# Cyclization of Acetylenic Alkyllithiums

**William F. Bailey*,[1a] and Timo V. Ovaska[1b]**

*Contribution from the Department of Chemistry, The University of Connecticut, Storrs, Connecticut 06269-3060, and the Department of Chemistry, Connecticut College, New London, Connecticut 06320-4196*

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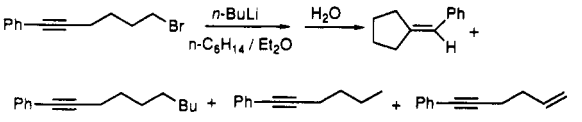
**Abstract:** The scope and limitations of cyclization reactions involving acetylenic alkyllithiums, which were prepared at −78 °C by lithium–iodine exchange between the corresponding iodide and *tert*-butyllithium in a solution of *n*-pentane–diethyl ether (3:2 by volume), have been investigated. 4-Pentynyllithiums, 5-hexynyllithiums, and 6-heptynyllithiums bearing a phenyl or trimethylsilyl substituent on the triple bond undergo regiospecific *exo-dig* cyclization to give 4-, 5-, and 6-membered rings, respectively, bearing an exocyclic lithiomethylene moiety. Cyclization of the analogous alkyl-substituted acetylenic alkyllithiums seems to be confined to the 5-*exo* mode. The vinyllithium products of the cyclizations may be trapped by reaction with electrophiles to afford functionalized cycloalkylidene derivatives in good yield. The cyclization reactions were found to be highly stereoselective: intramolecular addition of the C–Li unit to the triple bond to produce 4- or 5-membered rings proceeds in a syn fashion to generate isomerically pure exocyclic vinyllithiums that may be functionalized to give stereoisomerically pure products. At the higher temperatures needed to effect cyclization of 6-heptynyllithiums, the initially formed (*Z*)-vinyllithium intermediate is isomerized to the more stable *E*-isomer which, when trapped with an electrophile, affords stereoisomerically pure product formally derived from anti addition to the triple bond.

The construction of carbocycles with predictable regio- and stereocontrol remains a perennial challenge in organic chemistry. A conceptually simple approach to this synthetic problem involves intramolecular addition of a reactive center to a carbon–carbon multiple bond, and a number of general methods have evolved that exploit the reactivity of cationic, radical, and anionic intermediates.[2] While cationic[2,3] and radical-initiated[4] cyclization reactions are now widely used methods in organic synthesis, much less attention has focused on the formation of carbocycles via the anionic route. Indeed, the construction of ring systems by intramolecular addition of an anionic center to an unactivated carbon–carbon $\pi$-bond is a relatively recent development.[5-7] Various organolithium derivatives, in particular, have proved ideal for intramolecular cyclization reactions leading to cyclopentyl-containing products,[8,9] and the synthetic utility of such anionic cyclizations is further enhanced by the ease with which the organometallic product may be functionalized by reaction with an electrophile.

The successful utilization of the cyclization of olefinic alkyllithiums to prepare saturated carbocycles suggests that intramolecular addition of an organolithium reagent to an acetylenic moiety would be a potentially attractive alternative to radical-based strategies[4] for the construction of exocyclic alkenes. In fact, such an approach was investigated some 25 years ago: the discovery by Kandil and Dessy of an intramolecular addition of an aryllithium to a proximate alkyne[10] prompted Ward to investigate the generation and cyclization of an acetylenic alkyllithium.[11] In a now classical paper,[11] Ward reported that treatment of 6-bromo-1-phenyl-1-hexyne with *n*-BuLi in *n*-hexane–diethyl ether (5:1 by volume) at room temperature, followed by hydrolysis with water, gave a mixture of products that included a substantial proportion of benzylidenecyclopentane. Ward[11] and




others[12] have presented convincing evidence that these products result from the intermediacy of free radicals generated in the reaction of *n*-BuLi with the bromide. Subsequent investigations have demonstrated that this behavior is general:[13] lithium–bromine interchange between an alkyllithium and a primary alkyl bromide proceeds, at least in part, via single-electron transfer to give

(1) (a) University of Connecticut. (b) Connecticut College.
(2) For a recent review of cyclization reactions, see: Thebtaranonth, C.; Thebtaranonth, Y. *Tetrahedron* **1990**, *46*, 1385.
(3) Johnson, W. S. *Bioorg. Chem.* **1976**, *5*, 51.
(4) Representative examples may be found in the following: (a) Beckwith, A. L. J.; Ingold, K. U. *Rearrangements in Ground and Excited States*; de Mayo, P., Ed.; Academic: New York, 1980; Vol. 1, Essay 4. (b) Beckwith, A. L. J. *Tetrahedron* **1981**, *37*, 3073. (c) Surzur, J. M. *Reactive Intermediates*; Abramovitch, R., Ed.; Plenum: New York, 1982; Vol. 2, Chapter 3. (d) Hart, D. J. *Science* **1984**, *223*, 883. (e) Giese, B. *Radicals in Organic Synthesis*; Pergamon: New York, 1986. (f) Curran, D. P. *Synthesis* **1988**, 417 and 489. (g) Giese, B. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 969.
(5) For early reports on the cyclization of 5-hexenyllithiums, see: (a) St. Denis, J.; Dolzine, T.; Oliver, J. P. *J. Am. Chem. Soc.* **1972**, *94*, 8260. (b) Drozd, V. N.; Ustynyuk, Yu. A.; Tsel'eva, M. A.; Dmitriev, L. B. *J. Gen. Chem. USSR* **1969**, *39*, 1991. (c) Smith, M. J.; Wilson, S. E. *Tetrahedron Lett.* **1981**, *22*, 4615.
(6) Cyclization of unsaturated alkyl Grignard reagents: (a) Richey, H. G., Jr.; Rothman, A. M. *Tetrahedron Lett.* **1968**, 1457. (b) Kossa, W. C., Jr.; Rees, T. C.; Richey, H. G., Jr. *Tetrahedron Lett.* **1971**, 3455. (c) Hill, E. A. *J. Organomet. Chem.* **1975**, *91*, 123.
(7) Cyclization of unsaturated alkyl cuprates: (a) Crandall, J. K.; Battioni, P.; Wehlacz, J. T.; Bindra, R. *J. Am. Chem. Soc.* **1975**, *97*, 7171. (b) Normant, J. F.; Alexakis, A. *Synthesis* **1981**, 841.
(8) Bailey, W. F.; Patricia, J. J.; DelGobbo, V. C.; Jarret, R. M.; Okarma, P. J. *J. Org. Chem.* **1985**, *50*, 1999. (b) Bailey, W. F.; Nurmi, T. T.; Patricia, J. J.; Wang, W. *J. Am. Chem. Soc.* **1987**, *109*, 2442. (c) Bailey, W. F.; Rossi, K. *J. Am. Chem. Soc.* **1989**, *111*, 765. (d) Bailey, W. F.; Khanolkar, A. D. *J. Org. Chem.* **1990**, *55*, 6058. (e) Bailey, W. F.; Khanolkar, A. D. *Tetrahedron Lett.* **1990**, *31*, 5993. (f) Bailey, W. F.; Khanolkar, A. D. *Tetrahedron* **1991**, *47*, 7727. (g) 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. (h) Bailey, W. F.; Khanolkar, A. D.; Gavaskar, K. V. *J. Am. Chem. Soc.* **1992**, *114*, 8053.
(9) (a) Smith, M. J.; Wilson, S. E. *Tetrahedron Lett.* **1981**, *22*, 4615. (b) Ross, G. A.; Koppang, M. D.; Bartak, D. E.; Woolsey, N. F. *J. Am. Chem. Soc.* **1985**, *107*, 6742. (c) Cooke, M. P., Jr. *J. Org. Chem.* **1992**, *57*, 1495 and references therein. (d) Chamberlin, A. R.; Bloom, S. H.; Cervini, L. A.; Fotsch, C. H. *J. Am. Chem. Soc.* **1988**, *110*, 4788 and references therein. (e) Broka, C. A.; Shen, T. *J. Am. Chem. Soc.* **1989**, *111*, 2981. (f) Paquette, L. A.; Gilday, J. P.; Maynard, G. D. *J. Org. Chem.* **1989**, *54*, 5044. (g) Krief, A.; Barbeaux, P. *Synlett* **1990**, 511.
(10) Kandil, S. A.; Dessy, R. E. *J. Am. Chem. Soc.* **1966**, *88*, 3027.
(11) Ward, H. R. *J. Am. Chem. Soc.* **1967**, *89*, 5517.
(12) Ohnuki, T.; Yoshida, M.; Simamura, O. *Chem. Lett.* **1972**, 999.
(13) Bailey, W. F.; Patricia, J. J. *J. Organomet. Chem.* **1988**, *352*, 1.

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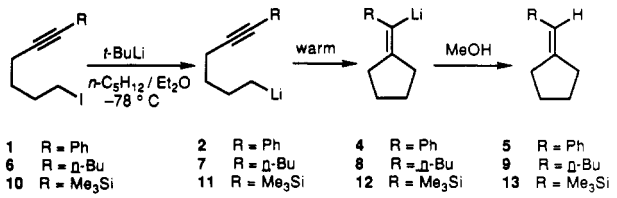
**Scheme I**



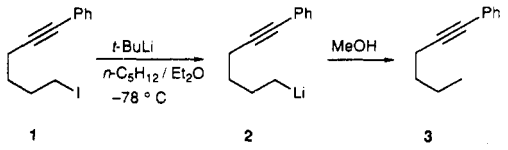

1 R = Ph; 6 R = n-Bu; 10 R = $Me_3Si$ — 2 R = Ph; 7 R = n-Bu; 11 R = $Me_3Si$ — 4 R = Ph; 8 R = n-Bu; 12 R = $Me_3Si$ — 5 R = Ph; 9 R = n-Bu; 13 R = $Me_3Si$

reactive alkyl radicals.[14] Since the lithium–iodine exchange of analogous substrates is, in contrast, an inner-sphere process that does not involve radical intermediates when conducted under appropriate conditions,[14,15] it occurred to us that the use of an acetylenic alkyl iodide rather than the bromide should allow for the clean generation of acetylenic alkyllithiums by lithium–iodine exchange. The experiments detailed below demonstrate that this is indeed the case.

Herein, we report the results of a comprehensive study probing the scope and limitations of the anionic cyclization of acetylenic organolithiums which are prepared by low-temperature lithium–iodine exchange.[16] As detailed below, this methodology provides a regiospecific and highly stereoselective route to 4-, 5-, and 6-membered rings bearing functionalized exocyclic alkene moieties.

## Results and Discussion

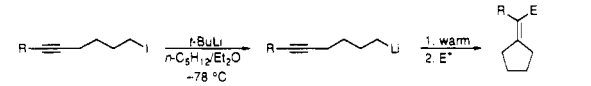
**5-*Exo* Cyclization of 5-Hexynyllithiums.** As expected from the results of mechanistic studies of the metal–halogen exchange reaction,[13,14] it was found that Ward's substrate could be converted to the corresponding acetylenic alkyllithium in virtually quantitative yield provided the iodide rather than the bromide was used. Thus, treatment of a solution of 6-iodo-1-phenyl-1-hexyne (**1**) in *n*-pentane–diethyl ether (3:2 by vol) with 2.0–2.2 equiv of *tert*-butyllithium (*t*-BuLi) in *n*-pentane at −78 °C cleanly generated the corresponding acetylenic alkyllithium (**2**) as demonstrated by the fact that quench of the reaction mixture with an excess of deoxygenated methanol afforded 1-phenyl-1-hexyne (**3**) in 96% isolated yield. Moreover, when MeOD was added to the cold solution of **2**, the isolated acetylene was found to contain 91% $d_1$ at the terminal carbon. Analogous results were obtained with other acetylenic alkyl iodides bearing a variety of substituents at the acetylenic carbon.




1 — 2 — 3

With a method in hand for the preparation of acetylenic alkyllithiums by low-temperature lithium–iodine exchange,[15] intramolecular cyclizations were investigated. As shown in Scheme I, 5-hexynyllithiums cleanly isomerize upon warming to room temperature to give exocyclic vinyllithiums via a regiospecific 5-*exo*-*dig* ring closure. Thus, for example, 6-phenyl-5-hexynyllithium (**2**), prepared at −78 °C as described above, undergoes facile isomerization upon warming to ca. 25 °C to give (1-cyclopentylidenebenzyl)lithium (**4**). Quench of the reaction mixture with deoxygenated methanol afforded benzylidenecyclopentane (**5**) in 98% isolated yield (Scheme I). The remaining 2% of the reaction mixture consisted of the uncyclized hydrocarbon (**3**): no trace of any other products could be detected by GC or NMR. Analogous results, presented in Scheme I, were obtained with 5-decynyllithium (**7**) and [6-(trimethylsilyl)-5-hexynyl]-lithium (**11**).

**Table I.** Cyclization of 5-Hexynyllithiums[a]




| entry | R | $E^+$ | E | yield,[b] % |
|---|---|---|---|---|
| 1 | Ph | $D_2O$ | D | 88 |
| 2 | Ph | $CH_2$=$CHCH_2Br$ | $CH_2$=$CHCH_2$ | 57[c] |
| 3 | Ph | $CH_3CHO$ | $CH_3CHOH$ | 86 |
| 4 | Ph | $CO_2$ | COOH | 76 |
| 5 | Ph | PhCHO | PhCHOH | 90 |
| 6 | *n*-Bu | MeOH | H | 84 |
| 7 | *n*-Bu | $CH_3COCH_3$ | $CH_3C(OH)CH_3$ | 69 |
| 8 | *n*-Bu | $CH_3(CH_2)_2CHO$ | $CH_3(CH_2)_2CHOH$ | 83 |
| 9 | *n*-Bu | $(CH_3)_2NCHO$ | CHO | 68 |
| 10 | $(CH_3)_3Si$ | MeOH | H | 96 |

[a] 5-Hexynyllithiums were generated at −78 °C by addition of 2.2 equiv of *t*-BuLi to a solution of the acetylenic alkyl iodide in *n*-petane–diethyl ether (3:2 by volume), the cooling bath was removed, and the mixture was allowed to warm and stand at room temperature for 15–60 min after which period the mixture was recoled to −78 °C and ~2 equiv of the electrophile was added. [b] Isolated yields of chromatographically pure product. [c] This reaction also produced ~25% of the vinyl bromide.

As would be expected, the exocyclic vinyllithium produced upon cyclization of a 5-hexynyllithium may be trapped by reaction with any of a variety of different electrophiles to deliver synthetically useful, functionalized derivatives in good to excellent isolated yields (60–90%). The results of these experiments are summarized in Table I. The functionalized cyclopentylidene-containing products were easily prepared by treatment of an approximately 0.1 M solution of the acetylenic alkyl iodide in *n*-pentane–diethyl ether (3:2 by volume) at −78 °C under argon with 2.0–2.2 equiv of *t*-BuLi in *n*-pentane. The resulting 5-hexynyllithium was then allowed to warm and stand at room temperature for 15–60 min to complete the cyclization after which period the solution was recooled to −78 °C and the electrophile, which was carefully purified immediately before use (usually by distillation in a flame-dried apparatus under nitrogen or argon), was added in excess (~2 equiv). After warming to room temperature, the functionalized product, which was obtained simply by solvent evaporation, was easily purified by flash chromatography or recrystallization. The only byproduct detected in greater than trace amounts from these reactions was typically 2–8% of the easily removed, unfunctionalized open-chain alkyne which, as noted elsewhere,[15] is produced during the initial lithium–halogen exchange by proton abstraction from the cogenerated *t*-BuI.

While intramolecular cyclization reactions of various organometallic derivatives of the 5-hexynyl system are known,[6,7] the relatively facile isomerization of the 5-hexynyllithiums (Scheme I and Table I) is unprecedented. The alkyl-substituted system, 5-decynyllithium (**7**), undergoes cleanly first-order cyclization to 1-(cyclopentylidene)pentyllithium (**8**) with a half-life of ~7 min ($k = (1.59 \pm 0.07) \times 10^{-3}$ s$^{-1}$)[17] at +28.8 °C. The activation parameters that characterize this reaction ($\Delta H^{\ddagger} = 23 \pm 0.9$ kcal/mol and $\Delta S^{\ddagger} = +4 \pm 3.3$ eu)[17] indicate that the rate of cyclization is strongly dependent on temperature; in fact, at temperatures below 0 °C the isomerization of **7** to **8** is quite sluggish. However, an equally important factor influencing the facility of ring closure of 5-hexynyllithiums is exerted by the nature of the substituent on the triple bond: the phenyl-substituted analog of **7**, (6-phenyl-5-hexynyl)lithium (**2**), cyclizes remarkably rapidly with a half-life of ~6 min at −50.6 °C ($k = (1.97 \pm 0.08) \times 10^{-3}$ s$^{-1}$).[17]

(14) (a) Bailey, W. F.; Patricia, J. J.; Nurmi, T. T.; Wang, W. *Tetrahedron Lett.* **1986**, *27*, 1861. (b) Bailey, W. F.; Patricia, J. J.; Nurmi, T. T. *Tetrahedron Lett.* **1986**, *27*, 1865.

(15) Bailey, W. F.; Punzalan, E. R. *J. Org. Chem.* **1990**, *55*, 5404.

(16) Preliminary accounts of some of these results have appeared, see: (a) Bailey, W. F.; Ovaska, T. V.; Leipert, T. K. *Tetrahedron Lett.* **1989**, *30*, 3901. (b) Bailey, W. F.; Ovaska, T. V. *Tetrahedron Lett.* **1990**, *31*, 627. Analogous studies of 5-hexynyllithium and 6-heptynyllithium cyclization have been reported by Negishi's group. See: Wu, G.; Cederbaum, F. E.; Negishi, E. *Tetrahedron Lett.* **1990**, *31*, 493.

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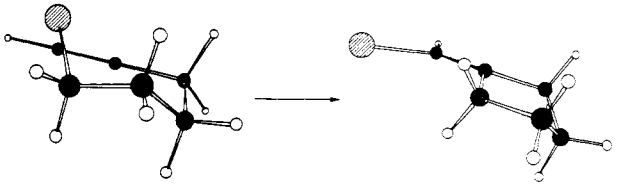
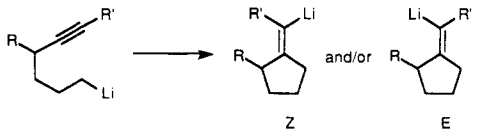


**Figure 1.** Transition state model for the cyclization of a 5-hexynyllithium.

Indeed, at this low temperature, isomerization of **2** to **4** is approximately $10^6$ times more rapid than is the cyclization of **7** to **8**! As noted elsewhere,[17] the rapid cyclization of **2** to **4** is most likely a consequence of a reduction in $\Delta H^{\ddagger}$ due to stabilization of the incipient vinyllithium product by the phenyl group.

The exclusive formation of 5-membered rings via 5-*exo* cyclization of 5-hexynyllithiums is in accord with observations that intramolecular additions of organometallic reagents to 4,5-, 5,6-, and 6,7-double bonds invariably form the smaller of the two possible rings.[18,19] Undoubtedly, the physical basis of these results lie in the stereochemical requirements of the transition states for the respective ring closures. As shown in Figure 1, a chair-like transition state complex can be invoked to account for the preferred 5-*exo* cyclization of 5-hexynyllithiums. This putative activated complex invokes coordination of the Li atom at C(1) with the C(5)–C(6) $\pi$-system to give a fairly rigid transition state geometry.[20] In view of the 180° dihedral angle imposed by the triple bond, the regiospecific 5-*exo* cyclization is conveniently rationalized by positing that the approach of the anionic center [i.e., C(1)] to the nearest carbon [i.e., C(5)] may be less energetically costly than approach to the more distant carbon [C(6)].

The transition-state model illustrated in Figure 1 implies that the cyclization reaction proceeds by a syn addition of the $CH_2Li$ moiety to the triple bond. None the less, as shown below, cyclization of a 4-substituted 5-hexynyllithium could, in principle, yield either the *Z*-isomer or the *E*-isomer or even a mixture of the two. On the assumption that the vinyllithium product is configurationally stable (vide infra), the *Z*-product would necessarily be derived from syn addition of $CH_2Li$ to the acetylenic moiety whereas the *E*-isomer would be generated by anti addition.




In an effort to address this stereochemical question, the cyclization of substrates bearing substituents at the propargylic position was investigated. As illustrated in Scheme II, treatment of either 4-ethyl-1-iodo-5-decyne (**14**) or 9-iodo-6,6-dimethyl-4-nonyne (**18**) with *t*-BuLi according to the general protocol for low-temperature lithium–iodine exchange,[15] followed by warming at room temperature for 1 h and then quench of the reaction mixture with deoxygenated methanol, resulted in the formation of (*Z*)-1-ethyl-2-pentylidenecyclopentane (**17**) and (*Z*)-1,1-dimethyl-2-butylidenecyclopentane (**21**) in 75% and 78% yield, respectively. The balance of the product in each case was the uncyclized alkyne. As shown in Scheme II, the isomerizations proceed in a totally stereoselective fashion to give the configurationally stable (*Z*)-vinyllithiums (**16** and **20**) via syn addition of the $CH_2Li$ to the acetylenic moiety. No trace of the *E*-isomers could be detected by either GC or $^1H$ NMR analysis of the product mixtures. For the sake of continuity, analysis of the stereochemistry of this and subsequent systems will be discussed in the section on configurational assignments (vide infra). It is, however, perhaps appropriate to note at this juncture that, in contrast to the complete stereocontrol observed in the cyclization of substituted 5-hexynyllithiums, the Wittig reaction of 2-ethylcyclopentanone with the ylide derived from butyltriphenylphosphonium iodide using *t*-BuOK as a base resulted in the formation of an approximately 1:1 mixture of the *E*- and *Z*-isomers of 1-ethyl-2-pentylidenecyclopentane [(*E*/*Z*)-**17**].

The configurational stability of the alkyl-substituted vinyllithium products generated in the cyclization reactions (Scheme II) is consistent with a wealth of literature precedents.[21] Thus, it is clear that vinylic organolithium compounds bearing alkyl substituents on the double bond do not readily isomerize at room temperature in diethyl ether solution. By contrast, vinyllithium compounds bearing aryl substituents are known to undergo facile cis–trans isomerization, and kinetic studies on the rate of isomerization of many such compounds have been reported.[22] It was no surprise, therefore, that cyclization at 20 °C of the phenyl-substituted hexynyllithium, **23**, prepared from 6-iodo-3,3-dimethyl-1-phenyl-1-hexyne (**22**) upon reaction with *t*-BuLi, afforded, as summarized in Scheme III, a 30:70 mixture of the *Z*-isomer (**26**) and the *E*-isomer (**27**) of the benzylidenecyclopentane product upon warming and quench with deoxygenated methanol. Undoubtedly, the formation of a mixture of isomeric products in this cyclization is a consequence of the fairly rapid equilibration of the (*Z*)- and (*E*)-vinyllithiums (Scheme III, **24** and **25**) at 20 °C.

Fortunately, as noted above, the insertion of an acetylenic moiety into a carbon–lithium bond is considerably accelerated by the presence of a phenyl substituent on the triple bond. Indeed, the relative rates for cyclization of a phenyl-substituted 5-hexynyllithium[17] and cis–trans isomerization of a phenyl-substituted vinyllithium[22] indicate that the cyclization should be complete well before equilibration of the product vinyllithiums. This analysis suggested that conducting the cyclization of phenyl-substituted 5-hexynyllithiums at lower temperatures might have a dramatic effect on the stereochemical outcome of the reaction. Trimethylsilyl-substituted acetylenic alkyllithiums might be expected to behave similarly; it is well-known that negative charges in the $\alpha$-position are stabilized by trialkylsilyl groups,[23] and a trimethylsilyl substituent would be expected to lower the $\Delta H^{\ddagger}$ of the cyclization through stabilization of the incipient vinyllithium. In the event, the ratio of cyclic isomers produced upon cyclization of phenyl- or trimethylsilyl-substituted 5-hexynyllithiums was found to be strongly dependent on the temperature at which the reaction was conducted. The results of such experiments are summarized in Table II.

As shown in Table II, dramatically different ratios of cyclic isomers were produced upon cyclization of **23** at various temperatures followed by quench with deoxygenated methanol. At −55 °C the isomerization proceeded to completion in 30 min and gave an approximately 8.5:1 ratio of **26** and **27**, respectively (Table II, entry 4). Further experiments revealed that the cyclization could be effected at temperatures as low as −78 °C; under these conditions the isomerization of **23** proceeds in 1 h with almost complete syn selectivity to give an approximately 15:1 ratio of the *Z*- and *E*-isomers (Table II, entry 3). The

(18) (a) Hill, E. A.; Richey, H. G., Jr.; Rees, T. C. *J. Org. Chem.* **1963**, *28*, 2161. (b) Richey, H. G., Jr.; Rees, T. C. *Tetrahedron Lett.* **1966**, 4297.

(19) (a) Cooke, M. P., Jr. *J. Org. Chem.* **1984**, *49*, 1144. (b) Cooke, M. P., Jr.; Widener, R. K. *J. Org. Chem.* **1987**, *52*, 1381.

(20) Recently reported molecular orbital calculations on 5-hexenyllithium indicate that there is an energetically favorable coordination of the lithium atom at C(1) with the C(5)–C(6) $\pi$-bond in the transition state leading to ring closure of this olefinic alkyllithium (for a discussion of the evidence, see ref 8g). A similar interaction may well be present in the activated complex formed during the isomerization of a 5-hexynyllithium.

(21) (a) Braude, E. A.; Coles, J. A. *J. Am. Chem. Soc.* **1951**, *73*, 2078. (b) Dreiding, A. S.; Pratt, R. J. *J. Am. Chem. Soc.* **1954**, *76*, 1902. (c) Curtin, D. Y.; Crump, J. W. *J. Am. Chem. Soc.* **1958**, *80*, 1922. (d) Miller, S. I.; Lee, W. G. *J. Am. Chem. Soc.* **1959**, *81*, 6313.

(22) Hunter, D. H.; Cram, D. J. *J. Am. Chem. Soc.* **1964**, *86*, 5478.

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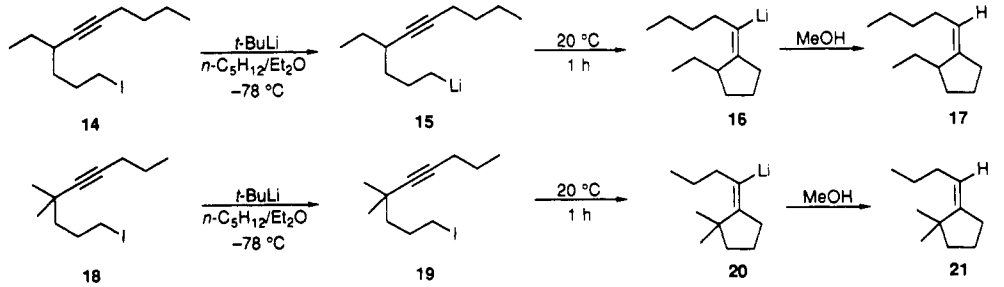
**Scheme II**




**Scheme III**

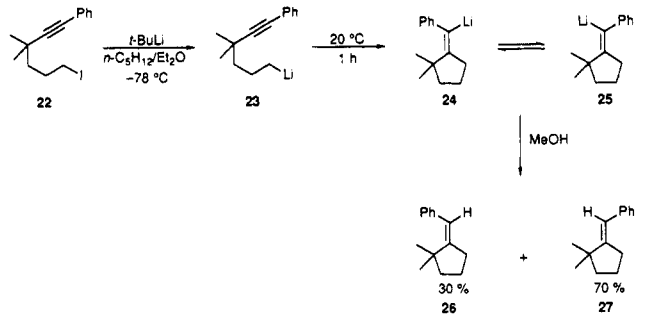
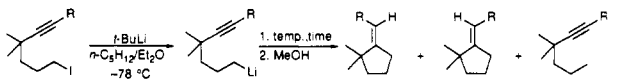



**Table II.** Stereochemistry of Cyclization of 5-Hexynyllithiums




| entry | R | temp, °C | time, min | *Z*-isomer, % | *E*-isomer, % | alkyne, % |
|---|---|---|---|---|---|---|
| 1 | Ph | −100 | 5 | 2 | 0 | 98 |
| 2 | Ph | −78 | 5 | 31 | 3 | 66 |
| 3 | Ph | −78 | 60 | 88 | 6 | 6 |
| 4 | Ph | −55 | 30 | 85 | 10 | 5 |
| 5 | Ph | 20 | 15 | 32 | 63 | 5 |
| 6 | Ph | 20 | 60 | 29 | 67 | 4 |
| 7 | $(CH_3)_3Si$ | −78 | 120 | 98 | 0 | 2 |
| 8 | $(CH_3)_3Si$ | −49 | 60 | 83 | 14 | 3 |
| 9 | $(CH_3)_3Si$ | 20 | 60 | 11 | 84 | 5 |

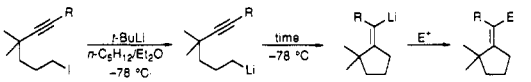
relatively rapid low-temperature cyclization of **23** is most likely a consequence of the Thorpe–Ingold effect[24] engendered by the presence of the *gem*-dimethyl substituents at the propargylic position. Indeed, ring closure of **23** is so facile that it was necessary to conduct the lithium–iodine exchange reaction at −100 °C in order to fully suppress cyclization (Table II, entry 1).

Similar results were obtained in a less extensive study involving the analogous trimethylsilyl-substituted compound (Table II, entries 7–9). Thus, treatment of trimethyl(6-iodo-3,3-dimethyl-1-hexynyl)silane (**28**) with *t*-BuLi at −78 °C followed by warming of the reaction mixture at 20 °C for 60 min gave a 1:7.6 ratio of the *Z*- and *E*-isomers, **30** and **31**, respectively, upon hydrolysis with deoxygenated methanol (Table II, entry 9). When the reaction was conducted at −49 °C the product ratio was almost completely reversed; quench of the reaction mixture after 1 h under these conditions afforded a 97% yield of **30** and **31** in a 6:1 ratio (Table II, entry 8). Exclusive formation of the *Z*-isomer (**30**) was observed when the reaction mixture was allowed to stand at −78 °C for 2 h prior to quench with deoxygenated methanol. Indeed, under these conditions the cyclization proceeds with complete stereoselectivity to give the less stable *Z*-isomer (Table III, entry 7).

The relatively rapid low-temperature cyclization of the phenyl- and trimethylsilyl-substituted 5-hexynyllithiums bearing two methyl groups at the propargylic position was exploited for the preparation of stereoisomerically pure, functionalized exocyclic derivatives. As indicated by the results presented in Table III, functionalization of the (*Z*)-vinyllithium produced upon cyclization at −78 °C of the 5-hexynyllithium derived from **22** or **28** proceeded without difficulty to deliver isomerically pure products in good yield.[25]

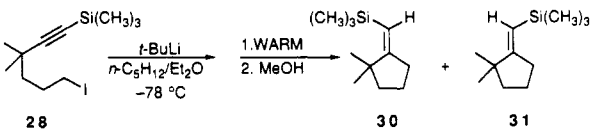
(24) Allinger, N. L.; Zalkov, V. *J. Org. Chem.* **1960**, *25*, 701.

**Table III.** Stereoselective Cyclization of 5-Hexynyllithiums[a]




| entry | R | time, min | $E^+$ | E | yield,[b] % |
|---|---|---|---|---|---|
| 1 | Ph | 60 | $CH_3OH$ | H | 88 |
| 2 | Ph | 60 | PhCHO | PhCHOH | 72 |
| 3 | Ph | 60 | $(CH_3)_3CCHO$ | $(CH_3)_3CCHOH$ | 84 |
| 4 | Ph | 60 | $CO_2$ | COOH | 76 |
| 5 | Ph | 60 | $CH_3CHO$ | $CH_3CHOH$ | 82 |
| 6 | $(CH_3)_3Si$ | 120 | $CH_3OH$ | H | 95 |

[a] The 5-hexynyllithiums were generated at −78 °C by addition of 2.2 equiv of *t*-BuLi to a solution of iodide **22** (R = Ph) or **28** (R = TMS) in *n*-pentane–diethyl ether (3:2 by volume), and the reaction mixture was stirred at −78 °C for the specified time after which period ~2 equiv of the electrophile was added. [b] Isolated yields of chromatographically pure product.




**4-*Exo* Cyclization of 4-Pentynyllithiums.** At the inception of this study the preferred mode of cyclization of a 4-pentynyllithium was an open question. Baldwin's rules for ring closure[26] hold that 4-*exo-dig* cyclization leading to a strained cyclobutylidene organolithium is disfavored vis-à-vis the 5-*endo-dig* process that would give a lithiocyclopentene. Indeed, in suitably constituted systems, 5-*endo* cyclization of acetylenic organometallics has been observed, and exclusive 5-*endo* ring closure has been reported for several aryllithiums bearing proximate carbon–carbon triple bonds.[27] On the other hand, 4-*exo* closure of several 4-pentynyl organometallics has been reported.[28,29]

In light of these isolated reports on the rather limited formation of 4-membered carbocycles via 4-*exo-dig* cyclization, we were delighted to discover that benzylidenecyclobutane (**34**, R = Ph) was formed in *nearly quantitative yield* when (5-phenyl-4-

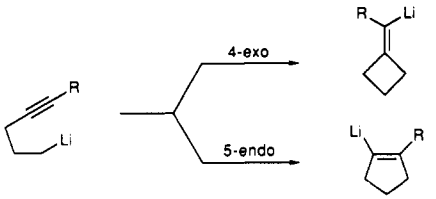
(25) It is perhaps worth noting explicitly that the stereochemical descriptor used to specify the configuration of the functionalized cycloalkylidene products will often differ from that used to name the vinyllithium precursor when a substituent having a higher priority than Li is introduced upon quench with an electrophile.

(26) Baldwin, J. E. *J. Chem. Soc.* **1976**, 734.

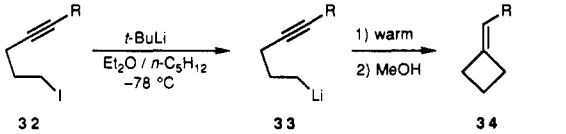
(27) (a) Dessy, R. E.; Kandil, S. A. *J. Org. Chem.* **1965**, *30*, 3857. (b) Johnson, F.; Subramanian, R. *J. Org. Chem.* **1986**, *51*, 5040.

(28) Crandall, J. K.; Keyton, D. J. *Tetrahedron Lett.* **1969**, *31*, 122. It is not clear whether the benzylidenecyclobutane observed in these studies resulted from isomerization of a 5-penten-1-yl radical or from cyclization of the corresponding organolithium.

(29) Fujikura, S.; Inoue, M.; Utimoto, K.; Nozaki, H. *Tetrahedron Lett.* **1984**, *25*, 1999.

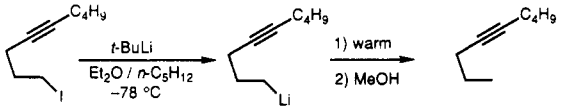



pentynyl)lithium (**33**, R = Ph), prepared from 5-iodo-1-phenyl-1-pentyne (**32**, R = Ph) by lithium–iodine exchange, was warmed at room temperature for 15 min followed by addition of methanol. The only byproduct (~5%) formed in the reaction was the uncyclized alkyne; no trace of the 5-*endo* product, 1-phenylcyclopentene, could be detected. Analogous results were obtained with the trimethylsilyl-substituted alkynyllithium (**33**, R = $Si(CH_3)_3$) which underwent facile isomerization to deliver trimethyl(cyclobutylidenemethyl)silane (**34**, R = $Si(CH_3)_3$) in 89% isolated yield upon hydrolysis and workup.




**32** **33** **34**
93 % (R = Ph)
89 % (R = TMS)

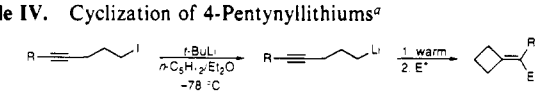
In contrast to these results, the alkyl-substituted 4-pentynyllithium was stable at room temperature for extended periods of time and, as shown below, gave only unrearranged alkyne upon quench with methanol. Attempts to facilitate the cyclization of 4-nonynyllithium by conducting the reaction in the presence of *N,N,N′,N′*-tetramethylethylenediamine (TMEDA) proved futile and resulted in the formation of at least six isomeric $C_9H_{16}$ hydrocarbons, none of which was identified as butylidenecyclobutane (**34**, R = *n*-Bu). In fact, we have been unable to find conditions that result in synthetically useful 4-*exo* cyclization of alkyl-substituted 4-pentynyllithiums.




The vinyllithiums derived from the facile 4-*exo* isomerization of trimethylsilyl- and phenyl-substituted 4-pentynyllithiums were efficiently trapped by addition of electrophiles to deliver functionalized products in good to excellent isolated yields (Table IV). On the basis of these results, it is clear that this methodology provides a convenient, regiospecific "one-pot" synthesis of highly strained *exo*-methylenecyclobutanes that are not easily obtained by other means.

The stereochemistry of the cyclization of phenyl- and trimethylsilyl-substituted 4-pentynyllithiums was probed in a series of experiments employing substrates bearing *gem*-dimethyl substituents at the propargylic position. Lithium–iodine exchange at −78 °C served to generate 3,3-dimethyl-5-phenyl-4-pentynyllithium (**36**) and 3,3-dimethyl-5-(trimethylsilyl)-4-pentynyllithium (**40**) from the corresponding iodides (**35** and **39**, respectively). As expected, the cyclization of these substrates was found to be a stereoselectively syn process when care was taken to conduct the isomerizations at a temperature low enough to preclude cis–trans isomerization of the vinyllithium products. As illustrated by the data presented in Table V, the rate of cyclization of the 4-pentynyllithium system is significantly slower than that of the 5-hexynyllithiums discussed above. When **36** was warmed at 20 °C for 15 min followed by quench with deoxygenated methanol, the product was found to be an approximately 1.3:1 ratio the *Z*- and *E*-isomers (Table V, entry 4). However, conducting the cyclization of **36** at −35 °C for 1 h produced pure (*Z*)-**38** in 93% yield; only a trace of the *E*-isomer could be detected by GC (Table V, entry 3). A preparative-scale reaction performed at −35 °C gave isomerically pure **38** in 91% isolated yield. The TMS derivative, **40**, behaved similarly (Table V, entries 5 and 6), and stereoisomerically pure (*Z*)-**42** was obtained in an isolated yield of 86% by conducting the cyclization at −50 °C for 30 min. Although no attempt was made to prepare isomerically pure functionalized derivatives of **37** or **41**, it is clear from the foregoing discussion that such products should be readily available by trapping of the isomerically pure vinyllithiums with suitable electrophiles.

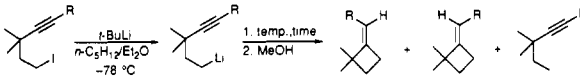
**Table IV.** Cyclization of 4-Pentynyllithiums[a]



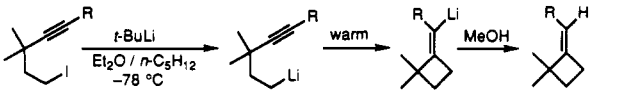

| entry | R | $E^+$ | E | yield,[b] % |
|---|---|---|---|---|
| 1 | Ph | $CH_3OH$ | H | 93 |
| 2 | Ph | $(CH_3)_2NCHO$ | CHO | 90 |
| 3 | Ph | PhCHO | PhCHOH | 84 |
| 4 | Ph | $H_2CO$ | $CH_2OH$ | 62 |
| 5 | $(CH_3)_3Si$ | $CH_3OH$ | H | 89 |
| 6 | $(CH_3)_3Si$ | $CH_3(CH_2)_2CHO$ | $CH_3(CH_2)_2CHOH$ | 90 |
| 7 | $(CH_3)_3Si$ | $CO_2$ | COOH | 84 |
| 8 | $(CH_3)_3Si$ | $(CH_3)_2CHCHO$ | $(CH_3)_2CHCHOH$ | 86 |
| 9 | $(CH_3)_3Si$ | $(CH_3)_3CCHO$ | $(CH_3)_3CCHOH$ | 90 |
| 10 | $(CH_3)_3Si$ | $ClCO_2Et$ | $CO_2Et$ | 75 |
| 11 | $(CH_3)_3Si$ | $(CH_3)_2NCHO$ | CHO | 92 |
| 12 | $(CH_3)_3Si$ | $CH_2CH_2O$ | $CH_2CH_2OH$ | 91 |
| 13 | $(CH_3)_3Si$ | $CH_3CHCH_2O$ | $CH_2CH(OH)CH_3$ | 81 |

[a] The 4-pentynyllithiums, generated from iodide **35** (R = Ph) or **39** (R = TMS) as described in footnote *a* of Table I, were allowed to warm and stand at room temperature (15 min in the case of R = Ph or 1 h in the case of R = TMS) after which period the mixture was recooled to −78 °C and ~2 equiv of the electrophile was added. [b] Isolated yield of chromatographically pure product.

**Table V.** Stereochemistry of Cyclization of 4-Pentynyllithiums




| entry | R | temp, °C | time, min | *Z*-isomer, % | *E*-isomer, % | alkyne, % |
|---|---|---|---|---|---|---|
| 1 | Ph | −78 | 60 | 0 | 0 | 100 |
| 2 | Ph | −50 | 60 | 45 | 0 | 55 |
| 3 | Ph | −35 | 60 | 93 | trace | 7 |
| 4 | Ph | 20 | 15 | 54 | 41 | 5 |
| 5 | $(CH_3)_3Si$ | −50 | 30 | 90 | 0 | 10 |
| 6 | $(CH_3)_3Si$ | 20 | 60 | 41 | 51 | 8 |

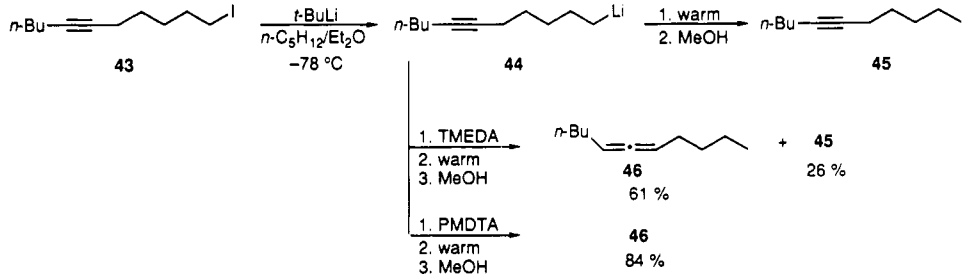



**35** R = Ph **36** R = Ph **37** R = Ph **38** R = Ph
**39** R = $Me_3Si$ **40** R = $Me_3Si$ **41** R = $Me_3Si$ **42** R = $Me_3Si$

**6-*Exo* Cyclization of 6-Heptynyllithiums.** The relatively facile isomerization of 5-hexynyllithiums to the corresponding (cyclopentylidenemethyl)lithium derivatives prompted us to explore the possibility of constructing 6-membered rings via 6-*exo-dig* cyclization. It was anticipated, however, that this mode of isomerization would be more difficult than 5-*exo-dig* cyclization leading to 5-membered rings. Consequently, in such situations, other reaction channels may become available that would consume the reactive acetylenic alkyllithium, and just such behavior was observed for alkyl-substituted 6-heptynyllithiums.

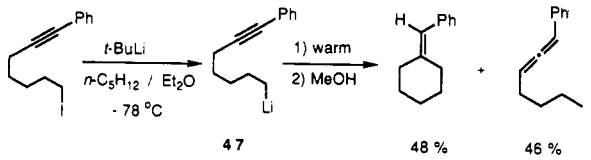
As illustrated in Scheme IV, treatment of 11-iodo-5-undecyne (**43**) with *t*-BuLi at −78 °C generated 6-undecynyllithium (**44**)

**Scheme IV**




in essentially quantitative yield. No isomerization of **44** occurred under the usual conditions employed for the cyclization of 5-hexynyllithiums. Even after several hours at 20 °C the only product that could be isolated, upon hydrolysis with methanol, was the open-chain hydrocarbon, 5-undecyne (**45**), derived from the initial lithium–iodine exchange. When the reaction was conducted in the presence of TMEDA, which has been found to significantly facilitate cyclization of olefinic alkyllithiums,[8] extensive prototropic rearrangement ensued, and the allene, **46**, was generated as the major product (Scheme IV). The tridentate ligand, *N,N,N',N'',N''*-pentamethyldiethylenetriamine (PMDTA), was found to be even more effective in promoting allene formation: the use of this additive under the conditions shown in Scheme IV afforded **46** in 84% isolated yield. Indeed, we have been unable to find conditions that result in a synthetically useful cyclization of such alkyl-substituted substrates.

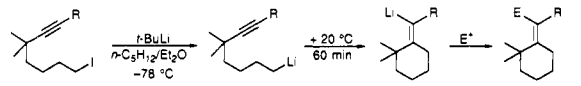
As shown below, the phenyl-substituted analog, **47**, behaves quite differently: quench of a reaction mixture that had been warmed at 20 °C for 1 h afforded an approximately 1:1 mixture of allene and benzylidenecyclohexane. Based on these results, it seems that ring closure of phenyl-substituted 6-heptynyllithiums and prototropic rearrangement leading to allenes are competitive processes at elevated temperatures; as cyclization becomes less favorable with increasing ring size, allene formation predominates.




Allene formation can obviously be totally suppressed by introduction of *gem*-dimethyl groups at the propargylic position of the 6-heptynyllithium and the relatively sluggish cyclization of such substrates would be expected, moreover, to benefit from operation of the Thorpe–Ingold effect.[24] Indeed, as shown below, organolithium **49**, which is prepared from iodide **48** in virtually quantitative yield, undergoes clean 6-*exo-dig* isomerization upon warming at room temperature for 1 h to give a vinyllithium (**50**) that may be trapped by addition of methanol (Table VI, entry 1) to give an 86% isolated yield of isomerically pure **51**. As indicated in Table VI, **50** could also be trapped with other electrophiles to give high isolated yields of functionalized products in which the phenyl substituent is trans with respect to the *gem*-dimethyl groups on the cyclohexane ring. Similarly, isomerization of 5,5-dimethyl-7-(trimethylsilyl)-6-heptynyllithium (**53**), prepared from the corresponding iodide (**52**), afforded the (*E*)-cyclohexylidene derivative (**55**) in 84% yield upon warming at room temperature for 1 h followed by hydrolysis with methanol (Table VI, entry 4).

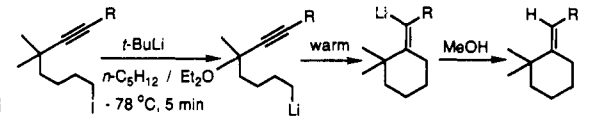
In light of the syn selectivity observed in the cyclization of 5-hexynyllithiums and 4-pentynyllithiums (vide supra), the stereochemical outcome of the isomerization of the 6-heptynyl system is intriguing. The products isolated from the 6-*exo* cyclization of **49** and **53** are stereoisomerically pure (Table VI) and were derived from reaction of the electrophiles with the

**Table VI.** Stereoselective Cyclization of 7-Heptynyllithiums[a]




| entry | R | $E^+$ | E | yield,[b] % |
|---|---|---|---|---|
| 1 | Ph | $CH_3OH$ | H | 86 |
| 2 | Ph | $CH_3CHO$ | $CH_3CHOH$ | 81 |
| 3 | Ph | $CH_3CH_2CHO$ | $CH_3CH_2CHOH$ | 78 |
| 4 | $(CH_3)_3Si$ | $CH_3OH$ | H | 84 |

[a] The 7-heptynyllithiums were generated at −78 °C buy addition of 2.2 equiv of *t*-BuLi to a solution of **48** (R = Ph) or **52** (R = TMS) in *n*-pentane–diethyl ether (3:2 by volume), the cooling bath was then removed, and the mixture was allowed to warm and stand at 20 °C for 1 h after which period ~2 equiv of the electrophile was added. [b] Isolated yields of chromatographically pure product.




**48** R = Ph, **52** R = $Me_3Si$ **49** R = Ph, **53** R = $Me_3Si$ **50** R = Ph, **54** R = $Me_3Si$ **51** R = Ph, **55** R = $Me_3Si$

*E*-isomer of the vinyllithiums (**50** and **54**). This stereochemical outcome is consistent with either (1) an anti addition of the $CH_2$-Li to the alkyne moiety or (2) a syn addition followed by rapid and complete isomerization of the configurationally labile (*Z*)-vinyllithium[30] to thermodynamically more stable *E*-isomer at the elevated temperatures (ca. 20 °C) needed to effect cyclization in this system. Investigation of the more rapid 5- and 4-*exo-dig* cyclizations of analogously substituted 5-hexynyllithiums and 4-pentynyllithiums (summarized in Tables II and V) clearly indicate that, while such cyclizations proceed in a stereoselectively syn manner, isomerization of the initially generated (*Z*)-vinyllithium to the more stable *E*-isomer is a very facile process at room temperature. On this basis, the formation of products derived from a formally anti addition in the 6-*exo-dig* cyclization is seen as a consequence of equilibration of an initially formed (*Z*)-vinyllithium to the *E*-isomer under the conditions of the cyclization reaction. Unfortunately, due to the higher temperatures needed to effect cyclization of **49** and **53**, it has not proved possible to trap the putative (*Z*)-vinyllithium intermediate in the 6-*exo-dig* isomerizations.

**Configurational Assignments.** The configurations of the products were established on the basis of a number of experimental observations including (1) NOE difference spectra and phase-sensitive NOESY experiments on selected compounds, (2) correlation of $^1H$ and $^{13}C$ chemical shifts, (3) analysis of the magnitude of four-bond allylic coupling constants,[31,32] (4) single-

(30) (a) Curtin, D. Y.; Koehl, W. J. *J. Am. Chem. Soc.* **1962**, *84*, 1967. (b) Panek, E. J.; Neff, B. L.; Chu, H.; Panek, M. G. *J. Am. Chem. Soc.* **1975**, *97*, 3996. (c) Negishi, E.; Takahashi, T. *J. Am. Chem. Soc.* **1986**, *108*, 3402.

(31) Full details are available in the Ph.D. Dissertation of Timo V. Ovaska, University of Connecticut, Storrs, CT, 1990.

(32) Gaudemer, A. *Stereochemistry, Fundamentals and Methods*; Kagan, H. B., Ed.; Georg Thieme: Stuttgart, 1977; Vol. 1, p 46 and references contained therein.

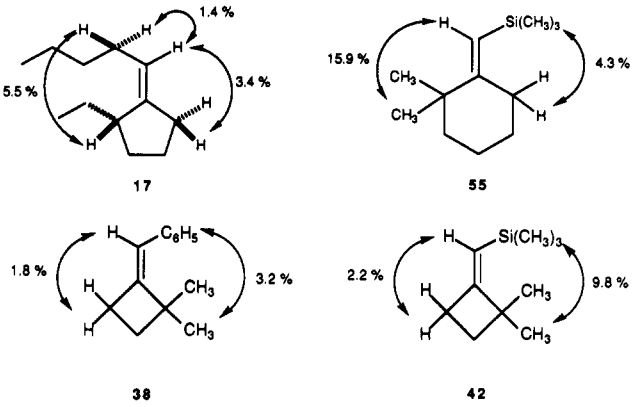



**Figure 2.** Summary of NOE studies performed on selected products.

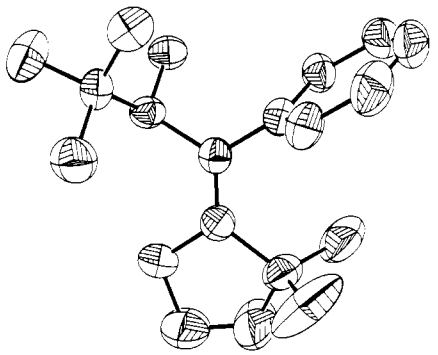


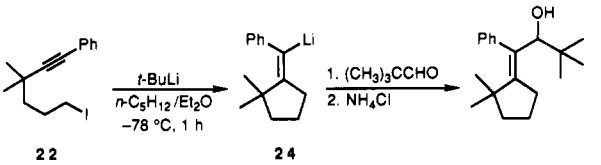
**Figure 3.** ORTEP drawing of (*E*)-1-(2,2-dimethylcyclopentylidene)-3,3-dimethyl-1-phenyl-2-butanol (with hydrogens omitted for clarity).

crystal X-ray analysis of a derivatized product, and (5) prediction of the relative stabilities of the isomeric products by MM2 molecular mechanics calculations[33] and comparison of these data with the proportions observed from experiments conducted under (presumably) equilibrium conditions. A summary of the data used to establish configuration is presented below.[31]

The $^1H$ and $^{13}C$ chemical shifts of isomeric cycloalkylidene products were easily assigned using standard COSY techniques. Unfortunately, there is very little literature data available for such compounds, and it was deemed imprudent to rely on precedent for the assignment of configuration based solely on chemical shifts and long-range proton–proton couplings. Unambiguous configurational assignments were established for representative products on the basis of NOE difference spectra and phase-sensitive NOESY experiments. Selected NOE enhancements observed for cyclopentylidene (**17**), cyclobutylidene (**38** and **42**), and cyclohexylidene (**55**) isomers are displayed pictorially in Figure 2. The configuration of related molecules was then assigned by analogy using chemical shift and coupling constant data.

The spectroscopic assignments of stereochemistry were validated by single-crystal X-ray analysis of one of the (few) crystalline derivatives of **24** (Table III, entry 3). The compound was prepared, as shown below, by treatment of a solution of **24** at −78 °C with pivalaldehyde followed by hydrolysis with a saturated aqueous ammonium chloride. The structure of the alcohol, displayed in Figure 3, clearly demonstrates the *E*-configuration of the material[25] and confirms the syn mode of cyclization.

As an aid for the assignment of structure, minimum-energy conformations of the alkylidenecycloalkanes were calculated using the MM2 parameter set.[34] This exercise would not be noteworthy were it not for an unexpected observation made in the course of




analysis of the isomeric composition of product mixtures formed in the room-temperature cyclization of acetylenic alkyllithiums bearing *gem*-dimethyl groups (Tables II, V, and VI). As discussed above, the fairly rapid *Z*/*E* isomerization of phenyl- or trimethylsilyl-substituted vinyllithiums at room temperature leads to formation of a mixture of isomeric products upon quench with a proton source. On the assumption that equilibration of the vinyllithiums is complete under the conditions of the experiments, the ratio of isomeric products is a measure of the relative stability of the organometallic precursors. Remarkably, the relative stabilities of the isomeric vinyllithiums seems, in most instances, to be well approximated by the calculated total steric energies of the hydrocarbon products. This observation is best appreciated by examination of the data presented in Table VII.

The total steric energy of each minimum energy conformation of the *E*- and *Z*-isomers of phenyl and trimethylsilyl-substituted exocyclic alkenes was taken as a measure of the relative thermodynamic stability of a given isomer, and the equilibrium proportions of a given pair of *E*- and *Z*-exocyclic alkenes were evaluated from the difference in total steric energies. As shown by the results presented in Table VII, the predicted *E*/*Z* ratios are generally in good agreement with the values observed from experiments in which the vinyllithium was allowed to isomerize prior to quench with methanol. Indeed, the predicted *E*/*Z* ratio is significantly different from the experimental values only in the case of the trimethylsilyl-substituted cyclobutylidene [(*E*)- and (*Z*)-**42**]: while the calculated energy difference (2.48 kcal/mol; Table VII, entry 3) clearly indicates that the equilibrium concentration of the *Z*-isomer should be negligible, the observed *E*/*Z* ratio is 55:45 (Table V, entry 6). It is, of course, entirely possible that the experimental ratio does not reflect an equilibrium value since quantities of the less stable *Z*-isomer would be formed through inadvertent quenching of the initially formed (*Z*)-vinyllithium by solvent molecules or adventitious traces of water as the reaction mixture was warmed. None the less, the results summarized in Table VII are all the more remarkable when it is recalled that the experimentally determined isomer ratios reflect the relative thermodynamic stabilities of the isomeric vinyllithiums and not necessarily those of the corresponding hydrocarbons modeled in the MM2 calculations. One of the (many) complicating factors ignored by the molecular mechanics calculation is the degree of aggregation of the vinyllithium intermediates which, under the reaction conditions, is unknown. Be that as it may, the MM2 calculations lend support to the stereochemical assignments: in every instance the isomer predicted to be the more stable was that found to predominate when the vinyllithiums were warmed at room temperature.

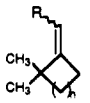
## Conclusions

Acetylenic alkyllithiums bearing a phenyl or trimethylsilyl substituent on the triple bond undergo totally regiospecific *exo-dig* cyclization to give 4-, 5-, or 6-membered rings bearing an exocyclic lithiomethylidene moiety. Cyclization of the corresponding alkyl-substituted acetylenic alkyllithiums seems to be confined to the 5-*exo* mode. The vinyllithium products of the isomerizations may be trapped by reaction with any of a variety of electrophiles to deliver synthetically useful, functionalized cycloalkylidene derivatives in high yield. Moreover, the ring closures are highly stereoselective: intramolecular addition of the C–Li bond to a pendent alkyne unit to produce 4- or 5-membered rings proceeds in a syn fashion to generate isomer-

(33) Molecular mechanics calculations were performed using the MM2 parameters incorporated in the Chem3D Plus package: Cambridge Scientific Computing, Cambridge, MA.

(34) Burkert, U.; Allinger, N. L. *Molecular Mechanics*; ACS Monograph 177; American Chemical Society: Washington, DC, 1982.

**Table VII.** Comparison of Predicted and Experimentally Observed $E/Z$ Ratios for the Cyclization of Acetylenic Alkyllithiums



| entry | R | $n$ | config | total steric energy, kcal/mol | $\Delta G°$, calc[a] | $E/Z$ calc[b] | $E/Z$ exp[c] |
|---|---|---|---|---|---|---|---|
| 1 | Ph | 1 | $E$ | 29.595 | −0.150 | 44:56 | 43:57 |
| 2 | Ph | 1 | $Z$ | 29.445 | | | |
| 3 | $(CH_3)_3Si$ | 1 | $E$ | 28.255 | 2.477 | 99:1 | 55:45 |
| 4 | $(CH_3)_3Si$ | 1 | $Z$ | 30.732 | | | |
| 5 | Ph | 2 | $E$ | 12.158 | 0.648 | 75:25 | 70:30 |
| 6 | Ph | 2 | $Z$ | 12.806 | | | |
| 7 | $(CH_3)_3Si$ | 2 | $E$ | 10.504 | 4.499 | 100:0 | 88:12 |
| 8 | $(CH_3)_3Si$ | 2 | $Z$ | 15.003 | | | |
| 9 | Ph | 3 | $E$ | 9.499 | 2.412 | 98:2 | 100:0 |
| 10 | Ph | 3 | $Z$ | 11.911 | | | |
| 11 | $(CH_3)_3Si$ | 3 | $E$ | 10.791 | 6.413 | 100:0 | 100:0 |
| 12 | $(CH_3)_3Si$ | 3 | $Z$ | 17.204 | | | |

[a] Evaluated as (MM2 steric energy of $Z$-isomer) − (MM2 steric energy of $E$-isomer). [b] Ratio of $E/Z$ isomers calculated from $\Delta G° = -RT \ln K$; where $T$ = 293.15 K, $K = E/Z$. [c] Experimentally observed $E/Z$ ratio from Tables II, V, and VI.

ically pure ($Z$)-vinyllithiums that may be functionalized to give stereoisomerically pure products. At the higher temperatures required to effect 6-*exo* cyclization of phenyl- or trimethylsilyl-substituted 6-heptynyllithiums, the initially formed ($Z$)-vinyllithium is completely isomerized to the more stable $E$-isomer which, in turn, can be trapped with electrophiles to afford stereoisomerically pure products formally derived from an anti addition to the triple bond.

Several features of this anionic route to functionalized exocyclic alkenes, which are not explicitly discussed in the preceeding sections, are worthy of note. (1) The acetylenic alkyllithiums are easily and conveniently generated using standard techniques in essentially quantitative yield by low-temperature lithium–iodine exchange.[15] (2) The requisite iodide precursors are available in multigram quantities from one- or two-step classical procedures.[35] (3) The cyclizations may be conducted on virtually any scale with little change in protocol: while we normally conduct the isomerizations using 0.1 M solutions of the acetylenic alkyllithiums in a solvent system composed of *n*-pentane–diethyl ether (3:2 by volume), the reactions may be run on much larger scale at much higher concentration (i.e., 0.5 M) using either pure diethyl ether or a hydrocarbon–diethyl ether mixture compatible with the exchange reaction used to generate the organolithium. (4) The generation and cyclization of acetylenic alkyllithiums are clean and highly efficient processes: the only side reaction observed in the methodology is the unavoidable formation of small quantities of unfunctionalized open-chain alkyne produced during the initial exchange reaction. Consequently, pure functionalized products may be isolated in high yield by simple chromatography or short-path distillation.

## Experimental Section

**General.** Spectroscopic and chromatographic procedures, methods used for the purification of solvents and reagents, and precautions regarding the manipulation of organolithiums have been previously described.[8g]

**Preparation of Acetylenic Alkyl Bromides.** The following unbranched acetylenic alkyl bromides were prepared as described by Crandell and Michaely:[36] 6-bromo-1-phenyl-1-hexyne, 5-bromo-1-phenyl-1-pentyne, 1-bromo-5-decyne, and 1-bromo-4-nonyne. Acetylenic alkyl bromides bearing *gem*-dimethyl groups at the propargylic position were prepared by regioselective coupling of 1,3-dibromo-3-methylbutane,[37] 1,4-dibromo-4-methylpentane,[38] or 1,5-dibromo-5-methylhexane,[39] as appropriate, with a trialkynylalane following the general procedure of Negishi and Baba.[40] The bromides prepared in this displayed the following properties.

**6-Bromo-3,3-dimethyl-1-phenyl-1-hexyne**: 59% yield; bp (Kugelrohr) 125–130 °C (0.3 mm); $^1$H NMR ($CDCl_3$) $\delta$ 1.29 (s, 6 H), 1.58–1.63 (m, 2 H), 2.04–2.15 (m, 2 H), 3.46 (t, $J$ = 6.70 Hz, 2 H), 7.25–7.40 (m, 5 H); $^{13}$C NMR ($CDCl_3$) $\delta$ 29.17, 29.26, 31.31, 34.22, 41.95, 80.83, 96.46, 123.80, 127.54, 128.13, 131.50; IR (neat) 3090, 3060, 2980, 2950, 2935, 2225, 1600, 1600, 1490, 1470, 1448, 1367, 1286, 1257, 759, and 690 cm$^{-1}$; mass spectroscopic molecular weight calcd for $C_{14}H_{17}Br$ 264.0514, found 264.0527.

**5-Bromo-3,3-dimethyl-1-phenyl-1-pentyne**: 77% yield; bp (Kugelrohr) 105–110 °C (0.2 mm); $^1$H NMR ($CDCl_3$) $\delta$ 1.31 (s, 6 H), 2.05–2.11 (m, 2 H), 3.55–3.61 (m, 2 H), 7.26–7.38 (m, 5 H); $^{13}$C NMR ($CDCl_3$) $\delta$ 29.16 (2 C), 32.41, 46.48, 81.47, 94.86, 123.41, 127.74, 128.09, 131.53; IR (neat) 3080, 3050, 2975, 2925, 2870, 2225, 1600, 1490, 1445, 1362, 1310, 1224, 910, 750, and 685 cm$^{-1}$; mass spectroscopic molecular weight calcd for $C_{13}H_{15}Br$ 250.0357, found 250.0355.

**7-Bromo-3,3-dimethyl-1-phenyl-1-heptyne**: 84% yield; bp (Kugelrohr) 145–150 °C (0.2 mm); $^1$H NMR ($CDCl_3$) $\delta$ 1.28 (s, 6 H), 1.44–1.51 (m, 2 H), 1.61–1.69 (m, 2 H), 1.90 (quintet, $J$ = 7.06 Hz, 2 H), 3.43 (t, $J$ = 6.79 Hz, 2 H), 7.23–7.40 (m, 5 H); $^{13}$C NMR ($CDCl_3$) $\delta$ 24.16, 29.20, 31.56, 33.14, 33.65, 42.43, 80.55, 96.91, 123.94, 127.42, 128.09, 131.52; IR (gas) 3069, 2976, 2879, 2226, 1662, 1598, 1491, 1315, 1203, 1028, 911, and 750 cm$^{-1}$; mass spectroscopic molecular weight calcd for $C_{15}H_{19}Br$ 278.0670, found 278.0669.

**Trimethyl(6-bromo-3,3-dimethyl-1-hexynyl)silane**: 39% yield; bp 78–80 °C (0.8 mm); $^1$H NMR ($CDCl_3$) $\delta$ 0.11 (s, 9 H), 1.17 (s, 6 H), 1.45–1.51 (m, 2 H), 1.94–2.05 (m, 2 H), 3.43 (t, $J$ = 6.73 Hz, 2 H); $^{13}$C NMR ($CDCl_3$) $\delta$ 0.26, 29.03, 29.20, 31.46, 34.31, 41.75, 83.97, 113.90; IR (gas) 2974, 2921, 2156, 1456, 1368, 1264, 942, 849, and 768 cm$^{-1}$; mass spectroscopic molecular weight calcd for $C_{11}H_{21}BrSi$ 260.0595, found 260.0596.

**Trimethyl(5-bromo-3,3-dimethyl-1-pentynyl)silane**: 48% yield; bp 59–60 °C (0.5 mm); $^1$H NMR ($CDCl_3$) $\delta$ 0.11 (s, 9 H), 1.19 (s, 6 H), 1.92–1.98 (m, 2 H), 3.45–3.51 (m, 2 H); $^{13}$C NMR ($CDCl_3$) $\delta$ 0.20, 29.16 [$CH_3$ and C(5)], 32.60, 46.33, 84.90, 112.13; IR (gas) 2976, 2909, 2156, 1455, 1330, 1253, 1196, 934, and 851 cm$^{-1}$. Anal. Calcd for $C_{10}H_{19}SiBr$: C, 48.58; H, 7.75. Found: C, 48.62; H, 7.93.

**Trimethyl(7-bromo-3,3-dimethyl-1-heptynyl)silane**: 43% yield; bp 71–73 °C (0.1 mm); $^1$H NMR ($CDCl_3$) $\delta$ 0.11 (s, 9 H), 1.15 (s, 6 H), 1.32–1.38 (m, 2 H), 1.51–1.62 (m, 2 H), 1.86 (apparent quintet, $J$ = 7.07 Hz, 2 H), 3.40 (t, $J$ = 6.80 Hz, 2 H); $^{13}$C NMR ($CDCl_3$) $\delta$ 0.30, 24.01, 29.15, 31.73, 33.12, 33.67, 42.27, 83.56, 114.38; IR (gas) 2974, 2921, 2156, 1456, 1368, 1264, 942, 849, and 768 cm$^{-1}$; mass spectroscopic molecular weight calcd for $C_{12}H_{23}BrSi$ 274.0752, found 274.0749.

**9-Bromo-6,6-dimethyl-4-nonyne**: 43% yield; bp (Kugelrohr) 80–90 °C (0.3 mm); $^1$H NMR ($CDCl_3$) $\delta$ 0.93 (t, $J$ = 7.32 Hz, 3 H), 1.15 (s, 6 H), 1.41–1.49 (m, 4 H), 1.94–2.03 (m, 2 H), 2.09 (t, $J$ = 6.98 Hz, 2 H), 3.41 (t, $J$ = 6.80 Hz, 2 H); $^{13}$C NMR ($CDCl_3$) $\delta$ 13.37, 20.64, 22.57, 29.21, 29.63, 30.71, 34.40, 42.21, 80.26, 87.02; IR (neat) 2972, 2940, 2885, 1460, 1440, 1385, 1363, 1295, 1271, and 1240 cm$^{-1}$; mass spectroscopic molecular weight calcd for $C_{11}H_{19}Br$ 230.0670, found 230.0682.

**Preparation of Acetylenic Alkyl Iodides.** Iodides were prepared from the corresponding bromide or alcohol via the mesylate. A mixture of the substrate in an approximately 0.65 M solution of 2.2 equiv of anhydrous NaI in dry acetone was stirred at room temperature under argon or nitrogen for 10–15 h followed by heating the mixture at reflux for additional 2–3 h. The cooled solution was then filtered by suction to remove inorganic salts, and the solid was washed well with acetone. Most of the solvent was removed by rotary evaporation under reduced pressure, the residue was partitioned between water and pentane, and the organic layer was washed with 10% sodium thiosulfate solution and water. Drying over $MgSO_4$ and solvent removal under reduced pressure afforded 90–98% product. The iodides obtained in this way were purified by passage through a short column of activated alumina eluting with pentane or hexane. The following iodides are known compounds whose physical and spectroscopic properties were in accord with literature data: 6-iodo-1-phenyl-1-hexyne (**1**),[36] 7-iodo-1-phenyl-1-heptyne,[36] 5-iodo-1-phenyl-1-pentyne,[41] trimethyl(5-iodo-1-pentynyl)silane[42] (via the mesylate from

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(40) Negishi, E.; Baba, S. *J. Am. Chem. Soc.* **1975**, *97*, 7385.
(41) Surzur, J.; Dupuy, C.; Bertrand, M. P.; Nouguier, R. *J. Org. Chem.* **1972**, *37*, 2782.

5-(trimethylsilyl)-4-pentyn-1-ol[43]), trimethyl(6-iodo-1-hexynyl)silane (**10**)[16] (via the mesylate from 6-(trimethylsilyl)-5-hexyn-1-ol[44]), 1-iodo-5-decyne (**6**),[36] 1-iodo-4-nonyne,[36] and 11-iodo-5-undecyne (**43**).[36] The structures of the remaining iodides were established on the basis of the following spectroscopic data.

**6-Iodo-3,3-dimethyl-1-phenyl-1-hexyne (22)**: $^1$H NMR ($CDCl_3$) $\delta$ 1.34 (s, 6 H), 1.57–1.65 (m, 2 H), 2.05–2.17 (m, 2 H), 3.28 (t, $J$ = 6.92 Hz, 2 H), 7.28–7.46 (m, 5 H); $^{13}$C NMR ($CDCl_3$) $\delta$ 7.27, 29.27, 29.85, 31.19, 44.17, 80.78, 96.51, 123.75, 127.51, 128.10, 131.51; IR (neat) 3050, 3020, 2910, 2860, 2200, 1570, 1430, 1355, 1225, 1170, 1060, 743, and 678 cm$^{-1}$; mass spectroscopic molecular weight calcd for $C_{14}H_{17}I$ 312.0377, found 312.0388.

**5-Iodo-3,3-dimethyl-1-phenyl-1-pentyne (35)**: $^1$H NMR ($CDCl_3$) $\delta$ 1.30 (s, 6 H), 2.10–2.17 (m [8 lines], 2 H), 3.32–3.39 (m [8 lines], 2 H), 7.25–7.40 (m, 5 H); $^{13}$C NMR ($CDCl_3$) $\delta$ 0.55, 28.87, 34.03, 48.07, 81.52, 94.86, 123.45, 127.75, 128.18, 131.55; IR (neat) 3080, 3060, 2970, 2925, 2225, 1600, 1488, 1445, 1310, 1190, 750, and 690 cm$^{-1}$; mass spectroscopic molecular weight calcd for $C_{13}H_{15}I$ 298.0221, found 298.0216.

**7-Iodo-3,3-dimethyl-1-phenyl-1-heptyne (48)**: $^1$H NMR ($CDCl_3$) $\delta$ 1.28 (s, 6 H), 1.44–1.53 (m, 2 H), 1.56–1.69 (m, 2 H), 1.87 (quintet, $J$ = 7.12 Hz, 2 H), 3.22 (t, $J$ = 7.01 Hz, 2 H), 7.23–7.41 (m, 5 H); $^{13}$C NMR ($CDCl_3$) $\delta$ 6.89, 26.50, 29.22, 31.55, 33.86, 42.18, 80.55, 96.93, 123.94, 127.42, 128.10, 131.54; IR (neat) 3069, 2976, 2940, 2223, 1597, 1490, 1315, 1183, 905, 755, and 689 cm$^{-1}$; mass spectroscopic molecular weight calcd for $C_{15}H_{19}I$ 326.0534, found 326.0523.

**Trimethyl(6-iodo-3,3-dimethyl-1-hexynyl)silane (28)**: $^1$H NMR ($CDCl_3$) $\delta$ 0.11 (s, 9 H), 1.16 (s, 6 H), 1.41–1.47 (m, 2 H), 1.83–1.99 (m, 2 H), 3.19 (t, $J$ = 6.92 Hz, 2 H); $^{13}$C NMR ($CDCl_3$) $\delta$ 0.29 ($(CH_3)_3Si$), 7.32, 29.23, 29.77, 31.37, 44.02, 83.93, 113.94; IR (gas) 2974, 2933, 2156, 1458, 1259, 1185, 941, 851, and 768 cm$^{-1}$; mass spectroscopic molecular weight calcd for $C_{11}H_{21}ISi$ 308.0460, found 308.0458.

**Trimethyl(5-iodo-3,3-dimethyl-1-pentynyl)silane (39)**: bp 72–73 °C (0.6 mm); $^1$H NMR ($CDCl_3$) $\delta$ 0.11 (s, 9 H), 1.17 (s, 6 H), 1.97–2.04 (m, 2 H), 3.21–3.28 (m, 2 H); $^{13}$C NMR ($CDCl_3$) $\delta$ 0.23, 0.49, 28.84, 34.19, 47.90, 84.91, 112.12; IR (gas) 2976, 2909, 2158, 1456, 1369, 1257, 1195, 920, and 850 cm$^{-1}$. Anal. Calcd for $C_{10}H_{19}SiI$: C, 40.82; H, 6.51. Found: C, 40.99; H, 6.60.

**Trimethyl(7-iodo-3,3-dimethyl-1-heptynyl)silane (52)**: $^1$H NMR ($CDCl_3$) $\delta$ 0.11 (s, 9 H), 1.15 (s, 6 H), 1.31–1.37 (m, 2 H), 1.47–1.58 (m, 2 H), 1.82 (quintet, $J$ = 7.12 Hz, 2 H), 3.18 (t, $J$ = 6.99 Hz, 2 H); $^{13}$C NMR ($CDCl_3$) $\delta$ 0.33, 6.85, 26.33, 29.17, 31.71, 33.81, 42.01, 83.57, 114.34; IR (gas) 2974, 2944, 2156, 1458, 1367, 1258, 1204, 954, 849, and 768 cm$^{-1}$; mass spectroscopic molecular weight calcd for $C_{12}H_{23}ISi$ 322.0616, found 322.0618.

**9-Iodo-6,6-dimethyl-4-nonyne (18)**: $^1$H NMR ($CDCl_3$) $\delta$ 0.94 (t, $J$ = 7.33 Hz, 2 H), 1.15 (s, 6 H), 1.39–1.53 (overlapping patterns, 4 H), 1.91–2.02 (m, 2 H), 2.09 (t, $J$ = 6.96 Hz, 2 H), 3.19 (t, $J$ = 7.00 Hz, 2 H); $^{13}$C NMR ($CDCl_3$) $\delta$ 7.51, 13.42, 20.67, 22.59, 29.68, 29.98, 30.66, 44.53, 80.15, 87.13; IR (neat) 2960, 2940, 2870, 2200, 1670, 1430, 1260, and 1180 cm$^{-1}$; mass spectroscopic molecular weight calcd for $C_{11}H_{19}I$ 278.0534, found 278.0543.

**Tetrahydro-2-[(4-ethyl-5-hexynyl)oxy]-2*H*-pyran.** A solution of 13.4 g (73.5 mmol) of tetrahydro-2-(5-hexynyloxy)-2*H*-pyran[45] in 70 mL of dry pentane was cooled in an ice/salt bath and stirred as 67.0 mL of a 2.74 M solution of *n*-BuLi (184 mmol) in hexanes was added slowly. The reaction mixture was then warmed to 10 °C and 17.0 mL of dry THF was added to dissolve the white, sticky solid which had formed upon addition of the organolithium reagent, the resultant mixture was recooled to 0 °C, and 12.8 g (118 mmol) of freshly distilled ethyl bromide was added dropwise to the stirred solution. Removal of the cooling bath resulted in spontaneous refluxing of the mixture and concomitant formation of a yellowish precipitate. After the violent reaction had subsided, the reaction mixture was stirred at room temperature overnight and then carefully quenched by addition of 70.0 mL of water. The layers were separated, the aqueous solution was saturated with NaCl and extracted twice with diethyl ether, and the combined organic layers were washed with brine and dried ($MgSO_4$). Solvent evaporation under reduced pressure gave 12.7 g (82%) of the crude product which was used for subsequent reactions: $^1$H NMR ($CDCl_3$) $\delta$ 0.99 (t, $J$ = 7.37 Hz, 3 H), 1.38–1.86 (m, 12 H), 2.03 (d, $J$ = 2.37 Hz, 1 H), 2.18–2.36 (m, 1 H), 3.35–3.52 (m, 2 H), 3.68–3.88 (m, 2 H), 4.56 (3 lines, $J$ = 3.38 Hz, 1 H); $^{13}$C NMR ($CDCl_3$) $\delta$ 11.49, 19.50, 25.41, 27.38, 27.43, 27.81, 30.64, 31.12, 31.20, 32.90, 32.96, 62.08, 67.10, 67.18, 69.29, 87.41, 98.62; mass spectroscopic molecular weight calcd for $C_{13}H_{22}O_2$ 210.1620, found 210.1612.

**4-Ethyl-5-decyn-1-ol.** A solution of 0.503 g (2.39 mmol) of tetrahydro-2-[(4-ethyl-5-hexynyl)oxy]-2*H*-pyran in 4.00 mL of anhydrous THF was cooled to −78 °C under argon, and 0.854 mL of a 2.80 M solution of *n*-BuLi (2.39 mmol) in hexanes was added over a period of 10 min. After the addition was complete, the mixture was stirred at −78 °C for 1 h followed by the addition of 0.451 g (2.45 mmol) of 1-iodobutane (purified by passage through a short column of activated alumina immediately before use). The resulting solution was allowed to warm and stir at room temperature for 14 h, heated at reflux for 3 h, and then poured into water. Standard ethereal workup following by drying ($MgSO_4$) and solvent removal under reduced pressure afforded 0.610 g of tetrahydro-2-[(4-ethyl-5-decynyl)oxy]-2*H*-pyran as a mixture of diastereomers. The crude product was dissolved in 19.0 mL of ethanol, and the pH of the solution was adjusted to ~3 by the dropwise addition of 0.1 M HCl. The mixture was then heated at reflux for 30 min, allowed to cool, and then poured into 20 mL of water and extracted with diethyl ether. The ethereal extract was dried ($MgSO_4$), and the solvent was removed under reduced pressure to give 0.429 g (~100%) of the crude alcohol which was purified by flash chromatography (30% EtOAc/hexanes, $R_f$ = 0.30) to give 0.365 g (84%) of the title compound as a clear liquid: $^1$H NMR ($CDCl_3$) $\delta$ 0.87 (t, $J$ = 7.11 Hz, 3 H), 0.95 (t, $J$ = 7.40 Hz, 3 H), 1.32–1.50 (m, 8 H), 1.59 (broad s, 1 H), 1.60–1.80 (m, 2 H), 2.13 (td, $J_t$ = 6.84 Hz, $J_d$ = 2.20 Hz, 2 H), 2.17–2.25 (m, 1 H), 3.63 (t, $J$ = 6.48 Hz, 2 H); $^{13}$C NMR ($CDCl_3$) $\delta$ 11.75, 13.57, 18.39, 21.88, 28.53, 30.70, 31.29, 33.24, 62.86, 81.75, 83.03; IR (gas) 3668, 2967, 2939, 2879, 1459, 1385, 1348, and 1056 cm$^{-1}$; mass spectroscopic molecular weight calcd for $C_{10}H_{17}O$ ($M^+ - CH_2CH_3$) 153.1279, found 153.1280.

**4-Ethyl-1-iodo-5-decyne (14).** The mesylate of 4-ethyl-5-decyn-1-ol, prepared from 1.39 g (7.62 mmol) of the alcohol, 1.15 g (11.4 mmol) of triethylamine, and 1.00 g (8.40 mmol) of methanesulfonyl chloride by the method of Crossland and Servis,[46] was converted to the iodide by using 2.64 g (17.6 mmol) of sodium iodide in 30 mL of anhydrous acetone as described above. Purification of the crude product by passage through a short column of activated alumina and elution with *n*-pentane gave 1.89 g (85%) of the title iodide: $^1$H NMR ($CDCl_3$) $\delta$ 0.91 (t, $J$ = 7.22 Hz, 3 H), 0.98 (t, $J$ = 7.36 Hz, 3 H), 1.26–1.52 (m, 8 H), 1.82–2.08 (m, 2 H), 2.13–2.30 (overlapping patterns [2.16 (t, $J$ = 6.78 Hz, 3 H), 3.21 (td, $J_t$ = 6.94 Hz, $J_d$ = 1.43 Hz, 2 H)]); $^{13}$C NMR ($CDCl_3$) $\delta$ 6.92, 11.74, 13.58, 18.37, 21.87, 28.48, 31.27, 31.45, 32.53, 35.77, 81.98, 82.47; mass spectroscopic molecular weight calcd for $C_{12}H_{21}I$ 292.0688, found 292.0678.

**General Procedure for the Generation and Cyclization of Acetylenic Alkyllithiums.** Acetylenic alkyl iodides were deoxygenated immediately prior to use by bubbling dry, oxygen-free argon gas through the neat liquid for several minutes. An approximately 0.1 M solution of the iodide in anhydrous *n*-pentane–diethyl ether (3:2 by volume) was stirred and cooled to −78 °C (or lower) under argon, 2.0–2.2 molar equiv of *t*-BuLi in pentane were added dropwise via syringe, and the mixture was stirred at −78 °C (or lower) for an additional 5 min. The reaction mixtures were then allowed to stand under argon for a period of time at the appropriate temperature to effect the isomerization: specific conditions of time and temperature used complete the cyclization of the various substrates are given in footnotes to Tables I, III, IV, and VI. Functionalized of the resulting vinyllithiums was accomplished by addition of an excess (typically 2 equiv) of the appropriate electrophile that had been carefully purified immediately prior to use. The reaction mixtures were worked up in the usual manner,[47] and products were purified by flash chromatography, short-path distillation, or recrystallization as appropriate. The yields of the products given in Tables I, III, IV, and VI refer to isolated, purified material. Benzylidenecyclopentane (**5**),[48] pentylidenecyclopentane (**9**),[36] trimethyl(cyclopentylidenemethyl)silane (**13**),[49] 2-cyclopentylidene-1-

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phenylacetic acid,[50] benzylidenecyclobutane,[51] benzylidenecyclohexane,[52] and 5,6-undecadiene[53] are known compounds whose physical and spectroscopic properties were fully in accord with those reported for these materials. The structures of the remaining derivatives prepared in this study were established on the basis of the data presented below and in the supplementary material (all products were liquids except where a melting point is given; product yields may be found in the appropriate tables).

**2-Cyclopentylidene-1,2-diphenylethanol** (Table I, entry 5): $^1$H NMR ($CDCl_3$) $\delta$ 1.50–1.66 (m, 2 H), 1.71–1.86 (m, 3 H), 1.96–2.17 (m, 2 H), 2.45–2.60 (m, 1 H), 2.62–2.75 (m, 1 H), 5.82 (s, 1 H), 6.86–7.34 (m, 10 H); $^{13}$C NMR ($CDCl_3$) $\delta$ 26.25, 26.51, 32.41, 30.52, 74.29, 125.76, 126.48, 126.75, 127.79, 127.91, 129.80, 133.58, 138.91, 142.86, 143.83; IR (neat) 3400, 3060, 3030, 2960, 2870, 2830, 1600, 1490, 1450, 1060, 1030, 1010, 695 cm$^{-1}$; mass spectroscopic molecular weight calcd for $C_{19}H_{20}O$ 264.1514, found 264.1522.

**1-Cyclopentylidene-1-phenyl-2-propanol** (Table I, entry 3): $^1$H NMR ($CDCl_3$) $\delta$ 1.17 (d, $J$ = 6.49 Hz, 3 H), 1.49–1.60 (m, 2 H), 1.71 (quintet, $J$ = 6.84, overlapping singlet from OH, 3 H), 2.29–2.41 (m, 1 H), 2.43–2.57 (m, 1 H), 4.80 (q, $J$ = 6.50 Hz, 1 H), 7.12–7.33 (m, 5 H); $^{13}$C NMR ($CDCl_3$) $\delta$ 21.92, 26.08, 26.45, 29.49, 32.15, 68.47, 126.34, 127.94, 129.67, 134.93, 139.53, 142.05; IR (neat) 3365, 3070, 3035, 2960, 2880, 2850, 1605, 1590, 1440, 1410, 1365, 1342, 1285, 1112, 1060, 970, 880, 863, 760, 705 cm$^{-1}$; mass spectroscopic molecular weight calcd for $C_{14}H_{18}O$ 202.1358, found 202.1362.

**(1-Cyclopentylidene-3-butenyl)benzene** (Table I, entry 2): $^1$H NMR ($CDCl_3$) $\delta$ 1.53–1.65 (m, 2 H), 1.72 (apparent quintet, $J$ = 7.05, 2 H), 2.22 (t, $J$ = 6.93 Hz, 2 H), 2.39 (t, $J$ = 7.25 Hz, 2 H), 3.13 (d, $J$ = 6.24 Hz, 2 Hz), 4.90–5.04 (m, 2 H), 5.69–5.84 (m, 1 H), 7.17–7.32 (m, 5 H); $^{13}$C NMR ($CDCl_3$) $\delta$ 26.37, 27.10, 30.69, 32.65, 39.68, 114.64, 125.83, 127.82, 128.23, 135.97, 141.89, 143.72; IR (neat) 3080, 3060, 3025, 2965, 2893, 2875, 2860, 1640, 1600, 1490, 1445, 1434, 990, 910, 698 cm$^{-1}$; mass spectroscopic molecular weight calcd for $C_{15}H_{18}$ 198.1409, found 198.1413.

**5-Cyclopentylidene-4-nonanol** (Table I, entry 8): $^1$H NMR ($CDCl_3$) $\delta$ 0.85–0.92 (m, [overlapping patterns], 6 H), 1.21–1.49 (m, 8 H), 1.57–1.66 (m, 5 H), 1.90–2.08 (m, 2 H), 2.15–2.42 (m, 4 H), 4.43 (t, $J$ = 6.72 Hz, 1 H); $^{13}$C NMR ($CDCl_3$) $\delta$ 13.94, 14.10, 19.27, 23.52, 26.34, 26.65, 28.47, 29.87, 30.58, 32.10, 37.65, 73.35, 132.28, 140.27; IR (gas) 3650, 2963, 2879, 1463, 1382, 1272, 1106, 1008 cm$^{-1}$; mass spectroscopic molecular weight calcd for $C_{14}H_{26}O$ 210.1985, found 210.1990.

**2-Cyclopentylidenehexanal** (Table I, entry 9): $^1$H NMR ($CDCl_3$) $\delta$ 0.87–0.92 (m, 3 H), 1.27–1.34 (m, 4 H), 1.68–1.84 (m, 4 H), 2.20 (apparent t, $J$ = 7.08 Hz, 2 H), 2.53 (t, $J$ = 7.05 Hz, 2 H), 2.82 (t, 6.99 Hz, 2 H), 9.94 (s, 1 H); $^{13}$C NMR ($CDCl_3$) $\delta$ 13.94, 22.91, 24.92, 26.59, 26.72, 29.81, 30.60, 33.17, 134.14, 167.74, 191.93; IR (neat) 2960, 2930, 2870, 2740, 1725, 1665, 1632, 1460, 1450, 1270, 1205, 1100, 900 cm$^{-1}$; mass spectroscopic molecular weight calcd for $C_{11}H_{18}O$ 166.1358, found 166.1362.

**2-Cyclobutylidene-1,2-diphenylethanol** (Table IV, entry 3): $^1$H NMR ($CDCl_3$) $\delta$ 2.01 (quintet, $J$ = 7.93 Hz, 2 H), 2.14 (br s, 1 H), 2.70–2.81 (m, 2 H), 2.92 (t, $J$ = 7.86 Hz, 2 H), 5.63 (s, 1 H), 7.01–7.36 (m, 10 H); $^{13}$C NMR ($CDCl_3$) $\delta$ 16.95, 30.60, 31.30, 73.08, 125.83, 126.47, 126.83, 127.85, 128.09, 128.86, 133.20, 136.83, 142.10, 142.87; IR (gas) 3620, 3067, 3030, 2988, 2955, 2928, 1598, 1493, 1447, 1181, 1031, 912 cm$^{-1}$; mass spectroscopic molecular weight calcd for $C_{18}H_{18}O$ 250.1358, found 250.1354.

**2-Cyclobutylidene-2-phenylethanol** (Table IV, entry 4): $^1$H NMR ($CDCl_3$) $\delta$ 1.56 (br s, 1 H), 2.01 (apparent quintet, $J$ = 7.90 Hz, 2 H), 2.86–2.95 (m, 4 H), 4.39 (s, 2 H), 7.18–7.36 (m, 5 H); $^{13}$C NMR ($CDCl_3$) $\delta$ 16.95, 30.52, 32.08, 61.19, 126.38, 127.19, 128.27, 129.99, 138.03, 143.26; IR (gas) 3644, 3066, 2986, 2936, 1598, 1493, 1381, 1298, 1192, 1060, 986 cm$^{-1}$; mass spectroscopic molecular weight calcd for $C_{12}H_{14}O$ 174.1045, found 174.1044.

**Trimethyl(cyclobutylidenemethyl)silane** (Table IV, entry 5): $^1$H NMR ($CDCl_3$) $\delta$ 0.03 (s, 9 H), 1.91 (quintet, $J$ = 7.97 Hz, 2 H), 2.67–2.78 (m, 4 H), 5.15 (apparent quintet, $J$ = 2.36 Hz, 1 H); $^{13}$C NMR ($CDCl_3$) $\delta$ –0.42, 16.41, 33.42, 35.46, 118.94, 160.23; IR (neat) 2965, 2920, 1640, 1245, 1030, 865, 828, 740, 675 cm$^{-1}$; mass spectroscopic molecular weight calcd for $C_8H_{16}Si$ 140.1021, found 140.1021.

**Ethyl cyclobutylidene(trimethylsilyl)acetate** (Table IV, entry 10): $^1$H NMR ($CDCl_3$) $\delta$ 0.13 (s, 9 H), 1.25 (t, $J$ = 7.16 Hz, 3 H), 1.99 (quintet, $J$ = 8.01 Hz, 2 H), 2.87–2.94 (m, 2 H), 3.06–3.12 (m, 2 H), 4.11 (q, $J$ = 7.13 Hz, 2 H); $^{13}$C NMR ($CDCl_3$) $\delta$ 0.01, 14.34, 17.11, 34.43, 36.62, 59.59, 125.64, 169.62, 173.27; IR (gas) 2979, 2964, 1719, 1631, 1252, 1227, 1202, 1105, 1042, 973, 845 cm$^{-1}$; mass spectroscopic molecular weight calcd for $C_{11}H_{20}SiO_2$ 212.1233, found 212.1231.

**3-Cyclobutylidene-3-(trimethylsilyl)-1-propanol** (Table IV, entry 12): $^1$H NMR ($CDCl_3$) $\delta$ 0.06 (s, 9 H), 1.46 (s, 1 H), 1.92 (apparent quintet, $J$ = 8.10 Hz, 2 H), 2.26 (t, $J$ = 6.90 Hz, 2 H), 2.73–2.80 (m, 4 H), 3.51 (t, $J$ = 6.90 Hz, 2 H); $^{13}$C NMR ($CDCl_3$) $\delta$ –0.35, 16.39, 32.23, 33.26, 34.44, 62.06, 125.99, 155.46; IR (gas) 3663, 2958, 1639, 1383, 1256, 1130, 1035, 960, 842 cm$^{-1}$. Anal. Calcd for $C_{10}H_{20}SiO$: C, 65.15; H, 10.94. Found: C, 65.52; H, 10.74.

**Cyclobutylidene(trimethylsilyl)acetic acid** (Table IV, entry 7): mp 84–85 °C; $^1$H NMR ($CDCl_3$) $\delta$ 0.15 (s, 9 H), 2.00 (quintet, $J$ = 7.99 Hz, 2 H), 2.94 (apparent t, $J$ = 8.15 Hz, 2 H), 3.15 (apparent t, $J$ = 7.94 Hz, 2 H); $^{13}$C NMR ($CDCl_3$) $\delta$ –0.01, 17.06, 34.73, 37.30, 124.85, 175.18, 177.04; IR (gas) 3568, 2964, 1733, 1631, 1408, 1258, 1136, 964, 846 cm$^{-1}$. Anal. Calcd for $C_9H_{16}O_2Si$: C, 58.65; H, 8.75. Found: C, 58.93; H, 8.80.

**4-Cyclobutylidene-4-(trimethylsilyl)-2-butanol** (Table IV, entry 13): $^1$H NMR ($CDCl_3$) $\delta$ 0.41 (s, 9 H), 1.12 (d, $J$ = 6.09 Hz, 3 H), 1.84 (s, 1 H), 1.89 (quintet, $J$ = 8.00 Hz, 2 H), 2.06 (d, $J$ = 6.79 Hz, 2 H), 2.70–2.79 (m, 4 H), 3.70 (hextet, $J$ = 6.36 Hz, 1 H); $^{13}$C NMR ($CDCl_3$) $\delta$ –0.29, 16.33, 22.61, 32.60, 33.23, 41.32, 67.13, 127.19, 155.60; IR (neat) 3350, 2940, 2905, 1638, 1392, 1242, 1065, 920, 830 cm$^{-1}$; mass spectroscopic molecular weight calcd for $C_{11}H_{22}OSi$ 198.1440, found 198.1435.

**(*Z*)-1-Ethyl-2-pentylidenecyclopentane (17)**: $^1$H NMR ($CDCl_3$) $\delta$ 0.85–0.92 (m, 6 H), 1.16–1.27 (m, 1 H), 1.28–1.35 (m, 4 H), 1.40–1.54 (m, 3 H), 1.59–1.82 (m, 2 H), 1.99 (apparent quartet, $J$ = 7.03 Hz, 2 H), 2.08–2.29 (m, 2 H), 2.39–2.52 (m, 1 H), 5.20 (tq, $J_t$ = 7.22 Hz, $J_q$ = 1.90 Hz, 1 H); $^{13}$C NMR ($CDCl_3$) $\delta$ 12.19, 14.06, 22.51, 24.10, 27.72, 28.97, 31.52, 32.42, 33.47, 41.84, 121.01, 146.72; IR (neat) 3000, 2980, 2920, 1650, 1460, 1375, 840 cm$^{-1}$; mass spectroscopic molecular weight calcd for $C_{12}H_{22}$ 166.1721, found 166.1728.

**(*Z*)-2-Butylidene-1,1-dimethylcyclopentane (21)**: $^1$H NMR ($CDCl_3$) $\delta$ 0.89 (t, $J$ = 7.32 Hz, 3 H), 1.15 (s, 6 H), 2.06 (t, $J$ = 7.47 Hz, 2 H), 2.27–2.33 (m, 2 H); $^{13}$C NMR ($CDCl_3$) $\delta$ 13.93, 23.58, 23.66, 28.10, 30.37, 36.65, 40.69, 45.75, 121.12, 149.66; IR (gas) 2964, 2882, 1667, 1466, 1371, 1000, 961 cm$^{-1}$; mass spectroscopic molecular weight calcd for $C_{11}H_{20}$ 152.1565, found 152.1562.

**(*Z*)-1,1-Dimethyl-2-benzylidenecyclopentane** (Table III, entry 1): $^1$H NMR ($CDCl_3$) $\delta$ 1.00 (s, 6 H), 1.52–1.57 (m, 2 H), 1.61–1.71 (m, 2 H), 2.55 (td, $J$ = 7.26 Hz, $J$ = 2.12 Hz, 2 H), 6.42 (br s, 1 H), 7.15–7.30 (m, 5 H); $^{13}$C NMR ($CDCl_3$) $\delta$ 22.45, 28.45, 36.31, 41.95, 45.45, 121.33, 125.83, 127.52, 129.28, 139.21, 153.34; IR (gas) 3072, 3033, 2965, 2881, 1604, 1497, 1468, 1130, 1028, 939 cm$^{-1}$; mass spectroscopic molecular weight calcd for $C_{14}H_{18}$ 186.1409, found 186.1417.

**(*E*)-1-(2,2-Dimethylcyclopentylidene)-1,2-diphenyl-2-ethanol** (Table III, entry 2): mp 108–109 °C; $^1$H NMR ($CDCl_3$) $\delta$ 0.76 (s, 3 H), 0.81 (s, 3 H), 1.54 (t, $J$ = 6.64 Hz, 2 H), 1.73 (quintet, $J$ = 6.99 Hz, 2 H), 1.85 (d, $J$ = 7.27 Hz, 1 H), 2.64–2.76 (m, 1 H), 2.81–2.92 (m, 1 H), 5.77 (d, $J$ = 6.92 Hz, 1 H), 7.18–7.27 (m, 10 H); $^{13}$C NMR ($CDCl_3$) $\delta$ 22.07, 28.18 and 28.39, 32.69, 42.99, 44.83, 74.15, 125.74, 126.72, 126.94, 127.87, 131.68, 133.76, 136.35, 142.64, 148.83; IR (gas) 3606, 3067, 2959, 2880, 1599, 1493, 1366, 1198, 1111, 1032 cm$^{-1}$. Anal. Calcd for $C_{21}H_{24}O$: C, 86.26; H, 8.27. Found: C, 86.27; H, 8.31.

**(*E*)-1-(2,2-Dimethylcyclopentylidene)-3,3-dimethyl-1-phenyl-2-butanol** (Table III, entry 3): mp 104–105 °C; $^1$H NMR ($CDCl_3$) $\delta$ 0.48 (s, 3 H), 0.82 (s, 9 H), 0.99 (s, 3 H), 1.43–1.49 (m, 2 H), 1.53–1.70 (m, 3 H), 2.50–2.73 (m, 2 H), 4.35 (d, $J$ = 8.34 Hz, 1 H), 7.23–7.28 (m, 5 H); $^{13}$C NMR ($CDCl_3$) $\delta$ 21.75, 26.76, 27.24, 29.23, 33.00, 36.54, 43.23, 45.03, 79.84, 126.62, 126.87, 127.12, 131.61, 132.47, 138.75, 150.09; IR (gas) 3619, 3065, 2959, 2880, 1598, 1472, 1367, 1198, 1113, 1002 cm$^{-1}$; mass spectroscopic molecular weight calcd for $C_{19}H_{28}O$ 272.2140, found 272.2137.

**(*E*)-2-(2,2-Dimethylcyclopentylidene)-2-phenylacetic acid** (Table III, entry 4): mp 157–158 °C; $^1$H NMR ($CDCl_3$) $\delta$ 0.79 (s, 6 H), 1.51 (t, $J$ = 6.55 Hz, 2 H), 1.67 (quintet, $J$ = 6.99 Hz, 2 H), 3.00 (t, $J$ = 7.29 Hz, 2 H), 7.15–7.32 (m, 5 H), 10.85 (s, 1 H); $^{13}$C NMR ($CDCl_3$) $\delta$ 22.04, 27.46, 36.10, 44.31, 45.47, 125.37, 127.12, 127.41, 130.85, 137.18, 170.83, 173.37; IR (gas) 3670, 3068, 2990, 2963, 2885, 1745, 1140, 756 cm$^{-1}$; mass spectroscopic molecular weight calcd for $C_{15}H_{18}O_2$ 230.1307, found 230.1308.

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**(Z)-Trimethyl[(2,2-dimethylcyclopentylidene)methyl]silane** (Table III, entry 6): $^1$H NMR ($CDCl_3$) $\delta$ 0.12 (s, 9 H), 1.11 (s, 6 H), 1.52–1.61 (m, 4 H), 2.43 (td, $J_t$ = 7.79 Hz, $J_d$ = 2.06 Hz, 2 H), 5.27 (t, $J$ = 2.06 Hz, 1 H); $^{13}$C NMR ($CDCl_3$) $\delta$ 1.82, 22.17, 28.14, 39.35, 42.56, 44.48, 117.38, 171.75; IR (gas) 2961, 2904, 1619, 1465, 1371, 1255, 870, 846 cm$^{-1}$; mass spectroscopic molecular weight calcd for $C_{11}H_{22}Si$ 182.1491, found 182.1483.

**(E)-Trimethyl[(2,2-dimethylcyclopentylidene)methyl]silane** (Table II, entry 9): $^1$H NMR ($CDCl_3$) $\delta$ 0.06 (s, 9 H), 0.99 (s, 6 H), 1.48 (t, $J$ = 6.38 Hz, 2 H), 1.63 (apparent quintet, $J$ = 7.07 Hz, 2 H), 2.39 (td, $J_t$ = 7.31 Hz, $J_d$ = 2.34 Hz, 2 H), 5.18 (t, $J$ = 2.34 Hz, 1 H); $^{13}$C NMR ($CDCl_3$) $\delta$ –0.23, 22.54, 28.88, 32.79, 41.35, 43.99, 114.60, 171.27; IR (gas) 2962, 2872, 1603, 1455, 1256, 874, 848 cm$^{-1}$.

**(E)-2-Benzylidene-1,1-dimethylcyclohexane** (Table VI, entry 1): $^1$H NMR ($CDCl_3$) $\delta$ 1.16 (s, 6 H), 1.43–1.53 (m, 4 H), 1.58–1.64 (m, 2 H), 2.38 (apparent t, $J$ = 5.83 Hz, 2 H), 6.29 (s, 1 H), 7.14–7.28 (m, 5 H); $^{13}$C NMR ($CDCl_3$) $\delta$ 22.53, 25.83, 28.06, 28.32, 36.97, 42.00, 119.81, 125.65, 127.90, 129.14, 139.19, 149.86; IR (gas) 3067, 3029, 2967, 2936, 2871, 1640, 1598, 1463, 1384, 1152, 914, 855 cm$^{-1}$; mass spectroscopic molecular weight calcd for $C_{15}H_{20}$ 200.1565, found 200.1566.

**(Z)-1-(2,2-Dimethylcyclohexylidene)-1-phenyl-2-propanol** (Table VI, entry 2): $^1$H NMR ($CDCl_3$) $\delta$ 1.07 (d, $J$ = 6.47 Hz, 3 H), 1.16 (m, 1 H), 1.23 (s, 3 H), 1.28 (apparent t, $J$ = 6.60 Hz, 2 H), 1.33 (s, 3 H), 1.36–1.41 (m, 2 H), 1.45–1.52 (m, 2 H), 1.74 (t, $J$ = 6.51 Hz, 2 H), 5.25 (q, $J$ = 6.47 Hz, 1 H), 6.91–7.28 (m, 5 H); $^{13}$C NMR ($CDCl_3$) $\delta$ 18.87, 22.66, 28.80, 29.60, 30.34, 36.64, 40.86, 65.88, 126.25, 127.80, 128.01, 130.24, 130.46, 137.87, 140.01, 144.47; IR (gas) 3618, 3066, 2941, 2878, 1601, 1472, 1374, 1258, 1183, 1101, 952, 882 cm$^{-1}$; mass spectroscopic molecular weight calcd for $C_{17}H_{24}O$ 244.1827, found 244.1821.

**(E)-Trimethyl[(2,2-dimethylcyclohexylidene)methyl]silane** (Table VI, entry 4): $^1$H NMR ($CDCl_3$) $\delta$ 0.07 (s, 9 H), 1.03 (s, 6 H), 1.35 (t, $J$ = 5.81 Hz, 2 H), 1.45–1.61 (m, 4 H), 2.24–2.29 (m, 2 H); $^{13}$C NMR ($CDCl_3$) $\delta$ 0.43, 22.27, 28.03, 26.68, 31.68, 38.50, 42.09, 116.87, 166.27; IR (gas) 2962, 2937, 2872, 1603, 1456, 1384, 1256, 874, 848 cm$^{-1}$; mass spectroscopic molecular weight calcd for $C_{12}H_{24}Si$ 196.1647, found 196.1649.

**(Z)-2-Benzylidene-1,1-dimethylcyclobutane** (Table V, entry 3): $^1$H NMR ($CDCl_3$) $\delta$ 1.28 (s, 6 H), 1.78 (t, $J$ = 8.04 Hz, 2 H), 2.68 (td, $J$ = 8.04 Hz, $J$ = 2.16 Hz, 2 H), 6.10 (t, $J$ = 2.13 Hz, 1 H), 7.15–7.40 (m, 5 H); $^{13}$C NMR ($CDCl_3$) $\delta$ 26.98, 27.01, 32.37, 45.29, 121.41, 125.88, 127.91, 128.21, 137.36, 152.15; IR (gas) 3069, 2960, 2873, 1789, 1598, 1367, 1225, 1167, 1074, 853 cm$^{-1}$; mass spectroscopic molecular weight calcd for $C_{13}H_{16}$ 172.1252, found 172.1259.

**(E)-2-Benzylidene-1,1-dimethylcyclobutane** (Table V, entry 4): $^1$H NMR ($CDCl_3$) $\delta$ 1.24 (s, 6 H), 1.91 (t, $J$ = 7.91 Hz, 2 H), 3.01 (td, $J$ = 7.92 Hz, $J$ = 2.55 Hz, 2 H), 6.06 (t, $J$ = 2.60 Hz, 1 H), 7.14–7.29 (m, 5 H); $^{13}$C NMR ($CDCl_3$) $\delta$ 27.61, 27.92, 33.25, 44.65, 118.07, 125.73, 127.24, 128.36, 136.33, 154.26; IR (gas) 3073, 3034, 2962, 2876, 1603, 1467, 1375, 891, 857 cm$^{-1}$.

**(Z)-Trimethyl[(2,2-dimethylcyclobutylidene)methyl]silane** (Table V, entry 5): $^1$H NMR ($CDCl_3$) $\delta$ 0.08 (s, 9 H), 1.19 (s, 6 H), 1.66 (t, $J$ = 8.09 Hz, 2 H), 2.57 (td, $J_t$ = 8.08 Hz, $J_d$ = 2.09 Hz, 2 H), 5.09 (t, $J$ = 2.09 Hz, 1 H); $^{13}$C NMR ($CDCl_3$) $\delta$ 0.96, 27.82, 29.54, 31.40, 46.39, 118.07, 169.11; IR (gas) 2963, 1641, 1459, 1367, 1254, 1033, 868, 843 cm$^{-1}$; mass spectroscopic molecular weight calcd for $C_{10}H_{20}Si$ 168.1334, found 168.1334.

**(E)-Trimethyl[(2,2-dimethylcyclobutylidene)methyl]silane** (Table V, entry 6): $^1$H NMR ($CDCl_3$) $\delta$ 0.02 (s, 9 H), 1.08 (s, 6 H), 1.72 (t, $J$ = 8.01 Hz, 2 H), 2.68 (td, $J_t$ = 8.01 Hz, $J_d$ = 2.57 Hz, 2 H), 5.12 (t, $J$ = 2.57 Hz, 1 H); $^{13}$C NMR ($CDCl_3$) $\delta$ 0.96, 27.82, 29.54, 31.40, 46.39, 118.07, 169.11.

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**Supplementary Material Available:** Details of the preparation and characterization of several of the derivatives listed in the Tables and copies of the $^1$H and $^{13}$C NMR spectra for all new compounds (104 pages). Ordering information is given on any current masthead page.