Stereocontrolled Double Ring Expansion of Fused Allylidenecyclopropanes. A Novel Route to Hydroazulenes and Other Fused Bicyclic Systems

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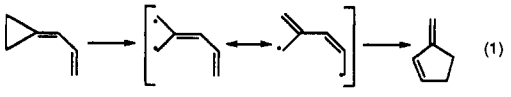
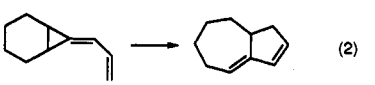
Abstract: A variety of 1-(phenylthio)-1-(trimethylsilyl)cyclopropanes, fused to five-, six-, and seven-membered rings, have been prepared by several procedures and reductively lithiated by means of aromatic radical anions. The resulting 1-lithio-1-(trimethylsilyl)cyclopropanes have been treated in most cases with α,β-unsaturated aldehydes, followed by potassium *tert*-butoxide to yield allylidenecyclopropanes. The latter, upon thermal rearrangement either in a sealed tube or in a flash vacuum pyrolysis apparatus, undergo a double ring expansion to cyclopentenocyclohexenes, -cycloheptenes (hydroazulenes), or -cyclooctenes. When the distal double bond of the allylidenecyclopropane possesses a terminal trans substituent, that substituent in the hydroazulene pyrolysis product is predominantly in the exo position (cis to the hydrogen atom at the ring junction carbon atom); cis substituents end up mainly in the endo position. Thus, the ring closure occurs mainly in a conrotatory sense. When the distal unsaturation is incorporated into a ring, a tricyclic system results. Carbonyl functionality can be introduced into either position of the five-membered rings and either of the two carbon atoms adjacent to the ring junction of the seven- or eight-membered ring of the ring expansion products by using appropriately substituted rearrangement substrates. Complete regioselectivity is observed when the original six- or seven-membered ring has a ketone group adjacent to the ring junction; the product is a completely conjugated dienone. Complete regioselectivity in the opposite sense is observed upon rearrangement of the corresponding kinetic silyl enol ether. This methodology is demonstrated by the synthesis of (+)-9-epiledene, containing the gross structural features of the aromadendrene sesquiterpenes, and of (±)-α-bulnesol, a guiazulene sesquiterpene.

Introduction

The allylidenecyclopropane rearrangement (eq 1) was discovered in 1968,[2] and its mechanism has been the subject of a number of investigations.[3] It is generally agreed that the reaction proceeds by a homolytic cleavage of the strained diallylic bond to a trimethylenemethane type diradical. Some possible resonance structures of the intermediate possessing an *S*-cis conformation of the original diene unit are shown. Analogous structures for the *S*-trans conformation, which cannot undergo ring closure, are also possible. To our knowledge, this rearrangement has never been used as a synthetic tool. The very general availability of allylidenecyclopropanes by methods developed in this laboratory now allows the use of this reaction for synthetic purposes.


(1)

All of the past studies have involved the basic structure shown in eq 1 with alkyl groups substituted at different positions of the skeleton. It occurred to us that if the cyclopropane were fused to another ring, the rearrangement would lead to a double ring expansion (e.g., eq 2). In the example shown, this ring expansion leads to the hydroazulene ring system, but, in principle, the ring fused to the cyclopropane could be virtually any size. In this paper, we describe the reduction to practice of this concept. In a subsequent paper, mechanistic insight gained from the study of such fused systems will be presented.


(2)

Our approach[4] to fused allylidenecyclopropanes involves the reductive lithiation of a fused geminal (phenylthio)(trimethylsilyl)cyclopropane, using the aromatic radical anions[5] lithium 1-(dimethylamino)naphthalenide (LDMAN)[6] or *p,p'*-di-*tert*-butylbiphenylide (LDBB),[7] treatment of the resulting α-lithiocyclopropylsilane with a conjugated enal, and replacement of the lithium cation with potassium,[8] leading to elimination; an example of this modification of the Peterson olefination[9] procedure in

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(1) (a) Deceased February 13, 1993. This paper is dedicated to the memory of Craig A. Shook. (b) Taken in part from the Ph.D. Theses of J. P. Sherbine (1985) and M. L. Romberger (1989) and the M. S. Thesis of C. A. Shook (1993), University of Pittsburgh.

(2) Shields, T. C.; Billups, W. E.; Lepley, A. R. *J. Am. Chem. Soc.* **1968**, *90*, 4749.

(3) (a) Roth, W. R.; Schmidt, T. *Tetrahedron Lett.* **1971**, 3639. (b) Kende, A. S.; Riecke, E. E. *J. Am. Chem. Soc.* **1972**, *94*, 1397. (c) Kende, A. S.; Riecke, E. E. *Tetrahedron Lett.* **1972**, 1857.

(4) (a) Cohen, T.; Sherbine, J. P.; Matz, J. R.; Hutchins, R. R.; McHenry, B. M.; Willey, P. R. *J. Am. Chem. Soc.* **1984**, *106*, 3245. (b) Cohen, T.; Jung, S.-H.; Romberger, M. L.; McCullough, D. W. *Tetrahedron Lett.* **1988**, *29*, 25.

(5) (a) Cohen, T.; Bhupathy, M. *Acc. Chem. Res.* **1989**, *22*, 152. (b) Cohen, T. In *Heteroatom Chemistry;* Block, E., Ed.; VCH Publishers: New York, 1990; Chapter 7.

(6) Cohen, T.; Matz, J. R. *Synth. Commun.* **1980**, *10*, 311.

(7) Freeman, P. K.; Hutchinson, L. L. *J. Org. Chem.* **1980**, *45*, 1924; **1983**, *48*, 4705.

(8) Lochmann, L.; Trekoval, J. *Collect. Czech. Chem. Commun.* **1988**, *53*, 76–97.

(9) Peterson, D. *J. Org. Chem.* **1968**, *22*, 4737. Ager, D. J. *Synthesis* **1984**, 384. Peterson, D. J. *Synthesis* **1984**, 385–398.

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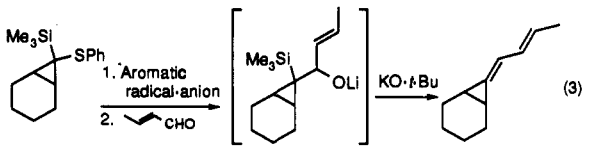
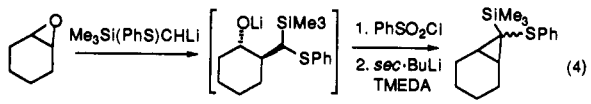
shown in eq 3. Other, somewhat less general, methods for the production of the α-lithiocyclopropylsilanes are also available.[10]



(3)

The generality of this procedure is due to the variety of methods available for the preparation of α-(phenylthio)(cyclopropyl)-trimethylsilanes. Of the several preparative methods that we previously developed,[4,11] the one-pot methods exemplified in eqs 4[11a] and 5[11b] are most suitable for fused ring systems. However, the method in eq 4 was deemed inappropriate for a number of substituted cases, and we describe below an additional method which, together with the earlier methods, allows the preparation of a considerable variety of such fused ring systems.



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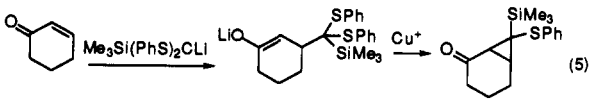
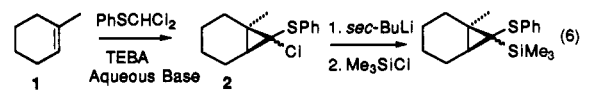


(5)

Results and Discussion

Carbenoid Route to Fused Ring Geminal (Phenylthio)(trimethylsilyl)cyclopropanes. The most general method that we have used to produce these reductive lithiation substrates involves a two step procedure (eq 6). The first step involves cyclopropanation of a cyclic olefin with chloro(phenylthio)carbene[12] generated by using a modification of Makozsa's phase transfer catalyzed base induced carbenoid α-elimination.[13]



(6)

During our initial studies we found that Makozsa's procedure for constructing cyclopropanes substituted at the bridgehead was unsatisfactory for multigram preparation of 1-chloro-1-(phenylthio)cyclopropanes, precursors of the desired 1-(phenylthio)-1-trimethylsilylcyclopropanes. In particular we needed cyclopropane **4** for our α-bulnesol synthesis. However the attempted cyclopropanation of **3** by using the reported method, utilizing 50% (19.1 M) NaOH and a catalytic quantity of benzyl(triethyl)-ammonium chloride (TEBA), resulted in poor yields (20–30%) of the isolated product. Table I summarizes the results of limited optimization studies for the cyclopropanation of **3** and the simpler 1-methylcyclohexene **1**, using different alkali bases and different concentrations. The results indicate that KOH is the base of choice and that a 10 M concentration gives quite satisfactory results, leading to an 84% yield in the case of **3**.

Several other examples of the modified phase-transfer cyclopropanation reaction using these optimum conditions are shown in Table II. It is seen that the procedure is satisfactory for some typical enol ethers but that the yield is below 40% for a nonconjugated dienol ether and an allylic alcohol.

Table I. Phase Transfer Cyclopropanation Optimization Studies

olefin	base	Chlorocyclopropane	Yield
 1	25 M NaOH	 2	46 %
	25 M KOH		63%
 3	25 M KOH	 4	62 %
	10 M KOH		84%

[a] The phase transfer catalyst was benzyl(triethyl)ammonium chloride (TEBA).

Table II. *gem*-Chloro(phenylthio)cyclopropanes Produced by Phase Transfer Catalysis

Cyclopropanation Product	Yield	Silylation Product	Yield
 5	77%	 6	57%
 7	64%		
 8	37%		
 9	33%	 10	53%

Conversion of the chlorocyclopropanes to the (trimethylsilyl)-cyclopropanes was carried out by a chlorine–lithium exchange[14] and capture of the resulting anion with trimethylsilyl chloride. We have found that in order to obtain reproducible results a reverse addition must be employed whereby the 1-chloro-1-(phenylthio)cyclopropanes are added to a solution of *s*-BuLi at −78 °C. It is probable that when the butyllithium is added to the chlorocyclopropane the α-lithiosilane induces elimination of HCl from unreacted substrate. While the tetrahydropyranyl analog **5** and the hydroxyl substituted compound **9** were successfully converted to the α-(phenylthio)silane, the methoxy substituted compounds **7** and **8** behaved quite differently. We were unable to gain access to the methoxy substituted α-(phenylthio)silanes. It is likely that once the α-lithiosulfide is generated by chlorine–lithium exchange, elimination of lithium methoxide produces a highly strained cyclopropene whose fate is unknown.

Allylidenecyclopropane Synthesis. A variety of allylidenecyclopropanes was synthesized by the reductive lithiation method (Table III). Although most were prepared in a straightforward fashion, a few comments are in order. The preparation of **19** is noteworthy in that the carbonyl compound used in the reductive lithiation sequence was an *E/Z* mixture of 3-(phenylthio)-propenal[15] that afforded a trans/cis (8:1) mixture of geometric isomers. Fortunately, these isomers could be separated by flash chromatography allowing the *cis*- and *trans*-phenylthio substituted allylidenecyclopropanes **20** to be prepared separately by Peterson olefination. The significance of this will become apparent when the rearrangement of these compounds is discussed; as will be seen, the stereochemistry of the rearranged product can be controlled by the geometry of the allylidenecyclopropane.

All of the previous studies were performed on allylidenecyclopropanes possessing a trans geometry.[2,3] Two different routes were used to synthesize allylidenecyclopropanes possessing a cis geometry. Rouessac's method[17] for preparing *cis*-crotonaldehyde,

(10) Krief, A. *Top. Curr. Chem.* **1987**, *135*, 1. Hiyama, T.; Kanakura, A.; Morizawa, Y.; Nozaki, H. *Tetrahedron Lett.* **1982**, *23*, 1279. Hässig, R.; Siegel, H.; Seebach, D. *Chem. Ber.* **1982**, *115*, 1990. Lewis, R. T.; Motherwell, W. B. *Tetrahedron Lett.* **1988**, *29*, 5033. Meijs, G. F.; Eichinger, P. C. H. *Tetrahedron Lett.* **1987**, *28*, 5559.

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(12) Remlinger, H. *Chem. Ind. (London)* **1966**, 1682. Schöllkopf, U.; Woerner, F. P.; Wiskott, E. *Chem. Ber.* **1965**, *98*, 2221. Schöllkopf, U.; Woerner, F. P.; Wiskott, E. *Chem. Ber.* **1966**, *99*, 806.

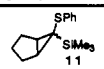
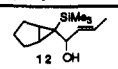
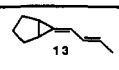
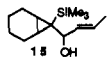
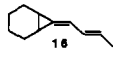
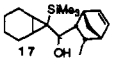
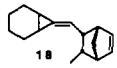
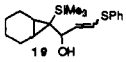
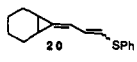
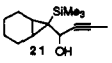
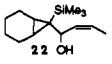
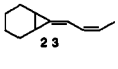
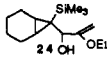
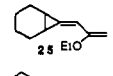
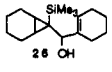
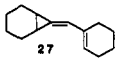
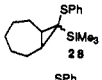
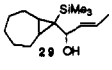
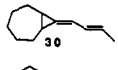
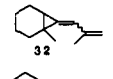
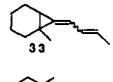
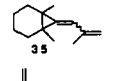
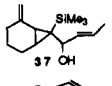
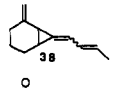
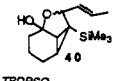
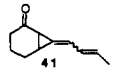
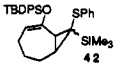
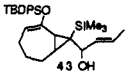
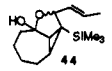
(13) Makozsa, M.; Bialecka, E. *Tetrahedron Lett.* **1971**, 4517.

(14) The reagent used was that developed originally for the conversion of vinyl bromides to vinyllithiums. Miller, R. D.; McGarvey, G. *J. Org. Chem.* **1979**, *44*, 4623.

(15) This compound has been prepared previously by the addition of thiophenol to 2-propyn-1-al, see: (a) Ha, D. C.; Hart, D. J.; Yang, T. K. *J. Am. Chem. Soc.* **1984**, *106*, 4819. (b) Englehard, N.; Kolb, A. *Ann. Chem.* **1964**, *673*, 136. During our synthesis of 3-(phenylthio)propenal,[16] a preparation identical to ours was reported, see: (c) Iwao, M.; Kuraishi, T. *Tetrahedron Lett.* **1985**, 6213.

(16) Romberger, M. L. Ph. D. Thesis, University of Pittsburgh, 1989.

Table III. Preparation of Allylidenecyclopropanes via Reductive Lithiation, Peterson Olefination

α-(phenylthio)silane	yield[a]	β-silylcarbinol	yield[a]	Olefin	yield[a,b]
 11	78%	 12	91%	 13	95%
 14	75%	 15	83%	 16	80%[c] 93%
		 17	93%[d]	 18	6%
		 19	72%[e]	 20	93%[f]
		 21	81%		
		 22	84%[g] 97%[h]	 23	94%
		 24	69%	 25	ND[i]
		 26	79%	 27	74%
 28	64%	 29	89%	 30	93%
 31	80%			 32	74%[c]
				 33	99%[c,j]
 34	36%[k]			 35	79%[c]
 36	99%[l]	 37	72%[m]	 38	99%[n]
 39	71%	 40	71%[o]	 41	90%[n]
 42	96%	 43	69%		
		 44	97%[p]		

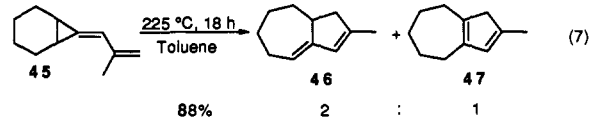
[a] For chromatographed material unless otherwise noted. [b] Yield for elimination step, from β-silylcarbinol, unless otherwise noted. [c] Overall yield of olefin from α-(phenylthio)silane; a one pot procedure was used. [d] Prepared from Dibal reduction product of Diels–Alder adduct of cyclopentadiene and cis crotononitrile; ref 17. [e] Mixture of trans/cis isomers, 8/1. [f] Elimination carried out separately for each β-silylcarbinol geometric isomer. [g] Yield for FVP of **17**. [h] Yield for hydrogenation of **21**. [i] Decomposed upon flash chromatography; the crude product was used for rearrangement. [j] 1:1 mixture of isomers. [k] Yield for two steps from 1,2-dimethylcyclohexene. [l] Yield from **39** via Wittig reaction. [m] 3.3:1.0 mixture of diastereomers. [n] Olefination carried out separately for each β-silylcarbinol diastereomer. [o] 12:1 mixture of diastereomers. [p] Yield from **43**.

involving the diisobutylaluminum hydride reduction product of the Diels–Alder adduct of cyclopentadiene and *cis*-crotononitrile, was used to prepare alkylidenecyclopropane **18**, the synthetic equivalent of **23**. By using flash vacuum pyrolysis (FVP), we could effect both the retro-Diels–Alder reaction, which produces the allylidenecyclopropane **23**, and the rearrangement of the latter. Alternatively, butynal could be used in the reductive lithiation sequence affording silylcarbinol **21**. *cis*-Allylidenecyclopropane **23** is obtained following hydrogenation to **22**, using the Lindlar catalyst,[18] and elimination.

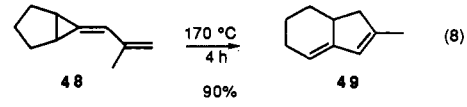
The synthesis of silylcarbinol **24** required a slight modification of the usual procedure. The process involved adding the α-lithiosilane, derived from **14** by reductive lithiation, to ethyl formate.[19] The resulting α-silyl aldehyde was then treated in situ with 1-ethoxy-1-lithioethene[20] to afford **24** in 69% yield. Because allylidenecyclopropane **25** was unstable toward chromatography it was subjected to rearrangement without purification.

Our initial attempts to reductively lithiate ketone **39** were unsuccessful but in situ generation and use of the trimethylsilyl enol ether, using lithium diisopropyl amide (LDA) and TMSCl, allowed the desired reduction of the cyclopropyl carbon–sulfur bond. The α-lithiosilane generated was treated with crotonaldehyde and upon workup afforded a separable (MPLC) diastereomeric mixture (12:1) of lactols **40**. As in all cases in this paper and in earlier work,[4a] only a single epimer about the C7 cyclopropyl position is produced by reductive lithiation followed by reaction with a carbonyl compound; from the present example, it is assumed that the trimethylsilyl group is in the exo position in all of these cases. This stereochemistry probably arises when the intermediate radical[5] arranges itself in the less crowded configuration in which the large trimethylsilyl group is exo. Each isomer of **40** was separately treated with potassium hexamethyldisilazide to yield different geometric isomers of **41** in excellent yield. Unfortunately, the in situ method failed with 7-(phenylthio)-7-(trimethylsilyl)bicyclo[5.1.0]octan-2-one, the one carbon homologue of **39**. In this case the trimethylsilyl group transferred from oxygen to the cyclopropyl anion, formed by reductive lithiation, and an enolate was generated. Once this transfer occurred, the nucleophilic addition is by the enolate anion instead of by the desired cyclopropyl anion. By using the more hindered *tert*-butyl diphenyl silyl (TBDPS) enol ether **42** to deter silyl transfer, 1,2-addition of crotonaldehyde occurred at the cyclopropyl anion leading to **43** in 69% yield. Lactol **44** was obtained by simply treating **43** with tetrabutylammonium fluoride.

Rearrangements of Allylidenecyclopropanes. The first example of this type of rearrangement in a fused system resulted in a double ring expansion when 7-(2-methylpropenylidene)bicyclo-[4.1.0]heptane[4a] (**45**) was heated at 225 °C for 18 h in a sealed tube. A 2:1 mixture of bicyclo[5.3.0]decadienes **46** and **47** was produced in 88% overall yield (eq 7). The presence of **47** is attributed to the acid catalyzed rearrangement of **46**.



Another example of this ring expansion is shown in eq 8. Compound **48**[4a] rearranged to **49** in 90% yield under milder conditions (170 °C, 4 h). Presumably, the increased strain in the ring fusion of a five- and three-membered ring is responsible for the more facile rearrangement.



Having demonstrated the general viability of the double ring expansion, we set out to probe the limitations, to expand the scope, and, ultimately, to develop a better understanding of the rearrangement reaction. With this in mind, several experiments which would explore some unanswered details of the rearrangement were devised. To investigate the effects of bridgehead substituents, allylidenecyclopropanes **33** and **35** were heated under

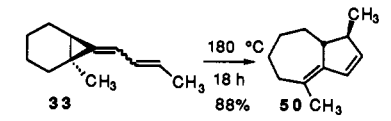
(17) Perrier, M.; Rouessac, F. *Nouv. J. Chem.* **1977**, *1(5)*, 367.

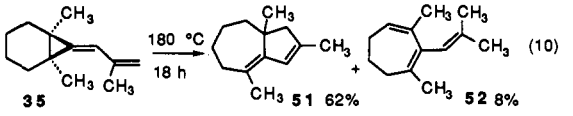
(18) Lindlar, H.; Dubuis, R. *Org. Synth.* **1973**, *5*, 880. Reed, M. W.; Moore, H. W. *J. Org. Chem.* **1988**, *53*, 4166. Doedens, R. J.; Meier, G. P.; Overman, L. E. *J. Org. Chem.* **1988**, *53*, 685.

(19) For the use of ethyl formate as a formylating agent, see; Pfeffer, P. E.; Silbert, L. S. *Tetrahedron Lett.* **1970**, 699.

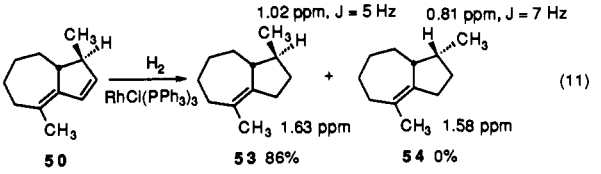
(20) Schöllkopf, U.; Hänssle, P. *Justus Liebigs Ann.* **1972**, *763*, 208. Baldwin, J. E.; Höfle, G. A.; Lever, O. W. *J. Am. Chem. Soc.* **1974**, *96*, 7125.

the described conditions. The results indicate that ring closure occurs at the less substituted bridgehead (eq 9) and that the yield is comparable to the unsubstituted case. When both bridgehead positions are substituted with methyl groups, the yield of double ring expansion product **51** is somewhat lower and is accompanied by 8% of a product (**52**) apparently resulting from a 1,6-hydrogen atom transfer in the intermediate diradical (eq 10).

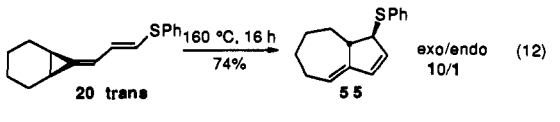


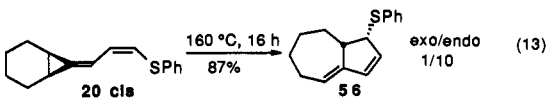


The thermolysis of **33** also led to a synthetically and mechanistically interesting stereochemical result. The *trans*-methyl group of the reactant was transformed exclusively to an *exo*-methyl group of the rearrangement product; the term *exo*-methyl indicates that the methyl substituent is cis to the hydrogen atom at the bridgehead and is thus less crowded than an endo methyl. The stereochemistry of **50** was determined by hydrogenation with Wilkinson's catalyst[21] to give the known compound **53** (eq 11).[22] The other known epimer **54** was not detected.

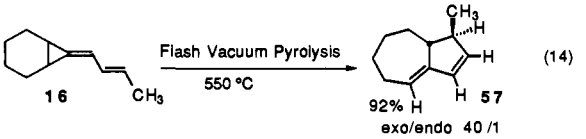


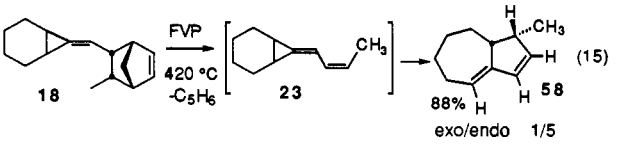
The above result led us to speculate that the stereochemistry of the C-8 substituent of the rearranged product could be controlled by the geometry of the disubstituted double bond of the allylidenecyclopropane. To examine the stereoselectivity of this rearrangement, the isomeric (phenylthio)allylidenecyclopropanes **20** were pyrolyzed. To obtain the separate cis and trans isomeric starting materials, separation of the precursor β-silylcarbinols was performed before olefination. In separate reactions **20-*cis*** and **20-*trans*** were heated in sealed tubes at 160 °C for 16 h. As hoped, each isomer produced mainly (10:1) one bicyclo[5.3.0]deca-1,9-diene (eqs 12 and 13).[23]



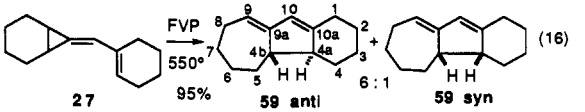


Similarly, the thermal rearrangement of the hydrocarbon analogs **16** and **23** were studied. Flash vacuum pyrolysis of the *trans* isomer **16** led very predominantly to the *exo*-methyl epimer **57** (eq 14), and pyrolysis of the spectroscopically pure *cis* isomer **23** or its equivalent **18** under optimum conditions (420 °C, slow distillation through a vertical column) gave a ratio of 5:1 of **58** and its *exo*-methyl epimer (eq 15).[24] The discovery that the endo methyl epimer **58** could be produced from the cis reactant is of importance because many of the naturally occurring hydroazulenes possess an endo C-8 methyl group.[25] As will be seen below, the trans-to-exo and cis-to-endo relationships (a conrotatory ring closure, assuming maintenance of the trans distal alkene linkage) were also demonstrated in the synthesis of racemic α-bulnesol.

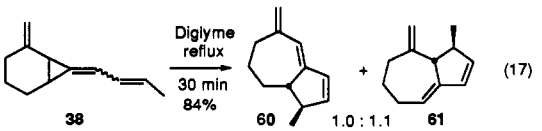




The same stereochemical pattern, albeit with lower selectivity, was evident upon pyrolysis of **27** in which the distal alkene is incorporated into a ring (eq 16). Because of the large preponderance of the anti isomer in the inseparable product mixture, it was possible to assign all of its proton and carbon peaks in the 500- and 125-MHz NMR spectra by the use of extensive 2D experiments. In the case of the ^{1}H NMR spectrum of the syn isomer, the ring fusion protons (HC-4a and HC-4b) only were clearly discernible and these as well as all of the carbon peaks were also assigned by 2D methods. 1D and 2D NOE experiments revealed magnetic interaction between the ring fusion protons (HC-4a and HC-4b) of the syn isomer but not those of the anti isomer, thus establishing the stereochemistry. However, the structure of **59-*syn***, while quite likely correct based on the two key proton peaks, the ^{13}C spectrum, the high resolution mass spectrum, and expectations derived from the other ring expansions, cannot be considered completely secure since a full proton spectrum is not attainable.



Thermolysis of either geometric isomer of **38**, obtainable by separation of the diastereomeric silylcarbinols precursors prior to Peterson olefination, was performed at reflux in diglyme (bp 162 °C) for 30 min. The low temperature required in this case is readily understandable on the basis of the extra delocalization of the diradical intermediate. The regioisomers **60** and **61** were produced in a 1.0:1.1 ratio regardless of the stereochemistry of the reactant (eq 17). The chemical shifts ($CDCl_3$) of the methyl groups of **60** and **61**, δ 1.10 and 1.09, respectively, are consistent with the exo stereochemistry expected on the basis of the results presented above.



The regioselectivity observed for bridgehead substituted substrates was attributed to the steric interactions of the bridgehead methyl group. However a remarkable and unanticipated feature

(21) Osborn, J. A.; Jardine, F. H.; Young, J. F.; Wilkinson, G. *J. Chem. Soc.* **1966**, 1911.

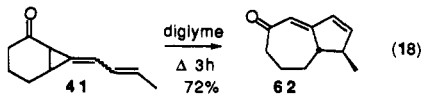
(22) Marshall, J. A.; Partridge, J. J. *Tetrahedron* **1969**, 2159.

(23) The stereochemical assignments of **55** and **56** are based on the stereochemistry of **50**, which is derived from the *trans*-allylidenecyclopropane **33**, after its conversion to the known **53** (eq 11). This analysis assumes that the phenylthio group would not alter the predicted stereochemical outcome of the rearrangement.

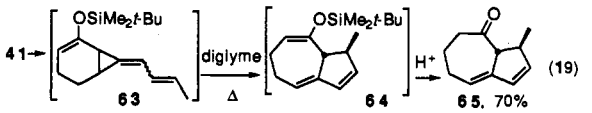
(24) The exo and endo assignments were made by comparing the chemical shifts of the *exo*-methyl group of **57** (δ 1.07) and the *endo*-methyl group of **58** (δ 0.86) with the chemical shifts of the closely analogous known compounds **53** and **54**, eq 11.

(25) Heathcock, C. L.; Graham, S. L.; Pirrung, M. C.; Plavac, F.; White, C. T. The Total Synthesis of Natural Products; ApSimon, J., Ed.; J. Wiley and Sons: New York, 1982; Vol. 5, pp 333–384.

of these rearrangements is that even substrates lacking a bridgehead methyl group can yield products with a high degree of regioselectivity as illustrated by the following examples. Heating either geometric isomer of allylidenecyclopropane **41** at reflux in diglyme for 3 h leads to a highly regioselective rearrangement producing enone **62** as the only product (eq 18). In gratifying contrast, thermolysis of **63**, derivable from **41** by silylation, under analogous conditions, shows a reversal of regiochemistry giving the opposite regioisomer **65** after hydrolysis of the enol silyl ether **64** (eq 19).[26] A ^{1}H NMR analysis of the crude reaction mixture (before hydrolysis) revealed that only one major product was formed and its spectrum is consistent with the structural features of **64**.[28] One would have expected the silyl group to perturb the product distribution in the opposite direction if steric crowding in the transition state for ring closure plays a major role in the reaction pathway.



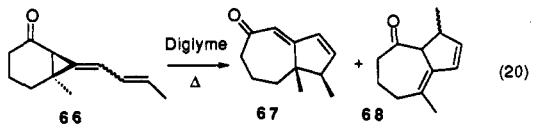
(18)



(19)

The gratifying regiochemical control demonstrated in eqs 18 and 19 is evidently the result of the distal nonring allylic radical site seeking out the most electron rich radical site of the ring. Consistent with this concept is the nonselectivity demonstrated in eq 17 in which the methylene substituent is intermediate between the carbonyl and enol silane substituents in electron donating ability.

A situation was then devised in which the "directing" effect of a bridgehead methyl group (see eq 9) and a carbonyl group are in opposition. The rearrangement of **66** allows for a competition between steric and electronic effects. This allylidenecyclopropyl ketone could be generated by PDC oxidation of the alcohol generated by reductive lithiation of **10** followed by Peterson olefination with *trans*-crotonaldehyde in the usual way. The rearrangement of either geometric isomer of **66** produced a 3:1 mixture of **67** and **68** (eq 20).[29] It should be noted that the major product results from radical recombination at the more sterically encumbered position. In all of the other cases that we have studied (including examples in the total synthesis section) in which the allylidenecyclopropane contains a bridgehead methyl group, the major product results from closure at the less substituted bridgehead.



(20)

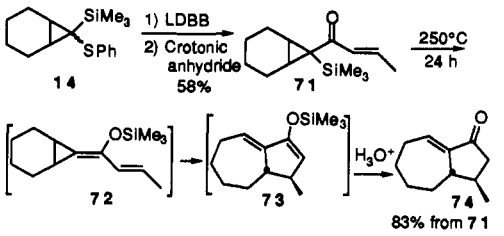
Having determined that carbonyl functionality can be incorporated into the seven-membered ring on the carbon atom adjacent to the ring junction or two removed from the junction, we turned our attention to the syntheses of hydroazulene type systems possessing carbonyl functionality on the five-membered ring. One

(26) The stereochemistry of **62** and **65** were assigned from prior results. The chemical shifts ($CDCl_3$) of their methyl groups are δ 1.17 and δ 1.07, respectively. Olefination of **62** with triphenylmethylenephosphorane[27] produced compound **60** that was identical to that obtained by rearrangement of **38**. Further evidence that **62** is not the (presumably less stable) endo isomer can be inferred from its failure to epimerize upon treatment with potassium *tert*-butoxide.

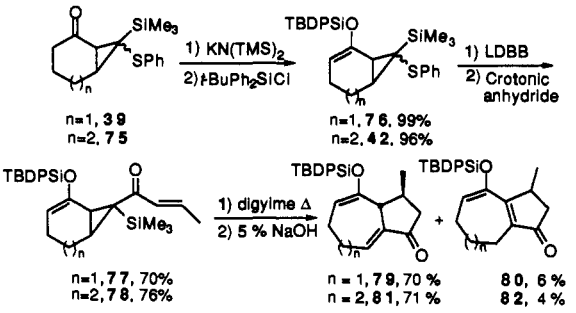
(27) Fitjer, L.; Quabeck, U. *Synth. Commun.* **1985**, *15*, 855.

(28) Significant ^{1}H NMR peaks of **64** in $CDCl_3$, δ 5.88 (dd, J = 5.5, 2.0 Hz, 1 H), δ 5.76 (dd, J = 5.5, 2.1 Hz, 1 H), δ 5.51 (m, 1 H), δ 4.96 (td, J = 7.1, 2.1 Hz, 1 H), δ 1.13 (d, J = 6.9 Hz, 3 H).

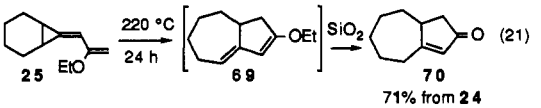
Scheme I



Scheme II



of the methods that we have developed involves masking the carbonyl as an enol ether, a procedure that is necessary for the rearrangement to take place. Sealed tube thermolysis of **25** afforded the rearranged enol ether **69** which was not isolated but could be hydrolyzed in the same vessel to the enone **70** produced in 71% yield from the Peterson olefination precursor **24** (eq 21).



(21)

Another extension of the allylidenecyclopropane rearrangement was possible via a related thermal ring expansion reaction whereby the allylidenecyclopropane is generated from a thermal Brook rearrangement[30] of an acylcyclopropylsilane. The general reaction sequence is shown in Scheme I. The acylcycloproplysilane is easily prepared by treating the α-lithiosilane, generated by reductive lithiation, with excess crotonic anhydride. Thermolysis of **71** involves rearrangement to **72** which then undergoes an allylidenecyclopropane rearrangement to **73**. Enone **74** was isolated from the one pot transformation from **71** in 83% yield after the rearranged product **73** was briefly treated with dilute acid.

We now had methods for introducing functionality on either of the fused rings. In order to further expand the utility of this rearrangement, we sought to combine the newly discovered regioselectivity and the method presented above which would lead to useful functionality on both rings of the rearrangement product. We also demonstrate that the allylidenecyclopropane rearrangement can be used to generate 8,5 ring systems.

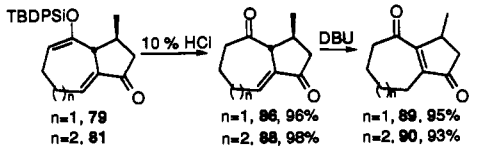
Using the general sequence shown in Scheme II, we were able to prepare the desired acyl(cyclopropyl)silanes **77** and **78**. First the cyclopropyl ketones had to be transformed into the silyl enol ethers which were subsequently reduced with LDBB. Trapping of the resultant anions with crotonic anhydride produced the desired acyl(cyclopropyl)silanes in good yields. The rearrangement of **77** and **78** for 4 h in refluxing diglyme once again proved to be remarkably regioselective. The enones **79** and **81** were

(29) A control experiment showed that the endo epimer of **68** is not stable to the reaction conditions and is converted to the exo isomer. Most of the endo epimer of **68** presumably arises by removal of the particularly acidic bridgehead proton α to the carbonyl group. The configurations of the endo and exo epimers of **68** were determined by a comparison NOE experiment of a 2.5:1.0 mixture of epimers. A strong NOE interaction between the methyl protons and the bridgehead proton was observed for the major isomer, while no interaction was observed for the minor isomer.

(30) Brook, A. G. *Acc. Chem. Res.* **1974**, *7*, 77.

isolated after briefly treating the reaction mixture with dilute base which selectively hydrolyzes the trimethylsilyl enol ether. There was also a small amount of the prototropic shift products **80** and **82** produced under the reaction conditions.

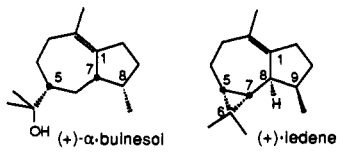
Because the trimethylsilyl enol ether could be selectively cleaved in the presence of the *tert*-butyl(diphenyl)silyl enol ether, it was possible to generate the monoprotected diketones **79** and **81**. This particular functionality could prove useful for further elaboration. Hydrolysis of **79** (or **81**) to the keto enone **86** (or **88**) could be carried out with 10% HCl without any double bond migration. However isomerization to a completely conjugated system could be accomplished by treating **86** (or **88**) with 1,8-diazabicyclo-[5.4.0]undec-7-ene (DBU) (eq 22).



(22)

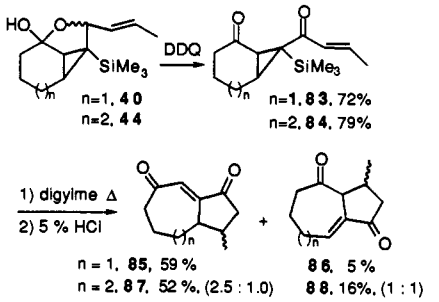
Our attempt to synthesize **83** and **84**, which were expected to be complementary in the regiochemistry of their rearrangement to **77** and **78**, initially presented difficulties. The attempted oxidation of **40** with manganese dioxide or under Swern[31] conditions gave no detectable amount of the desired product **83**. The attempted oxidation of lactol **40** with pyridinium dichromate (PDC)[32] gave mostly allylic rearrangement oxidation product of the ring-opened hydroxyketone. However, oxidation with 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ)[33] gave the desired diketones in good yields (Scheme III). As expected the major rearrangement product conforms to the regioselectivity expected with the carbonyl "directing group". However, the rearrangement of the two homologues show a significant difference in regioselectivity as well as stereoselectivity.[34]

Synthetic Studies on Racemic α-Bulnesol and (+)-Ledene. Thus, allylidenecyclopropanes in which the small ring is fused to a cyclohexane ring have been shown to be efficient synthetic tools for constructing the hydroazulene skeleton. Our fundamental strategy addressed the synthetic challenge that many of the naturally occurring sesquiterpenes possess an endo methyl group on C-8. The discovery of the partially stereospecific "*cis* to *endo*" ring expansion allows the construction of 8-(*endo*-methyl)bicyclo-[5.3.0]deca-1,9-dienes. Utilizing this new technology, we set out to attempt separate total syntheses of two naturally occurring hydroazulenic sesquiterpenes, the racemic form of α-bulnesol and (+)-ledene.

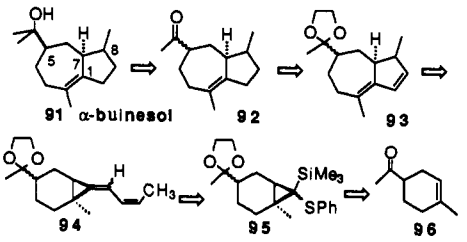


Prior to the synthetic work to be described in this report, five total syntheses,[22,35] and one synthesis from another natural product,[36] of α-bulnesol[37] had been reported. The major points of our retrosynthetic analysis of α-bulnesol are presented in

Scheme III



Scheme IV

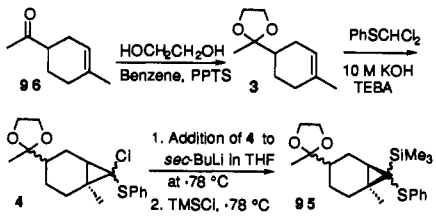


Scheme IV. The 1-hydroxy-1-methyl ethyl group appended to C-5 of α-bulnesol may be derived from the corresponding acetyl function of **92** via known methods.[38] Previous investigators[22,36] have demonstrated that the configuration at C-5 of **92** may be adjusted largely to the correct diastereomer by base induced epimerization α to the carbonyl functionality. This manipulative luxury renders the stereochemistry of this center inconsequential during further retrosynthetic analysis. Turning our attention to the proper installation of the thermodynamically less favorable C-8 *endo*-methyl group[22] of bicyclo[5.3.0]deca-1,9-diene **93**, we planned to exploit the newly discovered stereocontrol of the diradical rearrangement. The requisite *cis*-allylidenecyclopropane **94** for this proposed rearrangement could be assembled from the reductive lithiation–Peterson olefination sequence of 1-methyl-4-(2-methyldioxolan-2-yl)-7-(phenylthio)-7-(trimethylsilyl)bicyclo[4.1.0]heptane (**95**). The details of the total synthesis of α-bulnesol are reported below.

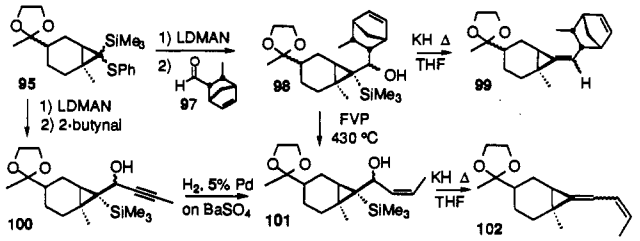
For the preparation of cyclopropane **95**, dioxolane **3**, produced in quantitative yield from Diels–Alder adduct **96**,[39] was cyclopropanated by our modified phase transfer catalysis conditions to afford a mixture of four chlorocyclopropane isomers collectively designated as **4** in 84% yield.[40] Because further chemical manipulations did not require separation, the isomeric mixture of chlorocyclopropanes **4** was subjected to chlorine–lithium exchange conditions and the resulting cyclopropyllithium was subsequently captured with TMSCl. The desired 7-(phenylthio)-

(31) Mancuso, A. J.; Huang, S.-L.; Swern, D. *J. Org. Chem.* **1978**, *43*, 2480.
(32) Corey E. J.; Suggs J. W. *Tetrahedron Lett.* **1975**, *17*, 2647.
(33) Braude E. A.; Linstead R. P.; Woolridge, K. P. H. *J. Soc. Chem.* **1956**, 3070.
(34) The major isomer of **87** was assigned an *exo*-methyl group based on NOE enhancement experiments. Presumably, stereochemical equilibration of the exo isomers of **87** and **88** occurs due to the high acidity of the bridgehead protons.
(35) Marshall, J. A.; Partridge, J. J. *J. Am. Chem. Soc.* **1968**, *90*, 1090. Kato, M.; Kosugi, H. L; Yoshikoshi, A. *J. Chem. Soc., Chem. Commun.* **1970**, 185. Heathcock, C. H.; Ratcliffe, R. *J. Am. Chem. Soc.* **1971**, *93*, 1746. Anderson, N. H.; Uh, H.-S. *Synth. Commun.* **1973**, *3*, 115. Tanaka, M.; Suemune, H.; Sakai, K. *Tetrahedron Lett.* **1988**, 1733.
(36) Paknikar, S. K.; Pednekar, P. R.; Chakravarti, K. K. *Indian J. Chem.* **1979**, *18B*, 178.
(37) For absolute stereochemistry determination, see: Sato, T.; Minato, H.; Shiro, H.; Koyanna, H. *J. Chem. Soc., Chem. Commun.* **1966**, 363. Minato, H. *Tetrahedron Lett.* **1961**, 280. Takeda, K.; Minato, H. J. *Tetrahedron Lett.* **1960**, 33. Dolejs, L.; Mironov, A.; Sõrm, F. *Tetrahedron Lett.* **1960**, 18.
(38) For preparations of the alcohol from the corresponding acid, see: Anderson, N. H.; Uh, H.-S. *Tetrahedron Lett.* **1973**, 2079. From the corresponding ketone, see: ref 36. From the corresponding ester, see: Kato, M.; Kosugi, H. L; Yoshikoshi, A. *J. Chem. Soc., Chem. Commun.* **1970**, 185; Tanaka, M.; Suemune, H.; Sakai, K. *Tetrahedron Lett.* **1988**, 1733; also ref 22.
(39) Lutz, E. F.; Bailey, G. M. *J. Am. Chem. Soc.* **1964**, *86*, 3899. Also commercially available from Aldrich Chemical Company.
(40) The relative configuration about the C-4 carbon atom of **4** was assigned from literature precedents[41] and from the chemical shift of the C-4 proton of each isomer. The assignments for the relative configuration at C-4 of **4** were supported by the chemical shifts of the C-4 proton resonance signals in their separate ^{1}H NMR spectra. The resonance of the C-4 proton of the major isomer was found to exhibit an upfield chemical shift (δ 2.05) relative to the corresponding proton signal (δ 2.21) of the minor isomer. This difference in chemical shift for axial and equatorial proton resonance signals has been noticed as a general trend for rigid cyclohexane rings.[42] Analytical HPLC analysis of the same product mixture indicated that the less polar, presumably endo,[43] phenylthio isomers were minor components (less than 10% of the mixture) and that the *endo*- to *exo*-dioxolanyl ratio of the *exo*-phenylthio isomer was approximately 9:1.

Scheme V



Scheme VI

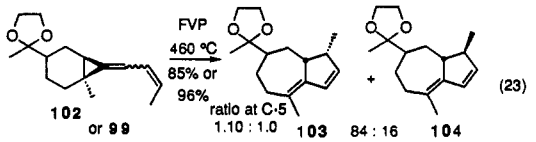


7-(trimethylsilyl)bicyclo[4.1.0]heptanes were then isolated in 90% yield as a mixture of isomers, collectively designated as **95** (Scheme V).[44]

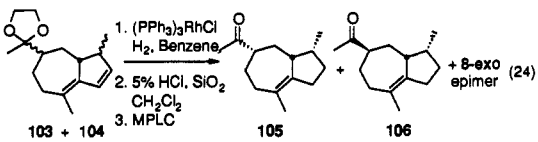
These efforts afforded an expeditious route to **95**, and we could focus our attention on synthesizing the racemic version of the natural product α-bulnesol **91**, a guaiazulene possessing an *endo*-methyl group at the C-8 position. This relative stereochemistry is energetically disfavored[22] (relative to its exo epimer) and presents itself as a synthetic challenge. Based upon our preliminary studies, we felt that we could assemble the bicyclo-[5.3.0]decane skeleton with concurrent installation of an endo C-8 methyl group by the stereospecific diradical rearrangement. Establishing a *cis* geometry about the distal or disubstituted allylidenecyclopropane olefinic group would provide the key for accessing the desired stereochemistry at the C-8 position of the bicyclo[5.3.0]decane ring skeleton.

We were able to prepare the aforementioned *cis*-olefin by three methods (Scheme VI). Our initial efforts utilized the endo aldehyde **97**[17] to prepare silylcarbinol **98** (61% yield). As found earlier for such reductive lithiation procedures (see above and footnote 4a), the epimeric mixture about C7 was converted to a single C7 epimer configuration in **100**. This material was then treated with potassium hydride to induce the Peterson olefination, and the resulting alkylidenecyclopropane **99**, a *cis* olefin equivalent via a retro Diels–Alder reaction, was isolated in 94% yield. In a variant of the above procedure, **98** was subjected to FVP conditions. As expected, the retro Diels–Alder elimination of cyclopentadiene took place and the resulting *cis*-olefin **101** was isolated in 53% yield; *trans*-olefin was not observed. This *cis* olefin (**101**) could also be prepared by a more conventional route. Treatment of the major isomer of **95** with LDMAN and then 2-butynal (available from the oxidation of 2-butynol[45]), followed by protic workup, afforded **100** in 96% yield as a mixture of two diastereomers (ratio of 6:1) which were separable by column chromatography. Hydrogenation of the major alkynol with Lindlar's catalyst produced in 96% yield the same compound (**101**) that was obtained by FVP of **98**. Olefination of **101**, a single diastereomer prepared from the reduction sequence, provided a single allylidenecyclopropane (**102**) in 94% yield.

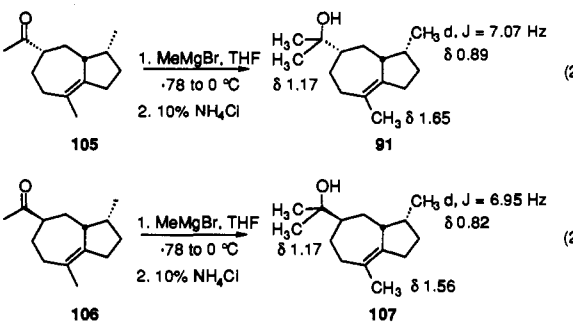
Subjecting **102** to FVP conditions produced the expected bicyclo[5.3.0]deca-1,9-dienes **103** as a pair of C-5 epimers in a 1.1:1.0 ratio (by capillary GC) and 85% yield. However, the sample was also tainted with approximately 15% of the C-8 epimer, **104**, as judged by integration of the methyl doublets in the ^{1}H NMR spectrum of the unchromatographed reaction oil.[46] Similarly, subjecting **99** to FVP at 460 ± 10 °C efficiently induced both the retro-Diels–Alder reaction and the double ring expansion reaction producing an inseparable mixture (84:16) of bicyclo-[5.3.0]deca-1,9-dienes, **103**, also as a pair of C-5 epimers in a 1.1:1.0 ratio, and **104**, in 91% overall yield (eq 23). Fortunately, derivatives of **104** could be removed by MPLC at a later stage.



Treating **103**, in the presence of **104**, with Wilkinson's catalyst under 1 atm of hydrogen led to the efficient reduction of the disubstituted olefin group of **103** resulting in the monoalkene (eq 24). After removal of the catalyst, the reaction mixture was treated with an aqueous slurry of silica gel and mineral acid in CH_2Cl_2[47] in order to liberate the diastereomeric ketones **105** and **106**. At this stage, the C-8 exo isomers, derived from **104**, were removed by MPLC from the endo epimers **105** and **106**, which were isolated in 47% and 43% yield, respectively.



To complete the synthesis of α-bulnesol, **105** was treated with methyl magnesium bromide to afford racemic α-bulnesol in 94% yield (eq 25).[22] The ^{1}H NMR spectrum of the isolated material (**91**) was identical to the published spectral data.[22] Alcohol **107** was prepared in similar fashion in 93% yield (eq 26). Since it has already been shown that base induced epimerization at C-5 bearing carbonyl functionality leads mainly (ester function),[22] and possibly almost completely (acetyl group)[36] to the desired stereochemistry, it appears that **106** could be converted mainly to **105**, thus considerably improving the overall yield of 16% for this approximately 10-step synthesis.



(+)-Ledene (**108**), a member of the aromadendrane family of sesquiterpenes, was first isolated from the essential oil of the liver wort *Bazzania trilobata*.[48] Its absolute configuration has been

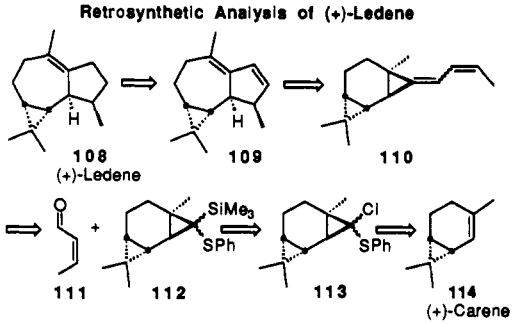
(41) Rickborn, B.; Lwo, S. *J. Org. Chem.* **1965**, *30*, 2212 and references cited therein.

(42) Silverstein, R. M.; Bassler, C. G.; Morill, T. C. *Spectrometric Identification of Organic Compounds*, 4th ed.; John Wiley & Sons, 1981; pp 188 and 229.

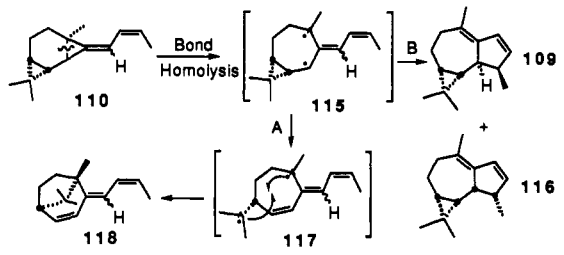
(43) Bhupathy, M. Ph. D. Thesis, University of Pittsburgh, 1985, p. 69.

(44) ^{1}H NMR spectral analysis of **95** revealed that the major component, 80% of the mixture, possessed an *exo*-phenylthio group[41] and an assumed *endo*-dioxolanyl functionality. The assignment of the latter aspect of the stereochemistry is based on mechanistic considerations and NMR analysis as described in the thesis of M. L. Romberger.[16] However it is inconsequential to the present study as the stereochemical relationship between the carbon atom bearing the dioxolanyl group and those at the bridge is destroyed during the ring expansion; furthermore, C-7 later becomes an sp^2 center. Therefore, the four isomers of **95** could be treated as a single substrate during the rest of the synthesis or, for purposes of ease of isolation and identification, the major isomer could be used. In order to provide conclusive evidence that **95** was indeed a mixture of *endo*- and *exo*-dioxolane isomers, a small amount of **95** was treated with LDMAN and the resulting α-lithiosilanes captured with TMSCl. The presence of four upfield (δ 0.18–δ 0.01) resonance signals in the ^{1}H NMR spectrum of the reaction product oil confirmed the presence of *endo*- and *exo*-dioxolane isomers in a ratio of 9:1.

Scheme VII



Scheme VIII

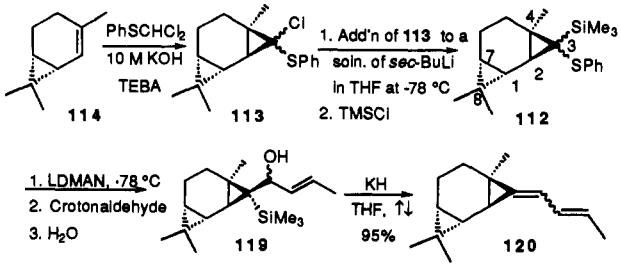


determined.[49] Aromadendranes are similar to hydroazulenes in that they both contain the bicyclo[5.3.0]decane carbon skeleton; however, aromadendranes, possess a geminal dimethyl cyclopropane ring fused to the C-5 and C-7 carbon atoms of the hydroazulene framework. (+)-Ledene also possess a contrathermodynamic architecture; the C-7 proton and the C-9 methyl group lie on opposite faces of the molecule, placing the methyl group in the endo orientation. We considered this molecule to be an attractive synthetic target and another test for our method of bicyclo[5.3.0]decane synthesis.

Our retrosynthetic dissection of (+)-ledene (**108**) proceeded as depicted in Scheme VII. We realized that our target molecule was merely the reduction product of diene **109**. This diene may in turn be synthesized by an allylidenecyclopropane to alkylidenecyclopentene rearrangement. We therefore focused our attention on preparing allylidenecyclopropane **110**. Based upon our previous results, we expected both *E* and *Z* isomers of **110** around the innermost carbon–carbon double bond to undergo the thermal rearrangement with equal ease. Allylidenecyclopropanes **110*E*** and **110*Z*** could be synthesized by standard protocol from "*cis*-crotonaldehyde" (**111**) and the tricyclo[5.1.0.0^{2,4}]octane derivative **112**.[50] This (phenylthio)(trimethylsilyl)cyclopropane was thought to be only two chemical transformations away from 3,7,7-trimethylbicyclo[4.1.0]hept-2-ene (**114**). Fortunately, **114** is the naturally occurring and commercially available (+)-2-carene whose absolute configuration is known.[51]

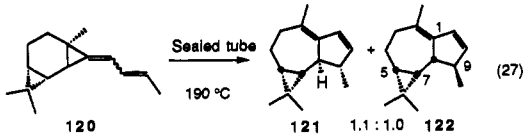
The critical step of the proposed synthesis would be the diradical rearrangement of **110** to **109**. Based upon our previous observations, we expected the thermolysis of **110** to produce a mixture of tricyclo[6.3.0.0^{5,7}]undeca-2,10-diene[52] isomers **109** and **116** (Scheme VIII). However, we also acknowledged the possibility of a competitive and detrimental process, the radical induced ring opening of the geminal dimethyl cyclopropane ring (i.e., **115** → **117**) to form triene **118**. This process (**115** → **117**), better known as the "cyclopropyl radical clock reaction",[53] has precedence and was considered to be a serious threat to our synthetic endeavor. Despite the apparent intermediacy of a notoriously unstable cyclopropylcarbinyl radical **115**, we were successful in the synthesis of (+)-9-epiledene, illustrating the remarkable efficiency of this intramolecular radical coupling process. However, synthesis of ledene itself turns out to be beyond the scope of this method as outlined below.

Scheme IX



In order to ascertain the magnitude of the "radical clock" reaction's interference with the desired rearrangement, a model study was deemed necessary. *trans*-Allylidenecyclopropane **120**, which is simpler to prepare than **110**, was envisaged as the logical chemical emulator of **110**. Thus, (1*R*,2*S*,4*R*,7*R*)-4,8,8-trimethyl-3-(phenylthio)-3-(trimethylsilyl)tricyclo[5.1.0.0^{2,4}]octane (**112**) was prepared from (+)-2-carene (**114**) in two steps (Scheme IX). Cyclopropanation of the trisubstituted olefin group of **114**, using our modified Makosza method, produced **113** in good yield and the carbenoid addition occurred with exclusive exo facial selectivity.[54] Conversion of the endo/exo phenylthio mixture of **113** to the (phenylthio)(trimethylsilyl)cyclopropane **112** was executed by slow addition of the chlorinated cyclopropanes **113** to a solution of *s*-butyllithium in THF at −78 °C, followed by addition of TMSCl.[55] Sequential treatment of **112** with LDMAN and crotonaldehyde produced a 7:1 mixture of silylcarbinols **119**, separable by MPLC, in 88% yield. The diastereomeric alcohols **119** were separately treated with KH in order to forge the trisubstituted olefins **120**.

Sealed tube thermolysis reactions of the separate geometric isomers of **120** were performed at various temperatures: 160, 190, 200, 210, and 217 °C. The optimum temperature for the rearrangement was found to be 190 °C, and the separable product mixture contained as the major components two isomeric dienes **121** and **122** in 88% overall yield (eq 27).[56]



Hydrogenation of the disubstituted olefin group of **121** using Wilkinson's catalyst under 1 atm of hydrogen gas quantitatively produced the corresponding monoalkene **123** (eq 28).[57] Comparing the ^{1}H NMR spectrum of **123** with the ^{1}H NMR spectrum of authentic (+)-ledene[58] indicated that it was merely epimeric with (+)-ledene at the C-9 carbon atom.

(45) Lunt, J. C.; Sondheimer, F. *J. Chem. Soc.* **1950**, 3361. Sauer, J. C. *Org. Synth.* **1950**, *36*, 66.

(46) For spectral comparison, an authentic sample of **104** as a 1.7:1 mixture of C-8 epimers could be prepared by a similar procedure starting from the trans isomer of **101**, prepared from *trans*-crotonaldehyde. See: Ph.D. Thesis of M. L. Romberger, pp 90, 91, 154–156.[16]

(47) Huet, F.; Pellet, M.; Conia, J. M. *Tetrahedron Lett.* **1977**, 3505. Huet, F.; Lechevallier, A.; Pellet, M.; Conia, J. M. *Synthesis* **1978**, 63.

(48) Konecny, K.; Streibl, M.; Vasickova, S.; Budesinsky, M.; Saman, D.; Ubik, K.; Herout, V. *Collect. Czech. Commun.* **1985**, *50*, 80.

(49) Kyrialov, N. P. *J. Gen. Chem. U.S.S.R.* **1951**, *21*, 2077; *Chem. Abstr.* **1952**, *46*, 6633,. Büchi, G.; Hofheinz, W.; Paukstelis, J. U. *J. Am. Chem. Soc.* **1966**, *88*, 4113.

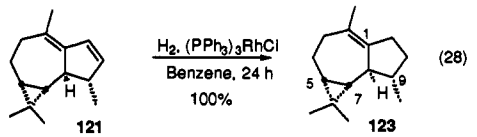
(50) The numbering and naming of the dicyclopropanated cyclohexane materials was derived from the examples published: Oku, A.; Tsuji, H.; Yoshida, M.; Yoshiura, N. *J. Am. Chem. Soc.* **1981**, *103*, 1244.

(51) Brown, H. C. *J. Am. Chem. Soc.* **1967**, *89*, 1925.

(52) For the IUPAC nomenclature of polycycles, see: *CRC Handbook of Chemistry and Physics*, 60th ed.; Weast, R. C., Ed.; CRC Press: Boca Raton, FL, 1981; pp C-1–32.

(53) Griller, D.; Ingold, K. U. *Acc. Chem. Res.* **1980**, *13*, 317. Also, see: Clive, D. *J. Chem. Soc., Chem. Commun.* **1989**, 332–35.

(54) Mühlstädt, M.; Phiet, H. V.; Graefe, J.; Frischleder, H. *Tetrahedron* **1968**, *24*, 6075. Mühlstädt, M.; Phiet, H. V.; Graefe, J.; Frischleder, H. *Tetrahedron* **1969**, *25*, 2081.

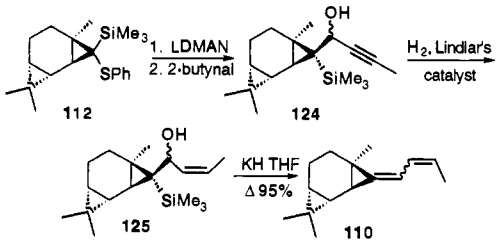


Having established the viability of our ring expansion method for synthesizing the tricyclo[6.3.0.0^{5,7}]undecane ring system, we prepared the necessary *cis*-allylidenecyclopropane **110** in the following manner (Scheme X). (Phenylthio)(trimethylsilyl)-cyclopropane **112** was sequentially treated with LDMAN and 2-butynal to give a 7:1 diastereomeric mixture of the propargylic alcohols **124**. After chromatographic separation of the mixture (MPLC), the major diastereomer was reduced to the *cis* olefin (**125**) by Lindlar's catalyst; overreduction was not observed. Treating **125** in the usual manner produced allylidenecyclopropane **110** of unassigned proximal alkene geometry.

In an attempt to effect the diradical rearrangement, a sample of **110** was distilled through a quartz tube (450 °C), and the distillate was analyzed by capillary GC and ^{1}H NMR. The GC trace of the FVP reaction product mixture appeared as a myriad of peaks with one major spike. ^{1}H NMR spectral analysis of the distillate indicates the presence of at least five different vinyl protons and one allylic methyl group appearing as a doublet of doublets at δ 1.81 (J = 6.94, 1.42 Hz). In an effort to isolate the compound representing the major peak of the GC trace, the reaction oil was subjected to flash column chromatography[59] (SiO_2, 12 in. × 30 mm, pentane, R_f 0.69), silver nitrate impregnated silica gel column chromatography (10% $AgNO_3$, 10 in. × 20 mm, pentane), and HPLC chromatography (Li-chrosorb, 4.6 mm × 25 cm column of noncommercial origin, hexane). All efforts to attain a single compound were unrewarded, and the structure of the compound which represents the major spike in the GC trace could not be definitively determined. Unable to secure the structure of the major component of the product mixture, we subjected the mixture to the identical hydrogenation conditions employed previously and then analyzed the product by capillary GC. A comparison of the retention times for the components of the hydrogenated mixture with that of authentic (+)-ledene[58] indicated its absence from the product mixture. At this stage our synthetic efforts were discontinued.

It is reasonable to assume that the allylic cyclopropane bond of **110** undergoes homolysis to the intermediate diradical **115** as appears to occur with the geometric isomer *trans*-allylidenecyclopropane **120**. Once formed, the diyl **115** has two likely pathways: pathway A, cyclopropylcarbinyl radical ring opening to homoallylic diradical **117** which may then recombine to triene **118**; pathway B, radical recombination to form a mixture of tricyclo[6.3.0.0^{5,7}]undec-1,10-dienes **109** and **116**. From our results, pathway B is far slower than A. It appears that the difference in reactivity between the *cis*- and *trans*-allylidenecyclopropane can be attributed to the steric interactions present during the formation of the alkylidenecyclopentene ring. Models show that in the case of the *cis*-allylidenecyclopropane, ring formation involves steric interactions between the methyl group and the cycloheptenyl ring. (This analysis assumes that the trans to exo–cis to endo stereoselectivity that we have observed is the direct result of the rotational barrier of 12–17 kcal of the allylic radical.[60] This rotational restriction of the appended allyl radical allows the relative configuration of the allyl radical to remain intact during the rearrangement.) Thus a decrease in the rate of cyclopentene formation may allow **115** to be consumed though other pathways. On the other hand, the *trans*-allylidenecyclopropane would not suffer from these steric interactions since the methyl group would project away from the cycloheptenyl ring. In this case the desired ring closure seems to be rapid enough to avoid destructive reaction pathways.

Scheme X



Conclusions

In addition to presenting a new, rather general, synthetic tool, the stereocontrolled double ring expansion of fused allylidenecyclopropanes, this work provides an excellent example of the power of reductive lithiation of phenyl thioethers for the preparation of carbanions. Because of the highly versatile nature of divalent sulfur, the methods presented here are far more general than any[10] now known to produce alkylidenecyclopropanes. The properties of divalent sulfur that are utilized here are α-chlorination, stabilization of carbene, a negative charge, and a positive charge on the carbon atom to which it is attached, ease of removal from a molecule by cuprous ion or reductive lithiation. Thus, a wide variety of geminal (phenylthio)silylcyclopropanes are readily available by several procedures and they are smoothly converted to α-lithiosilanes, substrates for the Peterson olefination.

With regard to the ring expansion, it is demonstrated that bicyclo[4.3.0], -[5.3.0], and -[6.3.0] systems can be prepared in this way. In addition a fused tricyclic system has been generated in this manner, and there is no reason to believe that tetracyclic systems would not result if another ring were to be fused to the ring that is fused to the cyclopropane ring in compounds such as **27**. Other useful features of the method are stereoselectivity and the ability to end up with ring systems bearing carbonyl groups at most of the positions of either or both of the two core rings of the product. Subsequent publications will report a mechanistic investigation of this type of reaction as well as a variation of the general concept that allows production of six-membered instead of five-membered rings by double ring expansions.

Experimental Section

General Methods. ^{1}H and ^{13}C NMR spectra were recorded on either a Bruker WH-300 or a Bruker AF-300, except where otherwise noted. Chemical shifts are reported in ppm relative to residual $CHCl_3$ or tetramethylsilane. Multiplicities are given as s (singlet), d (doublet), t (triplet), q (quartet), m (multiple), and br (broad). Infrared spectra were recorded using an IBM IR/32 FT-IR spectrophotometer and are reported in wave numbers (cm^{-1}). High resolution mass spectra were recorded on a CH-5 double focusing Varian MAT mass spectrometer or on a VG 70-SE mass spectrometer. Optical rotations were obtained as

(55) In order to remove any doubt of the geometric disposition of the adjacent cyclopropanes in **112**, the latter was treated with LDMAN and the resulting anion captured with TMSCl to afford a bis(trimethylsilyl) derivative **126** (see supplementary material) for which ^{1}H NMR analysis indicated that only one tricyclic compound was present. Drawing from the literature precedents[54] and the lack of coupling between the C-1 and C-2 protons in the ^{1}H NMR spectrum of **112** (this indicated that the dihedral angle between the aforementioned protons must then be very close to 90°), we concluded that the phase transfer cyclopropanation of (+)-2-carene had occurred exclusively onto the convex face during the cyclopropanation of 2-carene **114**.

(56) The relative ratio of isomers was determined by capillary GC and ^{1}H NMR spectra analysis to be 1.1:1.0. The relative stereochemistry of **121** and **122** rests upon the lack of proton–proton coupling between the C-7 and C-8 protons of **121** (their dihedral angle is approximately 90°) as well as later transformations.

(57) In our hands, the minor and less polar isomer (**122**) quickly underwent decomposition even when stored at low temperature under argon. Additionally, it was found to contain a very nonpolar impurity which was not possible to remove via conventional methods. Attempts to purify **122** led to the eventual destruction of this isomer.

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solutions in a 1-dm cell in a Perkin-Elmer 241 polarimeter. Silica gel 60 (40–60 um, E. Merck) was used for flash chromatography.

All reactions were performed under an argon atmosphere and standard precautions against moisture were taken. Tetrahydrofuran (THF) was distilled over sodium benzophenone ketyl. The preparation of lithium 1-(dimethylamino)naphthalenide (LDMAN)[61] and lithium 4,4′-di-*tert*-butylbiphenylide (LDBB)[62] has been described previously. In the reductive lithiations, nominal concentrations of 0.4 and 0.5 M, respectively, of LDMAN and LDBB were used. The actual concentrations were always somewhat less due to reaction of the lithium metal or the radical anion with moisture. Between 2.1 and 2.5 molar equiv of reducing agent were used depending on the relative humidity; in hot humid summer days the use of 2.5 equiv was found to be satisfactory, whereas in the winter the lower amounts were used.

7-Chloro-1-methyl-7-(phenylthio)bicyclo[4.1.0]heptane (2). To a one-necked, 50-mL round-bottomed flask which was capped with a rubber septum (pierced with an argon inlet and a small capillary tube) and contained a stirring bar, 25 mL of 10 M aqueous KOH, 1-methylcyclohexene (1.52 g, 15.8 mmol), and benzyltriethylammonium chloride (TEBA, 0.360 g, 1.58 mmol) was slowly added dichloro(phenylthio)methane[16,63] (4.58 g, 23.7 mmol) with the aid of a syringe pump (<1 mL/h). The resulting brown mixture was stirred for an additional 8 h after completion of addition. At this time, the reaction mixture was diluted with ether and water, transferred to a separatory funnel, and washed with water. After reextraction of the aqueous layer, the organic layers were combined, dried ($MgSO_4$), and concentrated under reduced pressure to yield 4.66 g of a dark brown oil. Flash chromatography (silica gel, hexanes) afforded 2.36 g (59%) a single isomer of **2** as a clear oil: IR (neat) 3050, 2936, 2866, 1699, 1653, 1586, 1480, 1026, 735, 689 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.28–7.36 (m, 4 H, phenyl), 7.10–7.21 (m, 1 H, phenyl), 1.93–2.10 (m, 2 H), 1.70–1.85 (m, 2 H), 1.34–1.50 (m, 2 H), 1.42 (s, 3 H, CH_3), 1.22–1.32 (m, 3 H); exact mass calcd for $C_{12}H_{17}ClS$ 254.0710, found 254.0709.

7-Chloro-1-methyl-4-(2-methyldioxolan-2-yl)-7-(phenylthio)bicyclo[4.1.0]heptane (4). The procedure was the same as for **2** starting with 1-methyl-4-(2-methyldioxolan-2-yl)cyclohexene (2.59 g, 14.2 mmol), dichloro(phenylthio)methane (4.14 g, 21.3 mmol), and TEBA (0.32 g, 1.4 mmol). Purification by flash chromatography (silica gel deactivated with 1% TEA, 5% ethyl acetate–hexanes) afforded 4.05 g (84%) of a 9:1 *endo*/*exo*-dioxolanylcyclopropane mixture in which the phenylthio groups were probably very predominantly in the exo configuration:[40] IR (neat, mixture of isomers) 3063, 1717, 1558, 1476, 1441, 1086, 1069, 1024 cm^{-1}; *endo*-dioxolanyl isomer ^{1}H NMR ($CDCl_3$) δ 7.29–7.39 (m, 4 H, exo phenyl), 7.18 (m, 1 H, exo phenyl), 3.85–4.00 (m, 4 H, OCH_2CH_2O), 2.05 (m, 1 H), 1.02–1.95 (m, 7 H), 1.41 (s, 3 H, bridge CH_3), 1.24 (s, 3 H, $C(OCH_2CH_2O)CH_3$); *exo*-dioxolanyl isomer ^{1}H NMR ($CDCl_3$) δ 7.29–7.39 (m, 4 H, exo phenyl), 7.18 (m, 1 H, exo phenyl), 3.85–4.00 (m, 4 H, ketal CH_2CH_2), 2.05 (m, 1 H), 1.02–1.95 (m, 7 H), 1.38 (s, 3 H, bridge CH_3), 1.23 (s, 3 H, $C(OCH_2CH_2O)CH_3$); exact mass calcd for $C_{18}H_{23}Cl$ 338.1107, found 338.1109.

7-Chloro-7-(phenylthio)bicyclo[4.1.0]-2-oxaheptane (5). The procedure was the same as for **2** starting with dihydropyran (4.61 g, 54.8 mmol), dichloro(phenylthio)methane (6.50 g, 33.7 mmol), and TEBA (0.050 g, 0.20 mmol). Standard workup and column chromatography (silica gel treated with 0.01% TEA, 25% benzene–hexane, R_f 0.29 and 0.22) gave 5.43 g (67.4%) of the probable[43] *exo*-phenylthio isomer of **5** and 0.78 g (9.6%) of the probable endo isomer: *exo*-phenylthio isomer IR (neat) 3098, 2965, 2930, 2863, 1480, 1439, 1239, 1156, 1067, 1026, 737, 691 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.30–7.43 (m, 4 H, phenyl), 7.19–7.27 (m, 1 H, phenyl), 3.80–3.88 (m, 1 H, equatorial OCH_2), 3.79 (d, J = 7.71 Hz, 1 H, cyclopropyl OCH), 3.41 (td, J = 11.29, 2.26 Hz, 1 H, axial OCH_2), 1.93–2.15 (m, 2 H) 1.72–1.88 (m, 1 H), 1.66 (ddd, J = 7.71, 7.71, 1.95 Hz, 1 H, cyclopropyl OCHC*H*), 1.37–1.48 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 134.1, 128.8, 127.8, 126.3, 64.3, 59.6, 54.1, 24.7, 20.6, 16.2; exact mass calcd for $C_{12}H_{13}OClS$ 240.0376, found 240.0375; *endo*-phenylthio isomer IR (neat) 3051, 2961, 2930, 2861, 1480, 1441, 1239, 1154, 1063, 1026, 739, 689 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.11–7.41 (m, 5 H, phenyl), 3.66–3.79 (m and d at δ 3.72, J = 7.67 Hz, 2 H, equatorial OCH_2 and OCH), 3.32 (ddd, J = 11.23, 11.23, 2.20 Hz, 1 H, axial OCH_2), 1.84–2.05 (m, 2 H), 1.63–1.81 (m, 1 H), 1.58 (ddd, J = 7.67, 7.67, 1.78 Hz, 1 H, cyclopropyl OCHC*H*), 1.27–1.39 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 131.2, 128.7, 128.1, 126.2, 64.0, 62.4, 53.0, 28.7, 20.8, 16.1; exact mass calcd for $C_{12}H_{13}OClS$ 240.0376, found 240.0376.

7-(Phenylthio)-7-(trimethylsilyl)bicyclo[4.1.0]-2-oxaheptane (6). A solution of the major isomer of **5**, probably exo, (0.330 g, 1.38 mmol) in THF (1 mL) was silylated by the procedure described for **31**. The resulting yellow mixture was then allowed to gradually warm to ambient temperature over a period of 10 h prior to the addition of a small amount of water. Standard workup and chromatography (silica gel, 5% ethyl acetate–hexane) afforded 0.220 g (57%, 80% based upon consumed starting material) of **6** as a single isomer: IR (neat) 3061, 2957, 2870, 1478, 1248, 1065, 841, 737, 693 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.21–7.26 (m, 4 H, phenyl), 7.03–7.09 (m, 1 H, phenyl), 3.73 (d, J = 6.60 Hz, 1 H), 3.65–3.73 (m, 1 H), 3.48 (dddd, J = 10.71, 9.27, 5.04, 1.44 Hz, 1 H), 2.16 (m, 1 H), 1.85–1.97 (m, 1 H), 1.63–1.79 (m, 1 H), 1.43–1.56 (m, 2 H), 0.18 (s, 9 H, endo $(CH_3)_3Si$); ^{13}C NMR ($CDCl_3$) δ 138.8, 128.4, 125.9, 124.2, 64.4, 63.6, 27.8, 20.5, 19.2, 17.2, 0.81; exact mass calcd for $C_{15}H_{22}OSSi$ 278.1161, found 278.1160.

7-Chloro-1-methoxy-7-(phenylthio)bicyclo[4.1.0]heptane (7). In a procedure identical to that for the preparation of **2**, 1-methoxycyclohexene (2.00 g, 17.8 mmol) was cyclopropanated to afford 2.85 g (64%) of **7** with the probable[43] *endo*-phenylthio isomer as the major component (6:1) after chromatography (silica gel treated with 0.01% TEA, 25% benzene–hexanes): IR (neat) 3061, 2940, 2860, 1583, 1480, 1440, 1206, 1105, 1073, 739, 691 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.36–7.43 (m, 2 H, phenyl), 7.25–7.36 (m, 2 H, phenyl) 7.18–7.24 (m, 1 H, phenyl), 3.48 (s, 3 H, OCH_3 of the *exo*-phenylthio isomer), 3.37 (s, 3 H, OCH_3 of the endo phenylthio isomer), 1.95–2.30 (m, 4 H), 1.61–1.73 (m, 1 H), 1.37–1.58 (m, 3 H), 1.22–1.37 (m, 1 H, cyclopropyl H); ^{13}C NMR ($CDCl_3$), endo phenyl thio isomer, δ 136.1 (s), 128.8 (d), 128.5 (d), 126.2 (d), 68.7 (s), 61.2 (s), 54.3 (q), 33.1 (d), 24.2 (t), 21.6 (t), 20.5 (t), 20.1 (t); exact mass calcd for $C_{14}H_{17}ClOS$ 268.0689, found 268.0690.

7-Chloro-1-methoxy-7-(phenylthio)bicyclo[4.1.0]hept-3-ene (8). In a procedure identical to that for the preparation of **2**, 1-methoxy-1,4-cyclohexadiene (2.00 g, 18.2 mmol) was cyclopropanated to afford 1.79 g (37%) of **8** with the probable[43] *endo*-phenylthio isomer as the major component (3:1) after chromatography (silica gel treated with 0.01% TEA, 25% benzene–hexane): IR (neat) 3032, 2934, 2897, 1584, 1480, 1107, 1049, 738, 711, 691, 662 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.36–7.43 (m, 2 H, phenyl), 7.25–7.36 (m, 2 H, phenyl) 7.18–7.24 (m, 1 H, phenyl), 5.50–5.63 (m, 2 H, vinyl H), 3.49 (s, 3 H, OCH_3 of the *exo*-phenylthio isomer), 3.40 (s, 3 H, OCH_3 of the *endo*-phenylthio isomer), 2.55–2.76 (m, 3 H), 2.16–2.28 (m, 1 H), 2.08 (d, J = 7.84 Hz, 1 H, cyclopropyl proton of *exo*-phenylthio isomer), 1.87 (d, J = 7.67 Hz, 1 H, cyclopropyl proton of *endo*-phenylthio isomer); ^{13}C NMR ($CDCl_3$), *endo*-phenylthio isomer, δ 138.6, 129.0, 128.4, 126.6, 123.0, 122.9, 66.8, 60.9, 54.8, 31.3, 25.4, 22.2; exact mass calcd for $C_{14}H_{15}ClOS$ 266.0530, found 266.0530.

7-Chloro-5-hydroxy-1-methyl-7-(phenylthio)bicyclo[4.1.0]heptane (9). In a procedure identical to that for the preparation of **2**, 3-methyl-2-cyclohexen-1-ol (1.89 g, 16.86 mmol) was cyclopropanated to afford 1.34 g (30%) of **9** as a mixture of isomers after chromatography (silica gel treated with 0.1% TEA, 15% ethyl acetate–hexanes): IR (neat) 3389, 2938, 2869, 1584, 1073, 967 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.18–7.49 (m, 5 H, phenyl), 4.23–4.32 (m, 1 H, C*H*OH major), 4.00–4.04 (m, 1 H, C*H*OH minor), 1.46 (s, 3 H, CH_3 major), 1.44 (s, 3 H, CH_3 minor), 1.22–2.08 (m, 8 H); exact mass calcd for $C_{14}H_{17}ClOS$ 268.0688, found 268.0689.

1-Methyl-5-(trimethylsiloxy)-7-(phenylthio)-7-(trimethylsilyl)bicyclo[4.1.0]heptane (10). A solution of **9** (0.51 g, 1.90 mmol) in THF (1 mL) was silylated by procedure described for **31**. Standard workup and chromatography (silica gel, 1% ethyl acetate–hexanes) afforded 0.38 g (53%) of **10** as a mixture of isomers. Some of the fractions contained the major isomer: IR (neat) 3060, 2950, 2859, 1584, 1482, 1250, 1007 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.48–7.52 (m, 2 H, phenyl), 7.17–7.22 (m, 2 H, phenyl), 7.01–7.06 (m, 1 H, phenyl), 4.42–4.51 (m, 1 H, SiOCH), 1.10–1.86 (m 10 H, including s at δ 1.44, CH_3), 0.20 (s, 18 H, both $(CH_3)_3Si$); exact mass calcd for $C_{20}H_{34}OSSi_2$ 378.1869, found 378.1854.

6-(Phenylthio)-6-(trimethylsilyl)bicyclo[3.1.0]hexane (11). Following the method for the preparation of **14**, cyclopentene oxide (4.6 g, 54.8 mmol) was cyclopropanated with the following reagents: *n*-BuLi (41.0 mL, 1.6 M, 66.0 mmol), (phenylthio)(trimethylsilyl)methane (13.0 g, 66.0 mmol), benzenesulfonyl chloride (11.7 g, 66.0 mol), *s*-BuLi (54 mL, 1.4 M, 75.6 mmol), and TMEDA (8.13 g, 70.0 mmol) to afford 11.1 g

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(78%) of **11** after flash chromatography (silica gel, hexanes): ^{1}H NMR ($CDCl_3$) δ 6.9–7.1 (m, 5 H, phenyl), 1.4–1.8 (m, 8 H), 0.0 (s, 9 H, $(CH_3)_3Si$); exact mass calcd for $C_{15}H_{22}SSi$ 262.1212, found 262.1212.

6-(1-Hydroxy-2-*trans*-buten-1-yl)-6-(trimethylsilyl)bicyclo[3.1.0]hexane (12). A solution of **11**[4a] (0.300 g, 1.14 mmol) in THF (0.5 mL) was treated with LDMAN for 45 min at -78 °C. A solution of crotonaldehyde (0.0880 g, 1.26 mmol) was added, and after 15 min the reaction mixture was quenched with moist THF. The following standard workup procedure for LDMAN reductive lithiations was performed. The solvent was partially removed under reduced pressure, and the residue was taken up in ether and successively washed with 5% NaOH (twice), water, 5% HCl (twice), and finally with basic brine. The solvent was removed from the dried ($MgSO_4$) organic phase and column chromatography (silica gel, 5% ethyl acetate–hexane) to afford 0.235 g (91%) of **12** after flash chromatography (silica gel, 5% ethyl acetate–hexane): IR (neat) 3463, 3041, 3001, 2951, 2872, 1456, 1246, 1003, 967, 839, 749, 685 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.60–5.68 (m, 2 H, vinyl H), 3.85 (br s, 1 H, C*H*OH), 1.85–2.12 (m, 3 H), 1.56–1.80 (m, 3 H), 1.71 (dd, J = 4.66, 1.03 Hz, 3 H, vinyl CH_3), 1.39–1.55 (m, 2 H), 1.32 (br s, 1 H, OH), –0.01 (s, 9 H, $(CH_3)_3Si$); ^{13}C NMR ($CDCl_3$) δ 134.19, 124.79, 72.34, 29.2, 29.1, 28.5, 25.7, 25.4, 23.3, 17.7, –0.42; exact mass calcd for $C_{13}H_{24}OSi$ 224.1596, found 224.1596.

6-(*trans*-2-Butenylidene)bicyclo[3.1.0]hexane (13). A solution of **12** (0.200 g, 0.891 mmol) in THF (10 mL) was stirred at ambient temperature as hexane-washed KH powder (0.0710 g, 1.78 mmol) was added all at once. The reaction mixture was heated at the reflux temperature of THF for 30 min, and the cooled mixture was then transferred to a separatory funnel containing brine overlaid with ether. Simple extraction, drying ($MgSO_4$) of the organic layer, and solvent removal under reduced pressure afforded 0.116 g (95%) of **13** in high purity and high yield: IR (neat) 3041, 2928, 2849, 1461, 1450, 1248, 970, 962 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 6.52 (d, J = 9.10 Hz, 1 H, CC*H*), 6.32 (ddd, J_{trans} = 15.43, J = 9.10, 1.02 Hz, 1 H, CCHC*H*), 5.61 (dq, J_{trans} = 15.43, J = 6.81 Hz, 1 H, CH_3CH), 1.70 (br d, J = 6.81 Hz, 3 H, CH_3) 1.15–1.52 (m, 6 H), 0.90–1.02 (m, 2 H, cyclopropyl H); ^{13}C NMR ($CDCl_3$), δ 133.1, 130.9, 126.7, 120.2, 30.0, 29.8, 21.5, 21.0, 20.8, 18.2; exact mass calcd for $C_{10}H_{14}$ 134.1096, found 134.1096.

7-(Phenylthio)-7-(trimethylsilyl)bicyclo[4.1.0]heptane (14).[4a,11a] A solution of (phenylthio)(trimethylsilyl)methane (11.0 g, 56.0 mmol) and tetramethylethylenediamine (TMEDA) (16.0 g, 138 mmol) in THF (125 mL) was stirred at 0 °C as *n*-BuLi (55.2 mL, 1.25 M, 69.0 mmol) was slowly added. After 1 h, cyclohexene oxide (7.00 g, 71.4 mmol) was slowly added to the yellow solution of organolithium and the resulting mixture was allowed to warm to room temperature and was stirred for 4 h. The solution was then cooled to 0 °C, and benzenesulfonyl chloride (12.6 g, 71.4 mmol) was slowly added. The resulting mixture was stirred for 30 min at 0 °C prior to the addition of TMEDA (16.1 g, 138 mmol) and *s*-BuLi (61.8 mL, 1.12 M, 69.2 mmol). This reaction mixture was stirred for 12 h at ambient temperature before being quenched with water. The aqueous phase was extracted with ether, and the resulting combined organic layer was successively washed with 5% HCl, 5% NaOH, and brine. The organic layer was dried with $MgSO_4$, and the solvent was removed by rotary evaporation. Column chromatography (silica gel, hexanes) afforded 11.6 g (75%) of an endo/exo mixture of **14**: IR (neat) 2950, 1590, 1490, 1440, 1250 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.2–7.4 (m, 5 H, phenyl), 1.0–1.8 (m, 10 H), 0.0 and –0.3 (s, 9 H, $(CH_3)_3Si$); ^{13}C NMR ($CDCl_3$) δ 138.4, 128.1, 126.3, 123.9, 22.0, 20.5, 19.3, –2.3; exact mass calcd for $C_{16}H_{24}SSi$ 276.1368, found 276.1358.

7-(1-Hydroxy-*trans*-2-buten-1-yl)-7-(trimethylsilyl)bicyclo[4.1.0]heptane (15). A solution of **14** (1.00 g, 3.62 mmol) in THF (1 mL) was treated with LDMAN for 30 min at -78 °C. A solution of crotonaldehyde (0.270 g, 3.89 mmol) in THF (0.5 mL) was added, and the mixture was worked up as for **12** to afford 0.863 g (83%) of **15**: IR (neat) 3476, 3020, 2930, 2860, 1448, 1246, 999, 837 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.58–5.65 (m, 2 H, vinyl H), 4.12 (br s, 1 H, C*H*OH), 1.99–2.07 (m, 1 H), 1.82–1.90 (m, 1 H), 1.72 (dd, J = 5.32, 1.38 Hz, 3 H, vinyl CH_3), 1.18–1.63 (m, 5 H), 1.32 (br s, 1 H, CHO*H*), 1.07–1.13 (m, 1 H), 1.00 (dt, J = 8.85, 3.50 Hz, 1 H, cyclopropyl), 0.85 (dt, J = 8.85, 2.23 Hz, 1 H, cyclopropyl), 0.03 (s, 9 H, $(CH_3)_3Si$); exact mass calcd for $C_{13}H_{23}OSi$ ($M^+ - CH_3$) 223.1518, found 223.1518.

7-(*trans*-2-Butenylidene)bicyclo[4.1.0]heptane (16). A solution of **14** (0.560 g, 2.02 mmol) in THF (1 mL) was treated with LDMAN for 30 min at -78 °C. A solution of crotonaldehyde (0.280 g, 2.60 mmol) in THF (0.5 mL) was added, and after complete formation of the alkoxide, potassium *tert*-butoxide (1.22 g, 10.0 mmol) was added. The reaction mixture was slowly warmed to room temperature, and after 8 h (overnight) the reaction was worked up as for **12**. The resulting oil was chromatographed (silica gel, hexanes) to afford 0.24 g (80%) of **16**, which rapidly decomposed upon exposure to air: IR (neat) 3003, 2976, 2930, 2855, 1448, 1174, 970, 943 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 6.32 (d, J = 10.52 Hz, 1 H, CH), 6.18 (dd, J_{trans} = 14.75, J = 10.52 Hz, 1 H, H_3CHCH), 5.77 (dq, J_{trans} = 14.75, J = 6.75 Hz, 1 H, H_3CH), 1.77 (d, J = 6.74 Hz, 3 H, CH_3), 1.70–1.00 (m, 10 H); exact mass calcd for $C_{11}H_{16}$ 148.1252, found 148.1252.

1-(6-*endo*-Methylbicyclo[2.2.1]hept-2-en-5-*endo*-5-yl)-7-(trimethylsilyl)-bicyclo[4.1.0]heptan-7-yl-1-hydroxymethane (17). A solution of **14** (2.00 g, 7.23 mmol) in THF (0.5 mL) was treated with LDMAN for 30 min at -78 °C. A solution of ***endo*-97**[17] (2.00 g, 9.10 mmol) in THF (2 mL) was added, and after 15 min the mixture was quenched with moist THF. Standard workup and MPLC chromatography (Lobar B, 2% ethyl acetate–hexane) afforded 2.04 g (93%) of **17**: IR (neat) 3561, 2956, 2930, 2870, 1455, 1375, 1343, 1250, 1022, 1001, 837, 727 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 6.22 (dd, J = 5.66, 2.91 Hz, 1 H, vinyl), 6.13 (dd, J = 5.66, 2.91 Hz, 1 H, vinyl H), 3.73 (br s, 1 H, C*H*OH), 3.06 (br s, 1 H), 2.42 (br s, 1 H), 2.01 (br s, 1 H, CHOHC*H*), 1.81–1.89 (m, 1 H, CH_3CH), 1.65–1.75 (m, 2 H,), 1.48–1.58 (m, 2 H), 1.26–1.36 (m, 6 H), 1.08 (d, J = 6.90 Hz, 3 H, CH_3), 1.03 (ddd, J = 8.85, 8.85, 3.21 Hz, 1 H, cyclopropyl H), 0.92 (br s, 1 H, OH), 0.83 (ddd, J = 8.85, 8.85, 2.84 Hz, 1 H, cyclopropyl H), 0.07 (s, 9 H, $(CH_3)_3Si$); exact mass calcd for $C_{14}H_{26}OSi$ ($-C_5H_6$) 238.1753, found 238.1753.

7-(6-*endo*-Methyl-5-*endo*-(vinylidenyl)bicyclo[2.2.1]hept-2-en-1-yl)-bicyclo[4.1.0]heptane (18). A solution of **14** (1.00 g, 3.62 mmol) in THF (0.5 mL) was treated with LDMAN for 30 min at -78 °C. A solution of ***endo*-97**[17] (0.650 g, 4.77 mmol) in THF (0.5 mL) was added, and after 15 min the reaction mixture was allowed to warm to ambient temperature at which time potassium *tert*-butoxide (2.03 g, 18.8 mmol) was added, and the resulting mixture was heated at the reflux temperature of THF for 2 h. Standard workup and chromatography (silica gel, hexane) afforded 0.590 g (76%) of **18** as a mixture of two diastereomers: IR (thin film) 3059, 2926, 2855, 1448, 1250, 866, 841, 731 cm^{-1}. MPLC allowed a partial separation and the two isomers could be obtained in fairly pure form. The isomers contained a small amount of inseparable impurity, which absorbed between δ 0.7 and 1.6 in the ^{1}HMR spectrum and therefore did not allow integration in this range: major isomer ^{1}H NMR ($CDCl_3$) δ 6.15–6.21 (m, 2 H, CH=CH), 5.28 (br d, J = 10.31 Hz, 1 H, C=CH), 2.95 (ddd, J = 10.31, 9.61, 3.61 Hz, 1 H, C=CHC*H*), 2.76 (m, 1 H, *H*CCH=CH), 2.71 (m, 1 H, CH=CHC*H*), 2.31 (dqd, J = 9.61, 7.26, 3.32 Hz, 1 H, C*H*CH_3), 1.65–1.85 (m), 1.47–1.67 (m), 1.32–1.47 (m), 1.18–1.32 (m), 0.75 (d, J = 7.26 Hz, 3 H, CH_3); minor isomer ^{1}H NMR ($CDCl_3$, δ 6.15–6.21 (m, 2 H, CH=CH), 5.63 (br d, J = 9.63 Hz, 1 H, C=CH), 3.05 (ddd, J = 10.31, 9.63, 3.61 Hz, 1 H, C=CHC*H*), 2.85 (br s, 1 H, *H*CCH=CH), 2.68 (br s, 1 H, CH=CHC*H*), 2.27 (m, 1 H, CH_3CH), 1.65–1.85 (m, 4 H), 1.20–1.64 (m), 1.04 (dd, J = 7.93, 2.76 Hz, cyclopropyl H), 0.85 (dt, J = 7.93, 2.04 Hz), 0.78 (d, J = 7.30 Hz, 3 H, CH_3); exact mass calcd for $C_{16}H_{22}$ 214.1721, measured 214.1721. A comparison of these NMR spectra with those of the stereoisomers derived from the epimeric bicyclic aldehyde prepared from the Diels–Alder adduct of cyclopentadiene and *trans*-crotonaldehyde[16] indicated that none of the epimer of **18** was present.

7-(1-Hydroxy-3-(phenylthio)-2-propen-1-yl-)-7-(trimethylsilyl)bicyclo-[4.1.0]heptane (19). A solution of **14** (1.00 g, 3.62 mmol) in THF (2 mL) was treated with LDMAN for 1 h at -78 °C. A solution of (*E*)- and (*Z*)-3-(phenylthio)propenal (0.650 g, 3.98 mmol) in THF (1 mL) was added, and the reaction mixture was slowly allowed to warm to ambient temperature prior to the addition of a small amount of water. Standard workup and MPLC chromatography (Lobar B column, 5% ethyl acetate–hexanes) gave 0.77 g (64%) of the *trans* isomer and 0.096 g (8%) of the *cis* isomer: *cis* isomer IR (neat) 3456, 3063, 2928, 2855, 1584, 1480, 1439, 1246, 1007, 837, 739, 691 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.41–7.43 (m, 1 H, phenyl), 7.15–7.32 (m, 4 H, phenyl), 6.32 (d, J_{cis} = 9.50 Hz, 1 H, SCH), 6.03 (dd, J_{cis} = 9.49, J = 7.90 Hz, 1 H, SCHC*H*), 4.52 (br d, J = 7.89 Hz, 1 H, allylic H), 2.01 (m, 1 H), 1.78 (m, 1 H), 1.47–1.56 (m, 5 H), 1.31–1.38 (m, 1 H), 1.15–1.25 (m, 1 H), 0.97 (dt, J = 8.93, 3.33, Hz, 1 H, bridge H), 0.84–0.90 (dt, J = 8.93–2.05 Hz, 1 H, bridge H), 0.01 (s, 9 H, $(CH_3)_3Si$); exact mass calcd for $C_{19}H_{28}OSSi$ 332.1630, found 332.1655; *trans* isomer IR (neat) 3457, 3010, 2928, 2859, 1664, 1583, 1479, 1441, 1246, 1089, 949, 837, 737, 689 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.12–7.29 (m, 5 H, phenyl), 6.36 (dd J_{trans} = 14.93, J = 1.63 Hz, 1 H, SCH), 5.86 (dd, J_{trans} = 14.95, J = 4.66 Hz, 1 H, SCHC*H*), 4.18 (broad singlet which upon addition of D_2O, sharpens to a doublet, J = 4.66 Hz, 1 H, allylic H), 1.90–2.20 (m, 1 H), 1.75–1.90 (m, 1 H), 1.31–1.49 (m, 5 H, including OH), 1.10–1.30 (m, 1 H), 0.95–1.10 (m, 1 H), 0.98 (dt, J = 8.99, 3.46 Hz, 1 H, bridge H), 0.79 (dt, J = 8.99, 2.24 Hz, 1 H, bridge

H), 0.12 (s, 9 H, $(CH_3)_3Si$); exact mass calcd for $C_{19}H_{28}OSSi$ 332.1630 found 332.1618.

7-(3-(Phenylthio)-*trans*-2-propenylidene)bicyclo[4.1.0]heptane (20-*trans*). A solution of potassium hydride (KH, 5.6 mg, 0.140 mmol) in THF (15 mL) was efficiently stirred as a dilute solution of **19*E*** (0.024 g, 0.070 mmol) in THF (1 mL) was added dropwise. After 30 min, the reaction mixture was carefully poured into ice water and extracted with ether. Removal of the solvent from the dried ($MgSO_4$) organic phase and chromatography (silica gel, hexane) afforded 0.016 g (93%) of **20-*trans***: IR (neat) 3060, 2954, 2928, 2856, 1651, 1480, 1206, 1021, 737, 689 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.16–7.40 (m, 5 H, phenyl), 6.61 (dd, J_{trans} = 14.81, J = 10.54 Hz, 1 H, SCHC*H*), 6.44 (d, J = 10.54 Hz, 1 H, C=CH), 6.33 (d, J_{trans} = 14.82 Hz, 1 H, SCH), 1.58–1.88 (m, 6 H), 1.16–1.36 (m, 4 H); exact mass calcd for $C_{16}H_{18}S$ 242.1128, found 242.1121.

7-(3-(Phenylthio)-*cis*-2-propenylidene)bicyclo[4.1.0]heptane (20 cis). Using the procedure described above, a solution of **19*Z*** (0.022 g, 0.066 mmol) in THF (5 mL) was olefinated to yield after workup and chromatography (chromatotron, 1 mm rotor, hexane) 0.015 g (93%) of **20-*cis***: IR (neat) 3060, 2926, 2853, 1653, 1478, 1439, 1202, 737, 689 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.29 (m, 2 H, phenyl), 6.82–7.02 (m, 4 H, phenyl and C=CH), 6.48 (dd, J_{cis} = 9.24, J = 10.07 Hz, 1 H, SCH=C*H*), 6.13 (d, J_{cis} = 9.24 Hz, 1 H, SCH), 1.45–1.69 (m, 6 H), 1.00–1.18 (m, 4 H); exact mass calcd for $C_{16}H_{18}S$ 242.1128, found 242.1121.

7-(1-Hydroxy-2-butyn-1-yl)-7-(trimethylsilyl)bicyclo[4.1.0]heptane (21). A solution of **14** (1.00 g, 3.62 mmol) in THF (2 mL) was treated with LDMAN for 45 min at -78 °C. A solution of 2-butynal (0.270 g, 3.98 mmol) in THF (0.5 mL) was added, and the resulting mixture was stirred for an additional 10 min at -78 °C. The ice bath was then removed, and the reaction mixture was allowed to warm to ambient temperature. Standard workup and purification by column chromatography (silica gel, 5% ethyl acetate–hexane) afforded 0.69 g (81%) of **21**: IR (neat) 3463, 3020, 2928, 2859, 1449, 1244, 1009, 945, 841, 735 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.32 (q, J = 2.12 Hz, 1 H, C*H*OH), 1.93–2.05 (m, 1 H), 1.82–1.92 (m, 1 H), 1.85 (d, J = 2.12 Hz, 3 H, CH_3), 1.62–1.71 (m, 1 H), 1.58 (br s, 1 H, CHO*H*), 1.36–1.50 (m, 2 H), 1.23–1.34 (m, 2 H), 1.03–1.16 (m, 1 H), 1.02 (dt, J = 8.61, 3.16 Hz, 1 H, cyclopropyl H), 0.91 (dt, J = 8.61, 2.36 Hz, 1 H, cyclopropyl H), 0.061 (s, 9 H, $(CH_3)_3$-Si); ^{13}C NMR ($CDCl_3$) δ 81.0, 80.8, 63.0, 22.6, 22.5, 20.0, 19.2, 18.8, 16.6, 15.9, 3.59, –1.03; exact mass calcd for $C_{14}H_{23}OSi$ (-H) 235.1510, found 235.1492.

7-(1-Hydroxy-*cis*-2-buten-1-yl)-7-(trimethylsilyl)bicyclo[4.1.0]-heptane (22). The titled compound could be synthesized from either one of two methods. Method A: Compound **17** (0.061 g, 0.199 mmol) was subjected to standard FVP conditions at 500 °C to afford the titled compound in 84% yield (0.040 g). Alternatively the desired *cis*-olefin could be synthesized from hydrogenation of the corresponding alkyne (**21**). Method B: A solution of palladium, saturated with H_2, on barium sulfate poisoned with lead (palladium content 5%) (0.250 g, 0.117 mmol) in THF (30 mL) was stirred at ambient temperature as **21** (0.500 g, 2.12 mmol) in THF (2 mL) was added, and the resulting solution was allowed to stir under an atmosphere of H_2 for 24 h. The catalyst was removed by filtration (florisil, $MgSO_4$), and the solvent was removed under reduced pressure. The remaining oil was chromatographed (silica gel treated with 0.01% TEA, 15% ethyl acetate–hexane) to afford 0.491 g (97%) of the *cis*-olefin **22** as a viscous oil: IR (neat) 3465, 3004, 2923, 2855, 1448, 1245, 1002, 963, 945, 833 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.78 (ddq, J_{cis} = 10.87, J = 8.74, 1.70 Hz, 1 H, CHOHC*H*), 5.61 (dq, J_{cis} = 10.87, J = 6.82 Hz, 1 H, C*H*CH_3), 4.45 (d, J = 8.74 Hz, 1 H, C*H*OH), 2.03–2.11 (m, 1 H), 1.76–1.84 (m, 1 H), 1.73 (dd, J = 6.82, 1.70 Hz, 3 H, CH_3), 1.18–1.64 (m, 6 H), 1.04–1.12 (m, 1 H), 1.02 (dd, J = 8.81, 3.45 Hz, 1 H, cyclopropyl H), 0.88 (dd, J = 8.81, 2.14 Hz, 1 H, cyclopropyl H), 0.02 (s, 9 H, $(CH_3)_3Si$); exact mass calcd for $C_{14}H_{26}OSi$ 238.1753, found 238.1759.

7-(*cis*-2-Butenylidene)bicyclo[4.1.0]heptane (23). A solution of **22** (0.019 g, 0.079 mmol) in THF (5 mL) was treated with KH (6.4 mg, 0.16 mmol) for 30 min at the reflux temperature of THF. Simple extraction, drying ($MgSO_4$) of the organic layer, and solvent removal under reduced pressure provided **23** in high purity and high yield (0.011 g, 94%): IR (neat) 3019, 2925, 2854, 1448, 1376, 1247, 836 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.66 (d, J = 11.24 Hz, 1 H, CH), 6.14 (ddd, J_{cis} = 10.80, J = 11.24, 1.07 Hz, 1 H, C*H*CHCH$_3$), 5.46 (dq, J_{cis} = 10.80, J = 6.96 Hz, 1 H, C*H*CH_3), 1.56–1.85 (m, 2 H), 1.79 (d, J = 6.96 Hz, 3 H, CH_3), 1.05–1.37 (m, 6 H), 0.75–0.92 (m, 2 H); exact mass calcd for $C_{11}H_{16}$ 148.1252, found 148.1252.

7-(1-Hydroxy-2-ethoxyprop-2-en-1-yl)-7-(trimethylsilyl)bicyclo[4.1.0]-heptane (24). A solution of **14** (0.588 g, 2.13 mmol) in THF (3 mL) was treated with LDBB (5.33 mmol) for 30 min at –78 °C. This anion was then cannulated to a precooled (– 78 °C) solution of ethyl formate (0.473 g, 0.516 mL, 6.39 mmol) in THF (10 mL), and the solution was stirred for 30 min. A THF solution of 1-lithio-1-ethoxyethene[20] was cannulated to the silyl aldehyde adduct, and the resulting mixture was stirred for 30 min prior to the addition of 5 mL of MeOH. Standard workup and chromatography (silica gel, 5% ethyl acetate–hexane, R_f 0.27) afforded 0.339 g (69%) of **24**: IR (neat) 3482 (br), 2979 (s), 2930 (m), 1660 (w), 1244 (s), 1084 (s), 841 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.31 (br s, 1 H, C=C*H*), 4.06 (br s, 1 H, C*H*OH, 3.99 (br s, 1 H, C=C*H*), 3.72 (q, J = 6.97 Hz, 2 H, CH_3CH_2O), 1.92–2.08 (m, 1 H), 1.78–1.90 (m, 2 H), 0.98–1.60 (m, 10 H, including a triplet at δ 1.30, J = 6.97 Hz, 3 H, CH_3CH_2O), –0.06 (s, 9 H, $(CH_3)_3Si$); ^{13}C NMR ($CDCl_3$) δ 163.5, 80.7, 71.7, 62.5, 22.8, 22.5, 20.2, 19.6, 19.1, 17.0, 16.5, 14.4, –1.09; exact mass calcd for $C_{14}H_{25}O_2Si$ ($M^+ - CH_3$) 253.1624, found 253.1610.

7-[1-Hydroxy-1-(1-cyclohexenyl)]methyl]-7-(trimethylsilyl)bicyclo-[4.1.0]heptane (26). A solution of **14** (0.600 g, 2.27 mmol) in THF (2.5 mL) was treated with LDBB at –78 °C for 30 min. A solution of cyclohexene-1-carboxaldehyde[64] (0.220 g, 2.00 mmol) in THF (2 mL) was added, and the resulting mixture was stirred for 30 min prior to addition of water. The following standard workup was performed for LDBB reductive lithiations. The resulting mixture was diluted with ether and successively washed with water and brine. Removal of the solvent *in vacuo* from the dried ($MgSO_4$) organic layer and purification by flash chromatography (3% ethyl acetate/hexanes, R_f 0.21) to yield 0.440 g (79%) of the titled compound: IR ($CHCl_3$) 3476 (br), 2928 (s), 2856 (s), 1244 (s), 837 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.88 (m, 1 H, CH=), 3.99 (m, 1 H, C*H*OH), 2.06–1.85 (m, 6 H), 1.70–1.50 (m, 6 H), 1.46–1.27 (m, 4 H), 1.22–1.14 (m, 1 H), 1.03–0.91 (m, 2 H), –0.06 (s, 9 H, $(CH_3)_3Si$); ^{13}C NMR ($CDCl_3$) δ 138.7, 120.6, 74.1, 26.0, 24.9, 22.7, 22.6, 22.3, 21.1, 19.6, 17.5, 15.6, –0.93; exact mass calcd for $C_{17}H_{30}OSi$ 278.2065, found 278.2048.

7-[(1-Cyclohexenyl)methylidene]bicyclo[4.1.0]heptane (27). A solution of **26** (0.420 g, 1.51 mmol) in THF (30 mL) was stirred at ambient temperature as KH power (0.182 g, 4.53 mmol) was added all at once. The reaction mixture was heated at reflux for 1 h, diluted with ether, and washed with brine. The organic layer was dried ($MgSO_4$), and the solvent was removed by rotary evaporation. The crude product was purified by flash chromatography (hexanes, R_f 0.56) to give 0.210 g (74%) of the diene: IR (neat) 3003 (m), 2928 (s), 2855 (s), 1446 (m), 1435 (m), 885 (m) cm^{-1}; ^1H NMR ($CDCl_3$) d 6.37 (s, 1 H, CH=), 5.72 (m, 1 H, CH=), 2.40–2.15 (m, 4 H), 1.84–1.55 (m, 9 H), 1.43 (t, 1 H, J = 8.3), 1.28–1.21 (m, 4 H); ^{13}C NMR ($CDCl_3$) d 137.0, 131.7, 126.3, 121.4, 25.8, 24.0, 23.1, 22.8, 22.5, 21.6, 21.2, 14.5, 10.6; exact mass calcd for $C_{14}H_{20}$ 188.1565, found 188.1559.

8-(Phenylthio)-8-(trimethylsilyl)bicyclo[5.1.0]octane (28). Following the method for the preparation of **14**, cycloheptene oxide (2.78 g, 24.8 mmol) was cyclopropanated with the following reagents: *n*-BuLi (18.2 mmol, 1.5 M, 27.3 mmol), (phenylthio)(trimethylsilyl)methane (5.35 g, 27.3 mmol), TMEDA (3.17 g, 27.3 mmol), benzenesulfonyl chloride (4.31 g, 27.3 mmol), *s*-BuLi (21.3 mL, 1.28 M, 27.3 mmol), and TMEDA (3.17 g, 27.3 mmol) to afford 4.63 g (64%) of **28**, which was rich in the *endo*-phenylthio isomer, after flash chromatography (silica gel, hexanes, R_f 0.73, 0.65): IR (neat) 3063, 2919, 2851, 1478, 1248, 882, 841, 735, 691 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.15–7.20 (m, 2 H, phenyl), 7.00–7.10 (m, 2 H, phenyl), 6.86–6.94 (m, 1 H, phenyl), 1.83–1.95 (m, 2 H), 1.63–1.80 (m, 3 H), 1.42–1.57 (m, 2 H), 1.19–1.38 (m, 3 H), 1.00–1.18 (m, 2 H, cyclopropyl), 0.01 (s, 9 H, endo $(CH_3)_3Si$), –0.18 (s, 9 H, exo $(CH_3)_3Si$); ^{13}C NMR ($CDCl_3$) ***endo*-**phenylthio isomer, δ 139.3, 128.1, 126.4, 124.1, 32.3, 29.0, 27.5, 26.2, 23.2, –2.3; exact mass calcd for $C_{17}H_{26}$-OSSi 290.1525, found 290.1523.

8-(1-Hydroxy-2-*trans*-buten-1-yl)-8-(trimethylsilyl)bicyclo[5.1.0.]-octane (29). A solution of **28** (0.570 g, 1.96 mmol) in THF (1 mL) was treated with LDMAN for 45 min at -78 °C. Crotonaldehyde (0.165 g, 2.36 mmol) was added, and after 15 min the reaction mixture was allowed to warm to 0 °C prior to the addition of moist THF. Standard workup and purification by column chromatography (silica gel, 5% ethyl acetate–hexane) gave 0.442 g (89%) of **29** as a clear oil: IR (neat) 3476, 2918, 2849, 1451, 1246, 1121, 1044, 1015, 970, 837, 747, 685 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.53–5.70 (m, 2 H, vinyl H), 4.25 (br s, 1 H, C*H*OH), 2.02 (dd, J = 12.45, 6.11 Hz, 1 H), 1.79–1.94 (m, 4 H), 1.70 (dd, J = 6.00, 1.06 Hz, 3 H, CH_3), 1.06–1.42 (m, 6 H), 0.82–0.98 (m, 2 H, cyclopropyl), –0.03 (s, 9 H, $(CH_3)_3Si$); ^{13}C NMR ($CDCl_3$) δ 133.9, 124.5, 72.9, 32.8, 29.9, 25.9, 25.11, 25.01, 23.5, 17.8, –0.64; exact mass calcd for $C_{15}H_{28}$-OSi 252.1909, found 252.1909.

8-(*trans*-2-Butenylidene)bicyclo[5.1.0]octane (30). A solution of **29** (0.270 g, 1.07 mmol) in THF (10 mL) was treated with KH powder

(0.128 g, 3.20 mmol) for 30 min at the reflux temperature of THF. Simple extraction, drying ($MgSO_4$) of the organic layer, and solvent removal under reduced pressure provided **30** in high purity and high yield (0.162 g, 93%): IR (neat) 3009, 2919, 2849, 1458, 1449, 972, 961, 781 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.15 (br d, J = 10.51 Hz, 1 H, C=C*H*), 5.96 (ddd, J_{trans} = 15.10, J = 10.51, 1.45 Hz, 1 H, CHC*H*), 5.51 (dq, J_{trans} = 15.10, J = 6.68 Hz, 1 H, CH_3C*H*), 1.80–1.97 (m, 2 H), 1.67 (d, J = 6.68 Hz, 3 H, CH_3), 1.14–1.39 (m, 10 H); ^{13}C NMR ($CDCl_3$) δ 134.3, 130.1, 125.2, 116.9, 31.4, 28.4, 28.3, 27.8, 27.6, 19.2, 19.0, 16.8; exact mass calcd for $C_{12}H_{18}$ 162.1409, found 162.1409.

1-Methyl-7-(phenylthio)-7-(trimethylsilyl)bicyclo[4.1.0]heptane (31). The following standard procedure for replacement of chlorine by trimethylsilyl was used. A solution of *s*-BuLi (10.2 mL, 1.01 M, 10.3 mmol) in THF (50 mL) was stirred at -78 °C as a solution of **2** (2.00 g, 7.91 mmol) in THF (2 mL) was slowly added. Addition was regulated to maintain a reaction solution temperature <–60 °C. The darkened solution was stirred at -78 °C for 1 h after completion of addition. A solution of TMSCl (1.29 g, 1.87 mmol) in THF was then slowly added to maintain a reaction temperature of <–60 °C. The resulting mixture was allowed to warm to approximately 0 °C prior to quenching the reaction by the addition of a small amount of water. After solvent evaporation *in vacuo*, the resulting dark oil was diluted with ether and washed with 5% aqueous $NaHCO_3$ and brine. After reextraction of the aqueous layers, the organic layers were combined, dried (Na_2SO_4), filtered through a small pad of florisil, and concentrated *in vacuo* to afford 2.20 g of dark oil. Flash column chromatography (silica gel, hexanes) yielded 1.83 g (80%) of **31** as a clear oil, rich in the *endo*-silyl isomer (9:1 endo/exo ratio by NMR spectral analysis): IR (neat) 3088, 3065, 2938, 2868, 1584, 1477, 1248, 855, 839, 735, 692 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.24–7.31 (m, 4 H, phenyl), 7.07–7.10 (m, 1 H, phenyl), 2.02–2.15 (m, 1 H), 1.68–1.82 (m, 3 H), 1.42–1.68 (m, 7 H, including a tall singlet at δ 1.47, CH_3), 1.12 (dd, J = 5.03, 8.48 Hz, 1 H, bridge H), 0.22 (s, 9 H, endo $(CH_3)_3Si$). In an otherwise identical spectrum, the exo isomer exhibited a signal at δ 0.13 (s, 9 H for the minor isomer, *exo*-silyl group): exact mass calcd for $C_{17}H_{26}SSi$ 290.1525, found 290.1523.

1 Methyl-7-(2-methyl-2-propenylidene)bicyclo[4.1.0]heptane (32). A solution of **31** (44.0 g, 1.50 mmol) was treated with LDMAN for 1 h at -78 °C. Methacrolein (0.210 g, 1.20 mmol) was added, and the mixture was allowed to warm to room temperature and was stirred for 4 h. Potassium *tert*-butoxide (1.12 g, 10.0 mmol) was added, and elimination was complete within 1 h. Workup as described for **33** and chromatography (silica gel, hexanes) afforded 0.18 g (74%) of **32**: IR (neat) 3080, 2970, 2940, 2860, 1610, 1450, 1440, 1375 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.43 and 6.46 (s, 1 H, approximately equal intensity), 4.88 and 4.91 (s, 2 H, approximately equal intensity), 1.12–1.94 (m, 15 H, containing four singlets at δ 1.14, 1.22, 1.86, and 1.94); exact mass calcd for $C_{12}H_{18}$ 162.1409, found 162.1408.

1-Methyl-7-(3-methyl-2-propenylidene)bicyclo[4.1.0]heptane (33). A solution of **31** (0.290 g, 1.00 mmol) in THF was treated with LDMAN for 1 h at -78 °C. Crotonaldehyde (0.400 g, 1.20 mmol) was added, and after this mixture had been stirred for 1 h at -78 °C, potassium *tert*-butoxide (0.280 g, 2.50 mmol) was added. The dry-ice bath was removed and the mixture was stirred at room temperature for 3 h. The mixture was taken up in hexanes and successively washed with 5% NaOH, water, 5% HCl, water, and saturated aqueous $NaHCO_3$. The organic layer was dried ($MgSO_4$) and concentrated *in vacuo*. Silica gel chromatography (hexanes) yielded 0.16 g (99%) of **33** as a 1:1 mixture of geometric isomers: IR (neat) 2960, 2930, 2850, 1450, 1375 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.25–6.29 (m, 1 H), 6.03–6.21 (m, 1 H), 5.56–5.71 (m, 1 H), 0.76–1.82 (15 H, containing two singlets at δ 1.04 and 1.16 and a doublet at δ 1.67, J = 6.8 Hz, 3 H); exact mass calcd for $C_{12}H_{18}$ 162.1409, found 162.1408.

1,6-Dimethyl-7-(phenylthio)-7-(trimethylsilyl)bicyclo[4.1.0]heptane (34). In a procedure identical to that for the preparation of **2**, 1,2-dimethylcyclohexene (0.57 g, 5.2 mmol) was cyclopropanated. The crude, chromatographically unstable product (1,6-dimethyl-7-chloro-7-(phenylthio)bicyclo[4.1.0]heptane) was silylated according to the procedure for **31** to afford 0.28 g (36%) of **34**: IR (KBr) 3070, 2970, 2940, 2860, 1580, 1475, 1450, 1440 cm^{-1}. Partial chromatographic separation of the C-7 epimers allowed individual ^1H NMR spectra of each to be obtained ($CDCl_3$ and CH_2Cl_2): isomer 1 δ 7.17–7.30 (m, 4 H, phenyl), 7.05–7.10 (m, 1 H, phenyl), 1.38–1.85 (m, 14 H, including a singlet at δ 1.39), 0.13 (s, 9 H, $(CH_3)_3Si$); isomer 2 δ 7.15–7.23 (m, 4 H, phenyl), 7.03–7.08 (m, 1 H, phenyl), 1.55–1.65 (m, 8 H), 1.24 (s, 6 H, methyl), 0.15 (s, 9 H, $(CH_3)_3Si$); exact mass calcd for $C_{18}H_{28}SSi$ 304.1681, found 304.1682.

1,6-Dimethyl-7-(2-methyl-2-propenylidene)bicyclo[4.1.0]heptane (35). A solution of **34** (0.15 g, 0.50 mmol) was treated with LDMAN for 1 h at -78 °C. Methacrolein (0.053 g, 0.75 mmol) was added, and the mixture was stirred for 1 h at -78 °C before being warmed to room temperature. Addition of potassium *tert*-butoxide (0.22 g, 2.0 mmol) completed the elimination within 1 h. Workup as described for **33** and chromatography (silica gel, hexanes) afforded 0.067 g (79%) of **35**: IR (neat) 3070, 2980, 2940, 2860, 1610, 1450, 1380 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.38 (s, 1 H), 4.89 (s, 1 H), 4.87 (s, 1 H), 1.55–1.85 (m, 8 H, containing a singlet at δ 1.85), 1.15–1.34 (m, 6 H, containing a singlet at δ 1.19), 1.11 (s, 3 H); exact mass calcd for $C_{13}H_{20}$ 176.1565, found 176.1565

2-Methylene-7-(phenylthio)-7-(trimethylsilyl)bicyclo[4.1.0]heptane (36). In a two-necked flask equipped with a reflux condenser, a mixture of methyltriphenylphosphonium bromide (5.54 g, 15.5 mmol) in THF (50 mL) was efficiently stirred at ambient temperature as potassium *tert*-butoxide (1.16 g, 10.3 mmol) was added all at once. After the bright yellow solution had been stirred for 20 min, a solution of **39** (1.50 g, 5.17 mmol) in THF (10 mL) was added. The reaction mixture was then heated to reflux for 30 min. After cooling, the resulting mixture was transferred to a separatory funnel containing brine overlaid with ether. The aqueous layer was extracted with ether, and after the combined organic layers were dried ($MgSO_4$) and concentrated *in vacuo*, the resulting oil was chromatographed (silica gel, 5% ethyl acetate–hexanes) to afford 1.43 g (99%) of **36** as a mixture of stereoisomers: IR (neat) 3074, 2935, 2860, 1630, 1585 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.02–7.26 (m, 5 H, phenyl), 5.29 and 5.07 (s, 1 H, exocyclic H), 4.98 (s, 1 H, exocyclic H), 2.08–2.32 (m, 3 H), 1.25–1.90 (m, 5 H), 0.95 and –0.06 (s, 9 H, $(CH_3)_3Si$, mixture of exo and endo undefined); ^{13}C NMR ($CDCl_3$) δ 143.7, 142.9, 140.1, 138.2, 128.4, 128.2, 126.6, 125.9, 124.3, 124.1, 115.6, 112.9, 32.6, 32.3, 30.9, 30.4, 25.4, 24.3, 23.7, 23.1, 22.9, 22.4, 22.2, 20.6, 1.42, –2.20; exact mass calcd for $C_{17}H_{24}SSi$ 288.1368, found 288.1361.

2-Methylene-7-(1-hydroxy-*trans*-2-buten-1-yl)-7-(trimethylsilyl)bicyclo-[4.1.0]heptane (37). A solution of **36** (0.245 g, 0.849 mmol) in THF (1.5 mL) was treated with LDBB for 30 min at -78 °C. A solution of crotonaldehyde (0.119 g, 1.70 mmol) in THF (0.5 mL) was then added, and stirring was continued for 20 min prior to the addition of an excess of water. After workup as for **26**, flash chromatography (silica gel, 2–5% ethyl acetate in hexanes, R_f 0.33 minor isomer, R_f 0.21 major isomer in 5% ethyl acetate in hexanes) afforded **37** as a separable mixture (3.3:1) of diastereomers in a combined yield of 0.153 g (72%): major IR (neat) 3610, 3471, 3014, 2935, 1628, 1450, 1247 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.49–5.70 (m, 2 H, vinyl H), 4.93 (br s, 2 H, exocyclic H), 4.05 (br s, 1 H, C*H*OH), 2.32 (m, 1 H), 2.04–2.16 (m, 1 H), 1.69 (d, J = 6.08 Hz, 3 H, CH_3), 1.25–1.83 (m, 7 H, including CHO*H*), 0.01 (s, 9 H, $(CH_3)_3$-Si); ^{13}C NMR ($CDCl_3$) δ 143.4, 133.2, 123.6, 113.9, 72.2, 32.9, 24.4, 23.7, 23.1, 20.8, 19.4, 17.7, –0.07; minor, IR (neat) 3584, 3484, 3070, 2935, 1625, 1449, 1247, 837 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.67 (dq, J_{trans} = 15.4, J = 6.18 Hz, 1 H, CH_3C*H*), 5.54 (dd, J_{trans} = 15.4, J = 4.79 Hz, 1 H, CH_3CHC*H*), 5.07 (s, 1 H, exocyclic H), 5.03 (s, 1 H, exocyclic H), 4.07 (br s, 1 H, C*H*OH), 2.30 (m, 1 H), 1.96–2.03 (m, 2 H), 1.70 (d, J = 6.18 Hz, 3 H, CH_3), 1.25–1.75 (m, 6 H, including CHO*H*), 0.002 (s, 9 H, $(CH_3)_3Si$); ^{13}C NMR ($CDCl_3$) δ 144.5, 132.5, 124.8, 113.0, 73.2, 32.6, 23.9, 23.7, 22.3, 20.0, 19.0, 17.7, –0.74; exact mass calcd for $C_{15}H_{26}$-OSi 250.1753, found 250.1753

***E* and *Z* Isomers of 2-Methylene-7-(*trans*-2-butenylidene)bicyclo[4.1.0]-heptane (38).** This procedure was carried out separately for each diastereomer of silylcarbinol **37**. A solution of **37** (0.120 g, 0.480 mmol) in THF (5 mL) was stirred at ambient temperature as KH powder (0.0577 g, 1.44 mmol) was added all at once. TLC analysis indicated that the starting material was completely consumed within 30 min. The resultant mixture was poured onto ice water overlaid with ether. Simple extraction, drying ($MgSO_4$), and chromatography (silica gel treated with 1% TEA, hexanes) afforded 0.108 g (90%) of **38** as a clear oil: IR (neat) 3005, 2934, 2857, 1633, 1446, 970, 857 cm^{-1}; major (from major silylcarbinol) ^1H NMR (C_6D_6) δ 6.45 (m, 2 H, C=C*H*C*H*), 5.59 (dq, J_{trans} = 14.1, J = 6.48 Hz, 1 H, CH_3C*H*), 4.99 (s, 1 H, exocyclic H), 4.86 (s, 1 H, exocyclic H), 2.26 (br d, J = 8.33 Hz, 1 H), 1.93–2.09 (m, 1 H), 1.85–1.91 (m, 1 H), 1.75–1.80 (m, 1 H), 1.61 (d, J = 6.48 Hz, 3 H, CH_3), 1.51–1.69 (m, 1 H), 1.15–1.41 (m, 3 H); ^{13}C NMR ($CDCl_3$) δ 145.1, 132.5, 129.7, 127.8, 119.5, 108.5, 30.6, 23.0, 21.5, 21.2, 18.2, 16.6; minor (from minor silylcarbinol) ^1H NMR (C_6D_6) δ 6.48 (br d, J = 10.5 Hz, 1 H, C=C*H*), 6.24 (ddd, J_{trans} = 15.2, J = 10.5, 1.58 Hz, 1 H, C=CHC*H*), 5.55 (dq, J_{trans} = 15.2, J = 6.70 Hz, 1 H, CH_3C*H*), 4.94 (s, 1 H, exocyclic), 4.84 (s, 1 H, exocyclic), 2.26 (br d, J = 8.33 Hz, 1 H), 2.03–2.11 (m, 1 H), 1.85–1.96 (m, 1 H), 1.52–1.80 (m, 2 H), 1.62 (d, J = 6.70 Hz, 3 H, CH_3), 1.20–1.39 (m, 3 H); ^{13}C NMR ($CDCl_3$) δ 145.6, 132.7, 130.2, 128.0, 119.5, 108.2, 30.5, 22.6, 21.6, 21.4, 18.3, 16.6; exact mass calcd for $C_{12}H_{16}$ 160.1252, found 160.1252.

7-(Phenylthio)-7-(trimethylsilyl)bicyclo[4.1.0]heptan-2-one (39).[65] A solution of bis(phenylthio)trimethylsilylmethane (7.00 g, 23.0 mmol) in

THF (90 mL) was stirred at -78 °C as *n*-BuLi (15.2 mL, 1.51 M, 23.0 mmol) was slowly added. After 1 h, a solution of cyclohexenone (1.11 g, 11.5 mmol) in THF (20 mL) was slowly added, and the mixture was stirred for an additional 2 h. CuBr·Me_2S (9.50 g, 46.0 mmol) was added all at once, and the resulting mixture was stirred for 15 min at -78 °C, warmed to ambient temperature by removing the ice bath, and stirred at this temperature overnight (8 h). The reaction mixture was then quenched with a saturated aqueous NH_4Cl solution prior to being filtered through a pad of Celite. The filtrate was diluted with ether and repeatedly washed with saturated NH_4Cl solution until the aqueous layer no longer turned blue. The organic layer was dried ($MgSO_4$), and the solvent was removed by rotary evaporation. Flash column chromatography (silica gel, 10% ethyl acetate–hexanes) yielded 2.42 g (71%) of **39** as a mixture of stereoisomers: IR (CH_2Cl_2, mixture of isomers) 2940, 1690 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.1–7.4 (m, 5 H, phenyl), 1.8–2.5 (m, 8 H), 0.20 and 0.07 (s, 9 H, $(CH_3)_3Si$, mixture of exo and endo undefined); ^{13}C NMR ($CDCl_3$) δ 210.4, 209.8, 127–140 (8 peaks, aromatic), 20–45 (four CH, six CH_2 and one quarternary C), two TMS peaks were observed; exact mass calcd for $C_{16}H_{18}OSSi$ 290.1161, found 290.1161.

7-(Trimethylsilyl)-8-(*trans*-1-propenyl)-9-oxatricyclo[4.3.0.0^{5,7}]nonan-1-ol (40). A solution of diisopropylamine (154 g, 1.53 mmol) in THF (4 mL) was stirred at 0 °C as *n*-BuLi (1.04 mL, 1.41 M, 1.46 mmol) was added. After 30 min, the reaction mixture was cooled to -78 °C, and a solution of **39** (0.403 g, 1.39 mmol) in THF (3 mL) was added slowly. After the reaction mixture had been stirred for several minutes, a solution of TMSCl (0.158 g, 1.46 mmol) in THF (1 mL) was added. This mixture was stirred for 2 h prior, and a second equiv of *n*-BuLi (1.09 mL, 1.41 M, 1.53 mmol) was added in order to deprotonate the diisopropylamine. The resulting mixture was stirred for 45 min at -78 °C before being transferred via cannulation to a precooled (-78 °C) 0.5 M solution of LDBB. Within 5 min a solution of crotonaldehyde (0.195 g, 2.78 mmol) in THF (2 mL) was added to the deep red reaction mixture which was stirred for 15 min before the addition of 10 mL of MeOH. The flask was then removed from the ice bath, and the contents were stirred for an additional 30 min. Standard workup and purification by MPLC chromatography (Lobar B, 14% ethyl acetate–hexanes, R_f 0.24 minor isomer, R_f 0.17 major isomer) afforded 0.0180 g of the fast moving isomer (mp 115–117 °C) and 0.230 g of the slower moving isomer (mp 97–100 °C) in a combined yield of 71%: major IR ($CHCl_3$) 3586, 3384, 3016, 2955, 2868, 1670, 1449, 1216, 839 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.76 (dq, J_{trans} = 15.1, J = 6.44 Hz, 1 H, CH_3CH), 5.56 (ddd, J_{trans} = 15.1, J = 6.32, 1.48 Hz, 1 H, CH_3CHCH), 4.78 (d, J = 8.64 Hz, 1 H, CHO), 2.40 (s, 1 H, CHO*H*), 1.71 (dd, J = 6.44, 1.48 Hz, 3 H, CH_3), 1.62–1.86 (m, 8 H), –0.02 (s, 9 H, $(CH_3)_3Si$); ^{13}C NMR ($CDCl_3$) δ 130.7, 129.3, 105.5, 82.5, 31.5, 28.9, 23.8, 22.3, 19.1, 17.8, 17.3, –2.55; minor, IR ($CHCl_3$) 3390, 3388, 3027, 2954, 2879, 1667, 1250, 909, 736 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.63 (m, 2 H, vinyl H), 4.26 (m, 1 H, C*H*OH) 2.44 (s, 1 H, CHO*H*), 1.72 (d, J = 4.61 Hz, 3 H, CH_3), 1.58–1.86 (m, 8 H), –0.35 (s, 9 H, $(CH_3)_3Si$); ^{13}C NMR ($CDCl_3$) δ 133.7, 127.0, 106.0, 83.1, 31.3, 28.1, 23.5, 22.2, 18.4, 17.6, 14.9, –1.30; exact mass calcd for $C_{14}H_{24}O_2Si$ 252.1546, found 252.1546.

7-(*trans*-2-Butenylidene)bicyclo[4.1.0]heptan-2-one (41). This procedure was carried out separately for each diastereomer of lactol **40**. A solution of $KN(TMS)_2$ (0.332 g, 1.67 mmol) in THF (10 mL) was stirred at -78 °C as a solution of **40** (0.210 g, 0.833 mmol) in THF (3 mL) was added slowly. After the reaction mixture had been stirred for 15 min, the flask was removed from the ice bath, and the contents were stirred overnight (8 h). The reaction mixture was diluted with ether, transferred to a separatory funnel, and washed with brine. The organic layer was dried ($MgSO_4$), and the solvent was removed *in vacuo*. Purification by flash column chromatography (silica gel, 10% ethyl acetate–hexane) yielded 0.134 g (99%) (yields typically ranged from 90–99%) of **41** as a clear oil: major (from major lactol) IR (neat) 2932, 2857, 1693, 1449, 1300, 945 cm^{-1}; ^1H NMR (C_6D_6) δ 6.33 (m, 2 H, C=C*H*C*H*), 5.62 (dq, J_{trans} = 14.0, J = 6.65 Hz, 1 H, CH_3CH), 2.39 (d, J = 7.24 Hz, 1 H), 2.08–2.21 (m, 1 H), 1.82–1.88 (m, 1 H), 1.22–1.79 (m, 7 H, including a d at δ 1.54, J = 6.65 Hz, CH_3), 1.02–1.15 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 206.3, 130.8, 129.1, 123.7, 122.5, 37.5, 30.4, 21.9, 21.3, 18.2, 17.8; minor (from minor lactol) IR (neat) 2926, 2855, 1693, 1448, 1300, 943 cm^{-1}; ^1H NMR (C_6D_6) δ 6.29 (br d, J = 10.5 Hz, 1 H, C=C*H*), 6.01 (dd, J_{trans} = 15.0, J = 10.5 Hz, 1 H, C=CHC*H*), 5.48 (dq, J_{trans} = 15.0, J = 6.64 Hz, 1 H, CH_3CH), 2.36 (d, J = 7.27 Hz, 1 H), 2.05–2.16 (m, 1 H), 0.95–1.78 (m, 9 H, including a d at δ 1.56, J = 6.60 Hz, CH_3); ^{13}C NMR ($CDCl_3$) δ 206.5, 131.0, 129.2, 123.7, 122.8, 37.2, 30.4, 21.5, 21.2, 18.3, 17.7; exact mass calcd for $C_{11}H_{14}O$ 162.1045, found 162.1045. For larger scale preparations of **41**, one can avoid MPLC separation of the lactols **40** if after the standard reductive lithiation reaction, the two diastereomeric lactols along with impurities were collectively separated by flash chromatography (silica gel wash column, 16% ethyl acetate–hexanes). The impure lactols are then treated with 2.5 equiv (based on theoretical yield) of $KN(TMS)_2$. The resulting allylidenecyclopropanes were purified by flash chromatography (silica gel, 10% ethyl acetate–hexane) in 64% yield (based on cyclopropane **39**) as an inseparable mixture (12:1) of geometric isomers.

2-(tert-Butyldiphenylsiloxy)-8-phenylthio-8-(trimethylsilyl)bicyclo-[5.1.0]oct-2-ene (42). In the manner described above, **75** (1.51 g, 5.00 mmol) was treated with $KN(TMS)_2$ (1.18 g, 5.96 mmol), and the enolate anion silylated with *tert*-butyldiphenylsilyl chloride (1.64 g, 5.96 mmol) to afford 2.58 g (96%) of **42** after purification by flash chromatography (silica gel, 3% ethyl acetate–hexanes): IR (neat) 3071, 2930, 2858, 1585, 1477, 1153, 1113, 737 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.03–7.92 (m, 15 H, phenyl), 4.43 (m, 1 H, SiOC=CH) 1.51–2.06 (m, 8 H), 1.05 (s, 9 H, $(CH_3)_3CSi$), 0.02 (s, 9 H, $(CH_3)_3Si$); exact mass calcd for $C_{33}H_{42}OSSi_2$ 542.2497, found 524.2481.

2-(*tert*-Butyldiphenylsiloxy)-8-(1-hydroxy-*trans*-2-buten-1-yl)-8-(trimethylsilyl)bicyclo[5.1.0]oct-2-ene (43). A solution of **42** (0.860 g, 1.59 mmol) in THF was treated with LDBB for 15 min at -78 °C. A solution of crotonaldehyde (0.220 g, 3.17 mmol) in THF was added, and stirring was continued for 20 min prior to the addition of excess water. Standard (LDBB) workup and purification by flash chromatography (silica gel, 3% ethyl acetate–hexane) afforded 0.55 g (69%) of **43**: IR (neat) 3590, 3497, 2932, 2859, 1136, 841 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.76–7.80 (m, 4 H, phenyl), 7.40–7.47 (m, 6 H, phenyl), 6.14 (m, 1 H, CH_3CH), 5.83 (m, 1 H, CH_3CH=C*H*), 4.62 (t, J = 4.69 Hz, 1 H, SiOC=C*H*), 4.36 (br s, 1 H, C*H*OH), 2.14–2.23 (m, 1 H), 1.85–2.08 (m, 1 H), 1.24–1.82 (m, 7 H), 1.73 (d, J = 6.45 Hz, 3 H, CH_3), 1.12 (s, 9 H, $(CH_3)_3CSi$), 0.12 (s, 9 H, $(CH_3)_3Si$); exact mass calcd for $C_{31}H_{44}O_2Si_2$ 486.2742, found 486.2806.

8-(Trimethylsilyl)-9-[*trans*-1-propenyl]-10-oxatricyclo[5.3.0.0^{6,8}]decan-1-ol (44). A solution of TBAF (1.0 M in THF, 0.68 mL, 0.68 mmol) was added to a solution of **43** (0.31 g, 0.62 mmol) in THF (10 mL) at -78 °C. The reaction mixture was stirred for 30 min at -78 °C, and then for an additional 30 min after the reaction flask was removed from the dry ice bath. The resulting mixture was then poured into water and extracted with ether. After removing the solvent in vacuo from the dried ($MgSO_4$) solution, the remaining oil was purified by column chromatography (silica gel, 15% ethyl acetate–hexane) to afford 0.16 g (97%) of **44** as a yellow oil: IR (neat) 3406, 2921, 2860, 1448, 1249, 967, 838 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.61–5.80 (m, 2 H, vinyl H), 4.77 (d, J = 7.82 Hz, 1 H, C*H*O), 2.98 (br s, 1 H, OH), 1.18–2.05 (m, 10 H), 1.67 (d, J = 5.81 Hz, 3 H, CH_3), –0.08 (s, 9 H, $(CH_3)_3Si$); ^{13}C NMR ($CDCl_3$) δ 130.7, 128.6, 104.8, 81.9, 38.8, 35.3, 28.1, 25.6, 23.6, 22.0, 17.8, –2.62; the peak at 25.6 is much taller and slightly broader than the other one-carbon peaks and probably represents two carbon atoms; exact mass calcd for $C_{15}H_{26}O_2Si$ 266.1702, found 266.1717.

Sealed Tube Thermal Rearrangement Reactions. The following is a standard procedure for the preparation of a sealed tube thermolysis reaction: A solution containing an allylidenecyclopropane and a trace of radical inhibitor (3-*tert*-butyl-4-hydroxy-5-methylphenylsulfide) in a heavy wall glass tube was frozen by placing the tube in a -78 °C dry ice bath. The tube was next sequentially evacuated (1 mmHg), interrupted from the vacuum source, and allowed to warm. Significant outgassing was noticed. This cycle (freeze–pump–thaw) was repeated until the cessation of outgassing (typically 4–5 cycles). After this time, the contents were again frozen, the system was evacuated, and the tube was sealed off with the aid of a torch. The contents were then allowed to warm prior to the tube being placed into a thermostated oil bath or Tecam sand bath. At the appropriate time, the heat source was removed, and after carefully removing the solvent the residue was subjected to chromatography.

9-Methylbicyclo[5.3.0]deca-1,9-diene (46) and 9-Methylbicyclo[5.3.0]-deca-1(7),9-diene (47). Following the standard protocol for a sealed tube thermolysis reaction, a solution of **45** (0.13 g, 0.87 mmol) in benzene was heated at 225 °C for 8 h in a preheated sand bath. Purification by column chromatography (silica gel wash column, hexanes) afforded 0.11 g (88%) of **46** and **47** in a ratio of 3:1 (by NMR): IR (neat) 2950, 2850, 1620, 1450 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.9 (s, vinyl H, **47**), 5.7 (s, vinyl H, **46**), 5.5 (m, vinyl, **46**), 2.9 (m), 2.7 (m), 2.3 (m), 2.0–2.2 (m, methyl, **47**), 1.0–1.9 (m, methyl, **46**); exact mass calcd for $C_{11}H_{16}$ 148.1252, found 148.1252. The structures were proved by heating at 140 °C for 44 h in a benzene solution containing 10% Pd on carbon and *trans*-cinnamic acid to yield 2-methylazulene the UV spectrum of which was identical to that reported.[66]

8-Methylbicyclo[4.3.0]nona-1,8-diene (49). Following the standard protocol for a sealed tube thermolysis reaction, a solution of **48** (0.080

g, 0.60 mmol) in benzene was heated at 175 °C for 7 h in a preheated sand bath. Purification by column chromatography (silica gel wash column, hexanes) afforded 0.072 g (90%) of **49** as an oil: IR (neat) 3100, 3000, 2900, 1630, 1530, 880 cm^{-1}; ^1H NMR at 60 MHz ($CDCl_3$) δ 5.7 (s, 1 H, vinyl H), 5.2 (m, 1 H, vinyl H), 2.5 (m, 1 H), 2.3 (m, 1 H), 1.9–2.1 (m, 4 H), 1.8 (m, 1 H), 1.7 (s, 3 H, CH_3), 1.4 (m, 1 H), 1.2 (m, 1 H); exact mass calcd for $C_{10}H_{14}$ 134.1096, found 134.1096.

2,8-Dimethyl[5.3.0]deca-1,9-diene (50). Following the standard protocol for a sealed tube thermolysis reaction, a solution of **33** (0.039 g, 0.24 mmol) in benzene was heated at 180 °C for 18 h in a preheated sand bath. Purification by column chromatography (silica gel, hexanes) afforded 0.023 g (58%) of **50**: IR (neat) 3060, 2960, 2925, 2850, 1450, 1380 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.20 (dd, J = 5.7, 1.9 Hz, 1 H), 5.77 (dd, J = 5.7, 2.3 Hz, 1 H), 2.21–2.41 (m, 3 H), 1.92–2.02 (m, 2 H), 1.15–1.88 (m, 7 H, containing a singlet at δ 1.79), 1.04 (d, J = 7.1 Hz, 3 H), 0.95–0.98 (m, 1 H); exact mass calcd for $C_{12}H_{18}$ 162.1409, found 162.1408.

2,7,9-Trimethylbicyclo[5.3.0]deca-1,9-diene (51). Following the standard protocol for a sealed tube thermolysis reaction, a solution of **35** (0.042 g, 0.24 mmol) in benzene was heated at 180 °C for 18 h in a preheated sand bath. Purification by preparative TLC (silica gel, hexanes) afforded 0.026 g (62%) of **51** and 0.0030 g (8%) of **52**: **51** IR (neat) 2960, 2940, 2850, 1450, 1380 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.87 (s, 1 H), 2.50 (m, 1 H), 2.34 (d, J = 17.0 Hz, 1 H), 2.10 (d, J = 17.0 Hz, 1 H), 1.50–1.90 (m, 11 H, containing singlets at δ 1.74 and 1.79), 1.25–1.30 (m, 2 H), 1.15 (s, 3 H); exact mass calcd for $C_{13}H_{20}$ 176.1565, found 176.1565; **52** IR (neat) 2960, 2930, 2850, 1440, 1370 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.75–5.80 (m, 1 H), 5.69 (s, 1 H), 1.92–2.02 (m, 4 H), 1.83–1.90 (m, 2 H), 1.79 (s, 3 H), 1.77 (d, J = 1.1 Hz, 3 H), 1.67 (s, 3 H), 1.55 (d, J = 0.8 Hz, 3 H); the structure was verified by appropriate decoupling experiments; exact mass calcd for $C_{13}H_{20}$ 176.1565, found 176.1565. The latter compound (**52**) was by far the major product when the pyrolysis was conducted at 145 °C for 2.5 days.

Selective Reduction of 50 to 53. Wilkinson's catalyst (0.020 g, 0.022 mmol) was dissolved in 5 mL of freshly distilled benzene, and H_2 gas was bubbled through the solution for 30 min. A solution of **50** (0.040 g, 0.24 mmol) in benzene (1 mL) was added, and the resulting solution was treated with H_2 gas for 18 h at room temperature. The reaction mixture was passed through a basic alumina column with pentane and evaporation of the eluant afforded 0.035 g (86%) of spectroscopically pure 2-methyl-8-*exo*-methyl[5.3.0]dec-1-ene (**53**) with identical spectra to that reported:[22] exact mass calcd for $C_{12}H_{20}$ 164.1565, found 164.1566.

8-*exo*-(Phenylthio)bicyclo[5.3.0]deca-1,9-diene (55). Following the standard protocol for a sealed tube thermolysis reaction, a solution of ***20-trans*** (0.061 g, 0.25 mmol) in benzene was heated at 160 °C for 16 h in a preheated oil bath. Purification by flash chromatography (silica gel, benzene/CCl_4/hexane, 1:1:2) afforded 0.044 g (72%) of a rapidly decomposing diene: IR (neat) 3054, 2915, 2845, 1584, 1480, 1437, 1024, 828, 737, 691 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.41–7.44 (m, 2 H, phenyl), 7.14–7.32 (m, 3 H, phenyl), 6.07 (d, J = 5.45 Hz, 1 H, HC-10), 5.89 (dd, J = 5.45, 1.06 Hz, 1 H, HC-9), 5.76 (m, 1 H, HC-2), 3.94 (br s, 1 H, HC-8), 2.79 (br d, J = 11.14 Hz, 1 H, HC-7), 2.00–2.26 (m, 3 H), 1.74–1.90 (m, 2 H), 1.45–1.60 (m, 1 H), 1.20–1.38 (m, 2 H); exact mass calcd for $C_{16}H_{18}S$ 242.1130, found 242.1148. Irradiation of the signal at δ 6.07 caused the dd at δ 5.88 to become a broad singlet and the signal at δ 3.94 to sharpen. Irradiation at δ 5.89 caused the doublet at δ 6.07 to collapse to a singlet and the br s at δ 3.94 to become an apparent doublet. Irradiation at δ 5.76 altered the shape of the multiplet centered at δ 2.15. Irradiation of the signal at δ 3.94 caused the doublet at δ 6.07 to sharpen, the dd at δ 5.88 to become a doublet with J = 5.41 Hz, and the doublet at δ 2.79 to sharpen. Irradiation of the signal at δ 2.79 caused the multiplet at δ 5.76 to become a dd with J = 8.06 and 4.83 Hz, the br s at δ 3.94 to sharpen, and the multiplet centered at δ 1.30 to alter its shape.

8-*endo*-(Phenylthio)bicyclo[5.3.0]deca-1,9-diene (56). With a procedure identical to the above, ***20-cis*** (0.050 g, 0.21 mmol) was thermally rearranged to **56** in 87% yield (0.044 g): IR (neat) 3056, 2918, 2849, 1480, 1437, 843, 826, 735, 691 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.20–7.43 (m, 5 H, phenyl), 6.14 (d, J = 5.24 Hz, 1 H, HC-10), 5.90 (dd, J = 5.24, 2.60 Hz, 1 H, HC-9), 5.90 (m, 1 H, HC-2), 4.62 (d, J = 7.67 Hz, 1 H, HC-8), 3.13 (m, 1 H, HC-7), 2.20–2.35 (m, 1 H), 1.97–2.18 (m, 2 H), 1.52–1.87 (m, 1 H), 1.20–1.64 (m, 4 H); exact mass calcd for $C_{16}H_{18}S$ 242.1130, found 242.1132.

8-*exo*-Methylbicyclo[5.3.0]deca-1,9-diene (57). Allylidenecyclopropane **16** (0.050 g, 0.33 mmol) was distilled under vacuum through a heated (550 °C) quartz tube packed with quartz helices. The distillate was immediately captured in a -78 °C cold trap. After complete distillation, the contents of the trap were removed and chromatographed (silica gel, hexanes) to yield 0.046 g (92%) of **57** as a clear oil with the odor of pine. Alternatively, the same transformation could be effected by sealed tube thermolysis (220 °C, 16 h, benzene) with identical results: IR (neat) 3050, 2953, 2919, 2849, 1445, 835, 818, 743 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.95 (dd, J = 5.45, 1.95 Hz, 1 H, HC-10), 5.78 (dd J = 5.45, 2.05 Hz, 1 H, HC-9), 5.67 (m, 1 H, HC-2), 2.45 (m, 1 H, CH_3CH), 2.17–2.28 (m, 2 H), 1.97–2.15 (m, 2 H), 1.72–1.83 (m, 2 H), 1.40–1.62 (m, 1 H), 1.18–1.38 (m, 2 H), 1.07 (d, J = 6.99 Hz, 3 H, CH_3); ^{13}C NMR ($CDCl_3$) δ 154.3, 140.2, 132.9, 120.8, 51.5, 48.7, 33.9, 32.1, 29.5, 29.2, 20.5; exact mass calcd for $C_{11}H_{16}$ 148.1252, found 148.1223.

8-*endo*-Methylbicyclo[5.3.0]deca-1,9-diene (58). With a procedure identical to the above, **18** (0.040 g, 0.26 mmol) or **23** (0.26 mmol) was distilled through a heated (430 °C) quartz tube to afford **58** and **57** as a 5:1 mixture in 88% yield: IR (neat, mixture) 3050, 2951, 2922, 2853, 1699, 1684, 1558, 1506, 1456, 839, 819, 743 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.97 (dd, J = 5.50, 1.05 Hz, 1 H, HC-10), 5.83 (dd, J = 5.50, 1.90 Hz, 1 H, HC-9), 5.59 (m, 1 H, HC-2), 2.52 (m, 1 H, CH_3CH), 1.80–2.24 (m, 3 H), 1.31–1.74 (m, 4 H), 1.11–1.32 (m, 2 H), 0.86 (d, J = 7.24 Hz, 3 H, CH_3); exact mass calcd for $C_{11}H_{16}$ 148.1252, found 148.1223.

anti*- and *syn*-1,2,3,4,4a,4b,5,6,7,8-Decahydrobenz[a]azulene (59).** Compound **27** (86 mg, 0.46 mmol) was evaporated at 550 °C under vacuum through a quartz tube that had been previously washed with a slurry of lead carbonate[67] in water and dried. The distillate was captured in a -78 °C cold trap. The crude condensate was chromatographed (pentane, R_f 0.51) to yield **59-*anti and ***-syn*** (82 mg, 95%) in a ratio of 6:1 (by GC and NMR): IR (neat) 3034 (m), 2922 (s), 2849 (s), 1445 (s), 870 (s) cm^{-1}; (C_6D_6) δ 5.73–5.70 (m, vinyl, HC-10 syn), 5.75–5.65 (m, vinyl, HC-10 anti, HC-9 anti, HC-9 syn), 2.85–2.78 (m, bridgehead H, HC-4a syn, $J_{4a,4b}$ = 11.9 Hz), 2.52–2.45 (m, bridgehead H, HC-4b, syn, $J_{4a,4b}$ = 11.9 Hz), 2.40–2.35 (br, bridgehead H, HC-4a anti, $J_{4a,4b}$ = 21.4 Hz, also HC-8 anti), 2.25–2.12 (m, HC-1 anti), 2.10–2.04 (br m, bridgehead H, HC-4b anti, $J_{4a,4b}$ = 21.4 Hz), 2.00–1.95 (m, HC-3 anti), 1.92–1.85 (m, HC-5 and HC-8 anti), 1.78–1.70 (m, HC-4 and HC-2 anti), 1.67–1.55 (m, HC-7 and HC-6 anti), 1.48–1.30 (m, HC-3, HC-4, and HC-2 anti), 1.20–1.10 (m, HC-7 and HC-6 anti), 1.05–0.80 (m, HC-5 anti); ^{13}C NMR (C_6D_6) δ 155.4 (C-9a syn), 154.2 (C-9a anti), 152.0 (C-10a syn), 151.1 (C-10a anti), 126.2 (C-10 anti), 126.0 (C-10 syn), 116.3 (C-9 anti), 116.0 (C-9 syn), 54.4 (C-4b anti), 51.3 (C-4a anti), 49.6 (C-4b syn), 45.7 (C-4a syn), 34.9 (C-5 anti and syn), 34.6 (C-4 anti and syn), 32.6 (C-3 anti and syn), 30.2 (C-1 syn), 29.84 (C-1 anti), 29.80 (C-2 anti), 29.4 (C-8 anti), 29.1 (C-2 syn), 28.8 (C-8 syn), 27.7 (C-7 syn), 27.5 (C-7 anti), 26.4 (C-6 syn), 26.3 (C-6 anti); exact mass calcd for $C_{14}H_{20}$ 188.1565, found 188.1552.

8-*exo*-Methyl-(3-methylene)bicyclo[5.3.0]deca-1,9-diene (60) and 8-*exo*-Methyl-(6-methylene)bicyclo[5.3.0]deca-1,9-diene (61) by Double Ring Expansion. The thermal rearrangement reaction was performed separately with each geometric isomer of allylidenecyclopropane **38**. A solution of **38** (0.110 g, 0.679 mmol) in 2.5 mL of 2-methoxyethyl ether (diglyme) and a trace of radical inhibitor (3-*tert*-butyl-4-hydroxy-5-methylphenyl sulfide) was heated at reflux for 30 min. When diglyme is used for the thermal rearrangement, the following workup procedure is used. The cooled reaction mixture was diluted with hexanes and repeatedly washed with water to remove the majority of the diglyme. Solvent removal from the dried ($MgSO_4$) organic layer and purification by flash chromatography (silica gel treated 1% TEA, hexanes) afforded 0.094 g (86%) as an inseparable mixture (1.1:1.0) of regioisomers. The ^1H NMR spectru was a superposition of those of the individual isomers (see below).

8-*exo*-Methyl-(3-methylene)bicyclo[5.3.0]deca-1,9-diene (60) by Ketone Methenylation. In a two-necked flask equipped with a reflux condenser, methyltriphenylphosphonium bromide (0.118 g, 0.330 mmol) in THF (1.5 mL) was efficiently stirred as potassium *tert*-butoxide (0.247 g, 0.220 mmol) was added all at once. After the reaction mixture had been stirred for 20 min, a solution of **62** (0.0178 g, 0.110 mmol) in THF (1 mL) was added to the bright yellow reaction mixture and stirring was continued for an additional 3 h. The reaction mixture was diluted with ether and washed with water. The organic layer was dried (Na_2SO_4), and the solvent was removed *in vacuo*. Flash column chromatography (silica gel deactivated with 1% TEA, hexanes) afforded 0.017 g (97%) of **60**: IR (neat) 2926, 2860, 1684, 1633, 1454, 1375, 1045 cm^{-1}; ^1H NMR (C_6D_6) δ 6.15 (s, 1 H, HC-2), 6.01 (dd, J_{cis} = 5.46, J = 1.73 Hz, 1 H, HC-10), 5.75 (dd, J_{cis} = 5.46, J = 2.07 Hz, 1 H, HC-9), 4.90 (s, 1 H, exocyclic H), 4.88 (s, 1 H, exocyclic H), 2.44–2.54 (m, 1 H), 2.28–2.42 (m, 2 H, HC-7 and HC-8), 2.21 (ddd, J = 13.9, 5.60, 4.08 Hz, 1 H), 1.41–1.80 (m, 4 H), 0.92 (d, J = 7.02 Hz, 3 H, CH_3); ^{13}C NMR (C_6D_6) δ 153.7, 148.5, 142.2, 134.2, 123.5, 113.6, 49.6, 48.6, 34.9, 32.0, 26.8, 19.9; exact mass calcd for $C_{12}H_{16}$ 160.1252, found 160.1252.

8-*exo*-Methyl-(6-methylene)bicyclo[5.3.0]deca-1,9-diene (61) by Ketone Methenylation. A solution of **65** (0.0317 g, 0.198 mmol) in CH_2Cl_2 (3 mL) was stirred at ambient temperature as aliquots of Lombardo's reagent[68] were added periodically until TLC analysis indicated that the reaction was complete. The reaction mixture was then taken up in ether and washed with 5% $NaHCO_3$. After being dried (Na_2SO_4) and removal of the solvent *in vacuo*, the reaction mixture was subjected to chromatography (silica gel treated with 1% TEA, hexanes) to afford 0.0225 g (71%) of **61** as a clear oil: IR (neat) 3051, 2928, 2855, 1639, 1452, 1259, 885 cm^{-1}; ^1H NMR (C_6D_6) δ 5.94 (dd, J_{cis} = 5.49, J = 1.49 Hz, 1 H, HC-10), 5.72, (dd, J_{cis} = 5.49, J = 1.43 Hz, 1 H, HC-9), 5.53 (m, 1 H, HC-2), 4.81 (s, 1 H, exocyclic H), 4.76 (s, 1 H, exocyclic H), 2.98 (br s, 1 H, HC-8), 2.46 (ddd, J = 13.3, 7.95, 4.63 Hz, 1 H), 1.99–2.21 (m, 4 H, including HC-7), 1.65–1.77 (m, 1 H), 1.38–1.52 (m, 1 H), 1.06 (d, J = 6.88 Hz, 3 H, CH_3); ^{13}C NMR (C_6D_6) δ 151.1, 149.8, 139.9, 132.1, 119.4, 107.5, 55.3, 44.7, 39.5, 28.1, 28.0, 20.7; exact mass calcd for $C_{12}H_{16}$ 160.1252, found 160.1252.

8-*exo*-Methyl-3-oxobicyclo[5.3.0]deca-1,9-diene (62). A solution of **41** (0.150 g, 0.926 mmol) in diglyme (2 mL) and a trace of radical inhibitor was heated at reflux for 3 h. Standard workup and purification by flash chromatography (silica gel, 18% ethyl acetate–hexanes) afforded 0.108 g (72%) of **62** as a clear oil: IR (neat) 3052, 2928, 2827, 1651, 1612, 1455, 1352, 1221 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.38 (dd, J_{cis} = 5.40, J = 2.43 Hz, 1 H, HC-9), 6.19 (dd, J_{cis} = 5.40, J = 1.93 Hz, 1 H, HC-10), 5.96 (br s, 1 H, HC-2), 2.51–2.66 (m, 4 H, including HC-7 and HC-8), 2.14–2.22 (m, 1 H), 1.74–2.02 (m, 2 H), 1.45–1.61 (m, 1 H), 1.17 (d, J = 7.11 Hz, 3 H, CH_3); ^{13}C NMR ($CDCl_3$) δ 203.4, 169.4, 151.6, 133.1, 122.5, 50.3, 49.0, 41.7, 29.8, 20.5, 19.4; exact mass calcd for $C_{11}H_{14}O$ 162.1045, found 162.1045.

8-*exo*-Methyl-6-oxobicyclo[5.3.0]deca-1,9-diene (65). A solution of $KN(TMS)_2$ (0.176 g, 0.882 mmol) in dry THF (3 mL) was cooled to -78 °C prior to the slow addition of a solution of **41** (0.0953 g, 0.588 mmol) in dry THF (2 mL). After the reaction mixture had been stirred for 15 min, a 1.0 M THF solution of TBDMSCl (0.880 mmol) was added, the ice bath was removed, and the reaction mixture was stirred for 30 min. The resulting mixture was diluted with ether and washed with cold saturated $NaHCO_3$. The organic layer was dried ($MgSO_4$), the solvents were removed *in vacuo*, and the resulting oil was rapidly chromatographed (silica gel deactivated with 1% TEA, 10% ethyl acetate–hexanes). Diglyme (2 mL) was added to this crude product which was then heated to reflux for 2 h. The reaction mixture was allowed to cool to ambient temperature, and it was diluted with ether and shaken with 5% HCl. Following the washing of the organic layer with saturated $NaHCO_3$ solution and reextraction of the aqueous layer, the combined organic layers were dried ($MgSO_4$) and concentrated *in vacuo*. Flash column chromatography (silica gel wash, 5% ethyl acetate-hexanes) afforded 0.067 g (70%) of **65** as a clear oil: IR (neat) 2953, 2928, 2867, 1709, 1620, 1456, 1179, 837 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.84 (m, 2 H, HC-9 and HC-10), 5.59 (m, 1 H, HC-2), 3.82 (m, 1 H, HC-7), 3.60 (m, 1 H, HC-8), 2.62–2.72 (m, 1 H), 2.50–2.61 (m, 2 H), 2.14–2.24 (m, 2 H), 1.79–1.84 (m, 1 H), 1.07 (d, J = 7.13 Hz, 3 H, CH_3); ^{13}C NMR ($CDCl_3$) δ 207.0 (s), 142.6 (s), 140.3 (d), 131.0 (d), 120.3 (d), 59.4 (d), 43.8 (t), 39.5 (d), 29.5 (t), 21.4 (t), 20.7 (q); exact mass calcd for $C_{11}H_{14}O$ 162.1045, found 162.1045.

7,8-Dimethyl-3-oxobicyclo[5.3.0]deca-1,9-diene (67) and 2,8-Dimethyl-6-oxobicyclo[5.3.0]deca-1,9-diene (68). A solution of **66** (0.05 g, 0.30 mmol; see supplementary material) in diglyme (1.5 mL) was heated at reflux for 3 h. Standard workup and chromatography (5% ethyl acetate–hexane to elute **68**, and 10% ethyl acetate–hexane to elute **67**) afforded 0.29 g (55%) of **67** and 0.0095 g (18%) of **68**: **67** IR (neat) 2936, 2872, 1653, 1617, 1445, 1260, 855 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.14 (m, 2 H, HC-9 and HC-10), 5.82 (s, 1 H, HC-2), 2.67–2.76 (m, 2 H, including CH_3CH), 2.49–2.60 (m, 1 H), 1.75–2.15 (m, 4 H), 1.05 (s, 3 H, CH_3), 1.04 (d, J = 5.9 Hz, 3 H, CH_3). ^{13}C NMR ($CDCl_3$) δ 204.3, 170.0, 148.1, 133.1, 121.2, 52.3, 49.9, 45.5, 36.6, 24.0, 20.4, 12.0; exact mass calcd for $C_{12}H_{16}O$ 176.1201, found 176.1225; **68-*exo*** IR (neat) 2957, 2930, 1708, 1653, 1455, 1109 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.12 (dd, J_{cis} = 5.7 Hz, J = 1.9 Hz, 1 H, HC-10), 5.86 (dd, J_{cis} = 5.7 Hz, J = 2.2 Hz, 1 H, HC-9), 3.80 (br s, 1 H, HC-7), 3.55 (m, 1 H, CH_3CH), 2.45–2.71 (m, 3 H), 2.08–2.30 (m, 2 H), 1.70–1.88 (m, 1 H), 1.75 (s, 3 H, CH_3), 1.05 (d, J = 7.1 Hz, 3 H, CH_3); ^{13}C NMR ($CDCl_3$) δ 207.4, 140.0, 136.3, 127.7, 127.4, 59.3, 43.8, 39.5, 36.1, 22.2, 21.5, 21.0; characteristic peaks of the **68-*endo*** isomer 6.31 (dd, J_{cis} = 5.6 Hz, J = 1.5 Hz, 1 H, HC-10), 5.92 (dd, J_{cis} = 5.6, J = 2.4 Hz, 1 H, HC-9), 3.71 (br d, 1 H, HC-7), 3.20 (m, 1 H, CH_3CH), 1.87 (d, J = 2.0 Hz, 3 H, CH_3), 1.00 (d, J = 7.2 Hz, 3 H, CH_3); exact mass calcd for $C_{12}H_{16}O$ 176.1201, found 176.1225.

Bicyclo[5.3.0]deca-1(10)-en-9-one (70). KH (0.15 g, 3.80 mmol) was added to a THF solution (10 mL) of **24** (0.34 g, 1.3 mmol), and after stirring for 18 h, the reaction mixture was diluted with ether and washed with water. The organic layer was dried (Na_2SO_4) and concentrated *in vacuo*. The residue was then subjected to standard sealed tube thermolysis conditions (220 °C, 24 h). Silica gel chromatography (18% ethyl acetate–hexanes) effected hydrolysis of the enol ether function of **69** and purification to afford 0.14 g (71%) of **70**: IR (neat) 2924, 2853, 1694, 1605, 1451, 1190 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.86 (d, J = 1.4 Hz, 1 H, HC-10), 2.92 (m, 1 H), 2.60–2.75 (m, 3 H), 1.20–2.20 (m, 9 H); ^{13}C NMR ($CDCl_3$) δ 209.0, 188.0, 129.8, 44.5, 44.4, 34.3, 32.3, 30.4, 28.6, 26.4; exact mass calcd for $C_{10}H_{14}O$ 150.1045, found; spectra data for the intermediate allylidenecyclopropane **25** IR (neat) 2979, 2930, 2857, 1628, 1304, 1078 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.30 (s, 1 H, C=C*H*), 4.20 (s, 1 H, OCC*H*), 4.02 (s, 1 H, OCC*H*), 3.54 (q, J = 7.0 Hz, 2 H, OCH_2CH_3), 0.95–2.10 (m, 13 H, including t at δ 1.12, J = 7.0 Hz, 3 H, OCH_2CH_3); ^{13}C NMR ($CDCl_3$) δ 160.1, 137.1, 115.5, 84.0, 62.6, 23.3, 22.7, 21.8, 21.6, 14.8, 14.7, 11.6.

7-(Trimethylsilyl)-7-(1-oxo-2-buten-1-yl)bicyclo[4.1.0]heptane (71). A solution of **14** (2.0 g, 7.2 mmol) in THF (10 mL) was treated with LDMAN for 30 min at -78 °C. This mixture was then added to a precooled (-78 °C) solution of crotonic anhydride (5.0 g, 33 mmol) in THF (20 mL) *via* a cannula syringe. The mixture was stirred for 2 h at -78 °C and then allowed to warm to ambient temperature. The reaction mixture was diluted with ether and successively washed with 5% HCl, 5% NaOH, and brine. The solvent was removed from the dried ($CaCl_2$) organic layer, and purification by flash chromatography (silica gel, 30% acetonitrile–hexane to remove phenylthio crotonate and then 5% ethyl acetate–hexane) afforded 0.95 g (58%) of **71**: IR (neat) 2933, 2863, 2360, 1727, 1659, 1445, 1176 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.82–6.74 (m, 1 H), 6.14 (dd, J_{trans} = 15.7 Hz, J = 1.5 Hz, 1 H), 1.89 (dd, J = 8.1, 1.1 Hz, 3 H, CH_3), 1.82–1.87 (m, 2 H), 1.13–1.26 (m, 6 H), 0.95–1.00 (m, 2 H), 0.21 (s, 9 H, $(CH_3)_3Si$); exact mass calcd for $C_{14}H_{24}OSi$ 236.1596, found 236.1597.

8-*exo*-Methylbicyclo[5.3.0]dec-1-ene-10-one (74). Following the standard protocol for a sealed tube thermolysis reaction, a solution of **71** (0.16 g, 0.69 mmol) in heptane was heated at 250 °C for 2 h in a preheated oil bath. The solution was transferred to a flask containing 5 mL of ether and 2 drops of 5% HCl, and the mixture was heated at reflux for 30 min. After removing the solvent from the dried ($MgSO_4$) organic layer, purification by flash chromatography (silica gel, 5% ethyl acetate–hexane) afforded 0.09 g (83%) of **74**. Using biphenyl as an internal standard, gas chromatography analysis indicated the intermediate enol silyl ether was produced in 90% yield: ^1H NMR ($CDCl_3$) δ 6.85–6.90 (m, 1 H), 2.43–2.54 (m, 2 H), 1.84–2.29 (m, 4 H), 1.60–1.79 (m, 2 H), 1.55 (s, 2 H), 1.23–1.50 (m, 2 H), 1.16 (d, J = 6.4 Hz, 3 H, CH_3); ^{13}C NMR ($CDCl_3$) δ 202.5, 144.4, 137.5, 50.0, 46.7, 35.4, 32.2, 29.3, 26.7, 16.8; exact mass calcd for $C_{11}H_{16}O$ 164.1182, found 164.1182.

8-(Phenylthio)-8-(trimethylsilyl)bicyclo[5.1.0]octan-2-one (75). In a manner described for the preparation of **39**, cycloheptenone (2.5 g, 22.7 mmol) was cyclopropanated. Standard workup and purification by column chromatography (silica gel, 5% ethyl acetate–hexanes) afforded 3.8 g (69%) of **75** as a white solid (mp 77.0–78.8): IR (CCl_4) 3057, 2930, 2857, 1701, 1583, 1248, 738 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.05–7.28 (m, 5 H, phenyl), 2.55 (t, J = 6.20 Hz, 1 H), 2.35 (m, 1 H), 1.52–1.99 (m, 8 H), –0.05 (s, 9 H, $(CH_3)_3Si$); ^{13}C NMR ($CDCl_3$) δ 207.3, 137.9, 128.2, 127.1, 124.7, 44.0 (two overlapping peaks), 35.6, 25.6, 25.1, 23.6, –2.29; exact mass calcd for $C_{17}H_{24}OSSi$ 304.1317, found 304.1322.

2-(*tert*-Butyldiphenylsiloxy)-7-(phenylthio)-7-(trimethylsilyl)bicyclo-[4.1.0]hept-2-ene (76). A solution of **39** (0.690 g, 2.38 mmol) in THF (10 mL) was added to a cooled (-78 °C) solution of $KN(TMS)_2$ (0.570 g, 2.86 mmol) in THF (5 mL). After the reaction mixture had been stirred for 15 min, a solution of *tert*-butyldiphenylsilyl chloride (0.660 g, 2.38 mmol) in THF (3 mL) was added. The dry-ice bath was removed, and the resulting mixture was allowed to warm to room temperature. The reaction mixture was diluted with ether, and the organic layer was washed with water, dried ($MgSO_4$), and concentrated *in vacuo*. Purification by flash chromatography (silica gel, 3% ethyl acetate–hexane) afforded 1.25 g (99%) of **76** as a viscous oil: IR (neat) 2932, 2857, 1657, 1391, 1179, 841 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.08–7.85 (m, 15 H, phenyl), 4.57–4.65 (m, 1 H, SiOCCH), 1.62–2.20 (m, 6 H), 1.12 and 1.19 (s, 9 H, $(CH_3)_3CSi$), 0.03 and 0.22 (s, 9 H, $(CH_3)_3Si$); exact mass calcd for $C_{32}H_{40}OSSi_2$ 528.2307, found 528.2325.

2-(*tert*-Butyldiphenylsiloxy)-7-(trimethylsilyl)-7-(1-oxo-2-buten-1-yl)-bicyclo[4.1.0]hept-2-ene (77). A solution of **76** (1.26 g, 2.39 mmol) in THF (5 mL) was treated with LDBB for 5 min at -78 °C. This mixture was then added to a precooled (-78 °C) solution of crotonic anhydride

(2.57 g, 16.7 mmol) in THF (15 mL) *via* a cannula syringe, and the resulting mixture was stirred for 15 min. The reaction mixture was transferred to a separatory funnel, diluted with ether, and washed with water. The solvent was removed from the dried ($MgSO_4$) organic layer and purification by flash chromatography (silica gel, 3% ethyl acetate-hexane) afforded 0.814 g (70%) of **77** as a pale yellow oil: IR (neat) 2932, 2859, 1669, 1624, 1250, 1181 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.71–7.76 (m, 4 H, phenyl), 7.35–7.45 (m, 6 H, phenyl), 6.89 (dq, J_{trans} = 15.5, J = 6.98 Hz, 1 H, CH_3CH), 6.38 (dd, J_{trans} = 15.5, J = 1.58 Hz, 1 H, CH_3CHCH), 4.38 (m, 1 H, SiOCCH), 1.97–2.08 (m, 1 H), 1.88 (dd, J = 6.98, 1.50 Hz, 3 H, CH_3), 1.36–1.74 (m, 5 H), 1.10 (s, 9 H, $(CH_3)_3$-CSi), 0.00 (s, 9 H, $(CH_3)_3Si$); exact mass calcd for $C_{30}H_{40}O_2Si_2$ 488.2566, found 488.2561.

2-(*tert*-Butyldiphenylsiloxy)-8-(trimethylsilyl)-8-(1-oxo-2-buten-1-yl)-bicyclo[5.1.0]oct-2-ene (78). A solution of **42** (0.640 g, 1.17 mmol) in THF (3 mL) was treated with LDBB for 5 min at -78 °C. This mixture was added to a precooled (-78 °C) solution of crotonic anhydride (1.28 g, 8.32 mmol) in THF (15 mL). After being stirred for 15 min, the mixture was worked up as described above to afford 0.45 g (76%) of **78** after purification by flash chromatography (silica gel, 3% ethyl acetate–hexane): IR (neat) 2932, 2859, 1671, 1620, 1428, 1144, 845 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.72–7.76 (m, 4 H, phenyl), 7.34–7.42 (m, 6 H, phenyl), 6.80–6.90 (m, 2 H, CH_3CHCH), 4.54 (m, 1 H, SiOCCH), 1.28–2.17 (m, 8 H), 1.80 (d, J = 5.38 Hz, 3 H, CH_3), 1.10 (s, 9 H, $(CH_3)_3CSi$), 0.08 (s, 9 H, $(CH_3)_3Si$); exact mass calcd for $C_{31}H_{42}O_2Si_2$ 502.2692, found 502.2724.

6-(*tert*-Butyldiphenylsiloxy)-8-methylbicyclo[5.3.0]deca-1,5-diene-10-one (79). Compound **77** (0.13 g, 0.26 mmol) was heated at reflux in diglyme for 3 h. After being cooled to room temperature, the reaction mixture was diluted with THF and treated with 5% aqueous NaOH for 5 min. Workup by the standard procedure and purification by flash chromatography (silica gel, 5% ethyl acetate–hexanes) afforded 0.074 g (70%) of **79** and 0.0065 g (6%) of **2-(*tert*-Butyldiphenylsiloxy)-10-methylbicyclo[5.3.0]deca-1(7),2-diene-8-one (80)**: **79** IR (neat) 2934, 2857, 1717, 1646, 1113, 702 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.68–7.80 (m, 4 H, phenyl), 7.32–7.50 (m, 6 H, phenyl), 6.76 (m, 1 H, HC-2), 4.59 (m, 1 H, HC-5), 3.76 (m, 1 H, HC-7), 2.70–2.86 (m, 1 H, CH_3CH), 2.62 (dd, J = 17.46, 7.55 Hz, 1 H), 2.13–2.28 (m, 2 H), 2.03 (dd, J = 17.46, 12.48 Hz, 1 H), 1.61–1.86 (m, 2 H), 1.42 (d, J = 6.22 Hz, 3 H, CH_3), 1.02 (s, 9 H, $(CH_3)_3CSi$); exact mass calcd for $C_{27}H_{32}O_2Si$ 416.2176, found 416.2168; **80** IR (neat) 3071, 2930, 2856, 1711, 1646, 1258, 742 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.71 (m, 4 H, phenyl), 7.36–7.43 (m, 6 H, phenyl), 5.65 (m, 1 H, HC-5), 2.48–2.72 (m, 3 H, including CH_3CH), 2.25–2.46 (m, 3 H), 1.88–2.04 (m, 1 H), 1.60–1.81 (m, 2 H), 1.12 (d, J = 7.02 Hz, 3 H, CH_3), 1.06 (s, 9 H, $(CH_3)_3CSi$); exact mass calcd for $C_{27}H_{32}O_2Si$ 416.2172, found 416.2199.

7-(*tert*-Butyldiphenylsiloxy)-9-methylbicyclo[6.3.0]undeca-1,6-diene-11-one (81). Compound **78** (0.22 g, 0.44 mmol) was heated at reflux in diglyme for 3 h. The resulting mixture is then treated as described above to afford 0.19 g (71%) of **81** and 0.0080 (4%) of **82** after chromatography (silica gel, 18% ethyl acetate–hexane): **81** IR (neat) 2932, 2859, 1723, 1653, 1647, 1144 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.73–7.79 (m, 4 H, phenyl), 7.34–7.46 (m, 6 H, phenyl), 6.43 (ddd, J = 10.54, 7.47, 3.11 Hz, 1 H, HC-2), 4.30 (m, 1 H, HC-6), 3.09 (m, 1 H, HC-8), 2.61 (dd, J = 17.61, 7.14 Hz, 1 H), 2.29–2.41 (m, 1 H, CH_3CH), 1.95–2.16 (m, 3 H, including dd, J = 17.61, 11.54 Hz, 1 H), 1.81–1.87 (m, 1 H), 1.50–1.62 (m, 1 H), 1.45 (d, J = 6.47 Hz, 3 H, CH_3), 0.88–1.20 (m, 2 H), 1.05 (s, 9 H, $(CH_3)_3CSi$); exact mass calcd for $C_{28}H_{34}O_2Si$ 430.2328, found 430.2317; **82** IR (neat) 3069, 2930, 2859, 1700, 1649, 1428, 1215 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.72–7.76 (m, 4 H, phenyl), 7.35–7.47 (m, 6 H, phenyl), 5.27 (s, 1 H, HC-6), 2.58–2.67 (m, 1 H, CH_3CH), 2.52 (dd, J = 18.38, 6.71 Hz, 1 H), 2.16–2.41 (m, 4 H), 1.90 (dd, J = 18.38, 1.90 Hz, 1 H), 1.51–1.78 (m, 4 H), 1.13 (d, J = 7.02 Hz, 3 H, CH_3), 1.08 (s, 9 H, $(CH_3)_3CSi$); exact mass calcd for $C_{28}H_{34}O_2Si$ 430.2328, found 430.2354.

7-(Trimethylsilyl)-7-(1-oxo-2-buten-1-yl)bicyclo[4.1.0]heptan-2-one (83). 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (0.24 g, 1.1 mmol) was added all at once to a solution of **40** (0.22 g, 0.89 mmol) in THF (20 mL) at 0 °C. Stirring was continued for 30 min at 0 °C and for an additional 5 h at room temperature. The reaction mixture was diluted with ether, and the organic layer was washed with water, saturated aqueous $NaHCO_3$ (until washings were pale yellow), and water. The organic phase was dried ($MgSO_4$) and concentrated *in vacuo*. Purification by flash chromatography (silica gel, 18% ethyl acetate–hexanes) afforded 0.16 g (72%) of **83**: IR (CCl_4) 2959, 1696, 1622, 1445, 1252, 843 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.86 (dq, J_{trans} = 15.45, J = 6.81 Hz, 1 H, CH_3CH), 6.10 (dd, J_{trans} = 15.45, J = 1.61 Hz, 1 H, CH_3CHCH), 1.42–2.18 (m, 8 H), 1.87 (dd, J = 6.81, 1.61 Hz, 3 H, CH_3), 0.05 (s, 9 H, $(CH_3)_3Si$); ^{13}C NMR ($CDCl_3$) δ 208.4, 197.2, 144.1, 131.8, 38.5, 37.8, 31.7, 25.9, 20.6, 19.7, 18.1, –2.92; exact mass calcd for $C_{14}H_{22}O_2Si$ 250.1358, found 250.1382.

2-Oxo-8-(trimethylsilyl)-8-(1-oxo-2-buten-1-yl)bicyclo[5.1.0]octane (84). In an identical procedure to that described above, **44** (0.16 g, 0.60 mmol) was oxidized with DDQ to afford 0.13 g (79%) of **84**: IR (neat) 2938, 1705, 1673, 1624, 1315, 1294, 845 cm^{-1}; ^1H NMR (C_6D_6) δ 6.79 (dq, J_{trans} = 15.48 , J = 6.91 Hz, 1 H, CH_3CH), 6.40 (dd, J_{trans} = 15.48 , J = 1.49 Hz, 1 H, CH_3CHCH), 1.99–2.21 (m, 3 H), 1.95 (d, J = 8.65 Hz, 1 H), 1.46 (dd, J = 6.91, 1.49 Hz, 3 H, CH_3), 1.26–1.47 (m, 3 H), 1.05–1.17 (m, 3 H), –0.08 (s, 9 H, $(CH_3)_3Si$); ^{13}C NMR (C_6D_6) 206.3, 195.3, 139.5, 133.9, 41.9, 39.0, 36.6, 25.8, 25.2, 24.9, 23.4, 17.6, –2.83; exact mass calcd for $C_{15}H_{24}O_2Si$ 264.1514, found 264.1553.

8-Methylbicyclo[5.3.0]deca-1-ene-3,10-dione (85). A solution of **83** (0.053 g, 0.21 mmol) in 1.5 mL of diglyme was heated at reflux for 4 h. The cooled reaction mixture was diluted with THF and treated with 5% HCl for 5 min. This mixture was then treated in the usual manner, and purification by HPLC chromatography (Si 83–121-C, 20% ethyl acetate–hexanes) afforded 0.022 g (58%) of **85** and 0.002 g (5%) of **86**: **85** IR (neat) 2963, 2930, 1732, 1684, 1636, 1507 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.57 (d, J = 3.23 Hz, 1 H, HC-2), 2.54–2.81 (m, 3 H), 2.47 (m, 1 H, HC-7), 2.25–2.38 (m, 1 H), 1.82–2.17 (m, 4 H, including CH_3CH), 1.40–1.58 (m, 1 H), 1.24 (d, J = 6.40 Hz, 3 H, CH_3); ^{13}C NMR ($CDCl_3$) δ 205.9, 203.3, 152.3, 129.2, 50.7, 46.4, 44.0, 35.3, 31.1, 23.0, 18.5; exact mass calcd for $C_{11}H_{14}O_2$ 178.0994, found 178.1004.

8-Methylbicyclo[5.3.0]dec-1-ene-6,10-dione (86). Treatment of **79** (0.20 g, 0.48 mmol) with 10% HCl in THF for 30 min effected hydrolysis of the enol silyl ether. The reaction mixture was diluted with ether, and the organic layer was washed with saturated aqueous $NaHCO_3$. Solvent removal from the dried ($MgSO_4$) organic layer and purification by flash chromatography (silica gel, 20% ethyl acetate–hexane) afforded 0.082 g (96%) of **86**: IR (neat) 2955, 2870, 1707, 1642, 1456, 1233, 1080 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.82 (m, 1 H, HC-2), 3.74 (m, 1 H, HC-7), 2.61–2.82 (m, 3 H, including CH_3CH), 2.43–2.60 (m, 2 H), 2.08–2.38 (m, 2 H), 2.10 (dd, J = 17.90, 11.19 Hz, 1 H), 1.82–1.92 (m, 1 H), 1.29 (d, J = 6.56 Hz, 3 H, CH_3); ^{13}C NMR ($CDCl_3$) δ 206.8, 203.8, 137.1, 134.2, 58.2, 45.2, 43.9, 29.4, 27.8, 20.3, 19.8; exact mass calcd for $C_{11}H_{14}O_2$ 178.1001, found 178.0993.

9-Methylbicyclo[6.3.0]undec-1-ene-3,11-dione (87). As above, **84** (0.059 g, 0.22 mmol) was thermalized for 3 h to yield 0.017 g (40%) of **87-*exo***, 0.0051 g (12%) of **87-*endo***, 0.0038 g (9%) of **88-*exo***, and 0.0030 g (7%) of **88-*endo*** after separation by HPLC chromatography (Si 83–121-C, 20% ethyl acetate–hexanes): **87-*exo*** IR (neat) 2961, 2924, 2865, 1717, 1655, 1630, 1194 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.67 (d, J = 2.67 Hz, 1 H, HC-2), 2.81–2.92 (m, 2 H, including HC-8), 2.48–2.64 (m, 2 H), 1.90–2.16 (m, 3 H, including CH_3CH), 1.38–1.88 (m, 5 H), 1.11 (d, J = 6.47 Hz, 3 H, CH_3); ^{13}C NMR ($CDCl_3$) δ 207.1, 205.2, 148.2, 130.7, 49.0, 44.5, 42.2, 34.8, 29.4, 25.3, 22.5, 20.8; exact mass calcd for $C_{12}H_{16}O_2$ 192.1151, found 192.1154; **86-*endo*** IR (neat) 2924, 2853, 1728, 1714, 1666, 1651, 1454, 1019 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.72 (d, J = 1.95 Hz, 1 H, HC-2), 3.32 (m, 1 H), 2.85–2.95 (m, 1 H), 2.46–2.60 (m, 3 H, including CH_3CH), 2.07–2.18 (m, 1 H), 1.68–1.94 (m, 4 H), 1.30–1.58 (m, 2 H), 1.04 (d, J = 6.61 Hz, 3 H, CH_3); exact mass calcd for $C_{12}H_{16}O_2$ 192.1151, found 192.1147; **88-*exo*** spectra identical to that obtained from the hydrolysis of **81**; **88-*endo*** IR (neat) 2926, 2853, 1698, 1682, 1651, 1634, 1204 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.96 (m, 1 H, HC-2), 3.72 (bd, J = 8.6 Hz, 1 H, HC-8), 2.40–2.81 (m, 4 H), 1.50–2.32 (m, 7 H), 0.98 (d, J = 6.5 Hz, 3 H, CH_3); exact mass calcd for $C_{12}H_{16}O_2$ 192.1151, found 192.1153.

9-Methylbicyclo[6.3.0]undec-1-ene-7,11-dione (88). As described above, **81** (0.05 g, 0.12 mmol) was hydrolyzed to afford 0.02 g (98%) of **88** after column chromatography (18% ethyl acetate–hexane): **88-*exo*** IR (neat) 2928, 2857, 1725, 1700, 1653, 1647, 1456 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.81 (ddd, J = 10.01, 7.32, 2.86 Hz, 1 H, HC-2), 3.26 (bd, J = 8.96 Hz, 1 H, HC-8), 2.56–2.65 (m, 2 H, including CH_3CH), 2.22–2.45 (m, 3 H), 2.05 (dd, J = 17.64, 10.10 Hz, 1 H), 1.82–1.94 (m, 4 H), 1.38–1.44 (m, 1 H), 1.16 (d, J = 6.58 Hz, 3 H, CH_3); ^{13}C NMR ($CDCl_3$) δ 212.4, 203.8, 138.4, 136.9, 61.6, 45.9, 38.5, 31.5, 27.1, 26.2, 25.2, 19.1; exact mass calcd for $C_{12}H_{16}O_2$ 192.1151, found 192.1165.

10-Methylbicyclo[5.3.0]dec-1(7)-ene-2,8-dione (89). Three drops of 1,8-diazobicyclo[5.4.0]undec-7-ene (DBU) was added to a solution of **86** (0.030 g, 0.17 mmol) in THF (5 mL). TLC analysis indicated that the isomerization was complete after 1 h. The reaction mixture was diluted with ether, and the organic layer was successively wash with 5% HCl, satutated aqueous $NaHCO_3$, and brine. The organic layer was dried ($MgSO_4$), and the solvent was removed *in vacuo*. Column chromatography (silica gel, 18% ethyl acetate–hexane) afforded 0.028 g (95%) of

89: IR (neat) 2924, 2853, 1709, 1674, 1652, 1019 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.23–3.32 (m, 1 H, CH_3CH), 2.61–2.81 (m, 3 H), 2.40–2.60 (m, 2 H), 2.11 (dd, J = 19.34, 1.95 Hz, 1 H), 1.78–1.93 (m, 4 H), 1.15 (d, J = 7.07 Hz, 3 H, CH_3); ^{13}C NMR ($CDCl_3$) δ 209.7, 203.1, 167.1, 148.1, 44.4, 43.2, 32.6, 25.0, 23.5, 22.7, 20.0; exact mass calcd for $C_{11}H_{14}O_2$ 178.0994, found 178.0997.

11-Methylbicyclo[6.3.0]undeca-1(8)-ene-2,9-dione (90). As described above, **88** (0.015 g, 0.078 mmol) was isomerized with DBU to afford 0.014 g (93%) of **90** after column chromatography (silica gel, 35% ethyl acetate–hexanes): IR (neat) 2934, 2870, 1703, 1638, 1410, 1141 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.26 (m, 2 H), 2.78–2.86 (m, 1 H, CH_3CH), 2.66 (dd, J = 18.78, 6.51 Hz, 1 H), 2.36–2.55 (m, 4 H), 2.04 (dd, J = 18.78, 1.89 Hz, 1 H), 1.75–1.88 (m, 4 H), 1.21 (d, J = 7.13 Hz, 3 H, CH_3); ^{13}C NMR ($CDCl_3$) δ 212.7, 207.0, 176.8, 134.9, 42.6, 42.4, 39.8, 37.3, 27.0, 26.3, 24.6, 19.1; exact mass calcd for $C_{12}H_{16}O_2$ 192.1151, found 192.1156.

2,8α-Dimethyl-7β-*H*-5α-(2-hydroxy-2-propanyl)bicyclo[5.3.0]dec-1-ene or Racemic α-Bulnesol (91). A solution of **105** (0.012 g, 0.059 mmol) in THF (2 mL) was treated with methyl magnesium bromide (3.0 M, 0.12 mmol, 39 μL) to afford, after standard workup and chromatography (silica gel treated with 0.01% TEA, 10% ethyl acetate–hexane), 12.3 mg (94%) of **91** as a clear oil: IR (neat) 3386, 2928, 2861, 1458, 1377, 1138, 1019, 930, 741 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.24–2.47 (m, 2 H), 1.81–2.20 (m, 4 H), 1.65 (br s, 3 H, vinyl CH_3), 1.01–1.48 (m, 4 H), 1.21 (br s, 1 H, OH), 1.06–1.25 (m, 3 H), 1.17 (s, 6 H, $(CH_3)_2C(OH)$), 0.89 (d, J = 7.07 Hz, 3 H, CH_3C-4); exact mass calcd for 222.1984, found $C_{15}H_{26}O$ 222.1984.

1-Methyl-4-(2-methyldioxolan-2-yl)-7-(phenylthio)-7-(trimethylsilyl)-bicyclo[4.1.0]heptane (95). A solution of **4** (1.69 g, 4.99 mmol) in THF (2 mL) was silylated by the procedure described for **31.** Standard workup and flash column chromatography (silica gel, 5% ethyl acetate–hexanes) afforded 1.69 g (90%) of **95** as a 9:1 mixture rich in the *endo*-dioxolanyl isomer (R_f 0.36 and 0.32 for the endo and exo isomers, respectively, in 10% ethyl acetate–hexanes): IR (neat, mixture of isomers) 2948, 2876, 1583, 1477, 1439, 1375, 1248, 1086, 1043, 839, 737, 692 cm^{-1}; *endo*-dioxolanyl isomer ^1H NMR ($CDCl_3$) δ 7.21–7.30 (m, 4 H, *exo*-phenyl), 7.07–7.13 (m, 1 H, *exo*-phenyl), 3.92–4.05 (m, 4 H, acetal CH_2CH_2), 1.15–2.10 (m, 8 H), 1.48 (s, 3 H, bridge CH_3), 1.31 (s, 3 H, $C(OCH_2CH_2O)CH_3$), 0.22 (s, 9 H, $(CH_3)_3Si$); *exo*-dioxolanyl isomer ^1H NMR ($CDCl_3$) δ 7.21–7.3 (m, 4 H, *exo*-phenyl), 7.07–7.13 (m, 1 H, *exo*-phenyl), 3.92–4.05 (m, 4 H, acetal CH_2CH_2), 1.15–2.10 (m, 8 H), 1.46 (s, 3 H, bridge CH_3), 1.29 (s, 3 H, $(OCH_2CH_2O)CCH_3$), 0.09 (s, 9 H, $(CH_3)_3$-Si); Exact mass calcd for $C_{21}H_{32}O_2SSi$ 376.1892, found 376.1893.

1-[1-Methyl-4-(2-methyldioxolan-2-yl)-7-exo-(trimethylsilyl)bicyclo-[4.1.0]heptan-7-yl]-1-*endo*-[6-*endo*-methylbicyclo[2.2.1]hept-2-en-5-*endo*-yl]-1-hydroxymethane (98). A solution of the major isomer of **95** (0.20 g, 0.53 mmol) in THF (0.5 mL) was treated with LDMAN for 30 min at -78 °C prior to the addition of a solution **97**-*endo*[17] (0.087 g, 0.64 mmol) in THF (0.5 mL). After 15 min the reaction mixture was quenched with moist THF. Standard workup and flash column chromatography (MPLC, Lobar B, 10% ethyl acetate–hexane) afforded 0.13 g (61%) of **98**: IR (neat) 3540, 3060, 2955, 2874, 1455, 1375, 1252, 1213, 1046, 837, 787 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.23 (dd, J = 5.66, 2.91 Hz, 1 H, vinyl H), 6.12 (dd, J = 5.66, 2.91 Hz, 1 H, vinyl H), 3.83–3.97 (m, 4 H, OCH_2CH_2O), 3.26 (d, J = 8.61 Hz, 1 H, $CHOH$), 3.10 (br s, 1 H, allylic H), 2.62 (br s, 1 H, allylic H), 2.51 (ddd, J = 9.24, 9.24, 3.17 Hz, 1 H, $CHOHCH$), 2.30 (dq, J = 7.38, 3.17 Hz, 1 H, CH_3CH), 1.68–1.80 (m, 3 H), 1.57–1.64 (m, 1 H), 1.44–1.50 (m, 1 H), 1.40 (d, J_{gem} = 8.44 Hz, 1 H, HC-7 exo), 1.28 (d, J_{gem} = 8.44 Hz, 1 H, HC-7 endo), 1.22 (s, 3 H, CH_3), 1.21 (s, 3 H, CH_3), 0.96–1.03 (m, 2 H), 0.89 (dd, J = 14.21, 6.53 Hz, 1 H, cyclopropyl H), 0.79 (d, J = 7.38 Hz, 3 H, $CHCH_3$), 0.20 (s, 9 H, $(CH_3)_3Si$); exact mass calcd for $C_{19}H_{34}O_3Si$ (-C_5H_6) 338.2277, found 338.2277.

1-Methyl-7-[6-*endo*-methylbicyclo[2.2.1]hept-2-en-5-*endo*-vinylidenyl)-4-*endo*-(2-methyldioxolan-2-yl)bicyclo[4.1.0]heptane (99). A solution of **95** (0.222 g, 0.599 mmol) in THF (0.5 mL) was treated with LDMAN for 1 h at -78 °C prior to the addition of a solution of **97** (0.104 g, 1.76 mmol) in THF (0.5 mL). The cold bath was then removed, and the reaction mixture was allowed to warm to ambient temperature. To this solution was added potassium *tert*-butoxide (0.331 g, 2.95 mmol), and the resulting mixture was heated at the reflux temperature of THF for 2 h. Standard workup and flash column chromatography (silica gel treated with 0.01% TEA, 2% THF–hexane) afforded 0.135 g (72%) of an inseparable mixture (7:1) of isomers of **99**: IR (neat) 3059, 2946, 2891, 1456, 1374, 1219, 1147, 1049, 866 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.08–6.14 (m, 2 H, vinyl H), 5.07 (d, J = 10.41 Hz, 1 H, CCH major isomer) 5.01 (d, J = 9.78 Hz, 1 H, CCH, minor isomer), 3.76–3.98 (m, 4 H, OCH_2CH_2O), 2.86 (ddd, J = 10.41, 9.24, 2.01 Hz, 1 H, $CCHCH$), 2.71 (br s, 1 H, HC-3), 2.66 (br s, 1 H, HC-6), 2.24 (ddq, J = 9.24, 6.94, 2.01 Hz, 1 H, CH_3CH), 1.60–1.90 (m, 2 H), 1.36–1.58 (m, 4 H), 0.96–1.35 (m, 4 H), 1.18 (s, 3 H, CH_3), 1.08 (s, 3 H, CH_3), 0.63 (d, J = 6.94 Hz, 3 H, endo $CHCH_3$); exact mass calcd for $C_{20}H_{27}O_2$ ($M^+ - CH_3$) 299.2011, measured 299.2011. Alternatively, the titled compound could be synthesized by subjecting **98** to the Peterson olefination conditions described above. In this manner, alkylidenecyclopropane **99** could be produced in 95% yield from the silylcarbinol.

7-*endo*-(1-Hydroxy-2-butyn-1-yl)-1-methyl-4-*endo*-(2-methyldioxolan-2-yl)-7-*exo*-(trimethylsilyl)bicyclo[4.1.0]heptane (100). A solution of the major isomer of **95** (1.00 g, 2.66 mmol) in THF (0.5 mL) was treated with LDMAN for 45 min at -78 °C prior to the addition of a solution of 2-butynal (0.270 g, 0.320 mL, 3.74 mmol) in THF (0.5 mL). After the mixture had been stirred for 10 min at -78 °C, the cold bath was removed, and the reaction mixture was allowed to warm to ambient temperature. Standard workup and flash column chromatography (silica gel treated with 0.01% TEA, 15% ethyl acetate–hexane) afforded **100** as a separable mixture (12:1 ratio) of two diastereomers in a combined yield of 0.865 g (96%): major isomer IR (neat) 3459, 2942, 2880, 1455, 1375, 1246, 1084, 1048, 1026, 841, 739 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.32 (br s, 1 H, $CHOH$), 3.81–3.94 (m, 4 H, OCH_2CH_2O), 2.04 (br dd, J = 14.35, 6.12 Hz, 1 H, axial HC-4), 1.81 (br s, 1 H, $CHOH$), 1.79 (d, J = 2.20 Hz, 3 H, $CCCH_3$), 1.36–1.76 (m, 4 H), 1.20 (s, 3 H, dioxolanyl CH_3), 1.19 (s, 3 H, bridge CH_3), 1.13–1.20 (m, 1 H), 1.10 (dd, J = 12.77, 4.62 Hz, 1 H), 0.88 (d, J = 7.42 Hz, 1 H, cyclopropyl), 0.15 (s, 9 H, $(CH_3)_3Si$); ^{13}C NMR ($CDCl_3$) δ 112.1, 81.13, 81.0, 64.8, 64.7, 64.2, 43.8, 42.6, 28.4, 26.5, 24.8, 23.4, 22.7, 21.4, 20.7, 3.59, 2.52; minor isomer ^1H NMR ($CDCl_3$) δ 4.10 (br s, 1 H, $CHOH$), 3.81–3.94 (m, 4 H, OCH_2CH_2O), 1.98 (br dd, J = 14.88, 7.13 Hz, 1 H, equatorial HC-4), 1.84 (d, J = 2.12 Hz, 3 H, $CCCH_3$), 1.35–1.79 (m including $CHOH$ at δ 1.63, 6 H), 1.23 (s, 3 H, CH_3), 1.20 (s, 3 H, CH_3), 1.14 (s, 1 H), 0.91 (d, J = 8.15 Hz, 1 H, cyclopropyl), 0.20 (s, 9 H, $(CH_3)_3Si$); exact mass calcd for $C_{18}H_{29}O_3Si$ ($M^+ - CH_3$) 321.1887, found 321.1869.

7-*endo*-(1-Hydroxy-*cis*-2-buten-1-yl)-1-methyl-4-*endo*-(2-methyldioxolan-2-yl)-7-*exo*-(trimethylsilyl)bicyclo[4.1.0]heptane (101). The titled compound could be synthesized from either one of two methods. Method A: **98** (0.078 g, 0.19 mmol) was subjected to standard FVP conditions at 470 °C to afford the titled compound in 53% yield (0.034 g). Alternatively the desired *cis* olefin could be synthesized from hydrogenation of the corresponding alkyne **100**. Method B: A H_2 saturated solution of palladium on barium sulfate poisoned with lead (palladium content 5%) (0.250 g, 0.117 mmol) in THF (30 mL) was stirred at ambient temperature as **100** (0.550 g, 1.63 mmol) was added, and the resulting solution was allowed to stir under 1 atm of H_2 for 24 h. The catalyst was then removed by filtration through florisil and $MgSO_4$, and the solvent was removed under reduced pressure. The remaining oil was chromatographed (silica gel treated with 0.01% TEA, 15% ethyl acetate–hexane) to afford 0.531 g (96%) of **101** as a viscous oil: IR (neat) 3494, 3021, 2944, 2884, 1375, 1250, 1211, 1086, 1045, 1009, 839, 696 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.75 (dd, J_{cis} = 10.79, J = 8.51 Hz, 1 H, $CHCHCH_3$), 5.59 (dq, J_{cis} = 10.79, J = 6.89 Hz, 1 H, $CHCH_3$), 4.19 (d, J = 8.51 Hz, 1 H, $CHOH$), 3.83–4.07 (m, 4 H, OCH_2CH_2O), 2.01 (dd, J = 14.91, 7.52 Hz, 1 H, HC-4), 1.80–1.86 (m, 1 H), 1.71 (d, J = 6.89 Hz, 3 H, $CHCH_3$), 1.48–1.67 (m, 4 H), 1.27 (s, 3 H, dioxolanyl CH_3), 1.18–1.24 (m, 1 H), 1.17 (s, 3 H, bridge CH_3), 1.09 (m, 1 H), 0.90 (d, J = 8.92 Hz, 1 H, cyclopropyl), 0.16 (s, 9 H, $(CH_3)_3Si$); exact mass calcd for $C_{19}H_{32}O_2Si$ (-H_2O) 320.2172, found 320.2172.

7-(*cis*-2-Butenylidene)-1-methyl-4-(2-methyldioxolan-2-yl)bicyclo-[4.1.0]heptane (102). A solution of **101** (0.016 g, 0.047 mmol) in THF (15 mL) was treated with KH powder (0.030 g, 0.075 mmol) for 30 min at the reflux temperature of THF. Simple extraction and removal of the solvent from the dried ($MgSO_4$) organic phase afforded 0.011 g (94%) of **102** as a clear oil judged pure by ^1H NMR spectroscopy: IR (neat) 3042, 2926, 2860, 1445, 1375, 1241, 1219, 1107, 1050, 721 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.52 (d, J = 11.19 Hz, 1 H, CCH), 6.10 (ddq, J_{cis} = 10.73, J = 11.19, 1.63 Hz, 1 H, $CHCHCH_3$), 5.42 (dq, J_{cis} = 10.73, J = 7.08 Hz, 1 H, $CHCH_3$), 3.84–3.95 (m, 4 H, OCH_2CH_2O), 1.90 (br d, J = 10.70 Hz, 1 H, HC-4), 1.84 (ddt, J = 13.84, 6.44, 2.87 Hz, 1 H), 1.78 (dd, J = 7.08, 1.63 Hz, 3 H, $CHCH_3$), 1.72 (dt, J = 13.84, 5.94 Hz, 1 H), 1.30–1.58 (m, 4 H), 1.20 (s, 3 H, dioxolanyl CH_3), 1.17 (s, 3 H, bridge CH_3), 1.04 (dd, J = 13.96, 6.44 Hz, 1 H, cyclopropyl); exact mass calcd for $C_{16}H_{24}O_2$ 248.1776, found 248.1775.

2,8α-Dimethyl-7β-*H*-5-(2-methyldioxolan-2-yl)bicyclo[5.3.0]deca-1,9-diene (103). Compound **99** (0.700 g, 2.23 mmol) or **102** was distilled under vacuum through a 500 °C quartz tube which was packed with quartz helices and the volatile distillate captured in a -78 °C cold trap.

The distillate was then chromatographed (MPLC, Lobar B, 5% ethyl acetate–hexane) to afford 0.503 g (91%) of an inseparable mixture of bicyclo[5.3.0]deca-1,9-dienes **103** and **104** whose ratio was calculated to be 5:1, respectively, from the integration of the C-8 methyl doublet signals in the ^{1}H NMR spectrum of the reaction product mixture: IR (neat) 2940, 2874, 1449, 1377, 1217, 1144, 1096, 1446, 868 cm^{-1}; **103**, major isomer, ^{1}H NMR ($CDCl_3$) δ 6.23 (dd, J = 5.69, 2.05 Hz, HC-9), 5.78 (m, HC-10), 3.83–3.92 (m, OCH_2CH_2O), 3.11–3.21 (m, HC-7), 2.80–2.92 (m, HC-5), 1.86–2.24 (m), 1.78 (br s, vinyl CH_3), 1.34–1.59 (m), 1.27 (s, dioxolanyl CH_3), 0.91 (d, J = 7.42 Hz, α-CH_3C-4); **103**, minor isomer (identical to the above spectrum with the following exceptions) ^{1}H NMR ($CDCl_3$) δ 6.17 (dd, J = 5.69, 1.94 Hz) 2.98 -3.07 (m, HC-7), 2.68–2.78 (m, HC-5), 1.69 (br s, vinyl CH_3), 1.25 (s, dioxolanyl CH_3), 0.99 (d, J = 7.38 Hz, α-CH_3C-4); exact mass calcd for $C_{16}H_{24}O_2$ 248.1776, found 248.1776.

2,8β-Dimethyl-7β-*H*-5-(2-methyldioxolan-2-yl)bicyclo[5.3.0]deca-1,9-diene (104):[46] IR (neat) 3075, 3050, 2951, 2872, 1457, 1378, 1146, 1083, 1048, 873, 735 cm^{-1}; major isomer ^{1}H NMR ($CDCl_3$), δ 6.25 (dd, J = 5.75, 2.08 Hz, 1 H, HC-10), 5.77 (br d, J = 5.75 Hz, 1 H, HC-9), 3.85–3.96 (m, 4 H, OCH_2CH_2O), 2.52 (m, 1 H, HC-7), 2.30–2.47 (m, 2 H, including HC-8), 2.07–2.23 (m, 2 H), 1.87–2.05 (m, 2 H), 1.71–1.81 (m, 2 H), 1.77 (br s, 3 H, vinyl CH_3), 1.23 (s, 3 H, dioxolanyl CH_3), 1.07 (d, J = 7.01 Hz, 3 H, exo CH_3C-4); minor isomer ^{1}H NMR (identical to the above spectrum with the following exceptions, $CDCl_3$) δ 6.18 (dd, J = 5.60, 1.66 Hz, 1 H, HC-10), 5.74 (br d, J = 5.60 Hz, 1 H, HC-9), 1.80 (br s, 3 H, vinyl CH_3), 1.20 (s, 3 H, dioxolanyl CH_3); exact mass calcd for $C_{16}H_{24}O_2$ 248.1776, found 248.1775.

5α-Acetyl-2,8α-dimethyl-7β-*H*-bicyclo[5.3.0]deca-1-ene (105) and 5β-Acetyl-2,8α-dimethyl-7β-*H*-bicyclo[5.3.0]deca-1-ene (106). Compound **103** (0.034 g, 0.137 mmol) was hydrogenated to afford 0.025 g (90%) of a mixture of C-5 epimeric ketones after chromatography (silica gel treated with 0.01% TEA, 5% ethyl acetate–hexane). Each isomer was separated by MPLC chromatography (Lobar B, 2% ethyl acetate–hexane, flow rate of 1.8 mL/min). The major component of the mixture (**105**, 0.0134 g) possessed a pseudo-equatorial acetyl group and exhibited the following spectral data: IR (neat) 2930, 2869, 1711, 1456, 1375, 1352, 1163, 737 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.52–2.60 (m, 1 H, pseudoaxial HC-5), 2.41–2.50 (m, 1 H), 2.23–2.35 (m, 1 H, CH_3CH), 2.14 (s, 3 H, $C(O)CH_3$), 1.08–1.98 (m, 10 H), 1.64 (br s, 3 H, vinyl CH_3), 0.88 (d, J = 6.98 Hz, 3 H, CH_3C-8). The minor component of the mixture (**106**, 0.012 g) possessed a pseudoaxial acetyl group and exhibited the following spectral data: IR (neat) 2926, 2867, 1707, 1375, 1350, 1289, 1248, 1157, 876 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.67–2.77 (m, 1 H, pseudoequatorial HC-5), 2.55–2.64 (m, 1 H), 2.01–2.32 (m, 1 H, CH_3CH), 2.13 (s, 3 H, $C(O)CH_3$), 1.73–1.99 (m, 2 H), 1.41–1.69 (m, 4 H), 1.58 (br s, 3 H, vinyl CH_3), 0.98–1.38 (m, 4 H), 0.74 (d, J = 7.07 Hz, 3 H, CH_3C-8); exact mass calcd for $C_{14}H_{22}O$ 206.1671, found 206.1671.

2,8α-Dimethyl-7β-*H*-5β-(2-hydroxy-2-propanyl)bicyclo[5.3.0]deca-1-ene (107). A solution of **106** (7.1 mg, 0.034 mmol) in THF (2 mL) was treated with methyl magnesium bromide (3 M, 18 μl, 0.055 mmol) to afford 0.0071 g (93%) of **107** as a clear oil after chromatography (silica gel treated with 0.01% TEA, 10% ethyl acetate–hexane): IR (neat) 3385, 2930, 2861, 1458, 1375, 1135, 1019, 740 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.70–2.80 (m, 1 H, HC-5), 2.23–2.38 (m, 1 H, HC-7), 1.73–2.20 (m, 2 H), 1.43–1.72 (m, 4 H) 1.56 (br s, 3 H, vinyl CH_3), 0.95–1.32 (m, 4 H), 1.18 (s, 6 H, $(CH_3)_2C(OH)$), 0.76–0.95 (m, 2 H), 0.82 (d, J = 6.95 Hz, 3 H, CH_3C-8); exact mass calcd for $C_{15}H_{26}O$ 222.1984, found 222.1984.

(1*R*,2*S*,4*R*,7*R*)-3-(*cis*-2-Butenylidene)-4,8,8-trimethyltricyclo[5.1.0.0^{2,4}]-octane (110). A solution of **126** (0.520 g, 1.78 mmol) in THF (30 mL) was stirred at ambient temperature as KH powder (0.142 g, 3.56 mmol) was added in one portion, and the resulting mixture was heated at the reflux temperature of THF for 30 min. The reaction mixture was allowed to cool to ambient temperature, and the excess KH was destroyed by the addition of wet ether. The solvent was then partially removed under reduced pressure, and the resulting slurry was taken up in ether and washed with brine. After removal of the solvent *in vacuo* from the dried ($MgSO_4$) solution, the desired diene was isolated (0.348 g, 97%) in high purity: R_f 0.57 in hexane; $[\alpha]_D$ = +66.65 ($CHCl_3$, c 0.0493, α = +3.286); IR (neat) 3021, 2940, 2863, 1449, 1375, 992, 725 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 6.60 (br d, J = 11.14 Hz, 1 H, CCH), 6.20 (ddq, J_{cis} = 10.80, J = 11.14, 1.57 Hz, 1 H, $CHCHCH_3$), 5.48 (dq, J_{cis} = 10.80, J = 7.09 Hz, 1 H, $CHCH_3$) 1.79 (dd, J = 7.09, 1.57 Hz, 3 H, allylic CH_3) 1.54–1.74 (m, 3 H), 1.08 (s, 3 H, methyl), 1.04 (s, 3 H, methyl), 0.98 (s, 3 H, methyl), 0.95–1.11 (m, 2 H, alicyclic and cyclopropyl H), 0.54–0.62 (m, 2 H, cyclopropyl H); ^{13}C NMR ($CDCl_3$) δ 143.2, 128.5, 123.9, 111.2, 29.7, 28.8, 23.4, 22.1, 18.7, 18.5, 17.8, 16.1, 15.9, 13.32; exact mass calcd for $C_{15}H_{22}$ 202.1788, measured 202.1788.

(1*R*,2*S*,4*R*,7*R*)-4,8,8-Trimethyl-3-(phenylthio)-3-(trimethylsilyl)tricyclo-[5.1.0.0^{2,4}]octane (112). A solution of (+)-2-carene (8.85 g, 65.0 mmol) and benzyltriethylammonium chloride (0.150 g, 0.650 mmol) in 10 M KOH (100 mL) under an atmosphere of argon was efficiently stirred as 1,1-dichloro(phenylthio)methane (18.8 g, 98.0 mmol) was slowly added *via* syringe pump (addition rate was about 2 mL/h). The resulting dark brown reaction mixture was allowed to stir for 8 h after addition was complete. Standard carbenoid cyclopropanation workup and chromatography (silica gel treated with 0.01% TEA, hexane) afforded the unstable **(1*R*,2*S*,4*R*,7*R*)-3-chloro-3-(phenylthio)-4,8,8-trimethyltricyclo[5.1.0.0^{2,4}]-octane (113)** as a mixture of *endo*- and *exo*-phenylthio isomers: IR (neat) 3017, 2944, 2869, 1586, 1482, 1455, 1441, 1377, 1026, 887, 895, 737, 689 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.37–7.38 (m, 1 H, phenyl), 7.28–7.33 (m, 3 H, phenyl), 7.15–7.18 (m, 1 H, phenyl), 1.85–1.88 (m, 1 H), 1.62 (ddd, J = 12.92, 12.92, 4.43 Hz, 1 H), 1.52–1.61 (m, 2 H), 1.27 (s, 3 H, CH_3C-4), 1.09 (s, 3 H, geminal CH_3), 0.87 (s, 3 H, geminal CH_3), 0.65–0.85 (m, 3 H, cyclopropyl); exact mass calcd for $C_{17}H_{21}ClS$ 292.1053, found 292.1053.

A solution of **113** (19.0 g, 64.9 mmol) in THF (20 mL) was silylated by the procedure described for **31.** Standard workup and chromatography (silica gel, hexane) afforded 13.4 g (63%) of **112** as a 9:1 mixture of isomers rich in the exo-phenylthio isomer: IR (neat) 3060, 2963, 2936, 2867, 1586, 1480, 1456, 1439, 1026, 843, 737, 691 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.18–7.28 (m, 4 H, phenyl), 7.04–7.07 (m, 1 H, phenyl), 1.74–1.78 (m, 1 H), 1.59 (ddd, J = 13.80, 4.46, 1.80 Hz, 1 H), 1.48–1.51 (m, 1 H), 1.38 (ddd, J = 13.80, 13.80, 4.46 Hz, 1 H), 1.30 (s, 3 H, CH_3), 1.12 (s, 3 H, CH_3), 0.90 (m, 1 H, cyclopropyl H), 0.85 (s, 3 H, CH_3), 0.70–0.88 (m, 2 H, cyclopropyl H), 0.14 (s, 9 H, endo $(CH_3)_3Si$). In an otherwise identical spectrum, the *endo*-phenylthio isomer exhibited the following signals; 1.31 (s, 3 H, CH_3), 1.08 (s, 3 H, CH_3), 0.92 (s, 3 H, CH_3), 0.05 (s, 9 H, *exo* $(CH_3)_3Si$); ^{13}C NMR (*exo*-phenylthio isomer, $CDCl_3$) δ 140.6, 128.2, 126.1, 123.8, 31.2, 26.7, 28.5, 28.2, 25.1, 23.4, 22.4, 20.2, 18.8, 16.3, 15.5, 1.98; exact mass calcd for $C_{20}H_{30}SSi$ 330.1838, found 330.1838.

(1*R*,2*S*,4*R*,7*R*,3*S*)-3-(1-Hydroxy-*trans*-2-buten-1-yl)-4,8,8-trimethyl-3-(trimethylsilyl)tricyclo[5.1.0.0^{2,4}]octane (119). A solution of **112** (1.00 g, 3.02 mmol) in THF (2 mL) was treated with LDMAN for 45 min at -78 °C prior to the addition of a solution of crotonaldehyde (0.270 g, 3.89 mmol) in THF (0.5 mL). The ice bath was then removed, and the reaction mixture was allowed to warm to ambient temperature. Standard workup and chromatography (silica gel, 5% ethyl acetate–hexane, R_f 0.27 minor isomer, R_f 0.21 major isomer) afforded 0.767 g (88%) of **119** as a mixture of (85:15) two isomers: minor isomer $[\alpha]_D$ = 114.6° ($CHCl_3$, c 0.419, α = –0.647); IR (neat) 3471, 2942, 1454, 1377, 1248, 970, 839, 735 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.53–5.63 (m, 2 H, vinyl H), 4.06 (br s, 1 H, $CHOH$), 1.74–1.79 (m, 1 H), 1.71 (dd, J = 4.71, 1.79 Hz, 3 H, vinyl CH_3), 1.50 (br s, 1 H, $CHOH$), 1.39 (ddd, J = 14.13, 4.62, 2.31 Hz, 1 H), 1.14 (dd, J = 13.78, 4.62 Hz, 1 H), 1.08 (s, 3 H, geminal CH_3), 1.07 (s, 3 H, geminal CH_3), 0.89 (s, 3 H, bridge CH_3), 0.80–0.88 (m, 1 H), 0.66 (d, J = 8.52 Hz, 1 H, HC-2), 0.58 (ddd, J = 8.52, 6.92, 6.92 Hz, 1 H, HC-7), 0.53 (s, 1 H, HC-2), 0.14 (s, 9 H, $(CH_3)_3Si$); ^{13}C NMR ($CDCl_3$) δ 133.4, 124.8, 74.7, 28.0, 26.4, 25.7, 24.6, 24.2, 22.7, 22.1, 18.4, 17.9, 17.8, 16.5, 16.0, 2.68; exact mass calcd for $C_{17}H_{29}OSi$ ($M^+ - CH_3$) 277.1988, found 277.1988; major isomer, $[\alpha]_D$ = +105.8° ($CHCl_3$, c 0.0150, α = +1.587); IR (neat) 3482, 2944, 2846, 1456, 1248, 972, 911, 853, 841, 735 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.76 (ddq, J_{trans} = 16.3, J = 8.3, 1.4 Hz, 1 H, $CHCHCH_3$), 5.56 (dqd, J_{trans} = 16.3, J = 6.9, 1.0 Hz, 1 H, $CHCH_3$), 4.12 (br s, 1 H, $CHOH$), 1.73–1.84 (m, 1 H), 1.72 (dd, J = 6.89, 1.03 Hz, 3 H, vinyl CH_3), 1.45 (ddd, J = 14.16, 5.36, 2.24 Hz, 1 H), 1.36 (dd, J = 13.27, 4.79 Hz, 1 H), 1.19 (br s, 1 H, OH), 1.13 (s, 3 H, CH_3), 1.05 (s, 3 H, CH_3), 0.80–0.97 (m, 1 H), 0.85 (s, 3 H, CH_3), 0.52 (ddd, J = 8.48, 5.23, 5.41 Hz, 1 H, HC-7), 0.48 (s, 1 H, HC-2), 0.40 (d, J = 8.48 Hz, 1 H, HC-2), 0.14 (s, 9 H, $(CH_3)_3Si$); ^{13}C NMR ($CDCl_3$) δ 134.6, 125.3, 74.4, 28.1, 26.3, 25.8, 24.5, 23.9, 22.5, 21.8, 18.9, 17.9, 17.5, 16.1, 15.7, 3.30; exact mass calcd for $C_{17}H_{29}OSi$ (M – CH_3) 277.1988, found 277.1988.

(1*R*,2*S*,4*R*,7*R*)-3-Z-(2-*trans*-Butenylidene)-4,8,8-trimethyltricyclo-[5.1.0.0^{2,4}]octane (120). A solution of **119** (major) (0.132 g, 0.450 mmol) in THF (10 mL) was stirred at ambient temperature as KH powder (0.036 g, 0.90 mmol) was added all at once, and the resulting mixture was heated at the reflux temperature of THF for 30 min. The reaction mixture was then allowed to cool, and excess KH was destroyed by the addition of wet ether. The solvent was then partially removed under reduced pressure and the resulting slurry was taken up in ether and washed with brine. After removal of the solvent *in vacuo* from the dried ($MgSO_4$) solution, **120** (major, isomer A) was isolated (0.086 g, 94%) in high purity: $[\alpha]_D$ = +19.12°, ($CHCl_3$, c 0.0205, α = +0.392); IR (neat) 2938,

2863, 1451, 1375, 989, 878, 845, 760 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 6.63 (d, J = 10.54 Hz, 1 H, CCH), 6.07 (ddq, J_{trans} = 15.11, J = 10.54, 1.62 Hz, 1 H, C*H*CHCH$_3$), 5.64 (dq, J_{trans} = 15.11, J = 6.93 Hz, 1 H, C*H*CH$_3$), 1.77 (br d, J = 6.93 Hz, 3 H, allylic CH$_3$), 1.58–1.72 (m, 2 H), 1.12 (s, 3 H, bridge CH$_3$), 1.00–1.10 (m, 2 H), 1.03 (s, 3 H, geminal CH$_3$), 0.98 (s, 3 H, geminal CH$_3$), 0.53–0.63 (m, 2 H, HC-1 and HC-4), 0.55 (s, 1 H, HC-2); ^{13}C NMR ($CDCl_3$) δ 140.6, 130.8, 126.5, 116.4, 28.5, 28.4, 23.4, 22.1, 19.0, 18.8, 18.7, 18.5, 18.3, 16.2, 16.0; exact mass calcd for $C_{15}H_{22}$ 202.1788, measured 202.1788. In an identical procedure a solution of **119** (minor) afforded **120** (minor, isomer B) in high purity: $[\alpha]_D$ = +16.26°, ($CHCl_3$, c 0.0438, α = +0.712); IR (neat) 2940, 2863, 1449, 1375, 992, 967, 876 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 6.18–6.29 (m, 2 H, CC*H*C*H*), 5.62–5.74 (m, 1 H, C*H*CH$_3$), 1.78 (d, J = 6.91 Hz, 3 H, allylic CH$_3$), 1.66–1.74 (m, 1 H), 1.54–1.63 (m, 1 H), 0.94–1.10 (m, 2 H), 1.06 (s, 3 H, CH$_3$), 1.05 (s, 3 H, CH$_3$), 1.03 (s, 1 H, HC-1), 0.98 (s, 3 H, CH$_3$), 0.62 (d, J = 9.04 Hz, 1 H, HC-1), 0.58 (ddd, J = 9.04, 7.71, 5.48 Hz, 1 H, HC-7); ^{13}C NMR ($CDCl_3$) δ 140.9, 130.7 (d), 126.9 (d), 115.8 (d), 28.8 (t), 28.3 (q), 23.5 (q), 22.1 (d), 18.7, 18.6 (d), 18.5 (d), 18.3, 18.0 (t), 16.2 (q), 15.9 (q); exact mass calcd for $C_{15}H_{22}$ 202.1718, found 202.1718.

5*R*,7*R*,8*S*,9*S*-2,6,6,9-Tetramethyltricyclo[6.3.0.0^{5,7}]undeca-1,10-diene (121) and 5*R*,7*R*,8*R*,9*R*-2,6,6,9-Tetramethyltricyclo[6.3.0.0^{5,7}]undeca-1,10-diene (122). Following the standard protocol for a sealed tube thermolysis reaction, a solution of **120** (0.200 g, 0.988 mmol) in benzene (4 mL) was heated at 190 °C for 16 h in a preheated oil bath. Column chromatography (silica gel, hexane, R_f 0.69 and 0.63) afforded 0.176 g (88%) as a 1.3:1.0 mixture of **121** and **122**, respectively: minor isomer (**122**) IR (neat) 3065, 3044, 2952, 2919, 2861, 1456, 1377, 821, 760 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 6.10 (dd, J = 1.83, 5.75 Hz, 1 H, HC-10), 5.82 (dd, J = 1.83, 5.75 Hz, 1 H, HC-11), 2.96 (br s, 1 H, HC-8), 1.92–2.08 (m, 3 H, including CH$_3$C*H*), 1.73 (s, 3 H, allylic CH$_3$), 1.41–1.61 (m, 2 H), 1.31 (d, J = 7.08 Hz, 3 H, CHC*H*$_3$), 0.99 (s, 3 H, geminal CH$_3$), 0.91 (s, 3 H, geminal CH$_3$), 0.71 (m, 1 H, HC-5), 0.67 (dd, J = 6.50, 7.98 Hz, 1 H, HC-7); exact mass calcd for $C_{15}H_{22}$ 202.1722, found 202.1722; major isomer (**123**) IR (neat) 3065, 3044, 2952, 2919, 2861, 2820, 1456, 1375, 760 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 6.30 (dd, J = 5.68, 2.16 Hz, 1 H, HC-10), 5.77 (br d, J = 5.68 Hz, 1 H, HC-11), 2.60 (br s, 1 H, HC-8), 2.20–2.32 (m, 2 H), 1.69–1.80 (m, 4 H, HC-9 and vinyl CH$_3$ overlapping), 1.44–1.62 (m, 2 H), 1.12 (s, 3 H, geminal CH$_3$), 1.05 (d, J = 6.99 Hz, 3 H, CH$_3$C-9), 1.04 (s, 3 H, geminal CH$_3$), 0.60–0.72 (m, 1 H, HC-5), 0.64 (s, 1 H, HC-7); exact mass calcd for $C_{15}H_{22}$ 202.1722, found 202.1722.

5*R*,7*R*,8*S*,9*S*-2,6,6,9-Tetramethyltricyclo[6.3.0.0^{5,7}]undeca-1-ene (123). A H_2 saturated solution of tris(triphenylphosphine)rhodium(I) chloride (0.010 g, 0.011 mmol) in benzene (10 mL) was stirred under an atmosphere of hydrogen as a solution of **121** (0.060 g, 0.30 mmol) in benzene (1 mL) was added. The resulting mixture was stirred for 12 h, and the catalyst was removed by filtration through a short column of florisil and $MgSO_4$. After solvent removal the dark oil was purified by column chromatography (silica gel, pentane, CH_2Cl_2 loading) to afford 0.059 g (96%) of **123** as a viscous oil: $[\alpha]_D$ = +26.72 ($CHCl_3$, c 0.0058, α = +0.155), IR (neat) 2948, 2863, 1456, 1374, 837, 787 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.57 (br s, 1 H, HC-8), 2.36–2.47 (m, 2 H, H_2C-3), 2.21–2.30 (m, 2 H, H_2C-11), 2.05 (m, 1 H, HC-9), 1.63–1.73 (m, 2 H, H_2C-4), 1.57 (br s, 3 H, allylic CH$_3$), 1.25–1.36 (m, 2 H, H_2C-10), 1.07 (s, 3 H, geminal CH$_3$), 1.04 (d, J = 6.98 Hz, 3 H, CHC*H*$_3$), 0.99 (s, 3 H, geminal CH$_3$), 0.67 (d, J = 9.52 Hz, 1 H, HC-7), 0.55 (dt, J = 9.52, 5.43 Hz, 1 H, HC-5); exact mass calcd for $C_{15}H_{24}$ 204.1879, found 204.1891.

1*S*,2*R*,4*R*,7*R*,8*S*-8-*endo*-(1-Hydroxy-2-butyn-1-yl)-3,3,7-trimethyl-8-*exo*-(trimethylsilyl)tricyclo[5.1.0.0^{2,4}]octane (124). A solution of **112** (1.00 g, 3.02 mmol) in THF (1.0 mL) was treated with LDMAN for 45 min at -78 °C prior to the addition of a solution of 2-butynal (0.250 g 3.63 mmol) in THF (0.5 mL). After stirring for an additional 10 min at -78 °C the cold bath was removed, and the reaction mixture was allowed to warm to ambient temperature. Standard workup and column chromatography (silica gel, 5% ethyl acetate–hexane) afforded 0.603 g (68%) of **124** as an oil: $[\alpha]_D$ = +50.19° ($CHCl_3$, c 0.0422, α = +2.118); IR (neat) 3461, 2944, 1456, 1375, 1248, 1021, 872, 843 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.30 (q, J = 2.20 Hz, 1 H, C*H*OH), 1.81 (d, J = 2.20 Hz, 3 H, CCCH$_3$), 1.72–1.81 (m, 1 H), 1.63 (br s, 1 H, CHO*H*), 1.40 (ddd, J = 14.31, 4.94, 2.08 Hz, 1 H), 1.19 (dd, J = 13.75, 4.94 Hz, 1 H), 1.02–1.16 (m, 1 H), 1.07 (s, 3 H, geminal CH$_3$), 1.05 (s, 3 H, geminal CH$_3$), 0.84 (s, 3 H, bridge CH$_3$), 0.65 (d, J = 8.43 Hz, 1 H, HC-2), 0.52 (dd, J = 8.43, 6.69 Hz, 1 H, HC-4), 0.47 (s, 1 H, HC-1), 0.20 (s, 9 H, (CH$_3$)$_3$Si); ^{13}C NMR ($CDCl_3$) δ 81.7, 81.4, 65.0, 27.9, 26.2, 25.8, 24.3, 24.1, 22.2, 21.5, 18.8, 16.9, 16.1, 15.7, 3.81, 2.55; exact mass calcd for $C_{17}H_{27}OSi$ (M^+–CH$_3$) 275.1825, found 275.1825.

1*S*,2*R*,4*R*,7*R*,8*S*-8-*endo*-(1-Hydroxy-*cis*-2-buten-1-yl)-3,3,7-trimethyl-8-*exo*-(trimethylsilyl)tricyclo[5.1.0.0^{2,4}]octane (125). A H_2 saturated solution of palladium on calcium carbonate in benzene (15 mL) was stirred at ambient temperature as a solution of **124** (0.570 g, 1.96 mmol) in benzene (2 mL) was added, and the resulting mixture was allowed to stir under 1 atm of hydrogen for 12 h. The reaction mixture was then filtered through florisil and $MgSO_4$ in order to remove the catalyst. The solvent was then removed *in vacuo*, and the remaining oil was chromatographed (silica gel, 5% ethyl acetate–hexane) to afford 0.570 g (99%) of **125** as a viscous oil: $[\alpha]_D$ = –26.90° ($CHCl_3$, c 0.077, α = –2.071); IR (neat) 3467, 3040, 2977, 2869, 1456, 1375, 1284, 1019, 853, 839 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.91 (ddq, J_{cis} = 10.97, J = 8.07, 1.67 Hz, 1 H, C*H*CHCH$_3$), 5.60 (ddq, J_{cis} = 10.97, J = 7.05, 0.87 Hz, 1 H, CHC*H*CH$_3$), 4.47 (d, J = 8.07 Hz, 1 H, C*H*OH), 1.78–1.88 (m, 1 H), 1.69 (dd, J = 7.05, 1.67 Hz, 3 H, CHC*H*$_3$), 1.24–1.52 (m, 3 H including CHO*H*), 1.15 (s, 3 H, geminal CH$_3$), 1.03, (s, 3 H, geminal CH$_3$), 0.86–0.96 (m, 1 H), 0.86 (s, 3 H, bridge CH$_3$), 0.50 (ddd, J = 8.45, 6.64, 6.64 Hz, 1 H, HC-3), 0.46 (s, 1 H, HC-1), 0.36 (d, J = 8.45 Hz, 1 H, HC-2), 0.20 (s, 9 H, (CH$_3$)$_3$Si); ^{13}C NMR ($CDCl_3$) δ 133.6 (d), 127.5 (d), 69.6 (d), 28.1 (q), 26.0 (t), 25.9, 24.5 (q), 23.3, 21.8 (d), 21.79 (d), 18.9, 17.2 (d), 16.1 (t), 15.6 (q), 13.4 (q), 3.17 (q); exact mass calcd for $C_{18}H_{30}Si$ ($M^+ - H_2O$) 274.2118, found 274.2104.

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Supplementary Material Available: Experimental procedures and characterization data for the preparation of 3-(phenylthio)-propanal, *E*- and *Z*-3-(phenylthio)propenal, 1-methyl-4-(2-methyldioxolan-2-yl)cyclohexene (**3**), 1-methyl-5-hydroxy-7-(*trans*-2-butenylidene)bicyclo[4.1.0]heptane, 1-methyl-7-(*trans*-2-butenylidene)bicyclo[4.1.0]heptan-5-one (**66**), and 1*S*,2*R*,4*R*,7R-3,7,7-trimethyl-8,8-bis(trimethylsilyl)tricyclo[5.1.0.0^{2,4}]octane (**126**) (4 pages). Ordering information is given on any current masthead page.