to examine mechanistic features of nucleophilic substitution reactions. For example, many analogies exist between a variety of phosphorus and silicon displacement reactions,[48,49] yet no accord has been reached, at least in silicon chemistry,[47] on the basic displacement processes.

One implication of the present study is that either retention or racemization processes for chiral derivatives, proceeding by way of Berry pseudorotation in activated five-coordinated states, will be energetically more common relative to inversion processes as one goes to heavier elements in each of these series. This is a direct consequence of the ease of intramolecular ligand exchange implied in going down a series. In order to test the validity of this proposal, a common reaction must be sought applicable to each member of the series.

Conclusion. In general, solid-state five-coordinated tin structures lie along the Berry pseudorotational coordinate as an expression of their structural nonrigidity, similar to that found for other elements of groups 14 and 15 that have been studied. Implications are that in going down a particular family, nonrigid character increases, Sn > Ge > Si;[1b,36] Sb > As > P[25] as determined by the ease of structural distortion produced by a common substituent effect and the fact that pseudorotation for five-coordinated tin is in general a low-energy process. The role of five-coordinated tin in mechanisms of nucleophilic displacement reactions should be more readily defined by application of the structural principles herein summarized governing this state.

Acknowledgment. The support of this research by the National Science Foundation (Grant CHE8504737) is gratefully acknowledged. We also thank the University of Massachusetts Computing Center for generous allocation of computer time.

Registry No. 1, 115162-45-3; **2**, 115162-50-0; **3**, 115162-47-5; **4**, 115162-48-6; Ph_3SnCl, 639-58-7; $PhSnCl_3$, 1124-19-2; $MeSnCl_3$, 993-16-8; (*n*-Bu)$SnCl_3$, 1118-46-3; disodium maleonitrile dithiolate, 5466-54-6.

Supplementary Material Available: Thermal parameters, hydrogen atom parameters, and additional bond lengths and angles (Tables S1-S3, respectively, for **1**, Tables S4-S6, for **2**; Tables S9-S11 for **4**) and thermal parameters and additional bond lengths and angles (Tables S7 and S8 for **3**) (11 pages); tables of observed and calculated structure factor amplitudes for **1-4** (32 pages). Ordering information is given on any current masthead page.

(48) Corriu, R. J. P.; Guerin, C. *Adv. Organomet. Chem.* **1982**, *20*, 265, and references cited therein.
(49) Corriu, R. J. P. *Phosphorus Sulfur* **1986**, *27*, 1, and references cited therein.

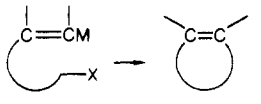
Novel Cyclialkylation Reactions of (ω-Halo-1-alkenyl)metal Derivatives. Synthetic Scope and Mechanism[1]

Ei-ichi Negishi,*,† Larry D. Boardman, Hiroyuki Sawada,[2] Vahid Bagheri, A. Timothy Stoll, James M. Tour, and Cynthia L. Rand

Contribution from the Department of Chemistry, Purdue University, West Lafayette, Indiana 47907. *Received January 19, 1988*

Abstract: (ω-Haloalkenyl)metals can undergo both σ- and π-type cyclization reactions. The σ-cyclialkylation reaction, which has so far been observed only with alkenyllithiums, can provide 3- through 7-membered rings in high yields. It requires the cis relationship between Li and the ω-haloalkyl group in the cyclization step. The presence of a trialkylsilyl group on the Li-bearing carbon atom facilitates configurational isomerization. However, it is not necessary for cyclization. The reaction proceeds with retention of regiochemistry. The cyclialkylation reactions of (ω-halo-1-silyl-1-alkenyl)metals containing Al, Zn, Zr, or Si, on the other hand, proceed via π-type cyclization processes. The relative ease of ring formation with respect to ring size is 3 and 4 ≫ 5 < 6. Formation of cyclobutenylsilanes is nonregiospecific. The stereochemistry of alkenylmetal intermediates is unimportant, but the presence of a silyl group as the second metal group is necessary. The reaction can be inhibited by some polar solvents, such as THF. All of these facts can be accommodated by π-cyclization mechanisms and Baldwin's cyclization rules.

Cyclization of alkenylmetals via cyclialkylation (eq 1) is a potentially useful synthetic methodology. Although the corresponding cyclialkylation of aryllithiums[3] is a well-established process, its alkenyl version remained essentially unknown at the outset of our study several years ago. Our interest in this area was further aroused by the following serendipitous discovery. In our study of the effects of heterosubstituents on the Zr-catalyzed carbometalation of alkynes,[4] 1-(trimethylsilyl)-4-bromo-1-butyne (**2b**) was treated with Me_3Al (2 equiv) in the presence of I equiv of Cl_2ZrCp_2 (Cp = η^5-C_5H_5) at 25 °C. The reaction did not give the expected carbometalation-protonolysis product **3b**. Instead, it produced within 6 h a cyclic product **4** in 92% yield (eq 2).

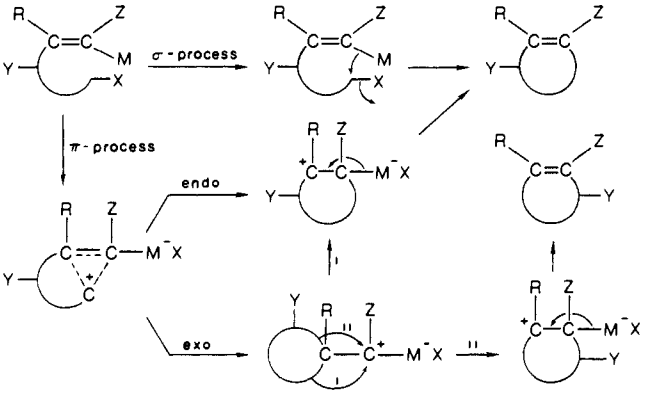


(1)

1

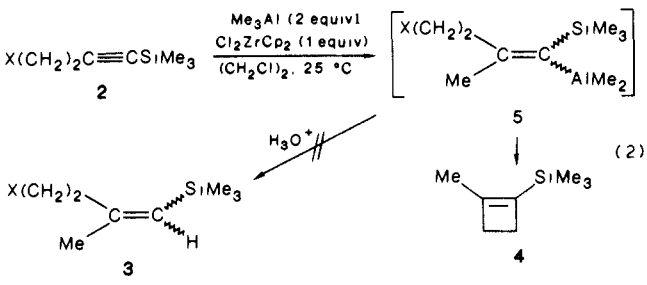
M = metal group; X = halogen or a related group

Scheme I



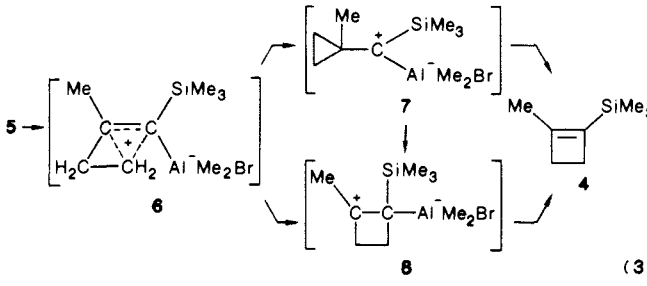
† John Simon Guggenheim Memorial Foundation Fellow (1987).

0002-7863/88/1510-5383$01.50/0



a, X = Cl; b, X = Br, c, X = I, d, X = OTs

Assuming that the reaction proceeds via a carbometalation product **5**, the results presented a few intriguing puzzles. First, alkenylalanes are known not to readily react with primary alkyl halides.[5] Second, the carbometalation reaction of Me_3Al–Cl_2ZrCp_2 has been shown to give exclusively or predominantly cis addition products,[4,6] indicating that the cyclization step either is not seriously affected by the alkene stereochemistry or can overcome the wrong stereochemistry. These considerations led us to propose the following π-type cyclization process (eq 3). A presumed π-complex **6** may

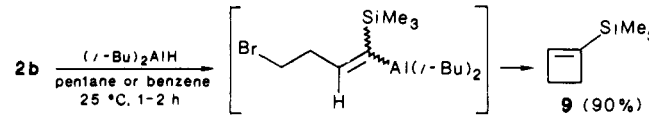


be converted to **4** via **7** and/or **8**. In this particular reaction, Baldwin's cyclization rule[7] would disfavor direct formation of **8**, a 4-endo-trig process. Intermediacy of **7** should lead to scrambling of the original regiochemistry.

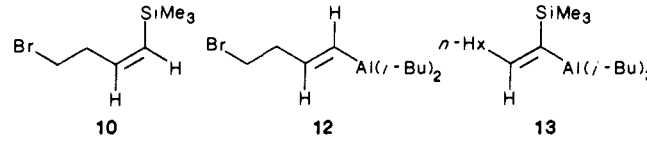
These results pointed to a hitherto unrecognized possibility that cyclialkylation of alkenylmetals may proceed via either σ- or π-type processes (Scheme I) and prompted us to discover and develop some such cyclization reactions and investigate their mechanistic details.

Results and Discussion

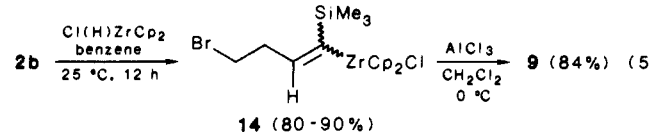
Cyclialkylation of [ω-Halo-1-(trimethylsilyl)-1-alkenyl]metals Containing Al, Zr, Zn, or Si. Scope and Mechanism of π-Cyclization Reactions. In order to investigate the detailed aspects of the cyclialkylation reaction represented by that shown in eq 2, a series of 4-halo-1-(trimethylsilyl)-1-butynes **2** containing Cl (**2a**), Br (**2b**), and I (**2c**) as well as the corresponding tosylate (**2d**) were prepared from 3-butyn-1-ol. Their reaction with Me_3Al (2 equiv) and Cl_2ZrCp_2 (1 equiv) in CH_2Cl_2 at 25 °C for 3 h produced **4** in 90, 85, 55, and 20% yields, respectively. The corresponding yields after 24 h were 95, 92, 85, and 35%. The reaction of **2b** with $(i\text{-Bu})_2AlH$ (DIBAH) in pentane or benzene at 25 °C gave within 1–2 h 1-(trimethylsilyl)cyclobutene (**9**) in 90% yield (eq 4), indicating that neither Cl_2ZrCp_2 nor the β-Me group is



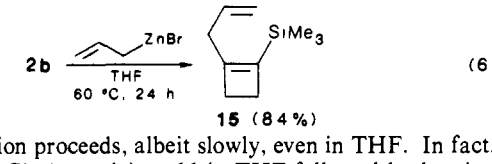
essential to the cyclization reaction. The same reaction run in Et_2O did not produce **9** but only the usual hydroalumination product **10** obtained via protonolysis of **11**, indicating that donor



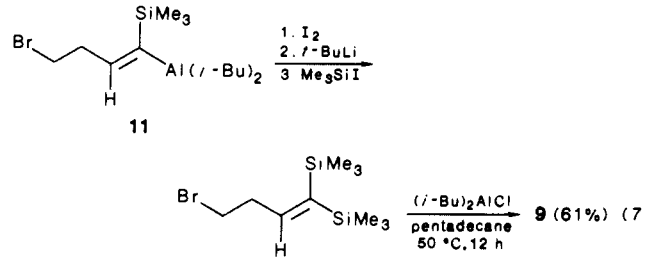
solvents may prevent the reaction. Both Al and Si appear to be necessary, since neither **10** nor **12** underwent cyclization under comparable conditions. It is also worth noting that there was no detectable reaction between **13** and homoallyl bromide. The results indicate that the scope of the reaction is limited to intramolecular cases only. Hydrozicronation of **2b** with $Cl(H)ZrCp_2$ in benzene for 12 h at 25 °C gave **9** only in 10% yield. Examination of the reaction mixture by ^1H NMR clearly indicated the formation of **14** as an *E* and *Z* mixture in 80–90% yield. Its treatment with $AlCl_3$ (1.1 equiv) in CH_2Cl_2 at 0 °C, however, produced **9** in 84% yield (eq 5), clearly indicating that hydrometalation or carbo-



metalation products can be intermediates for the cyclic products. Treatment of **2b** with allylzinc bromide (2 equiv) in THF for 24 h at 60 °C provided **15** in 84% yield (eq 6). It is noteworthy



that this reaction proceeds, albeit slowly, even in THF. In fact, addition of $ZnCl_2$ (1 equiv) to **11** in THF followed by heating the mixture for 1 h at 60 °C gave **9** in 40%, whereas no cyclization occurred in the absence of $ZnCl_2$ even after 3 h under otherwise the same conditions. Iodination of **11** followed by lithiation with *t*-BuLi (2 equiv) and silylation with Me_3SiI gave **16** in 76% yield based on **11**. Although **16** was stable for at least 12 h even at 100 °C in pentadecane, its treatment with $(i\text{-Bu})_2AlCl$ (1.1 equiv) in pentadecane for 12 h at 50 °C provided **9** in 61% yield, with an 18% of **16** remaining unreacted (eq 7).



To explore the scope of the cyclialkylation reaction with respect to ring size, 1-(trimethylsilyl)-3-bromo-1-propyne (**17**) was treated with Me_3Al (2 equiv) and Cl_2ZrCp_2 (1 equiv) in CH_2Cl_2 for 3 h under reflux. On protonlysis, **18** was obtained in 64% yield rather than the expected product **19**. Even when only 1 equiv of Me_3Al was used, **18** (50% yield) was essentially the only cyclization product, the balance of the material being the unreacted **17**. Evidently, **19** was formed but reacted further to give **20** at a faster rate. The formation of **20** was indicated by its conversion into **21** (≥95% D) upon deuteriolysis (eq 8).

(1) Metal Promoted Cyclization. 18. Part 17: Negishi, E.; Sawada, H.; Tour, J. M.; Wei, Y. *J. Org. Chem.* **1988**, *53*, 913. Some preliminary results of the work have been communicated: (a) Negishi, E.; Boardman, L. D.; Tour, J. M.; Sawada, H.; Rand, C. L. *J. Am. Chem. Soc.* **1983**, *105*, 6344. (b) Boardman, L. D.; Bagheri, V.; Sawada, H.; Negishi, E. *J. Am. Chem. Soc.* **1984**, *106*, 6105. (c) Stroll, A. T.; Negishi, E. *Tetrahedron Lett.* **1985**, *26*, 5671.

(2) On leave from Ube Industries, Ltd., Ube, Japan, Aug 1982–Jan 1985.

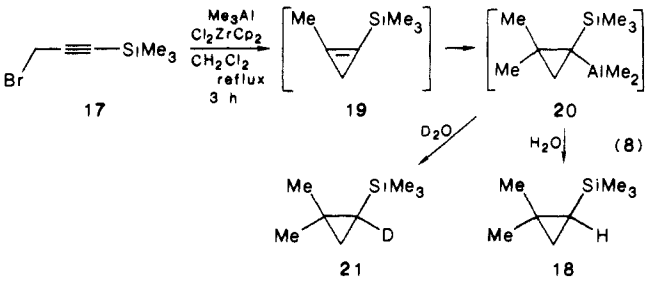
(3) For a review, see: Parham, W. E.; Bradsher, C. K. *Acc. Chem. Res.* **1982**, *15*, 300.

(4) (a) Rand, C. L.; Van Horn, D. E.; Moore, M. W.; Negishi, E. *J. Org. Chem.* **1981**, *46*, 4093. (b) For a review of this reaction, see: Negishi, E. *Pure Appl. Chem.* **1981**, *53*, 2333.

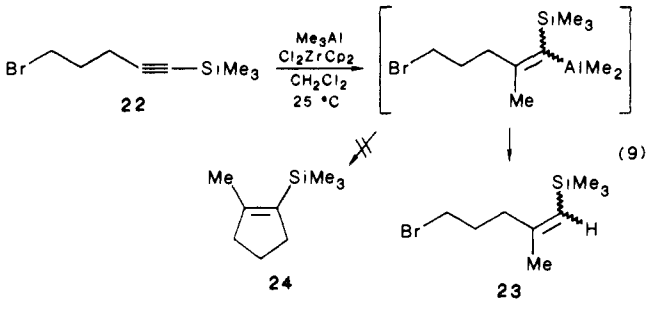
(5) For reviews, see: (a) Mole, T.; Jeffery, E. A. *Organoaluminum Compounds*; Elsevier: Amsterdam, *The Netherlands*, 1972. (b) Zweifel, G.; Miller, J. A. *Org. React. (N.Y.)* **1984**, *32*, 375.

(6) Snider, B. B.; Karras, M. *J. Organomet. Chem.* **1979**, *179*, C37.

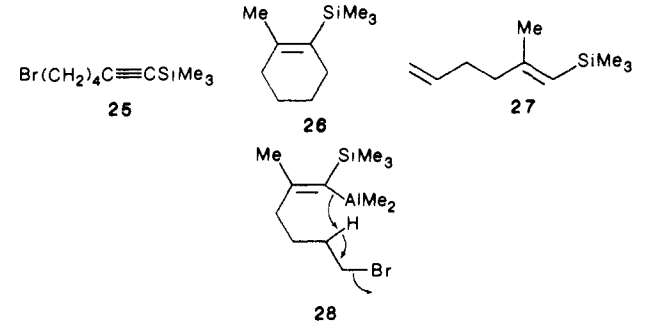
(7) Baldwin, J. E. *J. Chem. Soc., Chem. Commun.* **1976**, 734, 736, 738.



In sharp contrast with the reaction of **2** with Me_3Al–Cl_2ZrCp_2, the corresponding reaction of 5-bromo-1-(trimethylsilyl)-1-pentyne (**22**) gave, after protonlysis, only the carbometalation product **23** in 60% yield. Even after 24 h at 25 °C, the desired cyclization product **24** was not obtained in any significant yield (<5–10%) (eq 9). Somewhat surprisingly, the corresponding reaction of

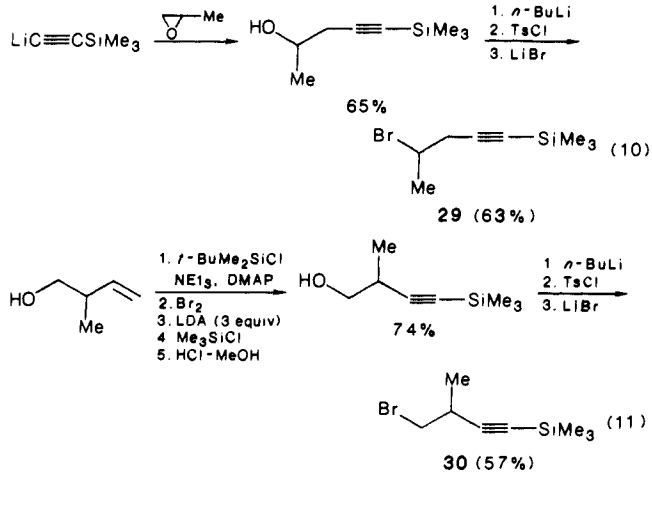


6-bromo-1-(trimethylsilyl)-1-hexyne (**25**) did produce **26** in 53% yield after 24 h at 25 °C along with a 20–25% yield of an acyclic byproduct **27**, which is essentially 100% E. The high stereoselectivity in the formation of **27** may be rationalized in terms of an intramolecular elimination process involving the *Z* isomer of **28**. No attempts have been made to see if the reaction is ap-

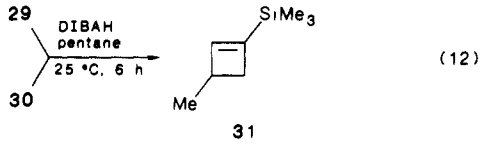


plicable to the formation of 7-membered and larger rings. On the basis of the above-described results, we conclude that the ease of cyclization with respect to ring size is 3 and 4 ≫ 5 < 6.

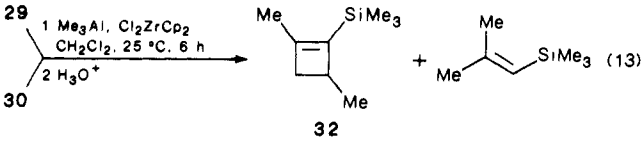
The regiochemistry of cyclization is important from both synthetic and mechanistic viewpoints. To probe this matter, **29** and **30** were prepared according to eq 10 and 11. The reaction



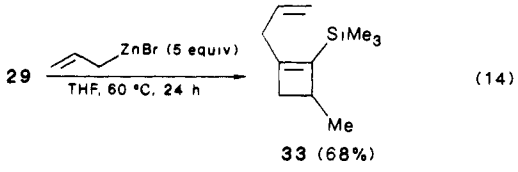
of **29** or **30** with DIBAH in pentane at 25 °C produced 3-methyl-1-(trimethylsilyl)cyclobutene (**31**) in 80 or 75% yield, respectively (eq 12). The yield of its regioisomer, if any, was <3%. Clearly, the reaction is nonregiospecific, although it is highly regioselective.



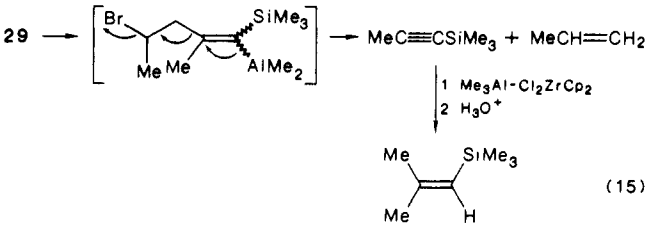
Further complications arose when **29** and **30** were treated with Me_3Al–Cl_2ZrCp_2. These reactions too were highly regioselective, producing **32** as essentially the only cyclic product in 75 and 39% yields, respectively, along with 2-methyl-1-(trimethylsilyl)propene produced in 25 and 10% yields, respectively (eq 13). Similarly,



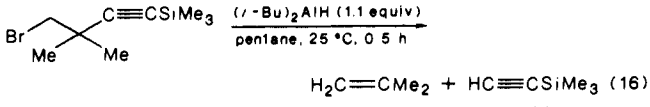
treatment of **29** with allylzinc bromide (5 equiv)[8] in THF at 60 °C for 24 h produced regioisomerically pure **33** in 68% yield (eq 14). In the reaction shown in eq 12, the Me group in **29** or **30**



ends up in the C-3 position, whereas the same Me group is in the C-4 position in the reaction shown in eq 13. The formation of the acyclic byproduct in the reaction shown in eq 13 may be readily explained in terms of a Grob-type fragmentation[9] followed by carbometalation (eq 15). In fact, the Grob-type fragmentation



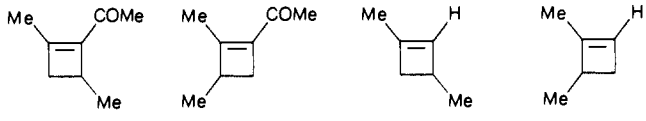
completely dominated in the reaction of 4-bromo-3,3-dimethyl-1-(trimethylsilyl)-1-butyne with DIBAH (eq 16).



In view of the diametrically opposed regiochemical results shown in eq 12 and 13, efforts were made to unequivocally establish the regiochemistry of **31** and **32**. The regiochemistry of **31** has been established by comparing its IR, ^1H NMR and ^{13}C NMR spectra with those of an authentic sample obtained by the σ-type cyclialkylation reaction, which has been shown to proceed with retention of regiochemistry (vide infra). Treatment of **32** with acetyl chloride and $AlCl_3$ in CH_2Cl_2 at 0 °C for 30 min provided **34** in 87% yield. Although this compound has not previously been reported, its regioisomer **35** has been reported.[10] Comparison of their ^1H NMR spectra clearly indicated them to be distinct. Specifically, the signals for the two Me groups on the cyclobutene

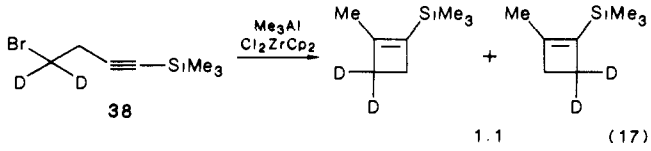
(8) Negishi, E.; Miller, J. A. *J. Am. Chem. Soc.* **1983**, *105*, 6761.
(9) For reviews, see: (a) Grob, C. A.; Schiess, P. W. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 1. (b) Grob, C. A. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 535.
(10) Bahurel, Y.; Meret, A.; Pautet, F.; Poncet, A.; Descotes, G. *Bull. Soc. Chim. Fr.* **1971**, 2215.

ring of **34** appeared at 1.03 (d, J = 7 Hz) and 1.88 (s) ppm, whereas the reported values for those of **35** are 1.20 (d, J = 7 H) and 1.65 (s) ppm. Furthermore, treatment of **32** with 50% HI in benzene at room temperature for 4 h gave **36** in 90% yield. Comparison of its ^{1}H NMR data with those reported in the literature[11] confirmed its identity. In particular, the observed chemical shift value of 5.73 ppm for the alkenyl proton is in good agreement with the reported value of 5.71 ppm but is substantially different from the reported value of 5.59 ppm for the alkenyl proton of the regioisomer **37**.

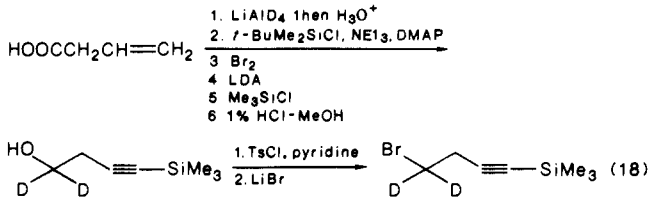


34 **35** **36** **37**

The nonregiospecific nature of the cyclialkylation reaction was further demonstrated by the reaction of 4,4-dideuterio-4-bromo-1-(trimethylsilyl)-1-butyne (**38**) with Me_3Al–Cl_2ZrCp_2, which provided an essentially 50:50 mixture of the 3,3- and 4,4-dideuterio derivatives of **4** (eq 17). The preparation of **38** was carried out as outlined in eq 18.

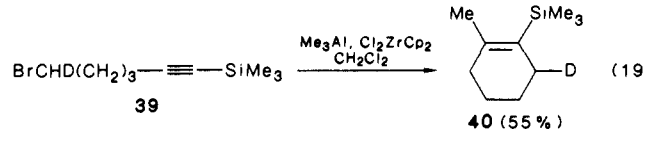


38 1:1 (17)



(18)

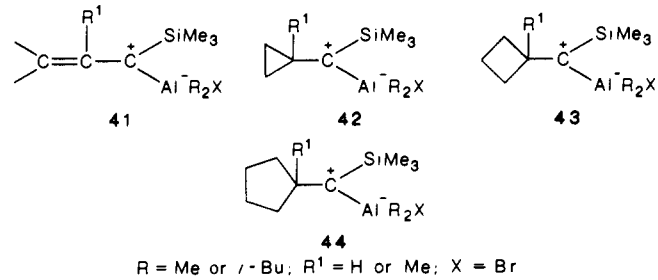
Interestingly, the reaction of 6-deuterio-6-bromo-1-(trimethylsilyl)-1-hexyne (**39**) with Me_3Al–Cl_2ZrCp_2 was highly regioselective and most probably regiospecific as well. We tentatively assign **40** to the sole cyclization product obtained in 55% yield (eq 19). Of seven distinct ^{13}C NMR signals, only the one



39 **40** (55%) (19)

at 29.00 ppm was split into a triplet due to the adjacent deuterium atom. The preparation of **39** consisted of oxidation of 5-hexyn-1-ol with PCC followed by reduction with $LiAlD_4$, bromination, and silylation.

All of the data presented above can be rationalized in terms of the π-cyclization process shown in Scheme I and Baldwin's cyclization rule.[7] Among noteworthy facts to be explained here are (i) the order of the ease of cyclization, i.e., 3 and 4 $\gg$ 5 < 6, (ii) nonregiospecificity of the cyclobutene formation, (iii) the unimportance of the stereochemistry of alkenylmetal intermediates, (iv) the necessity for two metals on the alkenyl moiety, and (v) the fact that polar solvents can prevent the reaction. The π-cyclization mechanism shown in Scheme I allows the cyclizing species to form an n-membered ring either directly or via $(n-1)$-membered intermediates. Since direct formation of 3- to 5-membered rings, i.e., 3- to 5-endo-trig processes, is expected to be unfavorable,[7] alternate exocyclic processes involving $(n-1)$-membered rings may be observed. Such processes for the formation of 3- and 4-membered rings would involve the intermediacy of allyl (**41**) and cyclopropylcarbinyl (**42**) cationic species, respectively. Since their formation involves normally facile β and γ elimination to produce resonance-stabilized species, it must be both kinetically and thermodynamically favorable. On the other hand, formation of cyclobutylcarbinyl cationic intermediate **43** is both kinetically and thermodynamically less favorable than the two cases mentioned above. Consequently, normally facile formation of 5-membered rings is highly unfavorable in the present reaction.

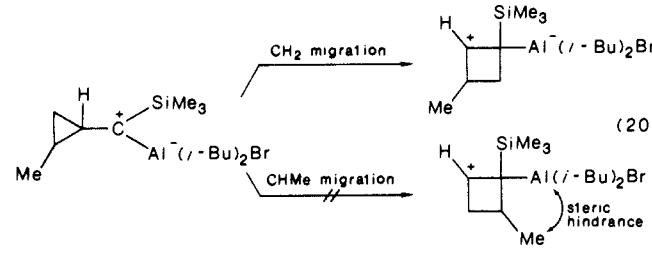


41 **42** **43** **44**

R = Me or t-Bu; R^1 = H or Me; X = Br

Formation of cyclohexenylsilanes may involve either direct cyclization by a favorable 6-endo-trig process[7] or intermediary formation of cyclopentylcarbinyl species by 5-exo-trig cyclization, another favorable process. In either case, it should be favored over the 5-membered ring case.

As mentioned earlier, the nonregiospecificity of cyclobutene formation is consistent with the intermediacy of **42** and has been conclusively demonstrated by the results shown in eq 17. The diametrically opposed regiochemical results observed in the formation of **31** and **32** must therefore be a mere consequence of variable steric hindrances at migration origins and termini. In the formation of **31**, the steric hindrance at the migration terminus may be greater than at the migration origin, causing selective migration of the sterically less demanding CH_2 group rather than the CHMe group (eq 20). In the reaction shown in eq 13, however, the steric hindrance at the migration origin must outweigh that at the migration terminus.



(20)

The fact that **40** was produced as the only cyclization product as a regioisomerically pure species rules out the intermediacy of **44**. The reaction must therefore produce directly **40** or its 6-membered precursor. The results are consistent with the π-cyclization mechanism involving 6-endo-trig processes. Although it is not possible to rigorously rule out the σ-cyclization mechanism for this particular case, such a σ-cyclization reaction would have produced the corresponding cyclopentenylsilanes, e.g., **24**, at comparable or faster rates.

The unimportance of the alkene stereochemistry is also a consequence of the π-cyclization process. However, the alkene stereochemistry appears to be important for the side reaction leading to the formation of **27**. One of the most intriguing findings in the present investigation is that the silyl group or a second metal group appears to be necessary to observe the above-described cyclization reaction. We suggest that the silyl group activates the adjacent alkenyl group as a nucleophile through σ-donation. It is known that Si can act as a combination of a σ-donor and a π-acceptor. Thus, for example, alkenylsilanes can react more readily with electrophiles via π-complexation than the parent alkenes.[12] Although it is thought that Si may somewhat destabilize an adjacent carbocation, this effect in the presumed intermediates **41** and **42** may be at least partially offset by the presence of the negatively charged Al group. Although we have not made a systematic investigation of the solvent effects, the data in hand indicate that either the metal atom, which leaves the

(11) Ripoll, J. L.; Conia, J. M. *Bull. Soc. Chim. Fr.* **1965**, 2755.

(12) For a review, see: Colvin, E. *Silicon in Organic Synthesis*; Butterworths: London, 1981.

Table I. Cyclialkylation of [ω-Halo-1-(trimethylsilyl)-1-alkenyl]lithiums[a]

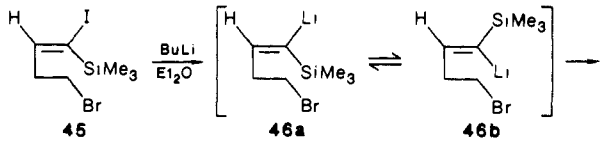
XR	R¹			% yield[b] of
$ClCH_2$	$CH_2CH{=}CH_2$	Z	t-BuLi	95
ClCHMe	$CH_2CH{=}CH_2$	Z	t-BuLi	95 (78)
$ClCH_2$	n-Pr	Z	t-BuLi	88 (58)
$ClCH_2$	Ph	Z	t-BuLi	90
$Br(CH_2)_2$	H	E	t-BuLi	81
$Br(CH_2)_2$	H	E	n-BuLi	80
$BrCH_2CHMe$	H	E	t-BuLi	31
$Cl(CH_2)_3$	H	E	n-BuLi	67
$Br(CH_2)_3$	n-Hx	Z (85%)	t-BuLi	87 (84)
$BrCHMe(CH_2)_2$	H	E	t-BuLi	85 (79)
$Br(CH_2)_4$	H	E	t-BuLi	64
$Br(CH_2)_4$	Me	E and Z	t-BuLi	70
$BrCH_2CHMe(CH_2)_2$	H	Z	t-BuLi	88 (82)
$BrCH_2CHMe(CH_2)_3$	H	Z	t-BuLi	77

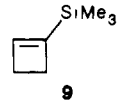
[a] The reaction was carried out in ether by addition of either t-BuLi (2 equiv) or n-BuLi (1 equiv) in a hydrocarbon solvent at −78 °C (30 min) followed by warming the mixture to 25 °C. [b] The yields were determined by either GLC (SE-30 column) or ^1H NMR. The numbers in parentheses are isolated yields.

starting compound, or an added reagent must act as a Lewis acid, suggesting polarization or even ionization of the carbon–halogen bond. This provides an explanation for the apparently much faster rates for the formation of 3- and 4-membered rings via allyl and cyclopropylcarbinyl cationic species relative to that for the formation of 6-membered rings.

Cyclialkylation Reactions of [ω-Halo-1-alkenyl]lithiums. Scope and Mechanism of σ-Cyclization Reactions. Although novel and interesting, the cyclization reaction discussed in the preceding section is associated with some difficulties and limitations. First, it does not provide cyclopentene derivatives. Nor does it produce cyclopropenes, although cyclopropanes have been obtained by the reaction. Second, the reaction may, in some cases, be nonregiospecific. Third, the need for a silyl group has limited its applicability to the synthesis of cycloalkenylsilanes. To overcome these difficulties, alternate cyclialkylation reactions were sought.

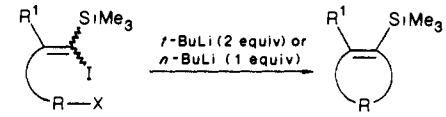
We treated (*E*)-4-bromo-1-iodo-1-(trimethylsilyl)-1-butene (**45**), obtained via hydroalumination in ether and iodinolysis of **2b**, with 5 mol % *t*-BuLi in the hope of obtaining the *Z* isomer of **45** by a literature procedure.[13] None of the *Z* isomer was obtained, with most of **45** remaining unchanged. However, the reaction did produce a small amount (5%) of 1-(trimethylsilyl)cyclobutene (**9**). Instead of catalyzing the desired isomerization, the presumed alkenyllithium intermediate **46** must have cyclized. Indeed, treatment of **45** with 2 equiv of *t*-BuLi or 1 equiv of *n*-BuLi in ether (−78 to +25 °C) gave **9** in ca. 80% yield (eq 21). It is noteworthy that the cyclization reaction must be considerably faster than an intermolecular reaction of **46** with *n*-BuI.





9 (21)

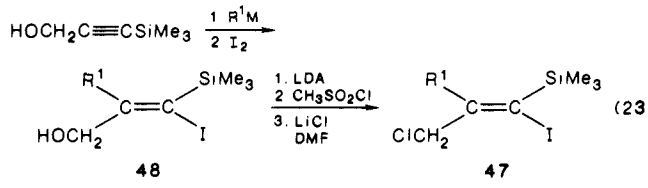
As the results summarized in Table I indicate, this reaction has indeed turned out to be more general with respect to ring size than those described in the preceding section. Three- through seven-membered cycloalkenylsilane derivatives have been obtained in good to excellent yields (eq 22) except that **31** was obtained in only 31% yield along with 4-bromo-3-methyl-1-(trimethylsilyl)-1-butene (31%). In no case was the desired cyclization



(22)

reaction completed by β-elimination. This is in contrast with the reaction producing 1-(trimethylsilyl)-2-methylcyclohexene (**26**) described in the preceding section.

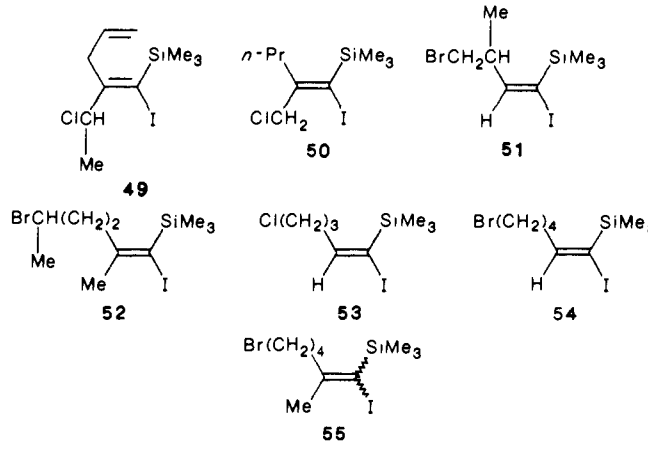
The preparation of some precursors (**47**) to cyclopropenylsilanes was carried out by carbometalation of 3-(trimethylsilyl)propargyl alcohol followed by iodinolysis and chlorination (eq 23). Oxi-



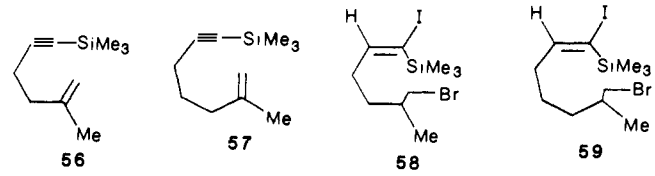
(23)

a, $R^1M = CH_2{=}CHCH_2ZnBr$ (2 equiv); b, R^1M = PhMgBr and CuI (10%)

dation of **48a** with pyridinium chlorochromate (PCC) followed by treatment with MeMgBr provided **49** in 73% yield, while the



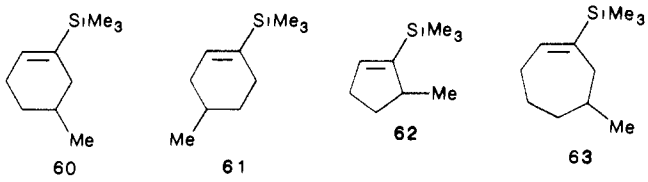
reaction of **48a** with $(i\text{-Bu})_3Al$ (3 equiv) and Cl_2ZrCp_2 (1 equiv) followed by protonolysis gave **50** in 72% yield. The preparation of **52–54** also involved hydroalumination of the corresponding ω-halo 1-trimethylsilanes with DIBAH in ether followed by iodinolysis, while treatment with Me_3Al–Cl_2ZrCp_2 followed by iodinolysis was used to prepare **55**. The reaction of methallylmagnesium bromide with 2,3-dichloropropene followed by treatment with LDA (2 equiv) and Me_3SiCl provided **56** in 80%



yield, while **57** was obtained in 77% yield by the reaction of 5-bromo-2-methyl-1-pentene with [2-(trimethylsilyl)ethynyl]-lithium. Hydroboration–oxidation of **56** and **57** with 9-BBN and $NaOH$–H_2O_2 followed by sequential treatment with CBr_4–PPh_3, DIBAH, and iodine provided **58** and **59**.

One noteworthy aspect of this cyclialkylation reaction is that each of those cases, which can, in principle, produce two regioisomeric products, gives only one regioisomer. Thus, **51** produced **31** as the only cyclic product, albeit in low yield. Similarly, cyclialkylation of **52**, **58**, and **59** gave only one cyclization product each, as judged by the ^{13}C NMR spectra of the products. That the product derived from **58** is **60** rather than **61** has been shown by comparing its spectra with those of an authentic sample of **61** prepared by treating 1-iodo-4-methyl-1-cyclohexene with *t*-BuLi (2 equiv) followed by silylation with Me_3SiCl. The ^1H NMR spectra of **60** and **61** are virtually indistinguishable, and the ^{13}C NMR signals for the Me_3Si, Me, and alkenyl carbon atoms are

(13) Zweifel, G.; Murray, R. E.; On, H. P. *J. Org. Chem.* **1981**, *46*, 1292.
(14) For a review with pertinent references on carbometalation of alkynes including propargyl alcohols, see: Normant, J. F.; Alexakis, A. *Synthesis* **1981**, 841.
(15) Negishi, E.; Yoshida, T. *Tetrahedron Lett.* **1980**, *21*, 1501.



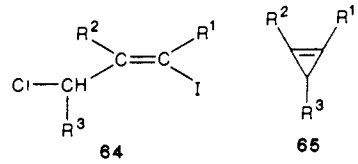
well within 0.1 ppm of each other. However, those for the four sp^3 ring carbon atoms are at 27.14, 28.75, 30.78, and 35.31 ppm for **60** and 26.90, 28.37, 31.35, and 35.52 ppm for **61**. The results clearly indicate that the cyclization reaction producing **60** have proceeded with complete retention of the regiochemistry of **58**. On the basis of the results obtained with **51** and **58**, as well as the difficulty in finding alternate explanations accounting for the formation of single regioisomers from **51**, **52**, **58**, and **59**, we judge that the cyclialkylation reaction of [ω-halo-1-(trimethylsilyl)-1-alkenyl]lithiums must generally proceed regiospecifically with retention. We therefore assign **62** and **63** as the structures of the products derived from **52** and **59**, respectively.

The results presented in this section strongly suggest a σ-cyclization mechanism (Scheme I). The intermediacy of [ω-halo-1-(trimethylsilyl)-1-alkenyl]lithiums has been clearly demonstrated for the reaction of **45**, since treatment of **45** with *t*-BuLi (2 equiv) at −78 °C in ether followed by quenching with Me_3SiI at this temperature gave **16** in 76% yield (eq 7).

Cyclialkylation of (ω-Halo-1-alkenyl)lithiums without a Silyl Group. If the cyclization reaction of (ω-halo-1-silyl-1-alkenyl)-lithiums indeed proceeds by a σ-cyclization mechanism, the role of the silyl group may merely be to facilitate configurational isomerization of (ω-halo-1-silyl-1-alkenyl)lithiums[16] in those cases where the ω-halogen-containing group and the metal group are initially trans to each other. In the σ-cyclization reactions of (ω-haloalkenyl)metals, the two reacting groups must be cis to each other for the desired cyclization to occur. It would then be essential to develop convenient procedures for preparing *cis*-ω-halo-1-iodo-1-alkenes, unless there is an auxiliary group, such as the Me_3Si group, that can facilitate configurational isomerization.

To test the above presumed configurational requirement, the *E* and *Z* isomers of 5-bromo-1-iodopentene and 6-bromo-1-iodo-1-hexene were prepared. The *E* isomers were obtained by hydroalumination (DIBAH)–iodinolysis of the corresponding ω-bromo-1-alkynes, while the *Z* isomers were prepared by hydroboration (disiamylborane)–protonolysis with HOAc of the corresponding ω-bromo-1-iodo-1-alkynes.[17] Treatment of the *Z* isomers with *n*-BuLi (1 equiv) gave cyclopentene and cyclohexene in 85 and 76% yields, respectively, whereas the same reaction of the *E* isomers did not yield any monomeric product. Since all starting compounds were consumed, the products in the latter reactions must be polymeric. These results not only demonstrate the configurational requirement but also strongly support the σ-cyclization mechanism for the cyclialkylation reaction of (ω-halo-1-alkenyl)lithiums.

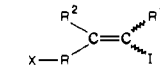
The required acyclic precursors with the correct configuration can, in many cases, be prepared stereoselectively via carbometalation–iodinolysis. Acyclic precursors **64** to cyclopropanes

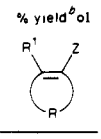


	R^1	R^2	R^3
a	Ph	*n*-Bu	H
b	*n*-Hx	Me	H
c	*n*-Hx	Me	Me
d	*n*-Hx	allyl	H
e	H	Ph	H

65 were prepared by treating the corresponding propargyl alcohols with Grignard reagents in the presence of CuI (10 mol %)[14] and

Table II. Cyclialkylation of (ω-Halo-1-alkenyl)lithiums[a]

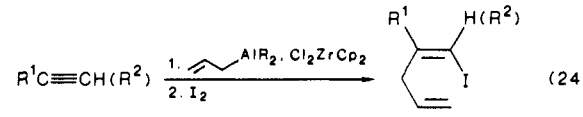




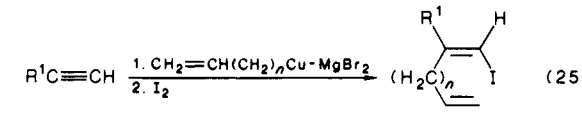
R^1	R^2	XR			
Ph	*n*-Bu	$ClCH_2$	*Z*	*n*-BuLi	83
n-Hz	Me	$ClCH_2$	*Z*	*t*-BuLi	84
n-Hx	Me	ClCHMe	*Z*	*t*-BuLi	70
n-Hx	$CH_2CH{=}CH_2$	$ClCH_2$	*Z*	*t*-BuLi	90
H	Ph	$ClCH_2$	*Z*	*c*	46[d]
H	H	$Br(CH_2)_3$	*Z*	*n*-BuLi	85
H	H	$Br(CH_2)_3$	*E*	*n*-BuLi	0
H	*n*-Hx	$Br(CH_2)_3$	*Z*	*n*-BuLi	80
H	H	$Br(CH_2)_4$	*Z*	*n*-BuLi	76
H	H	$Br(CH_2)_4$	*E*	*n*-BuLi	0
H	*n*-Bu	$Br(CH_2)_2CHMeCH_2$	*Z*	*n*-BuLi	(75)
H	*n*-Bu	$BrCH_2CHMe(CH_2)_2$	*Z*	*n*-BuLi	(56)
H	*n*-Hx	$Br(CH_2)_5$	*Z*	*t*-BuLi	(67)

[a,b] See the corresponding footnotes in Table I. [c] PhLi was used. [d] Isolated as 1-(trimethylsilyl)-2-phenylpropene after treatment with *t*-BuLi and $ClSiMe_3$.

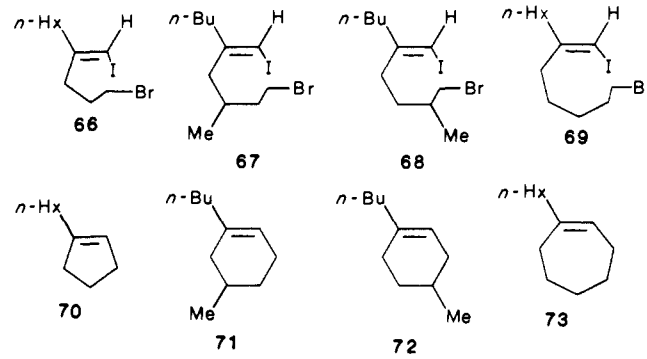
chlorinating the allylic alcohol intermediates as in the synthesis of silylated derivatives **47** (eq 23). Allylmetalation of terminal and internal alkynes can be achieved through the use of allyldialkylalanes and Cl_2ZrCp_2[18] (eq 24). Introduction of longer



alkenyl chains is most conveniently carried out by treating terminal alkynes with alkenylcopper–$MgBr_2$[14] (eq 25). The latter reaction



does not undergo allylmetalation. Treatment of these iododienes with $(i\text{-Bu})_3Al$ (1 equiv) in the presence of 1–5 mol % of Cl_2ZrCp_2[15] followed by brominolysis with NBS (3–3.5 equiv) produces ω-bromo-1-iodo-1-alkenes. In cases where the terminal alkenyl group is disubstituted, the hydroboration–oxidation–halogenation sequence has been used. Acyclic precursors **66–69** were prepared by these methods and treated with *t*-BuLi (2 equiv) or *n*-BuLi (1 equiv) to give the corresponding cyclic products **70–73**. The experimental results are summarized in Table II.



As expected, the cyclization reaction of **67** and **68** with *n*-BuLi in ether produced **71** and **72**, respectively, with complete retention of regiochemistry. The IR and ^1H and ^{13}C NMR spectra of **72** were superimposable with those of an authentic sample prepared by treating 4-methylcyclohexanone with *n*-BuLi and a catalytic amount of iodine. Two ^{13}C NMR signals of **71** at 25.34 and 37.06 ppm are distinctly different from the corresponding signals for **72** at 28.38 and 33.94 ppm, respectively, although all of the other signals are within ±0.5 ppm of each other. The cyclization yields are generally high for the formation of 3- and 5- through 7-membered rings. No attempts to prepare cyclobutenes by this

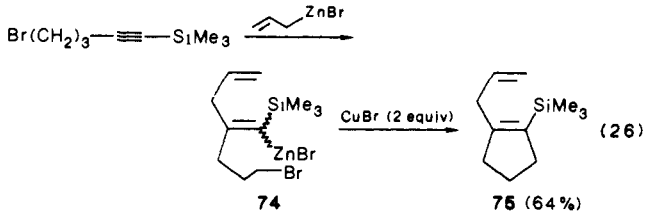
(16) Negishi, E.; Takahashi, T. *J. Am. Chem. Soc.* **1986**, *108*, 3402.
(17) Zweifel, G.; Arzoumanian, H. *J. Am. Chem. Soc.* **1967**, *89*, 5086.
(18) Miller, J. A.; Negishi, E. *Tetrahedron Lett.* **1984**, *25*, 5863.

Table III. Some Features of the σ- and π-Type Cyclization Reactions

feature	σ-process	π-process
metal	highly electropositive metals, e.g., Li; the second metal unnecessary	relatively electronegative metals, e.g., Al, Zn, Zr, or Si; the second metal, e.g., Si, necessary
alkene stereochemistry	Z geometry for the cyclizing grps reqd	unimportant
regiochemistry	regiospecific and retains regiochemistry	nonregiospecific in some cases
ease of cyclization	facile for the formtn of 3- through 7-membered rings	3 and 4 ≫ 5 < 6

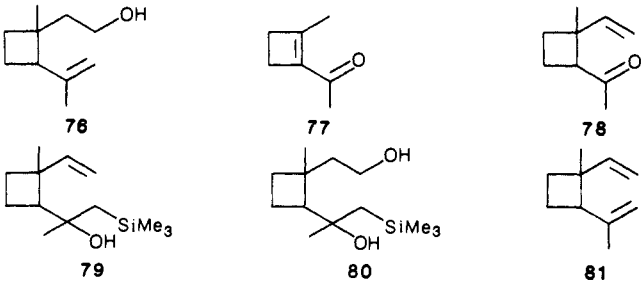
reaction have so far been made.

Subsequent to our initial development of the cyclialkylation reaction of (ω-haloalkenyl)lithiums,[1a] some related cyclialkylation reactions involving Li[19] and Mg in the presence of CuI[20] have been reported. In connection with the latter reaction, our own results on cyclialkylation of an (ω-bromoalkenyl)zinc derivative **74** to give **75** promoted by CuBr (eq 26) are also worth noting.[21]



74 75 (64%)

Synthesis of (±)-Grandisol. To demonstrate the synthetic utility of the cyclialkylation reactions herein reported, a synthesis of grandisol (*Anthonomus grandis* Boheman) (**76**)[22] was achieved



76 77 78 79 80 81

in 40% yield from **4**. Acetylation of **4** with AcCl and $AlCl_3$ in CH_2Cl_2 at 0 °C gave, after workup with 3 N NaOH in ether, an 88% yield of **77**. The reaction of **77** with $Li_2Cu(CH{=}CH_2)_2CN$ at −50 °C followed by treatment with MeOH–THF at −78 to 0 °C afforded a 2:1 mixture of (*Z*)- and (*E*)-1-acetyl-2-methyl-2-vinylcyclobutane (**78**) in 91% yield. The reaction of **78** with Me_3SiCH_2MgCl afforded **79**. Without purification, **79** was treated with disiamylborane and then with 30% H_2O_2–3 N NaOH to give **80**, which was then treated with KH in THF to produce an *Z* and *E* mixture of (±)-grandisol (**76**) in 50% yield based on **78**. The two-stage carbonyl olefination in place of the Wittig reaction avoided the intermediacy of **81**, which is known to readily undergo the Cope rearrangement even at room temperature.[23]

Summary

(ω-Haloalkenyl)metals can undergo both σ- and π-type cyclization reactions according to Scheme I. The σ-type cyclization reactions have so far been observed only with alkenyllithiums. Although not yet demonstrated, some other alkali metals and other highly electropositive metals might be expected to participate in similar σ-cyclization reactions. The σ-cyclialkylation reaction of alkenyllithiums can provide 3- through 7-membered rings in high yields. It requires the cis relationship between Li and the ω-haloalkyl group in the cyclization step. The presence of a trialkylsilyl group on the Li-bearing carbon atom facilitates configurational isomerization. However, the presence of the trialkylsilyl group is unnecessary for cyclization. The σ-cyclialkylation proceeds with retention of regiochemistry.

The cyclialkylation reactions of (ω-halo-1-silyl-1-alkenyl)metals containing Al, Zn, Zr, or Si, on the other hand, must proceed via π-type cyclization processes, as judged by the following observations. First, the relative ease of ring formation with respect to ring size is 3 and 4 ≫ 5 < 6. Second, formation of cyclobutenylsilanes is nonregiospecific. Third, the stereochemistry of alkenylmetal intermediates is unimportant, although (1-silyl-1-alkenyl)metals containing Al, Zn, Zr, or Si do not undergo facile configurational isomerization at room temperature.[16] Fourth, the presence of a second metal group, i.e., a silyl group, is necessary for observing the π-cyclization reactions reported in this work. All of these facts can be nicely accounted for in terms of π-cyclization mechanisms and Baldwin's cyclization rules. The apparent fact that polar solvents, such as ether or THF, can inhibit some π-cyclization reactions is also noteworthy. Some characteristic features of the σ- and π-cyclization reactions are summarized in Table III.

Experimental Section

General Methods. Manipulations involving organometallics were carried out under an atmosphere of N_2 or Ar. Flash chromatographic separations were carried out as described by Still[24] on 230–400-mesh silica gel 60. Alkyllithiums were titrated with either menthol–2,2′-bipyridyl or 2-butanol–1,10-phenanthroline,[25] and boron hydrides were determined in THF by pyrolysis with a 1:1:1 mixture of glycerol–water–THF and measurement of liberated H_2.[26] Gas chromatographic measurements were performed on SE-30 (Chromosorb W) columns using appropriate saturated hydrocarbon standards. THF and diethyl ether were distilled from sodium benzophenone ketyl; CH_2Cl_2, $(CH_2Cl)_2$, and CCl_4 were distilled from P_2O_5; pentane, hexane, benzene, and toluene were distilled from $LiAlH_4$; acetone, NEt_3, methanol, ethanol, cyclohexene, and AcCl were distilled from CaH_2; and HMPA was distilled from Ph_3CLi. $ZnCl_2$, LiCl, LiBr, and NaI were dried at 120 °C at ≤0.5 mm for 6–12 h. Other materials were purchased from appropriate sources and used as received.

4-Halo-1-(trimethylsilyl)-1-butynes. 4-Bromo-1-(trimethylsilyl)-1-butyne (2b) and 4-(Trimethylsilyl)-3-butynyl *p*-Toluenesulfonate (2d): Representative Procedure. To a solution of 3-butyn-1-ol (35.0 g, 0.50 mol) in THF (1 L) at −78 °C was added 2.3 N *n*-BuLi in hexane (453 mL, 1.00 mol). After 1 h, the reaction mixture was treated with Me_3SiCl (133 mL, 114 g, 1.05 mol), warmed to 25 °C over 1–2 h, treated with water, extracted with ether, and concentrated. The concentrate was treated with 3 N HCl, extracted with ether (3×), washed with saturated aqueous $NaHCO_3$ (3×) and NaCl (1×), dried ($MgSO_4$), and concentrated. After the concentrate was diluted in THF (500 mL), sequential treatment with 2.3 N *n*-BuLi in hexane (217 mL, 0.50 mol) at −78 °C for 1 h, *p*-toluenesulfonyl chloride (*p*-TsCl) (105 g, 0.55 mol) in THF (250 mL) at room temperature for 6 h, and water, followed by extraction with ether (1×), washing with saturated aqueous $NaHCO_3$ (1×) and NaCl (1×), drying ($MgSO_4$), and concentration, gave 140 g (93%) of **2d** (>95% pure by ^1H NMR): ^1H NMR ($CDCl_3$, Me_4Si) δ 0.15 (s, 9 H), 2.45 (s, 3 H), 2.60 (t, *J* = 7 Hz, 2 H), 4.10 (t, *J* = 7 Hz, 2 H), 7.3–7.5 (m, 2 H), 7.88.0 (m, 2 H).

The crude tosylate was treated with LiBr (87 g, 1.00 mmol) in acetone (1 L) at 25 °C for 12 h, and the reaction mixture was poured into water (4 L). Extraction with pentane (4×), washing with saturated aqueous $NaHCO_3$ (1×) and NaCl (1×), drying ($MgSO_4$), concentration, and distillation gave 92.0 g (90%) of **2b**: ≥95% pure by GLC; bp 70–75 °C (5.0 mmHg); ^1H NMR ($CDCl_3$, Me_4Si) δ 0.14 (s, 9 H), 2.73 (t, *J* = 7

(19) Chamberlin, A. R.; Bloom, S. H. *Tetrahedron Lett.* **1984**, *25*, 4901.
(20) Okuda, Y.; Morizawa, Y.; Oshima, K.; Nozaki, H. *Tetrahedron Lett.* **1984**, *25*, 2483.
(21) The results were obtained by S. J. Holmes of our laboratories.
(22) Tumlinson, J. H.; Hardee, D. D.; Gueldner, R. C.; Thompson, A. C.; Hedin, P. A.; Minyard, J. P. *Science (Washington, D.C.)* **1969**, *166*, 1010.
(23) Billups, W. E.; Cross, J. H.; Smith, C. V. *J. Am. Chem. Soc.* **1973**, *95*, 3438.
(24) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2933.
(25) Watson, S. C.; Eastham, J. F. *J. Organomet. Chem.* **1967**, *9*, 165.
(26) Brown, H. C. *Organic Synthesis via Boranes*; Wiley-Interscience: New York, 1975.

Hz, 2 H), 3.40 (t, J = 7 Hz, 2 H). The crude product thus obtained was used without further purification.

4-Chloro-1-(trimethylsilyl)-1-butyne (2a): 39% yield; bp 46–49 °C (17 mmHg); ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.12 ns, 9 H), 2.67 (t, J = 7 Hz, 2 H), 3.57 (t, J = 7 Hz, 2 H).

4-Iodo-1-(trimethylsilyl)-1-butyne (4c): 80% yield, bp 91–92 °C (5 mmHg); ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.14 ns, 9 H), 2.78 (t, J = 7 Hz, 2 H), 3.20 (t, J = 7 Hz, 2 H).

Reaction of 4-Halo- or 4-(Tosyloxy)-1-(trimethylsilyl)-1-butyne with Trimethylalane and Zirconocene Dichloride To Produce 2-Methyl-1-(trimethylsilyl)cyclobutene (4). The following procedure for the reaction of 4-bromo-1-(trimethylsilyl)-1-butyne is representative.

2-Methyl-1-(trimethylsilyl)cyclobutene (4) by Carbometalation of 2b. To Cl_2ZrCp_2 (0.44 g, 1.5 mmol) and Me_3Al (2.88 mL, 30 mmol) in CH_2Cl_2 (30 mL) was added **2b** (3.06 g, 15 mmol) in CH_2Cl_2 (7.5 mL). After the mixture was stirred overnight, it was quenched with ice-cold water and acidified (3 N HCl) until homogeneous. Extraction with ether (3 × 15 mL), washing with $NaHCO_3$ solution, drying ($MgSO_4$), concentration, and distillation provided 1.78 g (80%) of **4**: bp 52–56 °C (40 mmHg); IR (neat) 1625 (s), 1250 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.08 (s, 9 H), 1.73 (t, J = 2.5 Hz, 3 H), 2.30 (dq, J = 2.5 Hz, 2 H), 2.53 (bs, 2 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ −1.34, 18.09, 27.43, 34.05, 144.21, 157.72. Anal. Calcd for $C_8H_{16}Si$: C, 68.48; H, 11.50. Found: C, 68.29; H, 11.65. In a separate run, examination of the reaction mixture by GLC (SE-30) indicated that the yields of **4** after 3 and 24 h were 85 and 92%, respectively. The GLC yields of **4** obtained from **2a**, **2c**, and **2d** determined as above were 90, 55, and 20%, respectively, after 3 h and 95, 85, and 35%, respectively, after 24 h.

1-(Trimethylsilyl)cyclobutene (9). (a) Via Hydroalumination of 2b in Pentane. To **2b** (8.21 g, 40 mmol) in pentane (40 mL) at 25 °C was added dropwise DIBAH (8.8 mL, 6.86 g, 48 mmol).[27] After 1 h, analysis of a quenched aliquot by GLC indicated clean formation of a single product (90%). The reaction mixture was quenched at 0 °C with 3 N HCl washed with water, saturated aqueous $NaHCO_3$ (3×), and NaCl (1×), and dried ($MgSO_4$). Spinning-band distillation gave 3.78 g (80%) of **9**: bp 50–52 °C (85 mmHg); IR (neat) 1560 (w), 1247 (s), 935 (s), 831 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, C_6H_6) δ −0.09 (s, 9 H), 2.3–2.7 (m, 4 H), 6.36 (s, 1 H); ^{13}C NMR ($CDCl_3$, C_6H_6) δ −2.30, 31.82, 32.11, 147.59, 156.07. High-resolution MS for $C_7H_{14}Si$: calcd, 126.0865; found, 126.0852.

(b) Via Hydrozirconation of 2b. To a stirred slurry of $Cl(H)ZrCp_2$ (0.85 g, 3.3 mmol) in benzene (3 mL)[28] at 25 °C was added **2b** (0.62 g, 3.0 mmol) in benzene (3 mL). After 12 h, the mixture was concentrated, and its ^{1}H NMR spectrum indicated an approximately 1:1 mixture of the E and Z isomers of the hydrozirconation product (**14**) (90%): ^{1}H NMR (CH_2Cl_2, C_6H_6) δ 0.03 and 0.13 (s, 9 H), 2.3–2.7 and 3.0–3.6 (m, 4 H), 5.88 and 5.95 (s, 10 H). The alkenyl proton signal was not readily discernable. To a stirred slurry of $AlCl_3$ (0.20 g, 1.5 mmol) in CH_2Cl_2 (1 mL) at 0 °C was added **14** (1.5 mmol) in CH_2Cl_2 (1 mL). After 1 h, analysis of a quenched aliquot by GLC indicated the formation of **9** (84%).

(*E*)-4-Bromo-1-iodo-1-(trimethylsilyl)-1-butene (45). To **2b** (10.26 g, 50 mmol) in ether (100 mL) was added DIBAH (10.0 mL, 7.82 g, 55 mmol), and the reaction mixture was heated at 40 °C for 2 h.[27] After the mixture was cooled to −78 °C, I_2 (15.23 g, 60 mmol) in THF (50 mL) was added, and the mixture was warmed to 0 °C and quenched with ice-cold 3 N HCl. Extraction with pentane (1×), washing with saturated aqueous $NaHCO_3$ (3×) and NaCl (1×), drying ($MgSO_4$), concentration, and distillation provided 11.01 g (66%) of **45**: bp 76 °C (0.15 mmHg); IR (neat) 1263 (s), 1249 (s), 839 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.28 (s, 9 H), 2.63 (dt, J = 7, 7 Hz, 2 H), 3.36 (t, J = 7 Hz, 2 H), 7.14 (t, J = 8 Hz, 1 H). The crude material was used for cyclization.

(*Z*)-4-Bromo-1-(trimethylsilyl)-1-butene (10). Treatment of **2b** (6.16 g, 30 mmol) in ether (30 mL) with DIBAH (6.0 mL, 4.69 g, 33 mmol) was carried out as described above. The reaction mixture was quenched at 0 °C with 3 N HCl, extracted with pentane (3×), washed with saturated aqueous $NaHCO_3$ (3×) and NaCl (1×), dried ($MgSO_4$), and concentrated to give 5.88 g (95%) of **10**: bp 60–61 °C (4.9 mmHg); IR (neat) 1606 (m), 1247 (s), 1207 (m), 830 (s), 756 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, C_6H_6) δ 0.01 (s, 9 H), 2.55 (dt, J = 7, 7 Hz, 2 H), 3.23 (t, J = 7 Hz, 2 H), 5.57 (d, J = 14 Hz, 1 H), 6.15 (dt, J = 14, 7 Hz, 1 H). Anal. Calcd for $C_7H_{15}BrSi$: C, 40.58; H, 7.30. Found: C, 40.21; H, 7.46.

4-Bromo-1-butyne. 3-Butyn-1-ol (35.1 g, 0.50 mol) in THF (500 mL) was treated with 2.7 N n-BuLi in hexane (204 mL, 0.55 mol) followed by p-TsCl (114 g, 0.60 mol) in THF (250 mL), and the crude tosylate was treated with LiBr (87 g, 1.00 mol) in acetone (1 L). The title compound was obtained in 60% yield: bp 48 °C (91 mmHg); ^{1}H NMR ($CDCl_3$, Me_4Si) δ 2.11 (t, J = 3 Hz, 1 H), 2.75 (dt, J = 3, 7 Hz, 2 H), 3.45 (t, J = 7 Hz, 2 H).

Generation and Attempted Cyclization of (*E*)-(4-Bromo-1-butenyl)diisobutylalane (12). Hydroalumination of 4-bromo-1-butyne with DIBAH (1 equiv) was carried out in hexane at 40 °C, which produced, after hydrolysis, only 4-bromo-1-butene in 90% yield without giving cyclobutene.

Generation of [1-(Trimethylsilyl)-1-octenyl]diisobutylalane (13) and Its Reaction with 4-Bromo-1-butene. 1-(Trimethylsilyl)-1-octyne was treated in hexane with DIBAH (1 equiv). GLC examination of a hydrolyzed aliquot indicated the formation of 1-(trimethylsilyl)-1-octene in 90% yield. Addition of 4-bromo-1-butene (1 equiv) to **13** generated above did not induce any further reaction at 25 °C over 24 h.

2-(2-Propen-1-yl)-1-(trimethylsilyl)cyclobutene (15). Allyl bromide (3.5 mL, 4.84 g, 40.0 mmol) was added to a suspension of granular 20-mesh zinc metal (3.14 g, 48.0 mmol) in THF (20 mL) at such a rate that the temperature did not exceed 60 °C. After 30 min, the resultant solution of allylzinc bromide was added to **2** (4.10 g, 20.0 mmol) in THF (20 mL). The reaction mixture was heated at 60 °C for 24 h, poured into a mixture of ice and 3 N HCl, extracted with diethyl ether (3×), washed with saturated aqueous $NaHCO_3$ (3×) and NaCl (1×), and dried ($MgSO_4$). Distillation provided **15** (2.80 g, 84%): bp 64–68 °C (10 mmHg); IR (neat) 1642 (m), 1608 (s), 1247 (s), 904 (s), 830 (s), 749 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, C_6H_6) δ −0.07 (s, 9 H), 2.0–2.3 (m, 2 H), 2.3–2.5 (m, 2 H), 2.70 (d, J = 6 Hz, 2 H), 4.87 (d, J = 10 Hz, 1 H), 4.91 (d, J = 17 Hz, 1 H), 5.69 (ddt, J = 17, 10, 6 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ −1.25, 27.70, 31.95, 37.16, 115.41, 135.50, 145.20, 158.20, 158.60. High-resolution MS for $C_{10}H_{18}Si$: calcd, 166.1178; found, 166.1178.

1,1-Bis(trimethylsilyl)-4-bromo-1-butene (16). To **45** (3.08 g, 9.3 mmol) in ether (10 mL) at −78 °C was added 2.18 N t-BuLi in pentane (8.7 mL, 19.09 mmol). After 2 h, Me_3SiI (1.45 mL, 2.05 g, 10.2 mmol) was added, and the reaction mixture was warmed to 25 °C over 1–2 h, quenched with water, extracted with ether (1×), washed with saturated aqueous $NaHCO_3$ (1×) and NaCl (1×), dried ($MgSO_4$), and concentrated. Distillation provided **16** (1.97 g, 76%): bp 79–80 °C (0.65 mmHg); IR (neat) 1568 (m), 1263 (m), 1247 (s), 900–800 (s), 755 (7) cm^{-1}; ^{1}H NMR ($CDCl_3$, C_6H_6) δ −0.05 (s, 9 H), 0.04 (s, 9 H), 2.63 (dt, J = 7, 7 Hz, 2 H), 3.27 (t, J = 7 Hz, 2 H), 6.43 (t, J = 7 Hz, 1 H). Anal. Calcd for $C_{10}H_{23}BrSi_2$: C, 42.99; H, 8.30. Found: C, 43.12; H, 8.09.

Reaction of 16 with Diisobutylchloroalane. Treatment of **16** with $(i\text{-Bu})_2AlCl$ (1 equiv) in pentadecane at 50 °C for 12 h produced **9** in 61% yield (GLC).

1-(Trimethylsilyl)-3-bromo-1-propyne (17). This compound was prepared by a literature procedure[29] in 80% yield: IR (neat) 2180 (m), 1248 (s), 1203 (s, 1035 (s), 840 (s) cm^{-1}; ^{1}H NMR (CCl_4, C_6H_6) δ 0.15 (s, 9 H), 3.80 (s, 2 H) ppm.

(2,2-Dimethylcyclopropyl)trimethylsilane (18) and (2,2-Dimethylcyclopropyl)trimethylsilane-*1-d* (21). To Cl_2ZrCp_2 (1.75 g, 6 mmol) in 10 mL of CH_2Cl_2 was added at 25 °C Me_3Al (0.87 g, 1.15 mL, 12 mmol). To this was added **17** (1.17 g, 6 mmol) in 10 mL of CH_2Cl_2. The reaction mixture was refluxed for 3 h, treated at 0 °C with H_2O followed by acidification with 1 N HCl, washed with saturated aqueous $NaHCO_3$ and brine, and then dried over $MgSO_4$. Distillation provided 0.24 g (28%) of **18** (64% by GLC): IR ($CDCl_3$) 3052 (w), 1248 (s), 853 (s), 837 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, C_6H_6) δ −0.60 (dd, J = 8, 11 Hz, 1 H), 0.00 (s, 9 H), 0.0–0.6 (m, 2 H), 1.09 (s, 3 H), 1.12 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ −0.23, 12.46, 16.99, 18.46, 23.30, 29.03. Anal. Calcd for $C_8H_{18}Si$: C, 67.51; H, 12.75. Found: C, 67.38; H, 12.73.

The 1-deuterio analogue was prepared in the same manner except that D_2O was used to quench the reaction mixture. The yield and the physical properties of (2,2-dimethylcyclopropyl)trimethylsilane-*1-d* (**21**) are as follows: 26% yield by GLC; IR ($CDCl_3$) 3055 (w), 1248 (s), 840 (s), cm^{-1}; ^{1}H NMR ($CDCl_3$, C_6H_6) δ −0.10 (s, 9 H), 0.0–0.5 (m, 2 H), 0.98 (s, 6 H); ^{13}C NMR ($CDCl_3$) δ −0.25, 12.76 (t, J = 10 Hz), 16.91, 18.38, 23.30, 28.98.

1-(Trimethylsilyl)-5-bromo-1-pentyne (22). 5-(Trimethylsilyl)-4-pentyn-1-ol prepared by silylation of 4-pentyn-1-ol was tosylated and converted into the title compound[30] in 63% yield by bromination with LiBr: bp 48–50 °C (2 mmHg); IR (neat) 2180 (s), 1248 (s), 830 (s) cm^{-1}; ^{1}H NMR (CCl_4, C_6H_6) δ 0.06 (s, 9 H), 1.8–2.1 (m, 2 H), 2.31 (t, J = 6 Hz, 2 H), 3.40 (t, J = 6 Hz, 2 H).

Reaction of 22 with Trimethylalane and Zirconocene Dichloride.

(27) Zweifel, G.; Miller, J. A. *Org. React. (N.Y.)* **1984**, *32*, 375.
(28) Hart, D. W.; Schwartz, J. *J. Am. Chem. Soc.* **1974**, *96*, 8115.
(29) Miller, R. B. *Synth. Commun.* **1972**, *2*, 267.
(30) Flahaut, J.; Miginiac, P. *Helv. Chim. Acta* **1978**, *61*, 2275.
(31) Eaborn, C.; Jackson, R. A.; Pearce, R. *J. Chem. Soc., Perkin Trans. 1* **1975**, 470.

Treatment of **22** with Me_3Al (2 equiv) and Cl_2ZrCp_2 (1 equiv) in CH_2Cl_2 at 25 °C produced ca. a 50:50 mixture of the *E* and *Z* isomers of 1-(trimethylsilyl)-5-bromo-2-methyl-1-pentene (**23**) in 60% yield: bp 65–70 °C (2 mmHg); IR (neat) 1613 (s, 1240 (s), 830 (s) cm^{-1}; ^1H NMR (CCl_4, C_6H_6) δ 0.05 (s, 9 H), 1.73 and 1.78 (2 s, 3 H), 1.8–2.4 (m, 4 H), 3.30 (t, *J* = 6 Hz, 2 H), 5.16 (bs, 1 H); ^{13}C NMR ($CDCl_3$) (*Z* and *E* mixture) δ 0.03, 0.31, 21.52, 26.34, 30.94, 31.94, 33.19, 36.32, 36.17, 40.72, 124.42, 126.34, 152.90, 153.42. Anal. Calcd for $C_9H_{19}BrSi$: C, 45.95; H, 8.14. Found: 45.72; H, 8.37.

1-(Trimethylsilyl)-6-bromo-1-hexyne (25). This compound was prepared from 5-hexyn-1-ol via 6-(trimethylsilyl)-5-hexyn-1-ol and its tosylate in a similar manner as the preparation of **2b**.

(a) 6-(Trimethylsilyl)-5-hexyn-1-ol: 92% yield; bp 78–80 °C (4 mmHg); IR (neat) 3350 (s), 2175 (s), 1247 (s), 839 (m) cm^{-1}; ^1H NMR (CCl_4, C_6H_6) δ 0.05 (s, 9 H), 1.3–1.7 (m, 4 H), 2.0–2.3 (m, 2 H), 3.0–3.2 (m, 1 H), 3.3–3.7 (m, 2 H).

(b) 6-(Trimethylsilyl)-5-hexyn-1-yl *p*-Toluenesulfonate: 91% yield; IR (neat) 2175 (s), 1600 (m), 1364 (s), 1248 (s), 1175 (s), 836 (s) cm^{-1}; ^1H NMR (CCl_4, C_6H_6) δ 0.07 (s, 9 H), 1.3–1.9 (m, 4 H), 2.12 (t, *J* = 6 Hz, 2 H), 2.39 (s, 3 H), 3.96 (t, *J* = 6 Hz, 2 H), 7.25 (d, *J* = 8 Hz, 2 H), 7.69 (d, *J* = 8 Hz, 2 H).

(c) 1-(Trimethylsilyl)-6-bromo-1-hexyne (25): 64% yield; bp 71–74 °C (3 mmHg); IR (neat) 2170 (s), 1245 (s), 830 (s) cm^{-1}; ^1H NMR ($CDCl_3$, C_6H_6) δ 0.08 (s, 9 H), 1.4–2.0 (m, 4 H), 2.17 (t, *J* = 6 Hz, 2 H), 3.37 (t, *J* = 6 Hz, 2 H). The crudely distilled material was used for further transformations.

Reaction of 1-(Trimethylsilyl)-6-bromo-1-hexyne (25) with Trimethylalane–Zirconocene Dichloride. To Cp_2ZrCp_2 (1.46 g, 5 mmol) in 10 mL of CH_2Cl_2 was added Me_3Al (0.96 mL, 0.72 g, 10 mmol), and the mixture was stirred at 25 °C for 15 min. To this was added at 25 °C **25** (1.19 g, 5 mmol) in 10 mL of CH_2Cl_2. Treatment of the mixture after 24 h with 3 N HCl and ether, washing with saturated aqueous $NaHCO_3$ and brine, drying over $MgSO_4$, concentration, and distillation provided 0.45 g (53%) of **26**[13] and 0.17 g (20%) of 1-(trimethylsilyl)-2-methyl-1,5-hexadiene (**27**). **26**: bp 34–36 °C (2 mmHg); IR (neat) 1640 (m), 1245 (s), 824 (s) cm^{-1}; ^1H NMR (CCl_4, C_6H_6) δ 0.06 (s, 9 H), 1.3–1.7 (m, 4 H), 1.67 (bs, 3 H), 1.7–2.2 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 0.05, 23.05, 23.94, 29.09, 33.22, 128.98, 143.25. **27**: ^1H NMR (CCl_4, C_6H_6) δ 0.03 (s, 9 H), 2.0–2.3 (m, 4 H), 4.7–5.1 (7, 2 H), 5.12 (bs, 1 H), 5.4–5.9 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 0.08, 32.26, 41.86, 114.36, 123.33, 138.45, 154.43. Anal. Calcd for $C_{10}H_{20}Si$: C, 71.34; H, 11.97. Found: C, 71.06; H, 12.14.

5-(Trimethylsilyl)-4-pentyn-2-ol. To bis(trimethylsilyl)ethyne (17.04 g, 100 mmol) in THF (100 mL) at 0 °C was added 1.5 N MeLi in ether (74.0 mL, 111 mmol). After 30 min each at 0 and 25 °C, the mixture was cooled to −78 °C, and propylene oxide (7.7 mL, 6.39 g, 110 mmol) in THF (50 mL) was added. The reaction mixture was warmed to 25 °C over 1–2 h, poured onto cold water, extracted with ether, washed with water (1×) and saturated aqueous $NaHCO_3$ (1×), dried ($MgSO_4$), and concentrated. The crude alcohol (10.23 g, 65%) was 94% pure by GLC and was used without further purifcation: ^1H NMR ($CDCl_3$, Me_4Si) δ 0.14 s, 9 H), 1.23 (d, *J* = 6 Hz, 3 H), 2.38 (d, *J* = 6 Hz, 2 H), 3.7–4.1 (m, 1 H).

4-Bromo-1-(trimethylsilyl)-1-pentyne (29). Conversion of 5-(trimethylsilyl)-4-pentyn-2-ol into **29** was achieved in a similar manner as the preparation of **2b**. The title compound was obtained in 63% yield: bp 60–65 °C (3.5 mmHg); IR (neat) 2180 (m), 1249 (s), 838 (s) cm^{-1}; ^1H NMR ($CDCl_3$, Me_4Si) δ 0.02 (s, 9 H), 1.64 (d, *J* = 7 Hz, 3 H), 2.51 (dd, *J* = 17, 7 Hz, 1 H), 2.75 (dd, *J* = 17, 7 Hz, 1 H), 4.01 (sextet, *J* = 7 Hz, 1 H). The crudely distilled material was used for further transformations.

4-Bromo-3-methyl-1-(trimethylsilyl)-1-butyne (30). This compound was prepared in a similar manner as the preparation of **2b**.

(a) 1-(*tert*-Butyldimethylsiloxy)-2-methyl-3-butene. To *t*-$BuMe_2SiCl$ (4.15 g, 27.5 mmol), NEt_3 (4.2 mL, 3.04 g, 30.0 mmol), and 4-(dimethylamino)pyridine (0.18 g, 1.5 mmol) in CH_2Cl_2 (25 mL) at 25 °C was added 2-methyl-3-buten-1-ol (2.15 g, 25.0 mmol) in CH_2Cl_2 (10 mL). After 12 h, the reaction mixture was washed with water (1×), saturated aqueous NH_4Cl (1×) and NaCl (1×), dried ($MgSO_4$), and concentrated. Distillation provided the title compound (5.07 g, 99%): bp 79–81 °C (9.0 mmHg); IR (neat) 3100 (w) 1248 (s), 1090 (s), 910 (m), 833 (s), 771 (s) cm^{-1}; ^1H NMR ($CDCl_3$, C_6H_6) δ −0.10 ns, 6 H), 0.75 (s, 9 H), 0.86 (d, *J* = 7 Hz, 3 H), 1.9–2.6 (m, 1 H), 3.1–3.6 (m, 2 H), 4.85 (d, *J* = 10 Hz, 1 H), 4.88 (d, *J* = 17 Hz, 1 H), 5.65 (ddd, *J* = 17, 10, 7 Hz, 1 H).

(b) 1-(*tert*-Butyldimethylsiloxy)-2-methyl-4-(trimethylsilyl)-1-butyne. Bromine (1.23 mL, 3.84 g, 24.0 mmol) in CH_2Cl_2 (25 mL) was added over 5 min to 1-(*tert*-butyldimethylsiloxy)-2-methyl-3-butene (4.81 g, 24.0 mmol) in CH_2Cl_2 (25 mL) at 0 °C. The reaction mixture was stirred at 25 °C for 30 min, dried ($MgSO_4$), and concentrated. To the crude dibromide in THF (25 mL) at −78 °C was added over 30 min LDA in THF at 0 °C, prepared from 2.84 N *n*-BuLi in hexane (26.1 mL, 74 mmol) and diisopropylamine (10.4 mL, 7.5 g, 74 mmol) in THF (75 mL). After 1 h each at −78 and 0 °C, the reaction mixture was treated at −78 °C with Me_3SiCl (3.4 mL, 2.9 g, 27 mmol), warmed to 25 °C, stirred for 3 h, poured into 1 N HCl, extracted with ether (3×), washed with saturated aqueous $NaHCO_3$ (3×) and NaCl (1×), dried ($MgSO_4$), concentrated, and distilled to give the title compound (5.11 g, 79%): bp 80 °C (0.75 mmHg); IR (neat) 2170 (s), 1248 (s), 1175–1025 (s), 830 (s), 760 (s) cm^{-1}; ^1H NMR ($CDCl_3$, C_6H_6) δ −0.07 (s, 6 H), 0.00 (s, 9 H), 0.77 (s, 9 H), 1.03 (d, *J* = 7 Hz, 3 H), 2.3–2.7 (7, 1 H), 3.2–3.8 (m, 2 H).

(c) 2-Methyl-4-(trimethylsilyl)-3-butyn-1-ol. 1-(*tert*-Butyldimethylsiloxy)-2-methyl-4-(trimethylsilyl)-3-butyne (5.11 g, 18.9 mmol) was treated with 1% HCl in methanol (50 mL) at 25 °C for 1 h to give after the usual workup 2.80 g (95%) of the title alcohol: bp 85 °C (20 mmHg); IR (neat) 3600–3100 (s), 2170 (m), 1249 (s), 830 (s) cm^{-1}; ^1H NMR ($CDCl_3$, C_6H_6) δ 0.01 (s, 9 H), 1.03 (d, *J* = 7 Hz, 3 H), 2.2–2.8 (m, 1 H), 3.40 (d, *J* = 7 Hz, 2 H).

(d) 4-Bromo-3-methyl-1-(trimethylsilyl)-1-butyne (30). Conversion of the alcohol obtained above into **30** was achieved in the same manner as the preparation of **2b**: 57% isolated yield; bp 91–93 °C (14 mmHg); IR (neat) 2170 (m), 1248 (s), 835 (s), 754 (m), cm^{-1}; ^1H NMR ($CDCl_3$, C_6H_6) δ −0.01 (s, 9 H), 1.14 (d, *J* = 7 H, 3 H), 2.4–2.9 (m, 1 H), 2.9–3.5 (m, 2 H).

3-Methyl-1-(trimethylsilyl)cyclobutene (31). This compound was prepared in essentially the same manner as **9** by treating **29** (2.10 g, 9.6 mmol) in pentane (20 mL) with DIBAH (2.2 mL, 1.72 g, 12.1 mmol): 80% by GLC; IR (neat) 1559 (w), 1248 (s), 832 (s) cm^{-1}; ^1H NMR ($CDCl_3$, C_6H_6) δ −0.10 (s, 9 H), 1.00 (d, *J* = 7 Hz, 3 H), 1.86 (dd, *J* = 13, 2 Hz, 1 H), 2.54 (dd, *J* = 13, 4 Hz, 1 H), 2.6–3.0 (m, 1 H), 6.42 (s, 1 H); ^{13}C NMR ($CDCl_3$, C_6H_6) δ −2.27, 19.65, 39.14, 39.63, 152.53, 153.15. High-resolution MS for $C_8H_{17}Si$ ($M^+ + H$): calcd, 141.1100; found, 141.1090.

The identical compound was obtained in 75% yield from **30**.

2,4-Dimethyl-1-(trimethylsilyl)cyclobutene (32). This compound was prepared in an analogous manner as the conversion of **2b** into **4**. The GLC yield of **4** obtained from **29** was 75%, and 2-methyl-1-(trimethylsilyl)-1-propene was formed as a byproduct in 25% yield. The corresponding reaction of **30** led to the formation of **4** and the same byproduct in 39 and 10% yields, respectively. **32**: bp 75 °C (57 mmHg, Kugelrohr); IR (neat) 1617 (m), 1247 (s), 830 (s), 748 (m) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$, C_6H_6) δ −0.09 (s, 9 H), 0.96 (d, *J* = 7.0 Hz, 3 H), 1.55 (s, 3 H), 1.55–1.75 (m, 1 H), 2.25–2.45 (m, 1 H), 2.45–2.70 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ −1.30, 15.33, 17.92, 35.89, 40.55, 140.53, 162.40. High-resolution MS for $C_9H_{19}Si$ ($M^+ + H$): calcd, 155.1256; found, 155.1211.

4-Methyl-2-(2-propen-1-yl)-1-(trimethylsilyl)cyclobutene (33). This compound was prepared in essentially the same manner as **15** by treating **29** (1.00 g, 4.6 mmol) in THF (5 mL) at 60 °C for 24 h with allylzinc bromide in THF, prepared from allyl bromide (2.0 mL, 2.76 g, 22.8 mmol) and granular 20-mesh zinc metal (1.79 g, 27.4 mmol) in THF (20 mL). **23**: 68% yield; bp 85 °C (21 mmHg, Kugelrohr); IR (neat) 1645 (w), 1609 (m), 1249 (s), 830 (s) cm^{-1}; ^1H NMR ($CDCl_3$, C_6H_6) δ −0.05 (s, 9 H), 1.00 (d, *J* = 7 Hz, 3 H), 1.6–2.1 (m, 1 H), 2.4–2.8 (m, 4 H), 4.87 (d, *J* = 10 Hz, 1 H), 4.90 (d, *J* = 17 Hz, 1 H), 5.68 (ddd, *J* = 17, 10, 6 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ −1.26, 20.64, 35.91, 36.86, 39.73, 115.32, 135.52, 150.19, 156.78. Anal. Calcd for $C_{11}H_{20}Si$: C, 73.25; H, 11.18. Found: C, 73.60; H, 10.85.

4-Bromo-3,3-dimethyl-1-(trimethylsilyl)-1-butyne. To ethynyltrimethylsilane (5.89 g, 60.0 mmol) in hexane (100 mL) at 0 °C was added 2.1 N *n*-BuLi in hexane (28.6 mL, 60.0 mmol). After 30 min, $AlCl_3$ (2.67 g, 20.0 mmol) was added, and the reaction mixture was stirred for 30 min at 0 °C. Following concentration, the trialkynylalane was dissolved in $ClCH_2CH_2Cl$ (50 mL), and 1,2-dibromo-2-methylpropane (4.32 g, 20.0 mmol) was introduced at 0 °C.[32] After 15 min, $AlCl_3$ (2.67 g, 20.0 mmol) was added, and the reaction mixture was stirred at 0 °C for 1 h. The mixture was quenched with ice-cold 3 N HCl, extracted with ether (3×), washed with saturated aqueous $NaHCO_3$ (3×) and NaCl (1×), and dried ($MgSO_4$). Distillation afforded the title compound (2.52 g, 52%): bp 76–78 °C (20 mmHg); IR (neat) 2165 (s), 1248 (s), 1179 (s), 830 (s), 754 (s) cm^{-1}; ^1H NMR ($CDCl_3$, C_6H_6) δ −0.01 (s, 9 H), 1.17 (s, 6 H), 3.24 (s, 2 H). The crudely distilled material was used for further transformations.

Hydroalumination of 4-Bromo-3,3-dimethyl-1-(trimethylsilyl)-1-butyne with Diisobutylalane. Treatment of 4-bromo-3,3-dimethyl-1-(trimethylsilyl)-1-butyne with a 1.1 equiv of DIBAH in pentane at 25 °C led to a quantitative formation of (trimethyl)ethynylsilane within 0.5 h.

(32) Negishi, E.; Baba, S. *J. Am. Chem. Soc.* **1975**, *97*, 7385.

1-Acetyl-2,4-dimethyl-1-cyclobutene (34). To $AlCl_3$ (1.01 g, 7.6 mmol) suspended in CH_2Cl_2 (10 mL) at 0 °C were added sequentially acetyl chloride (0.54 mL, 0.60 g, 7.6 mmol) and 2,4-dimethyl-1-(trimethylsilyl)cyclobutene (1.06, 6.9 mmol) in CH_2Cl_2 (5 mL). After 30 min, the reaction mixture was poured into cold saturated aqueous $NaHCO_3$, extracted with ether (3×), washed with saturated aqueous NaCl (1×), dried ($MgSO_4$), and concentrated. Bulb-to-bulb distillation afforded 0.75 g (87%) of **34**: bp 90 °C (50 mmHg, Kugelrorh); IR (neat) 1700–1575 (s) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$, C_6H_6) δ 1.03 (d, J = 7.0 Hz, 3 H), 1.88 (s, 3 H), 1.80–2.00 (m, 1 H), 2.09 (s, 3 H), 2.40–2.70 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 14.55, 16.54, 28.19, 33.57, 36.57, 136.91, 161.71, 194.95. Anal. Calcd for $C_8H_{12}O$: C, 77.37; H, 9.74. Found: C, 77.62; H, 9.51.

1,3-Dimethylcyclobutene (36). To 2,4-dimethyl-1-(trimethylsilyl)-cyclobutane (0.31 g, 2.0 mmol) in benzene (1 mL) at 25 °C was added 50% aqueous HI (0.05 mL), and the mixture was vigorously stirred for 4 h. The organic phase was washed with saturated aqueous $NaHCO_3$ (1×) and dried ($MgSO_4$) to give a solution of **36** in benzene: ^1H NMR (C_6H_6) δ 1.12 (d, J = 7 Hz, 3 H), 1.58 (s, 3 H), 1.7–2.1 (m, 1 H), 2.4–2.9 (m, 2 H), 5.73 (s, 1 H); ^{13}C NMR (C_6H_6) δ 13.65, 17.45, 34.84, 39.29, 125.12, 150.51. Anal. Calcd for C_6H_{10}: C, 87.73; H, 12.27. Found: C, 87.51; H, 11.95.

Reaction of 4-Bromo-1-(trimethylsilyl)-1-butyne-*4,4-d*$_2$ with Trimethylalane and Zirconocene Dichloride To Afford 2-Methyl-1-(trimethylsilyl)-cyclobutene-*3,3-d*$_2$ and 2-Methyl-1-(trimethylsilyl)cyclobutene-*4,4-d*$_2$. To Cl_2ZrCp_2 (0.88 g, 3 mmol) and Me_3Al (0.60 mL, 6 mmol) in CH_2Cl_2 (10 mL) 6 mL) was added **38**. After 16 h, analysis of a quenched aliquot by GLC indicated the formation of the title compounds in a combined yield of 88%. The reaction mixture was treated with ice-cold 3 N HCl, extracted with pentane (3×), washed with saturated $NaHCO_3$ and NaCl, dried over $MgSO_4$, and concentrated. The crude material was distilled at 90–95 °C (90 mmHg, Kugelrohr) to afford approximately 1:1 mixtures of the title compounds: IR (neat) 2960 (s), 2910 (s), 2840 (m), 2210 (m), 2150 (w), 1615 (s), 1245 (s), 1200 (s), 1020 (s), 840 (s), 750 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.05 (s, 9 H), 1.75 (s, 3 H), 2.2–2.4 (m, 1 H), 2.57 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ −1.35, 18.06, 27.15, 33.78, 143.97, 144.31, 157.51, 157.81. The ^1H NMR signals at 2.2–2.4 and 2.57 ppm corresponding to 1.0 ± 0.1 H each indicate that the product is an essentially 1:1 mixture of the two regioisomers. This conclusion is further supported by two ^{13}C NMR signals at 27.15 and 33.78 ppm with comparable intensities as well as by a set of two signals for each alkenyl carbon atom.

4-Bromo-1-(trimethylsilyl)-1-butyne-*4,4-d*$_2$ (38). (a) 3-Buten-1-ol-*1,1-d*$_2$. Vinylacetic acid (8.18 g, 95 mmol) in ether (100 mL) was carefully treated with $LiAlD_4$ (5.00 g, 119 mmol) in ether (150 mL). After the reaction mixture was stirred for 4 h, water was added cautiously to decompose excess $LiAlD_4$. When 120 mL of 3 N HCl was added, a clear solution resulted. Extraction with ether (3×), washing with saturated $NaHCO_3$, drying over $MgSO_4$, evaporation, and distillation at 115–116 °C (760 mmHg) afforded 5.70 g (81%) of the title compound: IR (neat) 3400 (s), 2100 (s), 1640 (s), 970 (s), 910 (s) cm^{-1}; ^1H NMR ($CDCl_3$, Me_4Si) δ 1.95 (bs, 1 H), 2.30 (d, J = 7 Hz, 2 H), 5.0–5.3 (m, 2 H), 5.6–6.2 (m, 1 H).

(b) 1-(*tert*-Butyldimethylsiloxy)-3-butene-*1,1-d*$_2$. This compound was prepared in the same manner as that of 1-(*tert*-butyldimethylsiloxy)-1-methyl-3-butene. The crude product obtained in quantitative yield distilled at 85–86 °C (20 mmHg): IR (neat) 2180 (m), 2080 (m), 1630 (s), 1240 (s), 1130 (s) 1040 (s), 990 (m), 900 (s), 830 (s), 770 (s) cm^{-1}; ^1H NMR ($CDCl_3$, Me_4Si) δ 0.05 (s, 6 H), 0.90 (s, 9 H), 2.30 (d, J = 7 Hz, 2 H), 4.9–5.3 (m, 2 H), 5.6–6.1 (m, 1 H).

(c) 1-(*tert*-Butyldimethylsiloxy)-4-(trimethylsilyl)-3-butyne-*1,1-d*$_2$. This compound was prepared from 1-(*tert*-butyldimethylsiloxy)-3-butene-1,1-d_2 (13.18 g, 70 mmol) in a manner similar to the preparation of 1-(*tert*-butyldimethylsiloxy)-2-methyl-4-(trimethylsilyl)-1-butyne: yield 7.75 g (50%); bp 64–65 °C (0.5 mmHg); IR (neat) 2940 (s), 2850 (s), 2170 (s), 2080 (m), 1460 (s), 1400 (w), 1350 (m), 1300 (w), 1250 (s), 1130 (s), 1050 (s), 1000 (m), 930 (w), 840 (s), 770 (s) 690 (w) cm^{-1}; ^1H NMR ($CDCl_3$, Me_4Si) δ 0.05 (s, 6 H), 0.10 (s, 9 H), 0.90 (s, 9 H), 2.40 (s, 2 H).

(d) 4-(Trimethylsilyl)-3-butyn-1-ol-*1,1-d*$_2$. 1-(*tert*-Butyldimethylsiloxy)-4-(trimethylsilyl)-3-butyne-*1,1-d*$_2$ (5.40 g, 20.9 mmol) in 1% HCl in methanol (60 mL) was stirred at 25 °C for 1 h. After the standard workup, the crude material was distilled at 104–105 °C to afford 2.82 g (93%) of the title compound: IR (neat) 3340 (s), 2960 (s), 2900 (m), 2860 (w), 2180 (s), 2120 (m), 1415 (m), 1250 (s), 1125 (s), 1100 (s), 1030 (s), 975 (s), 900 (w), 850 (s), 760 (s), 700 (m) cm^{-1}; ^1H NMR ($CDCl_3$, Me_4Si) δ 0.10 (s, 9 H), 1.95 (s, 1 H), 2.40 (s, 2 H).

(e) 4-Bromo-1-(trimethylsilyl)-1-butyne-*4,4-d*$_2$ (38). The title compound was prepared in 80% yield in the same manner as **2b**. Its spectral data are as follows: IR (neat) 2960 (s), 2895 (w), 2180 (s), 1420 (w), 1310 (w), 1250 (s), 1050 (m), 980 (s), 940 (s), 845 (s), 760 (s), 700 (w) cm^{-1}; ^1H NMR ($CDCl_3$, Me_4Si) δ 0.15 (s, 9 H), 2.80 (s, 2 H).

5-Hexyn-1-ol-*1-d*. This compound was prepared in a manner analogous to 3-buten-1-ol-*1,1-d*$_2$ using 5-hexynal (3.84 g, 40 mmol), prepared by treatment of 5-hexyn-1-ol (4.90 g, 50 mmol) with pyridinium chlorochromate (16.17 g, 75 mmol) in CH_2Cl_2 (120 mL), and $LiAlD_4$ (1.47 g, 35 mmol). The product yield was 3.24 g (82%): IR (neat) 3300 (s), 2940 (s), 2860 (s), 2140 (m), 2120 (m), 1450 (s), 1430 (s), 1330 (w), 1095 (s), 1050 (s), 980 (w), 940 (s) cm^{-1}; ^1H NMR ($CDCl_3$, Me_4Si) δ 1.5–1.8 (m, 4 H), 1.9–2.1 (m, 3 H), 2.1–2.4 (m, 2 H), 3.65 (bs, 1 H).

6-Bromo-1-hexyne-*6-d*. This compound was prepared in a manner analogous to **2b**, using 5-hexyn-1-ol-*1-d* (2.97 g, 30 mmol) in $CHCl_3$ (40 mL), pyridine (8.5 mL, 8.30 g, 105 mmol), *p*-TsCl (13.35 g, 70 mmol), and LiBr (10.42 g, 120 mmol) in acetone (100 mL). The crude bromide was column chromatographed (pentane on a silica gel column) to afford 3.60 g (74%) of the title compound: IR (neat) 3290 (s), 2940 (s), 2860 (m), 2210 (w), 2120 (w), 1450 (m) 1430 (s), 1370 (w), 1330 (w), 1170 (m), 1080 (w), 1015 (w) cm^{-1}; ^1H NMR ($CDCl_3$, Me_4Si) δ 1.5–2.1 (m, 5 H), 2.1–2.4 (m, 2 H), 3.45 (t, J = 7 Hz, 1 H).

6-Bromo-1-(trimethylsilyl)-1-hexyne-*6-d* (39). This compound was prepared by the usual silylation of 6-bromo-1-hexyne-*6-d* in 92% yield: IR (neat) 2960 (s), 2170 (s), 1450 (w), 1430 (s), 1250 (s), 1050 (w), 1020 (w), 925 (w), 840 (s), 760 (s), 695 (w) cm^{-1}; ^1H NMR ($CDCl_3$, Me_4Si) δ 0.10 (s, 9 H), 1.5–2.1 (m, 4 H), 2.30 (t, J = 7 Hz, 2 H), 3.45 (t, J = 7 Hz, 1 H).

2-Methyl-1-(trimethylsilyl)-1-cyclohexene-*6-d* (40). This compound was prepared in a manner similar to the preparation of **26** from **25** using **39** (2.10 g, 9 mmol), Cl_2ZrCp_2 (2.60 g, 8.9 mmol), Me_3Al (1.70 mL, 17.5 mmol), and CH_2Cl_2 (35 mL). The reaction was complete after 72 h, and **40** was obtained in 65% yield: IR (neat) 2930 (s), 2860 (s), 2825 (m), 2150 (w), 1620 (s), 1445 (m), 1370 (w), 1245 (s), 990 (m), 840 (s), 750 (s), 685 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.05 (s, 9 H), 1.3–1.6 (m, 4 H), 1.70 (s, 3 H), 1.8–2.1 (m, 3 H); ^{13}C NMR ($CDCl_3$) δ 0.05, 23.01 (2 C), 23.93, 28.34, 28.70, 29.10, 33.23, 128.86, 143.24.

1-(Trimethylsilyl)cyclobutene (9). Reaction of (*E*)-4-Bromo-1-iodo-1-(trimethylsilyl)-1-butene with *tert*-Butyllithium in Ether. To **45** (0.33 g, 1.0 mmol) in ether (4 mL) at −78 °C was added 1.80 N *t*-BuLi in pentane (1.1 mL, 2.0 mmol). After 2 h, the reaction mixture was warmed slowly to 25 °C. Analysis by GLC indicated clean formation of **9** (78–89%). The use of 1 equiv of *n*-BuLi in place of *t*-BuLi led to a ca. 80% yield of **9**.

(*E*)-3-(Trimethylsilyl)-3-iodo-2-(2-propenyl)-2-propen-1-ol (48a). To 32.69 g (500 mmol) of dry zinc suspended in 80 mL of THF was added 48.39 g (400 mmol) of allyl bromide. After the mixture was stirred for 30 min, 40.08 g (200 mmol) of 3-(trimethylsilyl)-2-propyn-1-ol in 20 mL of THF was added. After it was heated for 16 h at 60 °C and cooled to −78 °C, the mixture was treated with 192.22 g (500 mmol) of I_2 in THF. After it was stirred for 30 min, the reaction mixture was poured into aqueous NH_4Cl, extracted with ether, washed with saturated aqueous $NaHCO_3$, NaCl, and $Na_2S_2O_3$. After concentration and flash column chromatography (4:1 hexane–ethyl acetate), 53.11 g (90%) of **48a** was obtained: IR (neat) 3400 (s, br), 1637 (m), 1248 (s), 1050 (s), 912 (s), 861 (s), 840 (s), 753 (s) cm^{-1}; ^1H NMR ($CDCl_3$, C_6H_6) δ 0.17 (s, 9 H), 1.97 (s, 1 H), 3.07 (dt, J = 5, 1 Hz, 2 H), 4.17 (s, 2 H), 4.8–5.2 (m, 2 H), 5.5–6.0 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 1.57, 37.44, 72.59, 109.36, 116.56, 135.20, 154.38.

(*Z*)-3-(Trimethylsilyl)-3-iodo-2-phenyl-2-propen-1-ol (48b). To a mixture of 7.69 g (60 mmol) of 3-(trimethylsilyl)-2-propyn-1-ol and 1.14 g (6 mmol) of CuI in 307 mL of ether was added 113 mL (150 mmol) of a 1.33 M solution of PhMgBr in ether at 0 °C. The reaction mixture was then warmed to 25 °C and allowed to stir over the weekend. Iodinolysis using 50.76 g (200 mmol) of I_2 and the workup procedure are the same as in the preparation of **48a**. The title compound was obtained in 56% yield (11.23 g): IR (neat) 3480 (m), 1610 (w), 1570 (w), 1500 (m), 1260 (s), 1070 (s), 1040 (s), 870 (s), 843 (s), 765 (s), 703 (s) cm^{-1}; ^1H NMR ($CDCl_3$, $ClCH_2CH_2Cl$) δ −0.13 (s, 9 H), 2.36 (s, 1 H), 4.45 (s, 2 H), 7.0–7.5 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 0.43, 73.78, 111.48, 127.52, 127.64, 128.43, 139.66, 157.77.

Preparation of 47 via Chlorination of 48. (a) (*E*)-1-(Trimethylsilyl)-1-iodo-2-(chloromethyl)-1,4-pentadiene (47a). To 4.44 g (15 mmol) of **48a** in 30 mL of THF was added 22.5 mL of 0.73 M (16.5 mmol) LDA in THF–hexane at 0 °C. After the mixture was stirred for 30 min, 1.80 g (15.8 mmol) of methanesulfonyl chloride was added at 0 °C. The mixture was warmed to 25 °C and evaporated under vacuum. To this was added 0.95 g (22.5 mmol) of LiCl dissolved in 15 mL of DMF. After it was stirred for 1 h at 25 °C, the reaction mixture was poured into water, extracted with a 1:1 mixture of pentane–ether, washed with saturated aqueous $NaHCO_3$, dried over $MgSO_4$, filtered, concentrated, redissolved in pentane, and filtered through a plug of silica gel with pentane as eluent. After concentration, 4.01 g (85% yield) of **47a** was

obtained: IR (neat) 1240 (s), 985 (m), 918 (m), 858 (s), 837 (s) cm^{-1}; ^1H NMR ($CDCl_3$, benzene) δ 0.06 (s, 9 H), 3.03 (d, J = 7 Hz, 2 H), 4.15 (s, 2 H), 4.7–5.1 (m, 2 H), 5.3–5.9 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 1.70, 37.30, 54.00, 114.89, 117.53, 134.45, 150.73.

(b) (*Z*)-1-(Trimethylsilyl)-1-iodo-2-phenyl-3-chloro-1-propene (47b): 85% yield; IR (neat) 1250 (s), 859 (s), 842 (s), 701 (s) cm^{-1}; ^1H NMR ($CDCl_3$, $ClCH_2CH_2Cl$) δ 0.21 (s, 9 H), 4.51 (s, 2 H), 7.1–7.5 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 0.59, 56.39, 117.59, 128.01, 128.09, 128.60, 139.38, 153.99.

(*Z*)-4-(Trimethylsilyl)-4-iodo-3-(2-propenyl)-3-buten-2-ol. A solution of 8.88 g (30 mmol) of **48a** in 30 mL of CH_2Cl_2 was added to a suspension of 9.70 g (45 mmol) of pyridinium chlorochromate in 30 mL of CH_2Cl_2. After the mixture was stirred for 45 min, 100 mL of ether was added, and the reaction mixture was filtered through a pad of Florisil (100–200 mesh). The remaining solids were triturated with ether and filtered. The filtrate was concentrated, dissolved in 150 mL of ether, and cooled to −78 °C. To this was added 11.6 mL (33 mmol) of 2.85 M MeMgBr in ether. The reaction mixture was warmed to 25 °C overnight, quenched with saturated aqueous NH_4Cl, extracted with pentane, washed with saturated aqueous $NaHCO_3$ and NaCl, dried over $MgSO_4$, concentrated, and subjected to flash column chromatography (9:1 hexane–ethyl acetate) to yield 6.83 g (73%) of the title compound: IR (neat) 3430 (s), 1260 (s), 864 (s), 847 (s) cm^{-1}; ^1H NMR ($CDCl_3$, C_6H_6) δ 0.05 (s, 9 H), 1.04 (d, J = 7 Hz, 3 H), 1.83 (s, 1 H), 2.9–3.1 (m, 2 H), 4.6–5.1 (m, 3 H), 5.5–6.0 (m, 1 H).

(*Z*)-1-(Trimethylsilyl)-1-iodo-2-(1-chloroethyl)-1,4-pentadiene (49). When a procedure similar to that for the preparation of **47** was used, 4.28 g (65%) of **49** was prepared from 6.21 g (20 mmol) of (*Z*)-4-(trimethylsilyl)-4-iodo-3-(2-propenyl)-3-buten-2-ol: bp 77–80 °C (0.1 mmHg); IR (neat) 1250 (s), 922 (s), 870 (s), 848 (s), 764 (s) cm^{-1}; ^1H NMR ($CDCl_3$, C_6H_6) δ 0.26 (s, 9 H), 1.44 (d, J = 7 Hz, 3 H), 3.23 (m, 2 H), 4.8–5.1 (m, 2 H), 5.32 (q, J = 7 Hz, 1 H), 5.5–6.0 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 1.64, 23.38, 34.28, 69.03, 113.48, 116.32, 136.76, 152.78.

(*Z*)-3-(Trimethylsilyl)-3-iodo-2-*n*-propyl-2-propen-1-ol. To 8.88 g (30 mmol) of **48a** in 30 mL of $(CH_2Cl)_2$ was added 2.9 mL (2.2 g, 30 mmol) of Me_3Al at −20 °C. After it was warmed to 25 °C, the mixture was stirred for 30 min and added to 15.2 mL (11.9 g, 60 mmol) of $(i\text{-}Bu)_3Al$ and 8.77 g (30 mmol) of Cl_2ZrCp_2 in 30 mL of $(CH_2Cl)_2$ at 0 °C.[15] After it was stirred at 0 °C for 4 h, the reaction mixture was poured onto ice and 3 N HCl, extracted with ether, washed with saturated aqueous $NaHCO_3$ and NaCl, dried over $MgSO_4$, filtered, concentrated, and subjected to flash column chromatography (9:1 hexane–ethyl acetate) to yield 6.46 g (72%) of **49**: IR (neat) 3400 (s), 1260 (s), 875 (s), 848 (s) cm^{-1}; ^1H NMR ($CDCl_3$, C_6H_6) δ 0.04 (s, 9 H), 0.68 (t, J = 7 Hz, 3 H), 1.17 (tq, $J_1 = J_2$ = 7 Hz, 2 H), 2.0–2.2 (m, 3 H), 4.12 (s, 2 H); ^{13}C NMR ($CDCl_3$) δ 1.70, 13.73, 22.50, 36.17, 113.46, 157.69.

(*Z*)-1-(Trimethylsilyl)-1-iodo-2-(1-chloroethyl)-1-pentene (50). When a procedure similar to that for **47** was used, 5.8 g (82%) of **50** was prepared from 5.96 g (20 mmol) of (*Z*)-3-(trimethylsilyl)-3-iodo-2-*n*-propyl-2-propen-1-ol and was purified by distillation at 80–82 °C (0.05 mmHg): IR (neat) 1260 (s), 952 (s), 877 (s), 848 (s), 769 (s), 719 (s), 719 (s) cm^{-1}; ^1H NMR ($CDCl_3$, C_6H_6) δ 0.07 (s, 9 H), 0.71 (t, J = 7 Hz, 3 H), 0.9–1.6 (m, 2 H), 2.25 (m, 2 H), 4.18 (s, 2 H); ^{13}C NMR ($CDCl_3$) δ 1.79, 13.70, 22.40, 35.99, 54.35, 113.58, 153.50.

Preparation of 1-(Trimethylsilyl)cyclopropenes. (a) 1-(Trimethylsilyl)-2-(2-propenyl)cyclopropene. Representative Procedure. To 0.623 g (2.00 mmol) of **47a** in ether was added 2.35 mL (4.0 mmol) of a 1.7 M solution of *t*-BuLi in pentane at −78 °C. After it was stirred for 20 min, the mixture was warmed to 25 °C, poured into saturated aqueous NH_4Cl, washed with saturated aqueous $NaHCO_3$, dried over $MgSO_4$, and filtered. To this were added 8.8 mg (0.04 mmol) of BHT and 2 mL of $CDCl_3$. The solution was carefully concentrated under N_2 at 0 °C (0.5 mmHg) to about 2 mL. An additional 2 mL of $CDCl_3$ was added, and the concentration process was repeated until no ether remained (GC and ^1H NMR). The product yield was 95% as determined by ^1H NMR: IR ($CDCl_3$) 2250 (m), 1795 (s), 1640 (s), 1620 (m), 1420 (s), 1407 (s), 1245 (s) 992 (s), 850 (s), 631 (s) cm^{-1}; ^1H NMR ($CDCl_3$, C_6H_6) δ 0.08 (s, 9 H), 0.71 (s, 2 H), 1.32 (d, J = 7 Hz, 2 H), 4.8–5.2 (m, 2 H), 5.5–6.2 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ −1.33, 6.48, 32.98, 106.69, 116.05, 133.32, 134.21. High-resolution MS for $C_9H_{16}Si$: calcd 152.1021; found, 152.1043.

(b) 1-(Trimethylsilyl)-2-(2-propenyl)-3-methylcyclopropene. The title compound was prepared in 78% yield from 0.066 g (2.0 mmol) of **49**. This product was sufficiently stable so that it was purified by bulb-to-bulb distillation at 50–55 °C (15 mmHg): IR (neat) 1650 (w), 1260 (s), 922 (s), 850 (s), 842 (s) cm^{-1}; ^1H NMR ($CDCl_3$, C_6H_6) δ −0.06 (s, 9 H), 0.82 (d, J = 5 Hz, 3 H), 1.22 (q, J = 5 Hz, 1 H), 3.07 (d, J = 7 Hz, 2 H), 4.8–5.2 (m, 2 H), 5.5–6.1 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ −0.80, 14.18, 22.14, 32.16, 115.56, 115.89, 134.62, 141.30. High-resolution MS for $C_{10}H_{18}Si$: calcd, 166.1180; found, 166.1178.

(c) 1-(Trimethylsilyl)-2-*n*-propylcyclopropene. The title compound was prepared from 0.95 g (3.0 mmol) of **50** as above and purified as follows. To the mixture containing the product were added 0.013 g (0.06 mmol) of BHT and 1.5 mL of hexadecane. The volatiles were removed at 0 °C (5.5 mmHg), and the title compound was distilled by heating the pot flask to 55 °C (0.4 mmHg) and trapping the distillate in a receiving flask kept at −78 °C. When the distillation was complete, the receiver was stoppered, and 1.51 g of $CDCl_3$ was added to 0.27 g (58%) of the title compound for spectral measurements: IR ($CDCl_3$) 2245 (m), 1796 (s), 1245 (s), 990 (s), 840 (s) cm^{-1}; ^1H NMR ($CDCl_3$, C_6H_6) δ 0.04 (s, 9 H), 0.61 (s, 2 H), 0.82 (t, J = 7 Hz, 3 H), 1.50 (tq, $J_1 = J_2$ = 7 Hz, 2 H), 2.42 (t, J = 7 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ −1.39, 6.16, 13.85, 20.63, 30.63, 105.30, 135.25. High-resolution MS for $C_9H_{18}Si$: calcd, 154.1178; found, 154.1182.

(d) 1-(Trimethylsilyl)-2-phenylcyclopropene. The title compound was prepared with 0.70 g (2.0 mmol) of **47b**. The yield of the title compound was 90% by both GLC and ^1H NMR. The use of *n*-BuLi (1 equiv) instead of *t*-BuLi (2 equiv) led to a yield of 78%: IR ($CDCl_3$) 2300 (w), 1810 (s), 1620 (m), 1260 (s), 1010 (s), 850 (s, br) cm^{-1}; ^1H NMR ($CDCl_3$, $ClCH_2CH_2Cl$) δ 0.22 (s, 9 H), 1.05 (s, 2 H), 7.2–7.8 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ −1.31, 5.69, 110.97, 128.51, 129.35, 130.97, 131.48. High-resolution MS for $C_{12}H_{16}Si$: calcd 188.1021; found, 188.1029.

(*E*)-1-(Trimethylsilyl)-1-iodo-ω-halo-1-alkenes. These compounds were prepared from the corresponding alkynes in a manner similar to the preparation of **45**.

(a) (*E*)-1-(Trimethylsilyl)-1-iodo-3-methyl-4-bromo-1-butene (51): 63% yield; bp 60 °C (0.10 mmHg, Kugelrohr); IR (neat) 1248 (s), 830 (s), cm^{-1}; ^1H NMR ($CDCl_3$, C_6H_6) δ 0.13 (s, 9 H), 0.96 (d, J = 7 Hz, 3 H), 2.3–2.9 (m, 1 H), 3.09 (d, J = 7 Hz, 2 H), 6.83 (d, J = 11 Hz, 1 H).

(b) (*E*)-1-(Trimethylsilyl)-1-iodo-2-methyl-5-bromo-1-hexene (52): 70% yield; bp 80–81 °C (0.1 mmHg); ^1H NMR ($CDCl_3$, Me_4Si) δ 0.30 (s, 9 H), 1.75 (d, J = 7 Hz, 3 H), 1.9–2.5 (m, 4 H), 4.20 (sextet, J = 7 Hz, 1 H), 7.30 (t, J = 7 Hz, 1 H).

(c) (*E*)-1-(Trimethylsilyl)-1-iodo-5-chloro-1-pentene (53): 74% yield; IR (neat) 1575 (m), 1235 (s), 820 (s) cm^{-1}; ^1H NMR ($CDCl_3$, C_6H_6) δ 0.16 (s, 9 H), 1.5–1.9 (m, 2 H), 1.9–2.3 (m, 2 H), 3.42 (t, J = 6 Hz, 2 H), 7.02 (t, J = 8 Hz, 1 H).

(d) (*E*)-1-(Trimethylsilyl)-1-iodo-6-bromo-1-hexene (54): 81% yield; IR (neat) 1580 (m), 1245 (s), 835 (s) cm^{-1}; ^1H NMR (CCl_4, C_6H_6) δ 0.22 (s, 9 H), 1.3–2.2 (m, 6 H), 3.29 (t, J = 6 Hz, 2 H), 6.99 (t, J = 7 Hz, 1 H).

(e) (*E*)-1-(Trimethylsilyl)-1-iodo-5-methyl-6-bromo-1-hexene (58): 55% yield; bp 97–98 °C (0.1 mmHg); ^1H NMR ($CDCl_3$, Me_4Si) δ 0.25 (s, 9 H), 1.03 (d, J = 7 Hz, 3 H), 1.2–1.9 (m, 3 H), 2.0–2.3 (m, 2 H), 3.38 (d, J = 6 Hz, 2 H), 7.20 (t, J = 8 Hz, 1 H).

(f) (*E*)-1-(Trimethylsilyl)-1-iodo-6-methyl-7-bromo-1-heptene (59): 67% yield; bp 100–103 °C (0.1 mmHg); IR (neat) 1250 (s), 840 (s), 760 (s) cm^{-1}; ^1H NMR ($CDCl_3$, Me_4Si) δ 0.25 (s, 9 H), 1.02 (d, J = 7 Hz, 3 H), 1.1–1.9 (m, 5 H), 3.38 (d, J = 6 Hz, 2 H), 7.20 (t, J = 7 Hz, 1 H).

1-(Trimethylsilyl)-1-iodo-2-*n*-hexyl-5-bromo-1-pentene. 1-(Trimethylsilyl)-1-iodo-2-*n*-hexyl-1,4-pentadiene was prepared in 63% yield from 1-(trimethylsilyl)-1-octyne and allyl bromide as previously reported:[8] bp 82–90 °C (0.05 mmHg); IR (neat) 1250 (s), 830 (s) cm^{-1}; ^1H NMR ($CDCl_3$, C_6H_6) δ 0.15 (s, 9 H), 0.6–0.9 (m, 3 H), 0.9–1.5 (m, 8 H), 2.0–2.3 (m, 2 H), 2.9–3.2 (m, 2 H), 4.8–5.2 (m, 2 H), 5.4–5.9 (m, 1 H). The above-prepared compound (3.50 g, 10 mmol) in 7 mL of $ClCH_2CH_2Cl$ was added to a mixture of Cl_2ZrCp_2 (2.92 g, 10 mmol) and $(i\text{-}Bu)_3Al$ (2.18 g, 11 mmol) in 15 mL of $ClCH_2CH_2Cl$ at 25 °C.[15] After 1 h, the mixture was added to NBS (6.47 g, 36 mmol) and 30 mL of ether kept at −35 °C. The reaction mixture was warmed to 25 °C, treated with water and pentane, washed with saturated aqueous $NaHCO_3$, Na_2SO_3, and brine, dried over $MgSO_4$, and concentrated to give 3.97 g (92%) of the title compounds: IR (neat) 1570 (m), 1245 (s), 835 (s) cm^{-1}; ^1H NMR ($CDCl_3$, C_6H_6) δ 0.15 (s, 9 H), 0.6–1.4 (m, 13 H), 1.7–2.6 (m, 4 H), 3.30 (t, J = 6 Hz, 2 H).

2-Methyl-6-(trimethylsilyl)-1-hexen-5-yne (56). This compound was prepared in 80% yield by the reaction of methallylmagnesium bromide (1.3 equiv) with 2,3-dichloropropene (1 equiv) followed by treatment with LDA (2 equiv) and Me_3SiCl (2 equiv), following the literature procedure:[33] bp 60–62 °C (7 mmHg); ^1H NMR ($CDCl_3$, Me_4Si) δ 0.15 (s, 9 H), 1.75 (s, 3 H), 2.2–2.5 (m, 4 H), 4.82 (m, 2 H).

2-Methyl-7-(trimethylsilyl)-1-hepten-6-yne (57). To $Me_3SiC{\equiv}CLi$, generated in situ by treating $Me_3SiC{\equiv}CSiMe_3$ (10.37 g, 61 mmol) with MeLi (1.3 M, 47 mL, 61 mmol) in 61 mL of THF at 0–25 °C, were

(33) Peterson, P. E.; Nelson, D. J.; Risener, R. *J. Org. Chem.* **1986**, *51*, 2381.

added at 25 °C diglyme (61 mL) and then 2-methyl-5-bromo-1-pentene (9.90 g, 61 mmol). After it was heated at 80 °C for 1 h, the mixture was quenched with 6 N HCl, extracted with pentane, washed with water and saturated $NaHCO_3$, dried over $MgSO_4$, and distilled to give 6.07 g (55%) of **57**: bp 78–82 °C (12 mmHg): IR (neat) 2180 (s), 1650 (w), 1250 (s), 835 (s), 755 (s) cm^{-1}; ^1H NMR ($CDCl_3$, Me_4Si) δ 0.12 (s, 9 H), 1.5–1.75 (m, 2 H), 1.70 (s, 3 H), 1.9–2.3 (m, 4 H), 4.73 (bs, 2 H).

2-Methyl-6-(trimethylsilyl)-5-hexyn-1-ol. This compound was prepared by hydroboration with 9-BBN (0.5 M in THF, 87 mL, 43 mmol) of **56** (6.64 g, 40 mmol) in 50 mL of THF at 60 °C for 2 h followed by oxidation with 15 mL each of 3 N NaOH and 30% H_2O_2:[26] 5.97 g (81%); IR (neat) 3350 (s), 2170 (s), 1250 (s), 1040 (s), 840 (s), 760 (s), cm^{-1}; ^1H NMR ($CDCl_3$, Me_4Si) δ 0.10 (s, 9 H), 0.92 (d, J = 7 Hz, 3 H), 1.2–1.9 (m, 3 H), 2.30 (t, J = 7 Hz, 2 H), 3.50 (d, J = 6 Hz, 2 H).

2-Methyl-7-(trimethylsilyl)-6-heptyn-1-ol. This compound was prepared in a manner analogous to the preparation of 2-methyl-6-(trimethylsilyl)-5-hexyn-1-ol using 2-methyl-7-(trimethylsilyl)-1-hepten-6-yne (2.40 g, 13.3 mmol). The title compound was obtained in 99% yield: IR (neat) 1250 (s), 1040 (s), 840 (s), 760 (s) cm^{-1}; ^1H NMR ($CDCl_3$, Me_4Si) δ 0.15 (s, 9 H), 0.95 (d, J = 7 Hz, 3 H), 1.2–2.1 (m, 6 H), 2.25 (t, J = 7 Hz, 2 H), 3.52 (d, J = 6 Hz, 2 H).

6-Bromo-5-methyl-1-(trimethylsilyl)-1-hexyne. To 2-methyl-6-(trimethylsilyl)-5-pentyn-1-ol (1.29 g, 7 mmol) and CBr_4 (4.64 g, 14 mmol) in ether (35 mL) was added PPh_3 (3.65 g, 14 mmol) at 25 °C. The standard extractive and distillative workup afforded 1.57 g (90%) of the title compounds: bp 54–56 °C (0.1 mmHg); IR (neat) 2170 (s), 1245 (s), 840 (s), 760 (s) cm^{-1}; ^1H NMR ($CDCl_3$, Me_4Si) δ 0.15 (s, 9 H), 1.03 (d, J = 7 Hz, 3 H), 1.2–2.0 (m, 3 H), 2.27 (t, J = 7 Hz, 2 H), 3.40 (d, J = 6 Hz, 2 H).

7-Bromo-6-methyl-1-(trimethylsilyl)-1-heptyne. This compound was prepared in a manner analogous to the preparation of 6-bromo-5-methyl-1-(trimethylsilyl)-1-hexyne using 2-methyl-7-(trimethylsilyl)-6-hepten-1-ol (2.50 g, 12.6 mmol): 91% yield; bp 63–65 °C (0.1 mmHg); IR (neat) 2175 (s), 1250 (s), 840 (s), 760 (s) cm^{-1}; ^1H NMR ($CDCl_3$, Me_4Si) δ 0.15 (s, 9 H), 1.02 (d, J = 7 Hz, 3 H), 1.3–2.0 (m, 5 H), 2.1–2.4 (m, 2 H), 3.40 (d, J = 6 Hz, 2 H). The crudely distilled material was used for further transformations.

Cyclialkylation of [ω-Halo-1-(trimethylsilyl)-1-alkenyl]lithiums. (a) 5-Methyl-1-(trimethylsilyl)-1-cyclopentene (62): Representative Procedure. To (*E*)-5-bromo-1-iodo-1-(trimethylsilyl)-1-hexene (**52**) (1.49 g, 4.1 mmol) in ether (16 mL) at −78 °C was added to *t*-BuLi (1.65 M in pentane, 5.0 mL, 8 mmol), and the mixture was warmed to 25 °C over 1 h. After stirring for 1 h, water was added. The organic phase was washed with saturated NaCl, dried over $MgSO_4$, and concentrated. Distillation afforded 0.50 g (79%) of **62**:[34] bp 100 °C (70 mmHg, Kugelrohr); IR (neat) 1580 (m), 1250 (s), 840 (s), 750 (s) cm^{-1}; ^1H NMR ($CDCl_3$, Me_4Si) δ 0.10 (s, 9 H), 1.05 (d, J = 7 Hz, 3 H), 1.8–2.9 (m, 5 H) 5.95 (t, J = 1 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 0.71 (q), 21.43 (q), 33.75 (t, 2 C), 44.00 (d), 140.69 (d), 149.72 (s).

(b) 1-(Trimethylsilyl)-1-cyclopentene. This compound was prepared by the reaction of (*E*)-1-(trimethylsilyl)-1-iodo-5-chloro-1-pentene (0.36 g, 1 mmol) with *n*-BuLi (2.3 M, 0.44 mL, 1 mmol). The yield and the physical properties of the title compound[34] are as follows: 67% GLC ield; bp 75–80 °C (100 mmHg); IR (neat) 3012 (m), 1582 (m), 1240 (s), 825 (s) cm^{-1}; ^1H NMR ($CDCl_3$, C_6H_6) δ −0.07 (s, 9 H), 1.4–1.9 (m, 2 H), 2.23 (t, J = 7 Hz, 4 H), 5.7–5.9 (m, 1 H).

(c) 1-(Trimethylsilyl)-2-*n*-hexyl-1-cyclopentene. This compound was prepared by the reaction of 1-(trimethylsilyl)-1-iodo-2-*n*-hexyl-5-bromo-1-pentene (2.16 g, 5 mmol) with *t*-BuLi (1.80 M, 5.6 mL, 10 mmol): 84% yield; bp 76 °C (1 mmHg); IR (neat) 1605 (m), 1240 (s) 820 (s) cm^{-1}; ^1H NMR ($CDCl_3$, C_6H_6) δ 0.02 (s, 9 H), 0.6–1.5 (m, 11 H), 1.5–1.9 (m, 2 H), 1.9–2.5 (m, 6 H); ^{13}C NMR ($CDCl_3$) δ −0.19, 14.12, 22.81, 24.00, 29.11, 29.66, 32.08, 38.20, 133.59, 154.79. Anal. Calcd for $C_{14}H_{28}Si$: C, 74.91; H, 12.57. Found: C, 74.76; H, 12.52.

(d) 1-(Trimethylsilyl)-1-cyclohexene. This compound**34** was prepared from **54** (3.91 g, 10 mmol) and *t*-BuLi (1.8 M, 11.1 mL, 20 mmol): 64% yield by GLC; bp 51 °C (10 mmHg); IR (neat) 1620 (m), 1248 (s), 830 (m) cm^{-1}; ^1H NMR (CCl_4, C_6H_6) δ −0.03 (s, 9 H), 1.4–1.7 (m, 4 H), 1.8–2.1 (m, 4 H), 5.8–6.0 (m, 1 H).

(e) 1-(Trimethylsilyl)-2-methyl-1-cyclohexene. This compound[35] was prepared by the reaction of **55** (1.56 g, 4.15 mmol) with 1.58 M *t*-BuLi (5.25 mL, 8.3 mmol): 70% GLC yield; bp 65 °C (8 mmHg); IR (neat) 1621 (s), 1235 (s), 835 (s) cm^{-1}; ^1H NMR (CCl_4, C_6H_6) δ 0.06 (s, 9 H), 1.3–1.7 (m, 4 H), 1.68 (bs, 3 H), 1.8–2.1 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 0.08, 23.06, 2396, 29.11, 33.24, 128.98, 143.27.

(f) 1-(Trimethylsilyl)-5-methyl-1-cyclohexene (60). This compound was prepared by (*E*)-1-(trimethylsilyl)-6-bromo-1-iodo-5-methyl-1-hexene (0.73 g, 1.95 mmol) and *t*-BuLi (1.7 M in pentane, 2.35 mL, 4.0 mmol): 82% yield; bp 95 °C (20 mmHg, Kugelrohr); IR (neat) 1620 (m), 1245 (s), 835 (s), 740 (s) cm^{-1}; ^1H NMR ($CDCl_3$, Me_4Si) δ 0.03 (s, 9 H), 0.97 (d, J = 6 Hz, 3 H), 1.2–1.9 (m, 3 H), 2.0–2.4 (m, 4 H), 5.9–6.1 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ −2.21, 22.09, 27.14, 28.75, 30.78, 35.31, 135.15, 138.17. Anal. Calcd for $C_{10}H_{20}Si$: C, 71.34; H, 11.98. Found: C, 71.58; H, 11.73.

(g) 1-(Trimethylsilyl)-6-methyl-1-cycloheptene (63). This compound was prepared from (*E*)-1-(trimethylsilyl)-7-bromo-1-iodo-6-methyl-1-heptene (0.52 g, 1.34 mmol) and *t*-BuLi (1.6 M in pentane, 1.75 mL, 2.80 mmol): 77% yield by GLC; IR (neat) 1615 (m), 1250 (s), 835 (s) cm^{-1}; ^1H NMR ($CDCl_3$, Me_4Si) δ 0.05 (s, 9 H), 0.8–1.0 (m, 3 H), 1.1–2.0 (m, 5 H), 2.0–2.3 (m, 4 H), 6.20 (t, J = 7 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 23.89, 25.90, 30.15, 32.62, 38.33, 41.47, 141.42, 143.85. Anal. Calcd for $C_{11}H_{22}Si$: C, 72.44; H, 12.16. Found: C, 72.59; H, 11.87.

1-Iodo-4-methyl-1-cyclohexene. 4-Methylcyclohexanone (34 g, 37 mL, 300 mmol) was converted into 1-chloro-4-methylcyclohexene in 50% yield by treatment with PCl_5 (125 g, 500 mmol) in CH_2Cl_2 (150 mL). The chloro compound (18 g, 138 mmol) was treated sequentially with Li wire (2.9 g, 414 mmol) in 100 mL of ether[36] and I_2 (46 g, 180 mmol) in THF (50 mL). The standard workup followed by distillation afforded 36 g (65% of the title compound:[37] bp 90–95 °C (36 mmHg); ^1H NMR ($CDCl_3$, Me_4Si) δ −0.12 (s, 9 H), 1.4–1.6 (m, 4 H), 1.8–2.0 (m, 4 H), 5.90 (m, 1 H).

1-(Trimethylsilyl)-4-methyl-1-cyclohexene (61). To 1-iodo-4-methyl-1-cyclohexene (0.68 g, 3.06 mmol) in ether (8 mL) at −78 °C was added *t*-BuLi (1.7 M in pentane, 3.60 mL, 6.12 mmol). After 30 min, the mixture was treated with Me_3SiCl (0.50 mL, 0.42 g, 3.9 mmol), warmed to 25 °C over 1 h, treated with water, extracted with ether, washed with saturated NaCl, dried over $MgSO_4$, and concentrated. Distillation afforded 0.43 g (84%) of **61**:[38] bp 95 °C (20 mmHg, Kugelrohr); IR (neat) 1620 (m), 1245 (s), 1060 (s), 835 (s), 745 (s), cm^{-1}; ^1H NMR ($CDCl_3$, Me_4Si) δ 0.03 (s, 9 H), 0.97 (d, J = 6 Hz, 3 H), 1.2–1.9 (m, 3 H), 2.0–2.4 (m, 4 H), 5.9–6.1 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ −2.13, 22.12, 26.90, 28.37, 31.35, 35.52, 135.19, 138.17.

ω-Bromo-1-iodo-1-alkynes. (a) 5-Bromo-1-iodo-1-pentyne. This compound was prepared by successively treating 5-bromo-1-pentyne (14.7 g, 100 mmol) with *n*-BuLi (2.60 M in hexane, 41.0 mL, 107 mmol, −78 °C, 1 h, THF) and iodine (35.7 g, 140 mmol, −78 to 25 °C, THF). Quenching with water, extraction with pentane, washing with $Na_2S_2O_3$, $NaHCO_3$, and NaCl, drying ($MgSO_4$), evaporation, and distillation gave the title compound in 68% yield: bp 62–63 °C (0.3 mmHg); IR (neat) 2140 (w), 1245 (s) cm^{-1}; ^1H NMR ($CDCl_3$, Me_4Si) δ 2.05 (q, J = 7 Hz, 2 H), 2.55 (t, J = 7 Hz, 2 H), 3.50 (t, J = 7 Hz, 2 H).

(b) 6-Bromo-1-iodo-1-hexyne. From 6-bromo-1-hexyne (5.20 g, 32 mmol): 7.78 g (85%); bp 68–70 °C (0.1 mmHg); IR (neat) 1250 (s) cm^{-1}; ^1H NMR ($CDCl_3$, Me_4Si) δ 1.5–2.2 (m, 4 H), 2.40 (t, J = Hz, 2 H), 3.40 (t, J = 7 Hz, 2 H).

(Z)-ω-Bromo-1-iodo-1-alkenes. (a) (Z)-5-Bromo-1-iodo-1-pentene. This compound was prepared by sequential treatment of 5-bromo-1-iodo-1-pentyne (16.4 g, 60 mmol) with 67.5 mmol of disiamylborane in THF, glacial acetic acid (5.50 mL, 96 mmol, 50 °C, 3 h), 3 N, NaOH (24 mL), and 30% H_2O_2 (24 mL):[17] 11.3 g (68%); IR (neat) 1610 (m), 1290 (s), 1260 (s) cm^{-1}; ^1H NMR ($CDCl_3$, Me_4Si) δ 1.8–2.4 (m, 4 H), 3.40 (t, J = 7 Hz, 2 H), 6.1–6.4 (m, 2 H).

(b) (Z)-6-Bromo-1-iodo-1-hexene. From 6-bromo-1-iodo-1-hexyne (7.20 g, 25 mmol): 5.01 g (70%); bp 60–62 °C (0.1 mmHg); ^1H NMR ($CDCl_3$, Me_4Si δ 1.5–2.0 (m, 4 H), 2.20 (q, J = 6 Hz, 2 H), 3.40 (t, J = 7 Hz, 2 H), 6.1–6.4 (m, 2 H).

(E)-ω-Bromo-1-iodo-1-alkenes. (a) (E)-5-Bromo-1-iodo-1-pentene. This compound was prepared by sequential treatment of 5-bromo-1-pentyne (4.41 g, 30.0 mmol) with DIBAH (5.62 M, 5.90 mL, 33.0 mmol, 50 °C, 4 h, hexanes) and iodine (9.14 g, 36.0 mmol, THF): 6.02 g (73%); bp 50–52 °C (0.1 mmHg); ^1H NMR ($CDCl_3$, Me_4Si) δ 1.8–2.4 (m, 4 H), 3.40 (t, J = 7 Hz, 2 H), 6.12 (d, J = 15 Hz, 1 H), 6.55 (dt, J = 15, 7 Hz, 1 H).

(b) (E)-6-Bromo-1-iodo-1-hexene. From 6-bromo-1-hexyne (3.30 g, 20 mmol): 2.90 g (50%); bp 81–82 °C (1 mmHg); IR (neat) 1607 (s), 941 (s) cm^{-1}; ^1H NMR ($CDCl_3$, Me_4Si) δ 1.4–2.3 (m, 6 H), 3.42 (t, J = 7 Hz, 2 H), 6.04 (d, J = 14 Hz, 1 H), 6.3–6.7 (m, 1 H).

Reaction of (Z or E)-ω-Bromo-1-iodo-1-alkenes with *n*-Butyllithium. (a) (Z)-5-Bromo-1-iodo-1-pentene. To (*Z*)-5-bromo-1-iodo-1-pentene

(34) (a) Paquette, L. A.; Fristad, W. E.; Dime, D. S.; Bailey, T. R. *J. Org. Chem.* **1980**, *45*, 2017. (b) Fristad, W. E.; Bailey, T. R.; Paquette, L. A. *J. Org. Chem.* **1980**, *45*, 3028.

(35) Eaborn, C.; Jackson, R. A.; Pearce, R. *J. Chem. Soc., Perkin Trans.* **1975**, 470.

(36) Braude, E. A.; Coles, J. A. *J. Chem. Soc.* **1950**, 2014.

(37) Bottini, A. T.; Cabral, L. J.; Dev, V. *Tetrahedron Lett.* **1977**, 615.

(38) Sato, T.; Tonegawa, T.; Naoi, K.; Murayama, E. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 285.

(0.55 g, 2.0 mmol) in ether (6.0 mL) at −78 °C was added *n*-BuLi (2.48 M, 0.80 mL, 2.0 mmol), and the mixture was warmed to 25 °C over 1 h and treated with water. The organic extract was analyzed by ^{1}H NMR using benzene (0.075 g, 0.96 mmol) as an internal standard, which showed a clean formation of cyclopentene (s, 5.72 ppm) in 85% yield.

(b) (*Z*)-6-Bromo-1-iodo-1-hexene. Treatment of the title compound (0.58 g, 2.0 mmol) as above produced cyclohexene (s, 5.70 ppm) in 73% yield.

(c) (*E*)-5-Bromo-1-iodo-1-pentene. Treatment of the title compound (0.57 g, 2.07 mmol) as above did not produce cyclopentene or any product detectable by GLC, even though all the starting compound was consumed.

(d) (*E*)-6-Bromo-1-iodo-1-hexene. Treatment of the title compound (0.58 g, 2.0 mmol) as above did not produce cyclohexene or any product detectable by GLC, even though all the starting compound was consumed.

(*Z*)-1-Iodoallyl Chlorides. These compounds were prepared by chlorinating the corresponding 3-iodoallyl alcohols as in the conversion of **48** into **47**. The 3-iodoallyl alcohol intermediates were, in turn, prepared from the corresponding propargyl alcohols as in the preparation of **48**.

(a) (*Z*)-1-Phenyl-1-iodo-2-(chloromethyl)-1-hexene: 92% yield for chlorination; IR (neat) 1480 (m), 757 (s), 697 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.78 (t, *J* = 7 Hz, 3 H), 0.9–1.6 (m, 4 H), 2.28 (t, *J* = 8 Hz, 2 H), 4.51 (s, 2 H), 7.2–7.6 (m, 5 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 13.61, 22.17, 30.36, 30.75, 52.43, 101.57, 127.85, 128.11, 143.10, 143.83.

(b) (*Z*)-1-Chloro-2-methyl-3-iodo-2-nonene. This compound was prepared in 33% yield by the reaction of 2-nonyn-1-ol (7.01 g, 50 mmol) with 150 mmol of 2.7 M MeMgBr in ether, followed by iodination and chlorination: bp 79–82 °C (0.08 mmHg); IR (neat) 1640 (m), 1470 (s), 1450 (s), 710 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.90 (t, *J* = 7 Hz, 3 H), 1.1–1.8 (m, 8 H), 1.93 (s, 3 H), 2.58 (t, *J* = 7 Hz, 2 H), 4.25 (s, 2 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 14.03, 16.33, 22.54, 28.04, 28.75, 31.62, 41.99, 56.40, 108.32, 135.21.

(c) (*Z*)-2-Chloro-3-methyl-4-iodo-3-decene. The allyl alcohol intermediate in the above synthesis was oxidized with pyridinium chlorochromate (16917 g, 75 mmol, 1.5 equiv), methylated with MeMgBr (55 mmol, 1.1 equiv), and chlorinated to give 4.68 g (30% based on 2-nonyn-1-ol) of the title compound: 1620 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.89 (t, *J* = 7 Hz, 3 H), 1.1–1.7 (m, 8 H), 1.49 (d, *J* = 7 Hz, 3 H), 1.86 (s, 3 H), 2.60 (t, *J* = 7 Hz, 2 H), 5.17 (q, *J* = 7 Hz, 1 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 12.60, 14.04, 22.58, 22.91, 28.08, 28.64, 31.66, 41.93, 67.63, 104.92, 138.49.

(d) (*Z*)-5-Iodo-4-(chloromethyl)-1,4-undecadiene. (*Z*)-3-Iodo-2-(2-propenyl)-2-nonen-1-ol, prepared in 59% yield from 2-nonyn-1-ol (14.02 g, 100 mmol), allylmagnesium bromide (250 mmol), and I_2 (76.14 g, 300 mmol), was chlorinated in 78% yield: IR (neat) 1640 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.91 (t, *J* = 7 Hz, 3 H), 1.1–1.8 (m, 8 H), 2.65 (t, *J* = 7 Hz, 2 H), 3.17 (d, *J* = 7 Hz, 2 H), 4.35 (s, 2 H), 5.0–5.3 (m, 2 H), 5.5–6.1 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 13.94, 22.45, 28.13, 299.27, 31.55, 34.06, 41.68, 54.03, 111.55, 116.81, 134.15, 137.12.

(e) (*Z*)-1-Iodo-2-phenyl-3-chloro-1-propene. (*Z*)-3-Iodo-2-phenyl-2-propen-1-ol was prepared in 35% yield from propargyl alcohol (5.61 g, 100 mmol), 250 mmol of 1.33 M PhMgBr in ether, and I_2 (300 mmol) and then chlorinated to give a 74% yield of the title compound: bp 90–93 °C (0.08 mmHg); IR (neat) 1596 (m), 1587 (m), 1564 (m), 1493 (m), 1440 (s), 1257 (s), 1200 (s), 762 (s), 692 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, Me_4Si) δ 4.68 (s, 2 H), 6.99 (s, 1 H), 7.53 (s, 5 H); ^{13}C NMR ($CDCl_3$) δ 47.56, 84.92, 125.92, 128.21, 128.33, 137.76, 146.35.

Cyclopropenes. The following five cyclopropenes were prepared by the representative procedure described for the preparation of 1-(trimethylsilyl)-2-(2′-propenyl)cyclopropene.

(a) 1-Phenyl-2-*n*-butylcyclopropene was obtained from 1.67 g (5.0 mmol) of (*Z*)-1-phenyl-1-iodo-2-(chloromethyl)-1-hexene and *n*-BuLi (1 equiv): 80% yield by NMR; IR ($CDCl_3$) 2230 (w), 1940 (w), 1810 (s), 1590 (s), 1480 (s), 1460 (s), 1440 (s), 1260 (s), 1025 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.95 (t, *J* = 7 Hz, 3 H), 1.20 (s, 2 H), 1.1–2.0 (m, 4 H), 2.69 (t, *J* = 7 Hz, 2 H), 7.2–7.8 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 7.12, 13.74, 22.54, 26.65, 29.83, 108.20, 115.23, 127.24, 128.32, 128.89, 130.51. High-resolution MS for $C_{13}H_{16}$: calcd, 172.1252; found, 172.1256.

(b) 1-*n*-Hexyl-2-methylcyclopropene was obtained from 0.60 g (2.0 mmol) of (*Z*)-1-chloro-2-methyl-3-iodo-2-nonene and *t*-BuLi (2 equiv): 84% yield by NMR; IR ($CDCl_3$) 2270 (w), 1900 (w), 1460 (s), 1020 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.7–1.1 (m, 5 H), 1.1–1.8 (m, 8 H), 2.05 (t, *J* = 2 Hz, 3 H), 2.41 (t, *J* = 7 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 8.13, 11.39, 13.99, 22.63, 26.01, 27.37, 29.10, 31.71, 105.29, 110.18. High-resolution MS for $C_{10}H_{18}$: calcd 138.1409; found, 138.1392.

(c) 2,3-Dimethyl-1-*n*-hexylcyclopropene was obtained from 0.63 g (2.0 mmol) of (*Z*)-2-chloro-3-methyl-4-iodo-3-decene and *t*-BuLi (2 equiv): 70% yield by NMR; IR ($CDCl_3$) 2245 (w), 1860 (w), 1456 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.90 (t, 3 H), 0.97 (d, *J* = 4 Hz, 3 H), 1.2–1.9 (m, 9 H) 2.01 (d, *J* = 2 Hz, 3 H), 2.40 (t, *J* = 7 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 9.87, 13.99, 14.59, 20.39, 22.64, 25.23, 27.69, 29.19, 31.76, 113.27, 118.10. High-resolution MS for $C_{11}H_{20}$: calcd, 152.1565; found, 152.1547.

(d) 1-*n*-Hexyl-2-(2-propenyl)cyclopropene was obtained from 0.653 g (2.0 mmol) of (*Z*)-5-iodo-4-(chloromethyl)-1,4-undecadiene and *t*-BuLi (2 equiv): 90% by NMR; IR ($CDCl_3$) 2220 (w), 1860 (m), 1710 (m), 1640 (s), 1450 (s), 1425 (s), 1020 (s), 995 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.71–1.1 (m, 5 H), 1.1–1.8 (m, 8 H), 2.48 (t, *J* = 7 Hz, 2 H), 4.9–5.4 (m, 2 H), 5.7–6.3 (m, 1 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 7.22, 14.07, 22.71, 26.16, 27.46, 29.17, 30.72, 31.78, 107.42, 111.07, 115.66, 134.39. High-resolution MS for $C_{12}H_{20}$: calcd, 164.1565; found, 164.1556.

(e) 1-Phenylcyclopropene. This compound was prepared from 0.139 g (0.50 mmol) of 1-iodo-2-phenyl-3-chloro-1-propene and 0.72 mL (1.0 mmol) of 1.39 M phenyllithium in ether. The reaction mixture was quenched with excess Me_3SiCl. The yield of 1-(trimethylsilyl)-2-phenylcyclopropene, identified by coinjection with an authentic sample, was 46%.

(*E*)-1-Iodo-2-*n*-hexyl-1,4-pentadiene.[18] This compound was prepared as reported previously[18] by the reaction of 1-octyne (0.44 g, 4.0 mmol) with allyldiisobutylalane, prepared from 5.72 mL (4.4 mmol) of 0.77 M allylmagnesium bromide and $(i\text{-Bu})_2AlCl$ (0.88 mL, 4.4 mmol) and Cl_2ZrCp_2 (1.16 g, 4.0 mmol) in $ClCH_2CH_2Cl$: 64% yield; IR (neat) 1640 (w), 980 (w), 905 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.85 (t, 3 H), 1.1–1.6 (m, 8 H), 2.18 (m, 2 H), 2.95 (d, *J* = 7 Hz, 2 H), 5.0–5.2 (m, 2 H), 5.5–6.0 (m, 1 H), 5.95 (s, 1 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 14.04, 22.57, 27.68, 28.84, 31.63, 37.25, 41.86, 75.40, 116.54, 133.92, 149.49.

1-*n*-Hexyl-1-cyclopentene (70). (*E*)-1-Iodo-2-*n*-hexyl-1,4-pentadiene (0.56 g, 2 mmol) was converted into (*Z*)-1-iodo-2-*n*-hexyl-5-bromo-1-pentene by its sequential treatment with $(i\text{-Bu})_3Al$ (2.4 equiv)–Cl_2ZrCp_2 (2 mmol) and NBS (7.5 mmol).[15] The crude product obtained after quenching with water, extraction, washing, and concentration was treated with *n*-BuLi (2 mmol) to give **70**[39] in 80% yield: IR (neat) 1640 (m), 820 (s) cm^{-1}; ^{1}H NMR (CCl_4, Me_4Si) δ 0.88 (t, 3 H), 1.2–1.4 (m, 10 H), 1.75–2.30 (m, 6 H), 5.28 (s, 1 H).

(*Z*)-1-Iodo Dienes via Carbocupration. (a) (*Z*)-1-Iodo-2-*n*-butyl-4-methyl-1,5-hexadiene: Representative Procedure. 4-Bromo-2-methyl-1-butene, prepared via mesylation and bromination of 2-methyl-3-buten-1-ol, was converted into (2-methyl-3-butenyl)magnesium bromide. To a suspension of CuBr (9.32 g, 65 mmol) in ether (50 mL) at −40 °C was added the above-preared Grignard reagent (0.65 M in ether, 74 mL, 48 mmol). After the mixture was stirred for 1 h at −40 °C, 1-hexyne (4.93 g, 60 mmol) was added, and the reaction mixture was stirred at −20 °C for 1 h. A solution of I_2 (19.04 g, 75 mmol) in THF (50 mL) was added at −50 °C. The mixture was warmed to 25 °C, treated with water, extracted with ether, washed with 3 N $Na_2S_2O_3$, $NaHCO_3$, and NaCl, dried ($MgSO_4$), and concentrated to give 6.94 g (52%) of the title compound: ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.8–1.1 (m, 6 H), 1.2–1.6 (m, 4 H), 2.1–2.4 (m, 5 H), 4.8–5.1 (m, 2 H), 5.6–6.0 (m, 2 H).

(b) (*Z*)-1-Iodo-2-*n*-butyl-5-methyl-1,5-hexadiene. This compound was prepared in 60% yield from 1-hexyne (9.04 g, 110 mmol), (3-methyl-3-butenyl)magnesium bromide (1.0 M in ether, 100 mL, 100 mmol), CuBr (18.6 g, 130 mmol), and I_2 (35.5 g, 140 mmol): ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.90 (t, *J* = 6 Hz, 3 H), 1.2–1.6 (m, 4 H), 1.80 (s, 3 H), 2.0–2.4 (m, 6 H), 4.75 (s, 2 H), 5.90 (s, 1 H).

(c) (*Z*)-1-Iodo-2-*n*-hexyl-1,6-heptadiene. This compound was prepared in 63% yield from 1-octyne (5.60 g, 50 mmol), 4-pentenylmagnesium bromide (0.80 M in ether, 60 mL, 48 mmol), CuBr (10.0 g, 70 mmol), and I_2 (17.0 g, 67 mmol): bp 94–95 °C (0.1 mmHg); IR (neat) 1640 (w), 985 (w), 905 (s), 760 (w) cm^{-1}, ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.85 (t, 3 H), 1.1–1.6 (m, 12 H), 2.0–2.3 (m, 6 H), 4.8–5.2 (m, 2 H), 5.6–6.1 (m, 2 H).

(*Z*)-1-Iodo-ω-bromo-1-alkenes via Hydroalumination–Bromination. (a) (*Z*)-1-Iodo-2-*n*-butyl-4-methyl-6-bromo-1-hexene (67). This compound was prepared in 75% yield from (*Z*)-1-iodo-2-*n*-butyl-4-methyl-1,5-hexadiene (2.78 g, 10.0 mmol), $(i\text{-Bu})_3Al$ (11.8 mmol), Cl_2ZrCp_2 (10.0 mmol), and NBS (36 mmol): ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.8–1.1 (m, 6 H), 1.2–1.6 (m, 5 H), 1.7–2.0 (m, 2 H), 2.1–2.4 (m, 4 H), 3.50 (t, *J* = 7 Hz, 2 H), 6.00 (s, 1 H).

(b) (*Z*)-1-Iodo-2-*n*-hexyl-7-bromo-1-heptene (69). This compound was prepared in 75% yield from (*Z*)-1-iodo-2-*n*-hexyl-1,6-heptadiene: bp 130–132 °C (0.1 mmHg); ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.85 (t, 3 H),

(39) Baba, T.; Avasthi, K.; Suzuki, A. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 1571.

1.1–1.7 (m, 14 H), 2.0–2.4 (m, 4 H), 3.40 (t, J = 7 Hz, 2 H), 5.85 (s, 1 H).

(*Z*)-1-Iodo-2-*n*-butyl-5-methyl-6-bromo-1-hexene (68). This compound was prepared in 32% yield from (*Z*)-1-iodo-2-*n*-butyl-5-methyl-1,5-hexadiene via hydroboration–oxidation followed by bromination: IR (neat) 2950 (s), 1620 (w), 1460 (s), 1380 (s), 1230 (w) cm^{-1}; ^1H NMR ($CDCl_3$, Me_4Si) δ 0.8–2.0 (m, 13 H), 2.1–2.4 (m, 4 H), 3.40 (d, J = 7 Hz, 2 H), 5.90 (s, 1 H).

1-*n*-Butyl-5-methyl-1-cyclohexene (71). To (*Z*)-1-iodo-2-*n*-butyl-4-methyl-6-bromo-1-hexene (0.63 g, 1.75 mmol) in ether (20 mL) at −78 °C was added *n*-BuLi (2.7 M in hexane, 0.67 mL, 1.81 mmol). The mixture was warmed to 25 °C over 1 h and treated with water. The organic phase was washed with saturated NaCl, dried over $MgSO_4$, and concentrated. Distillation afforded 0.20 g (75%) of **71**: bp 85 °C (23 mmHg, Kugelrohr); ^1H NMR ($CDCl_3$, Me_4Si) δ 0.8–1.1 (m, 6 H), 1.2–2.1 (m, 13 H), 5.3–5.5 (m, 1 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 13.98, 21.94, 22.47, 25.34, 28.97, 30.02, 30.92, 37.06, 37.60, 120.10, 137.59. Anal. Calcd for $C_{11}H_{20}$: C, 86.76; H, 13.24. Found: C, 86.49; H, 13.01.

1-*n*-Butyl-4-methyl-1-cyclohexene (72). (a) Via Cyclialkylation. This compound was prepared in 56% yield from 1-iodo-2-*n*-butyl-5-methyl-6-bromo-1-hexene (0.43 g, 1.2 mmol) ether (12 mL) and *n*-BuLi (2.8 M in hexane, 0.45 mL, 1.26 mmol): bp 85 °C (22 mmHg, Kugelrohr); ^1H NMR ($CDCl_3$, Me_4Si) δ 0.8–1.1 (m, 6 H), 1.2–2.1 (m, 13 H), 5.30–5.5 (m, 1 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 13.98, 21.78, 22.47, 28.38, 28.56, 30.03, 31.36, 33.94, 37.41, 120.08, 137.68.

(b) Via n-Butylation of 4-Methylcyclohexanone. *n*-Butyllithium (2.7 M in hexane, 9.7 mL, 26 mmol) was added to 4-methylcyclohexanone (2.80 g, 25 mmol) in THF (25 mL) at −78 °C, and the mixture was warmed to 25 °C and worked up in the usual manner. Dehydration was effected by heating the crude alcohol in toluene (50 mL) with iodine (0.10 g, 0.40 mmol). Water was removed under reflux at 140 °C for 6 h. The usual workup and distillation provided 1.80 g (47%) of **72**. Comparison of the ^1H and ^{13}C NMR spectra of **71** and **72** indicates that each of them is isomerically pure. Anal. Calcd for $C_{11}H_{20}$: C, 86.76; H, 13.24. Found: C, 86.37; H, 12.98.

1-*n*-Hexyl-1-cycloheptene (73). This compound[40] was prepared in 67% yield from (*Z*)-1-iodo-2-*n*-hexyl-7-bromo-1-heptene (0.62 g, 1.60 mmol) and *t*-BuLi (2.18 M in pentane, 1.5 mL, 3.27 mmol): ^1H NMR ($CDCl_3$, Me_4Si) δ 0.90 (t, 3 H), 1.2–1.8 (m, 14 H), 1.8–2.2 (m, 6 H), 5.55 (t, J = 7 Hz, 1 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 14.04, 22.65, 26.94, 27.48, 28.03, 28.34, 29.05, 31.83, 32.69, 32.80, 40.30, 125.56, 144.98.

1-(Trimethylsilyl)-2-(2-propenyl)-1-cyclopentene (75).[21] A mixture of 12.0 g (55.0 mmol) of 5-bromo-1-(trimethylsilyl)-1-pentyne and 170 mL (170 mmol) of 1.0 M allylzinc bromide in THF was heated at 65 °C for 14 h.[8] After the mixture was cooled to −78 °C, 15.8 g (110 mmol) of CuBr was added. The mixture was warmed to −20 °C for 2 h and then to 25 °C, treated with saturated aqueous NH_4Cl and pentane, washed with 3 N HCl, saturated $NaHCO_3$, and NaCl, dried over $MgSO_4$, filtered, concentrated, and distilled to provide 7.86 g (64%) of **75**: bp 77–80 °C (11 mmHg); IR (neat) 1640 (w), 1610 (m), 1245 (s), 989 (m), 905 (m), 825 (s) cm^{-1}; ^1H NMR ($CDCl_3$, Me_4Si) δ 0.11 (s, 9 H), 1.6–1.9 (m, 2 H), 2.1–2.5 (m, 4 H), 2.7–3.0 (m, 2 H), 4.9–5.2 (m, 2 H), 5.5–6.0 (m, 1 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ −0.38, 23.68, 36.23, 38.24, 115.12, 135.27, 136.57, 151.59. Anal. Calcd for $C_{11}H_{20}Si$: C, 73.25; H, 11.18. Found: C, 73.32; H, 10.91.

(40) Riemschneider, R.; Hoyer, G. A. *Monatsh. Chem.* **1968**, *99*, 642.

1-Acetyl-2-methylcyclobutene (77). This compound was prepared in a manner similar to the preparation of **34** from **4** (7.0 g, 50 mmol), AcCl (4.3 g, 55 mmol), and $AlCl_3$ (7.3 g, 55 mmol): 4.8 g (88%); bp 69–72 °C (16 mmHg); IR (neat) 1622–1660 (s), 1235 (s), 1185 (s) cm^{-1}; ^1H NMR ($CDCl_3$, Me_4Si) δ 2.09 (bs, 3 H), 2.20 (s, 3 H), 2.2–2.7 (m, 4 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 17.18, 25.50, 28.12, 30.20, 139.45, 157.52, 194.20. Anal. Calcd for $C_7H_{10}O$: C, 76.32; H, 9.15. Found: C, 76.25; H, 9.06.

1-Acetyl-2-methyl-2-vinylcyclobutane (78). A procedure by Lipshutz for conjugate additon[41] was followed by using CuCN (5.0 g, 56 mmol), vinyllithium (2.00 M in THF, 54 mL, 108 mmol), and **77** (4.4 g, 40 mmol) in ether (80 mL) at −50 °C for 2.5 h. The mixture was quenched at −78 °C by slowly adding methanol in THF and allowed to warm to 0 °C before following the published quenching procedure[41] to afford 4.2 g (76%) of a 2:1 mixture of the *Z* and *E* isomers of the title compound:[22] 92% yield by GLC; IR (neat) 1710 (s), 1640 (m), 1115 (m) cm^{-1}; ^1H NMR ($CDCl_3$, Me_4Si) δ 1.10 (s, for *E* methyl, 3 H), 1.42 (s, for *Z* methyl, 3 H), 1.5–2.5 (m with peaks at 1.95 for *Z* acetyl and 2.00 for *E* acetyl, 14 H), 3.0–3.3 (m, 2 H), 4.9–5.2 (m, 4 H), 5.8–6.3 (m, 2 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 16.14, 19.54, 26.42, 29.36, 29.47, 30.51, 30.87, 45.28, 45.71, 53.83, 57.23, 111.25, 112.60, 141.64, 146.72, 206.77.

1-(2-Hydroxymethyl)-2-isopropenyl-1-methylcyclobutane (76). A procedure by Chan and Chang[42] for carbonyl olefination was modified as follows. To a stirred stock solution of [(trimethylsilyl)methyl]magnesium chloride (0.96 M in ether, 12.5 mL, 12 mmol), prepared from Me_3SiCl (4.3 g, 35 mmol) and Mg turnings (1.3 g, 53 mmol) in ether (35 mL), was added at 25 °C **78** (1.4 g, 10 mmol) in ether (10 mL). After it was stirred for 10 min, the mixture was heated to reflux for 2 h, poured into cold saturated aqueous NH_4Cl, extracted with ether, washed with saturated aqueous $NaHCO_3$, and brine, dried over $MgSO_4$, and evaporated in vacuo (0.3 mmHg) for 6 h. To the silyl alcohol thus obtained was added at 0 °C THF (10 mL) and disiamylborane (25 mmol). After it was stirred for 2 h, the mixture was treated at 25 °C with 3 N NaOH (22 mL) and 30% H_2O_2 (15 mL), extracted with ether, and evaporated in vacuo (0.5 mmHg) for 6 h. The crude material was dissolved in THF (20 mL) and added at 25 °C to a suspension of KH (2.0 g, 50 mmol) in THF (20 mL). After it was stirred for 48 h, the mixture was poured into ice water, extracted with ether, washed with brine, dried over $MgSO_4$, and evaporated. The crude material thus obtained was purified by column chromatography (silica gel, 35% ethyl acetate in hexane) to afford 0.77 g (50%) of a 2:1 mixture of the *Z* and *E* isomers of **76**:[22] IR (neat) 3450–3250 (s), 1648 (m), 1050 (s), 880 (s) cm^{-1}; ^1H NMR ($CDCl_3$, Me_4Si) δ 0.92 (s, 3 H), 1.17 (s, 3 H), 1.3–2.1 (m with bs at 1.66, 20 H), 2.55 (t, J = 8 Hz, 2 H), 3.66 (t, J = 8 Hz, 4 H), 4.65 (bs, 2 H), 4.85 (bs, 2 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 19.23, 19.56, 19.80, 23.05, 23.23, 28.41, 29.40, 30.32, 37.02, 41.05, 41.40, 46.72, 50.58, 52.58, 59.91 (2 C), 109.81 (2 C), 145.21, 145.59.

Acknowledgment. We thank the National Science Foundation, the National Institutes of Health, and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. We also thank Drs. J. A. Miller and S. J. Holmes for providing some experimental data.

(41) Lipshutz, B. H.; Wilhelm, R. S.; Kozlowski, J. *Tetrahedron Lett.* **1982**, *23*, 3755.

(42) Chan, T. H.; Chang, E. *J. Org. Chem.* **1974**, *39*, 3264.