of an ongoing investigation of the mechanism of the metal–halogen interchange reaction,[10-13] we have found that such species may be easily prepared by treatment of the appropriate iodide with *t*-butyllithium (*t*-BuLi) in *n*-pentane–diethyl ether at −78 °C.[12] Under these conditions, as noted elsewhere,[13] the mechanism of the interchange reaction between a 1° RI and *t*-BuLi most likely involves rapid attack of the alkyllithium on the iodine atom of the substrate. Thus, addition of 2 equiv of *t*-BuLi in *n*-pentane to a −78 °C solution of 6-iodo-1-hexene (**1**) in n-C_5H_{12}–Et_2O (3:2 by vol) results in rapid, clean interchange to produce 5-hexen-1-yllithium (**2**). When such reaction mixtures are quenched with an excess of anhydrous, oxygen-free methanol, 1-hexene may be isolated in virtually quantitative yield (93–99%).[12] We have found, however, that the use of protio acids as quenching agents masks the fact that 5-hexen-1-yllithium (**2**) is generated in less than quantitative yield: 1-hexene is produced as a byproduct of the interchange reaction between **1** and *t*-BuLi.[14] The less than quantitative yield of **2** was revealed by the results of experiments employing deuteriated reagents.

Addition of 2 equiv of *t*-BuLi to a 0.1 M solution of **1** in n-C_5H_{12}–Et_2O (3:2 by vol) at −78 °C served to generate **2**. The reaction mixture was stirred for 5 min at −78 °C and then

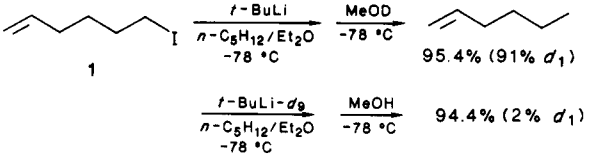
Scheme I



Isolated yield, %

E^+	E	4	5
CH_3OH	H	98	89
CH_3OD	D	87	67
CO_2	CO_2H	87	54
O_2	OH	78	78

quenched at −78 °C with an excess of anhydrous MeOD (>99.5% d_1) to give a 95.4% yield of 1-hexene that incorporated only 91% of the available deuterium. Thus, the yield of 5-hexen-1-yllithium



(**2**) at the time of the quench was ~87% (i.e., 95.4% × 91%). The origin of the nondeuteriated 1-hexene formed in this experiment is suggested by the outcome of an analogous experiment involving reaction of **1** with perdeuterio *t*-BuLi (*t*-BuLi-d_9). Treatment of **1** with *t*-BuLi-d_9 (>98% d_9) in n-C_5H_{12}–Et_2O (3:2 by vol), followed by addition of excess MeOH, gave a 94.4% yield of 1-hexene having a d_1 content of 2% above natural abundance. This low but nonnegligible deuterium incorporation from *t*-BuLi-d_9 is most likely the result of an elimination reaction between 5-hexen-1-yllithium (**2**) and the *t*-BuI-d_9 generated in the interchange to give 6-deuterio-1-hexene and $CD_2{=}C(CD_3)_2$.[14,15] The low deuterium incorporation, which presumably reflects the primary isotope effect on the elimination reaction, is consistent with the larger proportion of 1-hexene produced in the reaction of **2** with (protio) *t*-BuI. The significance of these observations to the matter at hand lies in the fact that alkenyllithiums generated via lithium–iodine interchange between an iodide and *t*-BuLi will often contain a small amount of hydrocarbon formally derived from reduction of the halide.

In contrast to this clean lithium–iodine exchange, the use of the analogous bromide results in the formation of a complex mixture of products[13] and the chloride is essentially inert when treated with *t*-BuLi at −78 °C.[13] The identity of the organolithium used to initiate the interchange was also found to be of importance: reaction of **1** with *n*-BuLi is so slow at −78 °C to be of little

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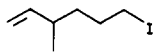
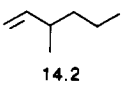
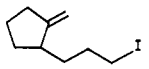
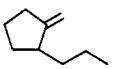
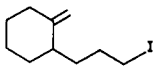
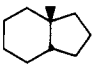
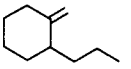
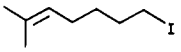
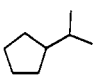
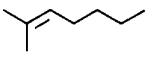
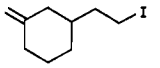
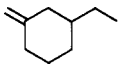
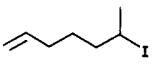
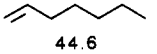
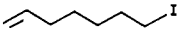
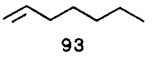
(13) Bailey, W. F.; Patricia, J. J.; Nurmi, T. T. *Tetrahedron Lett.* **1986**, *27*, 1865.

(14) The formation of hydrocarbon formally derived from reduction of the halide substrate appears to be a general occurrence in lithium–halogen interchange reactions that involve *t*-BuLi. The relevance of this observation to the mechanism of the interchange process will be discussed elsewhere (Bailey, W. F.; Patricia, J. J., unpublished results).

(15) The reaction of *t*-BuLi with the *tert*-butyl halide generated in the metal–halogen interchange is well-known. See: Corey, E. J.; Beames, D. J. *J. Am. Chem. Soc.* **1972**, *94*, 7210. And: Seebach, D.; Neuman, H. *Chem. Ber.* **1974**, *107*, 847.

(16) Organolithiums are known to exist as aggregates whose degree of association may be affected by such factors as solvent, concentration, and temperature (Wakefield, B. J. *The Chemistry of Organolithium Compounds*; Pergamon: New York, 1974). For the sake of pictorial clarity, monomeric species are used in mechanistic formulations.

Table I. Cyclization of Alkenyllithiums[a]

entry	precursor iodide	equiv TMEDA	time at room temp[b], h	products, % yield[c]		
1		0	1	 76	 5.6	 14.2
2		0	3	 15	 84	
3		2	4	(62)	15	
4		0	5	 65	 35	
5		2	4	(94)	5.1	
6		0	3	 5.6	 86.3	
7		2	3	 >98		
8[d]		0	0[e]	 5.3	 7.9	 44.6
9[d,f]		0	0[e]	44.0	<1	35.6
10		0	2	 6	 93	
11		2	2	67.6	30.9	

[a] Alkenyllithiums generated at −78 °C by addition of 2.0–2.2 molar equiv *t*-BuLi to a 0.1 M solution of the iodide in *n*-C_5H_{12}–Et_2O (3:2 by vol). [b] The cooling bath was removed 5 min after the addition of all reagents, and upon reaching +20 °C, the reaction mixture was allowed to sit for the specified period of time at ambient temperature. [c] Yields determined by GLC analysis of the quenched reaction mixture (deoxygenated CH_3OH) using internal standards and correction for detector response. Isolated yields of purified product in parentheses. [d] In addition to the products listed, the reaction mixture contained other hydrocarbons produced by Wurtz-type coupling and elimination. [e] Reaction quenched at −78 °C. [f] Iodide added to a −78 °C solution of *t*-BuLi in *n*-C_5H_{12}–Et_2O (3:2 by vol).

synthetic utility for the preparation of an alkenyllithium at low temperature. Thus, for example, treatment of a 0.1 M solution of **1** in *n*-C_5H_{12}–Et_2O (3:2 by vol) at −78 °C with 2.0–2.2 equiv of *n*-BuLi produced **2** cleanly but very slowly. The yield of 1-hexene generated upon hydrolysis of reaction mixtures at −78 °C was only 3.6% and 13.2% following reaction times of 5 min and 1 h, respectively.

Cyclization of Alkenyllithiums. With a method in hand for the facile preparation of organolithiums by low-temperature lithium–iodine interchange, intramolecular cyclization reactions of suitably constituted alkenyllithiums were investigated. We have recently demonstrated that 5-hexen-1-yllithium (**2**) undergoes isomerization analogous to that of the 5-hexen-1-yl radical (albeit more slowly) to give cyclopentylmethyllithium (**3**) in a totally regiospecific 5-exo-trig cyclization characterized[9] by $\Delta H^{\ddagger} = 11.8 \pm 0.5$ kcal mol^{-1} and $\Delta S^{\ddagger} = -30 \pm 2$ eu. As indicated by these activation parameters, the rate of rearrangement of **2** → **3** is a strong function of temperature: **2** is indefinitely stable at −78° C ($t_{1/2} \approx 114$ days), but it is rapidly converted to **3** upon warming to room temperature ($t_{1/2} = 5.5$ min at 23 °C). Consequently, 6-iodo-1-hexene (**1**) may be viewed as a synthon for either 5-hexen-1-yllithium (**2**) or cyclopentylmethyllithium (**3**) depending on the temperature at which the organolithium is used. The utility of this dual synthon approach is illustrated in Scheme I. Preparation of **2** at −78 °C followed by treatment with an electrophile provides a convenient route to 1-substituted-5-hexenes. Alternatively, simple warming of the reaction mixture to room temperature for 1 h prior to the addition of the electrophile serves to deliver functionalized methylcyclopentanes.

The scope of the cyclization step was surveyed in experiments employing substituted alkenyllithiums generated at −78 °C under an atmosphere of oxygen-free argon by slow addition (3–5 min) of 2.0 molar equiv of *t*-BuLi in pentane[17] to an approximately 0.1 M solution of the appropriate iodide in *n*-C_5H_{12}–Et_2O (3:2 by vol). The results are summarized in Table I. It should be noted that, although anhydrous CH_3OH was used to quench reaction mixtures in this exploratory study, other electrophiles have been used to prepare functionalized carbocycles (Scheme I) in yields comparable to those of the cyclic hydrocarbons produced upon protonation of the C–Li bond. The presence of small amounts of alkene in several of the product mixtures (Table I, entries 1, 3, and 5) does not necessarily reflect incomplete cyclization of the alkenyllithium since, as noted above, ca. 10% of the alkene is generated as a byproduct of the interchange. Thus, the observation of noncyclized hydrocarbon should not be construed as indicative of the presence of noncyclized alkenyllithium prior to the addition of CH_3OH. As a practical matter, the isolation of functionalized carbocyclic products (Scheme I) is not complicated by the presence of isomeric material derived from alkenyllithium provided that sufficient time is allowed for the cyclization to proceed to completion.

In several instances, the cyclization of the alkenyllithium is sluggish at room temperature. Such isomerizations were found to be facilitated by the addition of 2 equiv of TMEDA to the

(17) We have noted elsewhere[12] that commercial samples of "*t*-BuLi in pentane" invariably contain a small quantity of methylcyclopentane (presumably present in the pentane solvent used in their preparation). While this contaminant is often of no consequence, the presence of a significant amount of methylcyclopentane can complicate product analysis, and it is advisable to prepare solutions of *t*-BuLi in pure *n*-pentane (Kamienski, C. W.; Esmay, D. L. *J. Org. Chem.* **1960**, *25*, 1807) for use in reactions that produce C_6H_{12} hydrocarbons.

reaction mixture prior to the removal of the cooling bath.[18] This expedient was particularly effective in promoting the 6-exo-trig rearrangement of 6-hepten-1-yllithium (Table I, compare entries 10 and 11) as well as cyclizations that involve formation of a quaternary center adjacent to the CH_2Li moiety (Table I, compare entries 2 and 3, 4 and 5). It is significant that these bicyclic hydrocarbons are produced with virtually total regio- and stereocontrol by 5-exo-trig cyclization to give cis-fused product (Table I, entries 3 and 5). The complementarity of the anionic and radical strategies is illustrated by the fact that, whereas 6-methyl-5-hepten-1-yllithium undergoes very little rearrangement at elevated temperatures (Table I, entry 6), the corresponding radical is known to isomerize even more rapidly than the parent 5-hexen-1-yl radical.[3]

The behavior of the only 2° alkenyllithium studied (Table I, entries 8 and 9) is deserving of comment for several reasons. Firstly, in contrast to 1° alkyl iodides, treatment of a 2° iodide with *t*-BuLi at −78 °C leads to less than quantitative yield of RLi and reaction mixtures often contain hydrocarbons produced by Wurtz-type coupling and elimination. Secondly, cyclization of the 2° alkenyllithium is so much more rapid than isomerization of **2** that it is apparently complete within minutes at −78 °C. Consequently, the results presented in Table I (entries 8 and 9) are unaffected by warming of the reaction mixtures prior to the addition of CH_3OH. Finally, and perhaps most significantly, the stereoselectivity of the cyclization step is a function of the order of mixing of the reagents: addition of *t*-BuLi to the iodide in the normal way gives, following hydrolysis, a low yield (~13%) of cyclized product as a mixture of isomers (cis/trans ≈ 1.5); however, virtually pure *trans*-1,2-dimethylcyclopentane is produced in 44% yield upon addition of the iodide to the *t*-BuLi solution (Table I, entry 9). It should be noted, by way of contrast, that rearrangement of 4-methyl-5-hexen-1-yllithium (Table I, entry 1) produces an essentially equilibrium mixture[19] of 1,2-dimethylcyclopentanes. These observations, which will be explored in more detail in connection with our mechanistic studies, demonstrate that 2° systems are not as well behaved as are the 1° alkenyllithiums.

We are currently investigating extension of the work described above to the preparation of more complex systems by sequential, anion-initiated polyolefinic cyclization of alkenyl and alkynyllithiums.

Experimental Section

General Procedure. Melting points and boiling points are uncorrected. Bulb-to-bulb distillations were performed by using a Kügelrohr apparatus, and boiling points refer to the air-bath temperature. Proton magnetic resonance spectra were recorded on Varian EM-360 or IBM-200SY instruments, and shifts are referenced with respect to internal Me_4Si. Carbon-13 magnetic resonance spectra were obtained on an IBM-200SY spectrometer in the FT mode; shifts are referenced with respect to internal Me_4Si. Infrared spectra were recorded on a Perkin-Elmer 283 grating spectrometer. Analytical gas–liquid chromatography (GLC) was effected with a Perkin-Elmer Model 3920-B instrument fitted with flame ionization detectors and matched, $^1/_{16}$-in. stainless steel columns. Analytical GLC columns are coded as follows: (A) 20 ft, 20% SE-30 on Anakrom A (80/100 mesh); (B) 9 ft, 12% SE-30 on Chromosorb W (NAW) (80/100 mesh); 10 ft, 10% sodium sulfate on alumina[20] (80/100 mesh). Area ratios were determined by using a Linear Instruments Model 282 recording integrator. Unless otherwise noted, all yields determined by GLC analysis have been corrected for detector response under conditions of the analysis using weighed samples of pure product and standard. Preparative GLC was accomplished on a Varian Aerograph A-90P instrument fitted with one of the following $^1/_4$-in. aluminum columns: (A) 10 ft, 20% SE-30 on Chromosorb W (NAW) (60/80 mesh); (B) 10 ft, 20% SE-30 on Anakrom A (60/80 mesh); (C) 5 ft, 10% SE-30 on Anakrom U (60/80 mesh). High-resolution mass spectra (MS) were obtained on an AEI MS-902 instrument at 70 eV, and GC/MS was performed on a Hewlett-Packard 5970B system fitted with a 12-m × 0.33-μm SE-30 fused-silica capillary column using temperature programming (25 °C for 20 min; 10 °C/min to 250 °C). Miroanalyses were performed by either Galbraith Laboratories, Inc., Knoxville, TN, or MicAnal Organic Microanalyses, Tuscon, AZ.

All reactions involving the use of alkyllithiums were conducted under an atmosphere of dry, oxygen-free argon that had been passed through a 5-cm × 50-cm glass column packed with activated BASF R3-11 copper catalyst. All operations were performed in oven-dried glassware using standard syringe/cannula techniques.[11] Diethyl ether was freshly distilled under argon from dark-purple solutions of sodium/benzophenone. Dry, olefin-free *n*-pentane was obtained by repetitive washing of technical grade pentane with concentrated sulfuric acid until the acid layer remained clear, followed by washing with saturated, aqueous sodium carbonate and water, drying ($MgSO_4$) and distilling the purified pentane under argon from lithium aluminum hydride. The concentration of solutions of *t*-BuLi in *n*-pentane was determined immediately prior to each reaction by titration with 1,3-diphenyl-2-propanone *p*-tosylhydrazone in THF as described by Lipton and co-workers.[21] All alkyl iodides were freshly distilled prior to use.

Literature procedures were followed for the preparation of 6-iodo-1-hexene (**1**),[11] 6-iodo-1-heptene,[22] 4-methyl-5-hexen-1-ol,[23] 6-methyl-5-hepten-1-ol,[24] 3-(2-methylenecyclopentyl)propan-1-ol,[25] 3-(2-methylenecyclohexyl)propan-1-ol,[26] and ethyl (3-oxocyclohexyl)acetate.[27] The following samples of pure hydrocarbons were purchased from commercial sources: 3-methyl-1-hexene (Wiley Organics), methylcyclopentane and methylcyclohexane (Aldrich), *cis*-1,2-dimethylcyclopentane (ICN/K&K Laboratories), and 1-heptene (Aldrich).

Isopropylcyclopentane. Room-temperature hydrogenation of 10.62 g (100.0 mmol) of dimethylfulvene[28] in 100 mL of dry *n*-pentane over 0.534 g of 10% palladium-on-charcoal at 40 psi was accomplished by using a Parr hydrogenation apparatus. Reduction was continued until hydrogen uptake ceased, the catalyst was removed by filtration, and the filtrate was concentrated to give a clear residue that was distilled through a 3-in. vacuum-jacketed Vigreux column to afford 9.66 g (86%) of product: bp 118–120 °C [lit.[28] bp 126.4 °C]; ^{1}H NMR ($CDCl_3$) δ 0.48–2.08 [overlapping patterns, 16 H, i.e., 0.48–2.08 (m, 10 H), 0.93 (d, J = 6.0 Hz; 6 H)].

2-Methyl-2-heptene. A slurry of 80.00 g (185.0 mmol) of isopropyltriphenylphosphonium iodide (mp 196–197.5 °C [lit.[29] mp 195–196 °C]) in 400 mL of anhydrous diethyl ether was rapidly stirred under argon with a mechanical stirrer, and 84.0 mL of a 2.37 M solution of *n*-BuLi (199 mmol) in hexanes (Aldrich) was added over a 160-min period. The resulting dark-red solution was stirred at room temperature for an additional 165 min, and 15.93 g (185.0 mmol) of freshly distilled *n*-pentanal in 30 mL of anhydrous diethyl ether was slowly added to the ylide under argon over 130 min. The mixture was heated at reflux for 74 h, allowed to cool to room temperature, and then hydrolyzed by the addition of 200 mL of water. The mixture was filtered through a pad of Celite to remove triphenylphosphine oxide, the two-phase filtrate was separated, and the aqueous layer was extracted with ether. The combined extracts were dried ($MgSO_4$), volatile components were removed by simple distillation, and the residue was fractionated through a 6-in. Vigreux column to give 12.30 g (59%) of the alkene: bp 113 °C [lit.[30] bp 122–123 °C]; IR (neat) 2985, 2951, 2897, 2881, 1676, 1455, and 1379 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.48–2.45 [overlapping patterns, 15 H, i.e., 0.48–2.45 (m, 9 H), 1.65 (s, 3 H), 1.73 (s, 3 H)], 5.21 (t, J = 7.2 Hz, 1 H).

***trans*-1,2-Dimethylcyclopentane.** One crystal of iodine was added to 6.75 g (59.1 mmol) of a mixture of the isomeric of 1,2-dimethylcyclopentan-1-ols,[31] and the resulting dark-brown–black solution was distilled

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by using an oil bath and an ice-cooled receiver. The first portion of the two-phase distillate was collected at 76–77 °C and the bulk of the product distilled at 80–85 °C. The organic layer was taken up into pentane and dried over $MgSO_4$. Pentane was removed by distillation through a short Vigreux column, and the residue was fractionated to yield 4.96 g (87%) of 1,2-dimethylcyclopent-1-ene contaminated with ~15% of an isomeric alkene (bp 92–94 °C [lit.[32] bp 103.5–104.5 °C]; ^1H NMR ($CDCl_3$) δ 1.67 (s, 6 H), 0.81–2.72 (m, 6 H)). A solution of 4.00 g (41.6 mmol) of this alkene in 50 mL of glacial acetic acid was hydrogenated at 15 psi over 0.291 g of 10% palladium-on-carbon until hydrogen uptake ceased (ca. 17 min). The catalyst was removed by filtration through a pad of Celite, and the filtrate was partitioned between water and pentane. The organic phase was washed with saturated, aqueous sodium bicarbonate and water and then dried over $MgSO_4$. Solvent was removed by distillation through a short Vigreux column, and the residue was fractionated to give 2.89 g (71%) of a mixture of *trans*- and *cis*-1,2-dimethylcyclopentanes in a ratio (trans/cis) of approximately 3/1: bp 91–92 °C [trans isomer, lit.[33] bp 91.78 °C; cis isomer, lit.[33] bp 99.23 °C]. The isomers were identified on the basis of their ^{13}C chemical shifts which agreed well with those reported[34] for these compounds: ^{13}C NMR ($CDCl_3$) trans isomer δ 18.78 (CH_3), 23.24 (C(4)), 34.88 (C(3,5)), 42.55 (C(1,2)); ^{13}C NMR ($CDCl_3$) cis isomer δ 15.18 (CH_3), 23.06 (C(4)), 33.02 (C(3,5)) 37.36 (C(1,2)). An authentic sample of pure *cis*-1,2-dimethylcyclopentane was purchased from ICN/K&K Laboratories.

7-Bromo-1-heptene. This procedure represents a modification of that described by Kraus and Landgrebe.[35] A 50-mL, three-necked, round-bottomed flask fitted with a magnetic stirring bar, pressure-equalizing addition funnel, and condenser for downward distillation was charged with 8.00 g (31.0 mmol) of neat 1,7-dibromoheptane. The flask was heated to 240 °C (oil bath temperature), and 6.50 g (36.3 mmol) of hexamethylphosphoric triamide (HMPA) was added dropwise over an 8-min period. The distillate which formed was collected in an ice-cooled receiver. At the end of the addition, the oil bath temperature had risen to 258 °C. The distillate was subjected to rotary evaporation at 28 °C (ca. 20 mm) for 20 min to remove the 1,6-heptadiene that had formed in the reaction, and the residue was taken up into pentane, washed with several portions of water, and dried ($MgSO_4$). Solvent was removed under reduced pressure, 2 mL of *n*-heptadecane was added to the residue as a "distillation chaser", and the mixture was fractionated through a 5-in. Vigreux column to give 2.14 g (39%) of the bromoalkene: bp 81–82 °C (24 mm) [lit.[36] bp 64 °C (10 mm)]; ^1H NMR ($CDCl_3$) δ 1.03–2.50 (m, 8 H), 3.48 (t, J = 6.8 Hz, 2 H), 4.79–5.37 (m, 2 H), 5.37–6.39 (m, 1 H).

7-Iodo-1-heptene. A mixture of 1.77 g (10.0 mmol) of 7-bromo-1-heptene, 3.75 g (25.0 mmol) of anhydrous sodium iodide, and 25 mL of dry acetone was stirred at room temperature under argon for 14.5 h and then at reflux for an additional 2.5 h. Inorganic salts was removed by filtration and washed well with acetone, and the combined filtrate and washings were concentrated by rotary evaporation. The residue was taken up in pentane and washed successively with water, 10% aqueous sodium thiosulfate, and water. After drying ($MgSO_4$), solvent was removed by rotary evaporation, and the residue was distilled to give 2.20 g (98%) of the iodide: bp (Kugelrohr) 79–80 °C (8.0 mm); ^1H NMR ($CDCl_3$) δ 1.25–2.69 (m, 8 H), 3.31 (t, J = 6.8 Hz, 2 H), 4.83–5.43 (m, 2 H), 5.43–6.39 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 6.71, 27.76, 29.91, 33.39, 114.55, 138.46. An analtyical sample was prepared by preparative GLC on column A at 180 °C: mass spectroscopic molecular weight calcd for $C_7H_{13}I$ 224.0068, found 224.0062. Anal. Calcd for $C_7H_{13}I$: C, 37.52; H, 5.85. Found: C, 38.00; H, 6.07.

6-Iodo-3-methyl-1-hexene. The mesylate of 4-methyl-5-hexen-1-ol,[23] prepared from 2.50 g (22 mmol) of the alcohol by the method of Crossland and Servis,[37] was added to a solution of 4.95 g (33 mmol) of anhydrous sodium iodide in 50 mL of dry acetone. The mixture was stirred overnight at ambient temperature and then heated at gentle reflux for an additional 0.5 h. The mixture was filtered, the filtrate was concentrated at reduced pressure, and the residue was taken up in pentane and washed successively with water, 10% aqueous sodium thiosulfate, and water. After drying ($MgSO_4$), solvent was removed by rotary evaporation and the residue was distilled to give 3.91 g (79% from the alcohol) of the iodide: bp 85–87 °C (22 mm). An analytical sample was prepared by preparative GLC on column C at 130 °C: IR (neat) 3036, 2908, 2876, 1604, 1463, 1425, 993, and 900 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.00 (d, J = 6.70 Hz, 3 H), 0.85–1.89 (overlapping m, 4 H), 2.08–2.25 (m, 1 H), 3.17 (t, J = 7.00 Hz, 2 H), 4.91–4.96 (m, 2 H), 5.57–5.75 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 6.79, 20.19, 31.33, 36.98, 37.37, 113.04, 143.89. Anal. Calcd for $C_7H_{13}I$: C, 37.52; H, 5.85. Found: C, 37.42; H, 5.86.

2-(3-Iodopropyl)-1-methylenecyclopentane. The mesylate of 3-(2-methylenecyclopentyl)propan-1-ol[25] was prepared from 3.50 g (25 mmol) of the alcohol following the general procedure of Crossland and Sevis.[37] The crude mesylate was added to a solution of 7.50 g (50 mmol) of anhydrous sodium iodide in 75 mL of dry acetone, and the mixture was stirred overnight at room temperature under a nitrogen atmosphere. Inorganic salts were removed by filtration, the filtrate was concentrated at reduced pressure, and the residue was distilled to give 5.0 g (80% from the alcohol) of the iodide: bp (Kügelrohr) 95 °C (0.9 mm); ^1H NMR ($CDCl_3$) δ 1.2–2.3 (m, 11 H), 3.1–3.2 (complex m, 2 H), 4.78 (apparent s, 1 H), 4.88 (apparent s, 1 H); ^{13}C NMR ($CDCl_3$) δ 6.85, 24.07, 31.74, 32.53, 32.95, 35.15, 42.87, 104.48, 155.84; mass spectroscopic molecular weight calcd for $C_9H_{15}I$ 250.0225, found 250.0215.

2-(3-Iodopropyl)-1-methylenecyclohexane. Following the general procedure of Crossland and Servis,[37] 3.70 g (24 mmol) of 3-(2-methylenecyclohexyl)propan-1-ol[26] was converted to its mesylate. The crude mesylate was added to a solution of 7.15 g (48 mmol) of anhydrous sodium iodide in 75 mL of dry acetone; the mixture was stirred overnight at room temperature under a nitrogen atmosphere and then heated to reflux for an additional 2 h. The reaction mixture was cooled, inorganic salts were removed by filtration, and the filtrate was concentrated at reduced pressure. The residue was taken up in pentane and washed successively with water, 10% aqueous sodium thiosulfate, water, and brine. The organic extract was dried ($MgSO_4$) and concentrated to afford an oil. The residue was distilled to give 5.10 g (80% from the alcohol) of the iodide: bp 78–80 °C (0.65 mm); ^1H NMR ($CDCl_3$) δ 1.2–2.2 (m, 13 H), 3.15 (t, J = 6.8 Hz, 2 H), 4.52 (apparent s, 1 H), 4.62 (apparent s, 1 H); ^{13}C NMR ($CDCl_3$) δ 7.16, 23.88, 28.58, 31.49, 32.86, 33.73, 34.32, 42.17, 105.93, 151.87; mass spectroscopic molecular weight calcd for $C_{10}H_{17}I$ 264.0381, found 264.0377.

2-(3-Methylenecyclohexyl)ethanol. A suspension of 5.10 g (46 mmol) of freshly sublimed potassium *tert*-butoxide and 16.48 g (46 mmol) of methyltriphenylphosphonium bromide in 60 mL of anhydrous diethyl ether was stirred under nitrogen for 7 h at 0 °C. A solution of 8.5 g (46 mmol) of ethyl (3-oxocyclohexyl)acetate[27] in 30 mL of anhydrous diethyl ether was added to the bright-yellow suspension, and the mixture was stirred for 4 h at 0 °C and then at room temperature for an additional 36 h. Water was added, the reaction mixture was filtered through a pad of Celite, the two-phase filtrate was separated, and the aqueous layer was extracted with ether. The combined ethereal layers were dried ($MgSO_4$) and concentrated to give 8.5 g (~100%) of **ethyl (3-methylenecyclohexyl)acetate** as an oil [^{13}C NMR ($CDCl_3$) δ 13.89, 26.19, 31.79, 34.35, 35.52, 40.82 (two resonances), 59.63, 107.56, 147.41, 172.10]. A solution of 8.5 g of the crude ester in 50 mL of anhydrous diethyl ether was then added dropwise to a stirred slurry of 2.66 g (70 mmol) of lithium aluminum hydride in 150 mL of anhydrous diethyl ether. After addition was completed, the mixture was stirred for 2 h at room temperature and then hydrolyzed by sequential, dropwise addition of 2.7 mL of water, 2.7 mL of 15% aqueous sodium hyroxide, and 8.1 mL of water. The mixture was filtered and the solids were washed thoroughly with ether. The combined filtrate and washings were dried ($MgSO_4$) and concentrated to give an oil which was distilled to afford 5.1 g (79% from the keto ester) of the title alkenol: bp (Kügelrohr) 70–72 °C (0.2 mm); IR (neat) 3360, 3100, 1654, 888 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.5–2.2 (complex pattern, 11 H), 3.08 (br s, 1 H), 3.64 (t, J = 6.61 Hz, 2 H), 4.60 (apparent s, 2 H); ^{13}C NMR ($CDCl_3$) δ 26.74, 32.37, 34.88, 35.49, 39.25, 41.49, 60.23, 107.05, 148.69; mass spectroscopic molecular weight calcd for C_9H_{14} ($M^+ - H_2O$) 122.1096, found 122.1098.

3-(2-Iodoethyl)-1-methylenecyclohexane. The mesylate of 2-(3-methylenecyclohexyl)ethanol was prepared from 3.50 g (25 mmol) of the alcohol by the method of Crossland and Servis.[37] The crude mesylate was added to a solution of 7.50 g (50 mmol) of anhydrous sodium iodide in 75 mL of dry acetone; the mixture was stirred overnight at room temperature under a nitrogen atmosphere and then heated at gentle reflux for 2 h. The reaction mixture was cooled, inorganic salts were removed by filtration, and the filtrate was taken up in pentane and washed successively with water, 10% aq sodium thiosulfate, and brine. The organic extract was dried ($MgSO_4$), concentrated, and distilled to afford 4.81 g (77% from the alcohol) of the iodide: bp (Kügelrohr) 60–65 °C (0.15 mm); ^1H NMR ($CDCl_3$) δ 1.1–2.3 (overlapping multiplets, 11 H), 3.20 (t, J = 7.35 Hz, 2 H), 4.62 (br s, 2 H); ^{13}C NMR ($CDCl_3$) δ 4.29, 26.51, 31.41, 34.84, 39.55, 40.14, 40.54, 107.60, 147.93; mass

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spectroscopic molecular weight calcd for $C_9H_{15}I$ 250.0225, found 250.0223.

***tert*-Butyllithium in *n*-Pentane.** This procedure was adapted from that of Kamienski and Esmay.[17] A 30% dispersion of lithium (containing 1% sodium) in mineral oil (Alfa, catalog no. 89347) was placed in a medium-porosity, sintered-glass funnel under a blanket of oxygen-free argon. The mineral oil was removed by using suction by repeated washings with dry, freshly distilled *n*-pentane to give dry, finely divided pyrophoric lithium metal. In a typical experiment, a three-necked, round-bottomed Morton flask fitted with a reflux condenser, pressure-equalizing addition funnel, magnetic stirring bar, and gas inlet–outlet lines was flame-dried under argon and charged with 3.08 g (444 mmol) of the lithium metal and 25 mL of dry *n*-pentane. The mixture was heated to reflux under argon by using a heating mantle, and a solution of 9.26 g (100 mmol) of *tert*-butyl chloride in 25 mL of dry *n*-pentane was added dropwise over a 2-h period to the stirred mixture. Three minutes into the addition, the heating mantle was removed and gentle reflux was continued by the exotherm of the reaction. After addition of the halide was completed, the reaction mixture was stirred at room temperature for 30 min. The light-yellow solution was transferred via a stainless-steel cannula under a positive pressure of argon through a flame-dried, medium porosity, fritted Schlenk funnel into a flame-dried, round-bottomed flask. The concentration of the clear *t*-BuLi in *n*-pentane solution was determined to be 1.52 M by the method of Lipton et al.[21] Perdeuterio *t*-BuLi (*t*-BuLi-d_9) was prepared in an analogous manner from *t*-BuCl-d_9 (Aldrich).

General Procedure for the Generation and Cyclization of Alkenyllithiums. A 50-mL, three-necked, round-bottomed flask was fitted with rubber septa, a Telfon-coated magnetic stirring bar, and a low-temperature thermometer. The flask was swept with a stream of dry, oxygen-free argon (introduced through the septa with 20-gauge needles), and the entire assembly was flame-dried by using a Bunsen burner. The cooled, dry flask was charged with an accurately weighed sample of the appropriate alkyl halide (typically 1.0–2.0 mmol) and enough dry *n*-pentane–diethyl either (3:2 by volume) to give a 0.1 M solution of the halide (typically 10–20 mL). All additions were conducted under an atmosphere of dry, oxygen-free argon by using standard syringe techniques, and a positive pressure of argon was maintained within the flask during all subsequent operations. The solution was cooled to −78 °C by using a dry ice/acetone bath and 2.0–2.2 molar equiv of *t*-BuLi in *n*-pentane was added via syringe over a 2–4-min period. The temperature of the reaction mixture was maintained at ≤−70 °C during the addition of *t*-BuLi, and the mixture was stirred for an additional 5 min at −78 °C before treatment in one of the following ways. **(A) Cold Quench.** One milliliter of deoxygenated, anhydrous methanol (or an excess of the appropriate electrophile; see Scheme I) was added at −78 °C to the stirred reaction mixture, and the cooling bath was removed. **(B) Room-Temperature Quench.** The cooling bath was removed, the mixture was allowed to warm over 10–30 min to +20 °C, argon lines were removed, and the mixture was allowed to stand without stirring under a positive pressure of argon for 1 h at room temperature. At this point, the argon sweep and stirring were reemployed and the reaction mixture was quenched by the addition of 1.0 mL of deoxygenated, anhydrous methanol (or an excess of the appropriate electrophile; Scheme I). **(C) Cyclization in the Presence of TMEDA.** The alkenyllithium solution was maintained at −78 °C under an atmosphere of argon and 2.10–2.20 molar equiv of dry, deoxygenated *N,N,N′,N′*-tetramethylethylenediamine (TMEDA) was added dropwise by syringe over 1–3 min such that the temperature of the reaction mixture was maintained at ≤75 °C. The addition of TMEDA was generally accompanied by the immediate formation of a thick, white precipitate and a change in the color of the solution from clear to pale yellow. The mixture was stirred for 5–10 min at −78 °C, the cooling bath was removed, and the flask and its contents were allowed to warm over 15–25 min to +20 °C. The reaction mixture then sat under a blanket of argon for 1–5 h at room temperature before the addition of 1.0 mL of deoxygenated, anhydrous methanol. The reaction mixtures were washed with two 10-mL portions of water, dried over $MgSO_4$, and analyzed. Reaction products were, for the most part, identified by comparison of their GLC retention times and mass spectra with those of authentic samples. When samples of authentic material were unavailable, quantities of such products were isolated by preparative GLC from reactions conducted on a larger scale and structures were established on the basis of physical and spectroscopic properties. Unless otherwise noted, all yields determined by GLC analysis (Table I) were corrected for detector response under conditions of the analysis using accurately weighed samples of pure product and standard.

The structures of the following hydrocarbons indicated in Table I were established by comparison of their GLC retention times and mass spectra with those of either commercially available samples or authentic material prepared as described above: *cis*- and *trans*-1,2-dimethylcyclopentane (entries 1, 8, and 9), 3-methyl-1-hexene (entry 1), isopropylcyclopentane (entry 6), 2-methyl-2-heptene (entry 6), 1-heptene (entries 8–11), methylcyclohexane (entries 10 and 11). Structures of the remaining hydrocarbons were established on the basis of the physical and spectroscopic properties exhibited by isolated samples.

Reaction of 2-(3-Iodopropyl)-1-methylenecyclopentane with *t*-BuLi. Preparation of 2-*n*-Propyl-1-methylenecyclopentane. A solution of 1.039 g (4.153 mmol) of 2-(3-iodopropyl)-1-methylenecyclopentane in a mixture of 24.90 mL of dry *n*-pentane and 16.60 mL of anhydrous diethyl ether was cooled to −78 °C (acetone/dry ice bath) under argon, and 3.60 mL of 2.52 M solution of *t*-BuLi in *n*-pentane (9.07 mmol of *t*-BuLi) was added dropwise over an 8-min period as described in the General Procedure (A) section. The mixture was stirred for an additional 10 min at −78 °C and then quenched at −78 °C by the addition of 5.0 mL of deoxygenated, anhydrous methanol. The cooling bath was then removed, and the flask was allowed to warm to room temperature. The mixture was washed with two portions of water, dried ($MgSO_4$), and concentrated by rotary evaporation to give 428 mg (83.1%) of product: ^{1}H NMR ($CDCl_3$) δ 0.92 (t, J = 6.9 Hz, 3 H), 1.16–1.91 (m, 8 H), 2.27–2.33 (m, 3 H), 4.77 (apparent s, 1 H), 4.85 (apparent s, 1 H); ^{13}C NMR ($CDCl_3$) δ 14.24, 21.02, 24.25, 32.79, 33.24, 36.95, 43.83, 103.90, 156.99. An analytical sample was prepared by preparative GLC on column C at 100 °C: mass spectroscopic molecular weight calcd for C_9H_{16} 124.1253, found 124.1235. Anal. Calcd for C_9H_{16}: C, 87.02; H, 12.98. Found: C, 87.07; H, 13.13.

Reaction of 2-(3-Iodopropyl)-1-methylenecyclopentane with *t*-BuLi: Preparation of *cis*-1-Methylbicyclo[3.3.0]octane. A solution of 1.141 g (4.562 mmol) of 2(3-iodopropyl)-1-methylenecyclopentane in a mixture of 27.4 mL of dry *n*-pentane and 18.2 mL of dry diethyl ether was cooled to −78 °C (acetone–dry ice bath) under an argon atmosphere, and 4.00 mL of a 2.52 M solution of *t*-BuLi in *n*-pentane (10.1 mmol of *t*-BuLi) was added over a 6-min period at such a rate that the temperature never rose above −71 °C. The mixture was stirred for an additional 10 min at −78 °C and then 1.52 mL (10.1 mmol) of dry TMEDA was added via syringe over 30 min at such a rate that the temperature of the reaction mixture remained below −75 °C. During the addition, the solution became a bright yellow in color and a copious white solid formed. Five minutes after complete addition of the TMEDA, the cooling bath was removed, the reaction was allowed to warm to +20 °C over 27 min, and the mixture remained at room temperature for 4 h under a blanket of argon (General Procedure, C). The reaction mixture was hydrolyzed by the addition of 5.0 mL of deoxygenated, anhydrous methanol, washed with two 10-mL portions of water, and dried over $MgSO_4$. Solvent was removed by rotary evaporation to give 436.7 mg (77.1%) of product as a 4:1 mixture of the title compound (62% yield) and 2-*n*-propyl-1-methylenecyclopentane. An analytical sample of *cis*-1-methylbicyclo-[3.3.0]octane was isolated by preparative GLC on column A at 110 °C: ^{1}H NMR ($CDCl_3$) δ 1.05 (s, 3 H), 1.27–1.81 (m, 13 H); ^{13}C NMR ($CDCl_3$) δ 25.94 (C(3,7)), 29.10 (CH_3), 34.50 (C(4,6)), 41.86, (C(2,8)) 49.74 (C(1)), 50.90 (C(5)) [lit.[38] ^{13}C NMR δ 25.9, 29.2, 34.5, 41.9, 49.8, 50.9]; mass spectroscopic molecular weight calcd for C_9H_{16} 124.1253, found 124.1257.

Reaction of 2-(3-Iodopropyl)-1-methylenecyclohexane with *t*-BuLi: Preparation of 2-*n*-Propyl-1-methylenecyclohexane. A solution of 870.3 mg (3.29 mmol) of 2-(3-iodopropyl)-1-methylenecyclohexane in a mixture of 19.7 mL of dry *n*-pentane and 13.2 mL of dry diethyl ether was cooled to −80.5 °C (acetone/dry ice bath) under an atmosphere of argon, and 2.60 mL of a 2.83 M solution of *t*-BuLi in pentane (7.36 mmol of *t*-BuLi) was added dropwise over an 8-min period with the temperature never increasing above −74 °C. Fifteen minutes later the −80 °C reaction mixture was quenched with the cautious addition of 3.0 mL of anhydrous, deoxygenated methanol, and the cooling bath was removed. After warming to room temperature, the mixture was washed twice with water and dried ($MgSO_4$) and solvent removed by rotary evaporation to give 424 mg (93.2%) of product: ^{1}H NMR ($CDCl_3$) δ 0.83 (t, J = 6.0 Hz, 3 H), 1.19–2.11 (m, 13 H), 4.48 (apparent s, 1 H), 4.55 (apparent s, 1 H); ^{13}C NMR ($CDCl_3$) δ 14.27, 20.58, 24.32, 28.96, 33.89, 34.47, 34.83, 42.94, 105.33, 153.10. An analytical sample was prepared by preparative GLC on column C at 110 °C: mass spectroscopic molecular weight calcd for $C_{10}H_{18}$ 138.1409, found 138.1400. Anal. Calcd for $C_{10}H_{18}$: C, 86.88; H, 13.12. Found: C, 86.79; H, 13.48.

Reaction of 2-(3-Iodopropyl)-1-methylenecyclohexane with *t*-BuLi: Preparation of *cis*-1-Methylbicyclo[4.3.0]nonane. A solution of 986 mg (3.73 mmol) of 2-(3-iodopropyl)-1-methylenecyclohexane in a mixture of 22.4 mL of dry *n*-pentane and 14.9 mL of dry diethyl ether was cooled to −80 °C (acetone/dry ice bath) under argon and 2.95 mL of a 2.83 M solution of *t*-BuLi in *n*-pentane (8.35 mmol of *t*-BuLi) was added dropwise over a 7-min period with the temperature never exceeding −71 °C. The mixture was stirred for 15 min at −78 °C, and then 1.26 mL (8.35 mmol) of freshly distilled, deoxygenated, dry TMEDA was added via

syringe over a 6-min period with the temperature rising only 1 °C. The mixture was stirred for an additional 5 min at −78 °C, the cooling bath was removed, and the mixture was then allowed to warm to +20 °C over 26 min. After stirring at ca. 23 °C for 4.0 h under a blanket of argon (General Procedure, C), the reaction mixture was quenched by the cautious addition of 3.0 mL of dry, deoxygenated methanol and then washed twice with 10-mL portions of water. The organic phase was dried ($MgSO_4$), and solvent was removed by rotary evaporation to give 509.2 mg (98.7%) of product as a 95:5 mixture of the title compound (93.8% yield) and 2-*n*-propyl-1-methylenecyclohexane. An analytical sample of *cis*-1-methylbicyclo[4.3.0]nonane was isolated by preparative GLC on column A at 130 °C: ^1H NMR ($CDCl_3$) δ 0.93 (s, 3 H), 0.85–1.69 (m, 15 H); ^{13}C NMR ($CDCl_3$) δ 20.69 (C(8)), 22.46 (C(3)), 22.82 (C(4)), 26.80 (C(5) and CH_3), 29.03 (C(7)), 33.85 (C(2)), 38.24 (C(9)), 40.53 (C(1)), 45.04 (C(6)) [lit.[39] ^{13}C NMR δ 20.8, 22.5, 22.9, 26.8, 26.8, 29.1, 33.8, 38.3, 40.6, 45.1]; mass spectroscopic molecular weight calcd for $C_{10}H_{18}$ 138.1409, found 138.1417.

Reaction of 3-(2-Iodoethyl)-1-methylenecyclohexane with *t*-BuLi: Preparation of 3-Ethyl-1-methylenecyclohexane. A solution of 137.1 mg (0.548 mmol) of 3-(2-iodoethyl)-1-methylenecyclohexane in a mixture of 3.30 mL of dry *n*-pentane and 2.20 mL of anhydrous diethyl ether was cooled to −78 °C (dry ice/acetone bath) under argon, and 0.46 mL of a 2.59 M solution *t*-BuLi in *n*-pentane (1.19 mmol of *t*-BuLi) was added dropwise over a 2-min period. The mixture was stirred for 5 min at −78 °C and then 0.18 mL (1.20 mmol) of freshly distilled, deoxygenated, dry TMEDA was added via syringe over a 1-min period such that the temperature never rose above −77 °C. The mixture was stirred for an additional 3 min at −78 °C, the cooling bath was removed, and the mixture was then allowed to warm to +20 °C over a 15-min period. The mixture was allowed to sit at ca. 23 °C for 3 h (General Procedure, C) before the addition of 1.0 mL of dry, deoxygenated methanol. The mixture was extracted with two 10-mL portions of water, dried ($MgSO_4$), and concentrated by rotary evaporation to give the known[40] 3-ethyl-1-methylenecyclohexane that was found to be essentially pure by GLC on column B. In a separate experiment, the alkenyllithium–TMEDA mixture was heated at reflux for 4.5 h; GLC analysis of the product mixture indicated that 3-ethyl-1-methylenecyclohexane was the only tractable product of the reaction.

6-Heptenoic Acid. A solution of 423 mg (2.01 mmol) of 6-iodo-1-hexene (**1**) in a mixture of 12 mL of *n*-pentane and 8 mL of diethyl ether was cooled to −78 °C and treated with 1.34 mL of a 2.26 M solution of *t*-BuLi in *n*-pentane following the General Procedure (A) for the preparation of alkenyllithiums. Dry CO_2 was bubbled through the solution of 5-hexen-1-yllithium at −78 °C for ca. 10 min. The cooling bath was then removed, the mixture was allowed to warm to 10 °C, and 10 mL of 10% aqueous HCl was added. The organic phase was separated, the aqueous phase was extracted with three 10-mL portions of ether, and the combined organic layers were extracted with three 15-mL portions of saturated, aqueous sodium bicarbonate. The aqueous, basic solution was acidified with concentrated aqueous HCl to pH ≈ 1 and extracted with three 10-mL portions of ether. The combined ethereal exctracts were dried ($MgSO_4$) and concentrated by rotary evaporation to give 225 mg (87%) of the known[41] title acid: ^1H NMR ($CDCl_3$) δ 1.4–1.7 (m, 4 H), 2.07 (4 line pattern, 2 H), 2.36 (t, J = 7.04 Hz, 2 H), 4.9–5.1 (m, 2 H), 5.7–6.0 (m, 1 H), 11.4 (br s, 1 H); ^{13}C NMR ($CDCl_3$) δ 24.1, (C(3)), 28.2 (C(4)), 33.3 (C(5)), 33.9 (C(2)), 114.7 (C(7)), 138.2 (C(6)), 180.3 (C=O).

5-Hexen-1-ol. A soltuion of 1.05 g (5.0 mmol) of 6-iodo-1-hexene in a mixture of 20 mL of *n*-pentane and 13 mL of diethyl ether was cooled to −78 °C and treated with 6.40 mL of a 1.70 M solution of *t*-BuLi in *n*-pentane following the General Procedure (A). Dry O_2 was bubbled through the reaction mixture for 1 h, the cooling bath was removed, and the mixture was allowed to warm to ca. 0 °C. Water (10 mL) was added to the reaction mixture, the organic layer was separated, dried over $MgSO_4$, and concentrated by rotary evaporation. The residue was distilled by using a Kügelrohr apparatus [bath temperature 77–82 °C (30 mm)] to give 390 mg (78%) of the alkenol that was identical in all respects (IR, ^1H NMR, and ^{13}C NMR) with an authentic sample of this material (Aldrich).

Cyclopentylacetic Acid. Cyclopentylmethyllithium (**3**) was prepared, following the General Procedure (B), from 1.49 mL of 2.75 M *t*-BuLi in *n*-pentane and 478.5 mg (2.28 mmol) of 6-iodo-1-hexene (**1**) in a mixture of 15 mL of *n*-pentane and 9 mL of diethyl ether. After cyclization was completed (1 h at room temperature), the mixture was cooled to −78 °C and dry CO_2 was bubbled through the solution for 10 min. The cooling bath was removed, the mixture was allowed to warm to ca. 10 °C, and 10 mL of 10% aqueous HCl was added. The organic phase was separated, the aqueous phase was washed with three 10-mL portions of ether, and the combined organic phases were extracted with three 15-mL portions of saturated, aqueous sodium bicarbonate. The basic, aqueous solution was acidified to pH ≈ 1 with concentrated hydrochloric acid and extracted with three 10-mL portions of ether. The ethereal extracts were dried ($MgSO_4$) and concentrated to give 234 mg (80%) of the crude acid. Kügelrohr distillation of the residue [bath temperature 140 °C (26 mm)] afforded 157 mg (54%) of cyclopentylacetic acid that was identical in all respects (IR, ^1H NMR, ^{13}C NMR) with an authentic sample of the material (Aldrich).

Cyclopentylmethanol. Cyclopentylmethyllithium (**3**) was prepared, following the General Procedure (B), from 3.20 mL of 1.53 M *t*-BuLi in *n*-pentane and 466.4 mg (2.22 mmol) of 6-iodo-1-hexene in a mixture of 13 mL of *n*-pentane and 9 mL of diethyl ether. After cyclization was completed (1 h at room temperature), the mixture was cooled to 0 °C and dry oxygen gas was bubbled through the solution for 30 min. The cooling bath was then removed, 1 mL of water was added to the mixture, and the organic phase was separated, dried ($MgSO_4$), and concentrated by rotary evaporation. Kügelrohr distillation of the residue [bath temperature 79 °C (28 mm)] gave 173.4 mg (78%) of the alcohol that was identical in all respects (IR, ^1H NMR, ^{13}C NMR) with an authentic sample of the material (Aldrich).

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