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Generation, Some Synthetic Uses, and 1,2-Vinyl Rearrangements of Secondary and Tertiary Homoallyllithiums, Including Ring Contractions and A Ring Expansion. Remarkable Acceleration of the Rearrangement by an Oxyanionic Group

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Abstract: A very general preparative method for homoallyllithiums consists of reductive lithiation of homoallyl phenyl sulfides by lithium 4,4′-di-*tert*-butylbiphenylide. The sulfides can be prepared by a variety of methods including (1) the triethylamine-catalyzed addition of thiophenol to a conjugated enal or enone followed by a Wittig or Peterson olefination, (2) the reaction of a silyl enol ether with a diphenyl dithioacetal catalyzed by stannic chloride, followed by a Peterson olefination, or (3) the treatment of the lithio derivatives of phenyl thioethers or thioacetals or the corresponding cuprates with allyl halides. Secondary and tertiary homoallyllithiums, which can be prepared readily by reductive lithiation, can often be induced to rearrange to less substituted homoallyllithiums via intermediate (cyclopropylcarbinyl)lithiums. Optimum conditions for such rearrangements have been developed. By the use of appropriate reactants, ring contractions and expansions can be the results of such rearrangements. A very considerable acceleration of the rearrangement of a tertiary homoallyllithium that bears a CH_2CH_2OLi or a $CH_2CH_2CH_2OLi$ substituent on the lithium-bearing carbon atom has been discovered. It is believed that coordination of the oxyanion to the lithium ion associated with carbon is responsible for such acceleration; the stereochemistry of the intermediate (cyclopropylcarbinyl)lithium, which can be detected in the former case, is consistent with this explanation.

Reductive lithiation of phenyl thioethers by means of aromatic radical anions is proving to be an exceptionally general method of preparation of organolithium compounds.[1,2] The generality is due largely to the extraordinary ease of incorporating the phenylthio group into organic molecules. Another very satisfying feature of this method is that, unlike the conventional preparative method, electrophile removal, the less stable the organolithium, the greater the ease of its generation by reductive lithiation.

Among the wide variety of organolithiums that have been prepared in this way are cycloalkenyllithiums (**1**, $n = 1$–3),[3] other vinyllithiums,[4] and allyllithiums (**2**).[5]

We now report that reductive lithiation of readily prepared homoallyl phenyl thioethers is a simple preparative method for a wide variety of homoallyllithiums (**3**), presently rare materials that are of considerable synthetic and mechanistic interest. Unlike the organolithiums **1** and **2**, this type of molecule has no special

(1) Cohen, T.; Bhupathy, M. *Acc. Chem. Res.* **1989**, *22*, 152–61.
(2) Early reports of the preparation of organolithiums by reductive lithiation of phenyl thioethers: See: Screttas, C. G.; Micha-Screttas, M. *J. Org. Chem.* **1978**, *43*, 1064–71. Cohen, T.; Daniewski, W. M.; Weisenfeld, R. B. *Tetrahedron Lett.* **1978**, 4665–68.
(3) Cohen, T.; Doubleday, M. D. *J. Org. Chem.* **1990**, *55*, 4784–86.
(4) (a) Cohen, T.; Weisenfeld, R. B. *J. Org. Chem.* **1979**, *44*, 3601–3603. (b) Cohen, T.; Matz, J. R. *Synth. Commun.* **1980**, *10*, 311–317. (c) Duhamel, L.; Chauvin, J.; Messier, A. *J. Chem. Res., Synop.* **1982**, 48; *J. Chem. Res., Miniprint* **1982**, 619–653. Doubleday, M. D. Ph.D. Thesis, University of Pittsburgh, 1991. Adam, W.; Richter, M. *Chem. Ber.* **1992**, *125*, 243–246.

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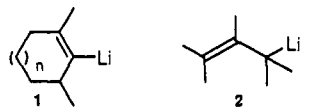
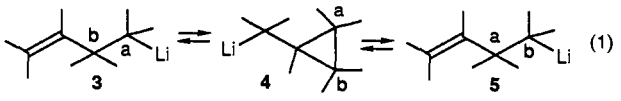
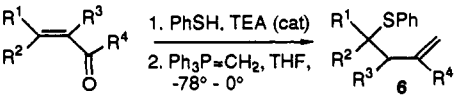


stabilizing features. Furthermore, whereas previously only primary homoallyllithiums had been prepared in a synthetically useful manner,[6,7] the present method allows ready access to secondary and tertiary homoallyllithiums as well. With the exception of commercially available *tert*-butyllithium, tertiary organolithiums of any kind are very uncommon.[8] A particularly intriguing feature of homoallyllithiums is that in many cases they can be induced to undergo 1,2-vinyl rearrangements of tertiary to primary or secondary and of secondary to primary organolithiums (eq 1). Such rearrangements have been well studied in Grignard reagents[9] but somewhat less in organolithiums,[6,10] in which they are far more facile;[11] however, until now, these rearrangements have been almost entirely mechanistic curiosities.[12]

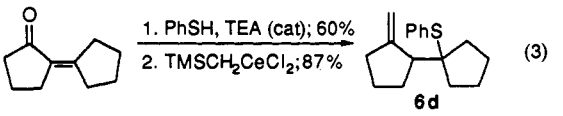


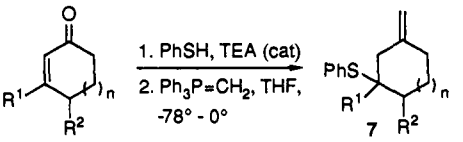
Results and Discussion

Preparation of Homoallyl Phenyl Sulfides. Three methods were used to prepare the precursors of the homoallyllithiums. Method A involves triethylamine-catalyzed conjugate addition of thiophenol to an enone or enal followed by Wittig olefination or the Johnson modification of the Peterson olefination[13] (eqs 2–4). The yields in eq 2 are for steps 1 and 2 since the conjugate addition products were used directly in the next step without purification; the yields of conjugate adducts were estimated to be 85–90%. Method B, like method A, involves olefination of a β-(phenylthio) ketone, but in this case the latter is prepared by the treatment of a diphenyl dithioacetal with an enol silyl ether in the presence of stannic chloride, a procedure developed by Reetz[14] (Scheme I). The Reetz method should be applicable to the preparation of a variety of β-(phenylthio) ketones that could otherwise be prepared only from enones that are attainable with difficulty or that do not bear a hydrogen atom at the α-position, a requisite for the conjugate addition method. Since our study emphasizes the 1,2-vinyl rearrangement which proceeds best, at least in the case of Grignard reagents,[15] without a distal alkyl group on the alkene, the olefination reactions consisted of simple methylenations. However, it is likely that the preparative procedure could



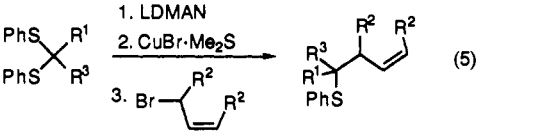
6a, R^1 = Me, R^2 = R^3 = R^4 = H; 80%
6b, R^1 = R^2 = Me, R^3 = R^4 = H; 76%
6c, R^1 = R^2 = R^4 = Me, R^3 = H; 81%





7a, R^1 = Me, R^2 = H, n = 1; step 1, 70%; step 2, 80%
7b, R^1 = *n*-Bu, R^2 = H, n = 1; step 1, 60%; step 2, 90%
7c, R^1, R^2 = -$(CH_2)_3$-, n = 1; step 1, 90%; step 2, 95%
7d, R^1 = Me, R^2 = H, n = 2; step 1, 90%; step 2, 76%

be generalized by the use of other Wittig and Peterson reagents. In the methylenations shown in eq 3 and Scheme I, the Johnson–Peterson procedure gave a far better yield than the Wittig reaction presumably due to the hindered nature of the ketones; in these cases, the Wittig reagent caused a great deal of elimination of thiophenol. Method C also utilizes a diphenyl dithioacetal (Schemes II and III and eq 5). In Scheme II, the diphenyl



8l, R^1, R^3 = $(CH_2)_5$, R^2 = H; 57%
8l, R^1, R^3 = -$(CH_2)_4$-, R^2 = -$(CH_2)_2$-; 70%
8k, R^1 = Et, R^2 = H, R^3 = CH_2CH_2-*t*-Bu; 57%

dithioacetal derived from an aldehyde is deprotonated and treated with an allyl bromide. The resulting diphenyl dithioacetal is reductively lithiated with lithium 1-(dimethylamino)naphthalenide[1,4b] (LDMAN) and the resulting α-lithio thioether is treated with an electrophile. In Scheme III, the diphenyl dithioacetal of formaldehyde is deprotonated and treated with ethylene oxide; the resulting thioacetal is reductively lithiated with lithium 4,4′-di-*tert*-butylbiphenylide (LDBB)[16] and allylated. In eq 5,[17] a diphenyl dithioacetal derived from a ketone is reductively lithiated, using LDMAN, and the resulting α-lithio thioether is allylated.

Preparation and Rearrangements of Homoallyllithiums. As in most of the reductive lithiations that we have performed recently, LDBB was used. In those cases in which the alkene function was a simple vinyl group, the temperature was –78 °C and the solvent tetrahydrofuran (THF). In cases in which the proximal terminus of the alkene function was disubstituted, it was necessary to replace some of the THF with hexanes in order to decrease the degree of proton abstraction (see below) from the solvent during the 1,2-vinyl rearrangements. When optimal rearrangement conditions were used in these cases, the reductive lithiation was performed in a 2:1 hexanes/THF solution and the temperature had to be maintained higher than –78 °C because at that temperature a great deal of precipitation of the LDBB occurred.

(5) Cohen, T.; Guo, B.-S. *Tetrahedron* **1986**, *42*, 2803–2808. Guo, B.-S.; Doubleday, W.; Cohen, T. *J. Am. Chem. Soc.* **1987**, *109*, 4710. Screttas, C. G.; Smonou, J. C. *J. Organomet. Chem.* **1988**, *342*, 143–152. Abraham, W. D.; Cohen, T. *J. Am. Chem. Soc.* **1991**, *113*, 2314–2316. McCullough, D. W.; Bhupathy, M.; Piccolino, E.; Cohen, T. *Tetrahedron* **1991**, *47*, 9727–9736. Cabral, J. A.; Cohen, T.; Doubleday, W. W.; Duchelle, E. F.; Fraenkel, G.; Guo, B.-S.; Yü, S. H. *J. Org. Chem.* **1992**, *57*, 3680–84.

(6) Maercker, A.; Theysohn, W. *Liebigs Ann. Chem.* **1971**, *747*, 70–83.

(7) Maercker, A.; Bsata, M.; Buchmeier, W.; Engelen, B. *Chem. Ber.* **1984**, *117*, 2547–2554.

(8) We have recently reported the preparation of a carbonyl-protected tertiary β-lithio ketone by reductive lithiation. See: Cherkauskas, J. P.; Cohen, T. *J. Org. Chem.* **1992**, *57*, 6–8.

(9) (a) Silver, M. S.; Shafer, P. R.; Nordlander, J. E.; Rüchardt, C.; Roberts, J. D. *J. Am. Chem. Soc.* **1960**, *82*, 2646–47. (b) Hill, A. *J. Organomet. Chem.* **1975**, *91*, 123–71.

(10) (a) Grovenstein, E. J. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 313–332. (b) Grovenstein, J. E.; Black, K. W.; Subhash, C. G.; Hughes, R. L.; Northrop, J. H.; Streeter, D. L.; VanDerveer, D. *J. Org. Chem.* **1989**, *54*, 1671–79.

(11) Maercker, A.; Weber, K. *Liebigs Ann. Chem.* **1972**, *756*, 43–78.

(12) One exception is the Grignard rearrangement of Julia, which, however, apparently proceeded in fairly poor yield. See: Julia, M.; Noël, Y. *Bull. Soc. Chim. Fr.* **1968**, 3749–54.

(13) Johnson, C. R.; Tait, B. D. *J. Org. Chem.* **1987**, *52*, 281–83.

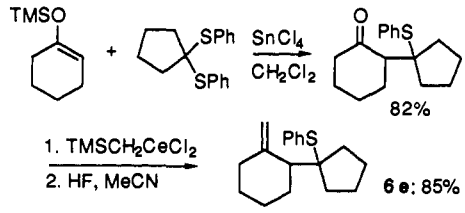
(14) Reetz, M. T.; Giannis, A. *Synth. Commun.* **1981**, *11*, 315–322.

(15) Maercker, A.; Streit, W. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 542–43.

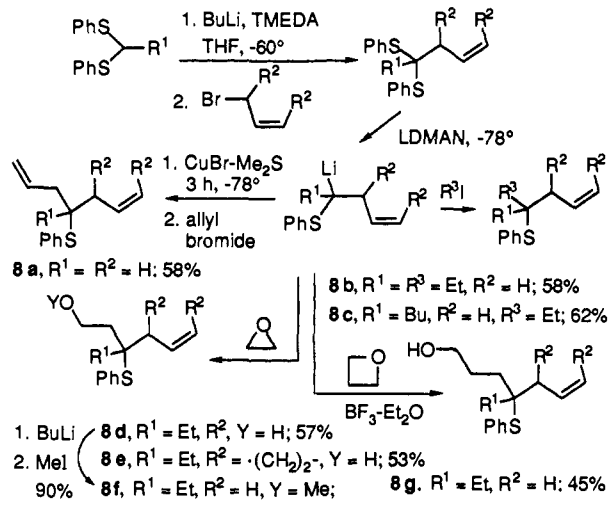
(16) Freeman, P.; Hutchinson, L. *J. Org. Chem.* **1980**, *45*, 1924–30.

(17) The thioacetal used in the preparation of **8k** was prepared in 80% yield by alkylation of the lithio derivative of the diphenyl dithioacetal of propanal using *t*-$Bu(CH_2)_2OTos$.

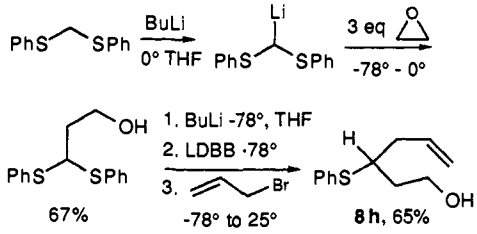
Scheme I



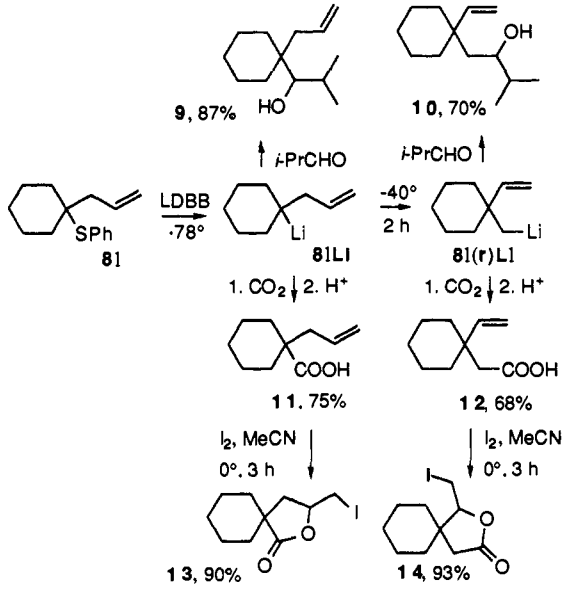
Scheme II



Scheme III

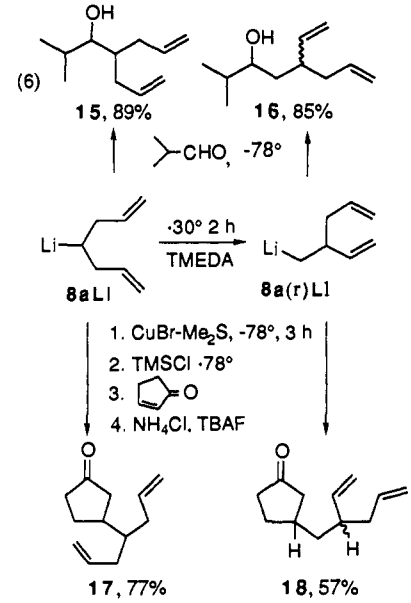


Scheme IV



A rather typical example of the generation of a tertiary homoallyllithium and its 1,2-vinyl rearrangement product and of their capture by electrophiles is shown in Scheme IV. Because of its high reactivity toward nucleophiles and its low acidity, isobutyraldehyde was the standard electrophile used in the work.

Scheme V



As is usual, the unsaturated alcohol derived from the proximate tertiary organolithium was formed in good yield while the alcohol derived from the rearranged primary organolithium was produced in a somewhat lower yield. In this particular case, each of the homoallyllithiums was also captured with carbon dioxide and the resulting unsaturated acids were converted to iodolactones. Thus, as is the case in much of the present work, a single homoallylic thioether can be converted to either of two homoallyllithiums.

A few secondary homoallyllithiums were also generated and allowed to rearrange to primary homoallyllithiums. In the example shown in Scheme V, in addition to the aldehyde quenches, both the secondary and primary organolithiums were converted to cuprates which were allowed to add in a conjugate fashion to an enone.

The results of many experiments in which secondary and tertiary homoallyllithiums were generated by reductive lithiation and induced to rearrange to primary organolithiums are summarized in Table I. The relative amounts of unsaturated alcohol derived from unrearranged (U) and rearranged (R) homoallyllithiums upon reaction with isobutyraldehyde are given in addition to the yields of combined alcohols of both types. The proximate homoallyllithiums are given numbers that are the same as their thioether precursors with an added Li; in the schemes, the rearranged homoallyllithiums are given the same designation except that Li is preceded by (r).

A competition experiment revealed an interesting feature of these rearrangements; the secondary homoallyllithium **6aLi** rearranges slightly faster than the tertiary analog **6bLi**. This is consistent with the results of Richey and co-workers who found that secondary organomagnesiums add more rapidly than either tertiary or primary organomagnesiums to alkenes in an intramolecular fashion to form a 5-membered ring[18] or in an intermolecular fashion.[19] This was reasonably attributed to the extra alkyl group exerting a rate-enhancing electronic effect and a rate-retarding steric effect. However, in the present work, an added complication is the formation of the intermediate cyclopropane ring. To the extent that the transition state resembles this intermediate, such a process could be accelerated by the Thorpe–Ingold effect[20] in

(18) Kossa, J. W. C.; Rees, T. C.; Richey, J. H. G. *Tetrahedron Lett.* **1971**, 3455–3458.
(19) Watkins, E. K.; Richey, H. G. *Organometallics* **1992**, *11*, 3785–3794.
(20) Beesley, R. M.; Ingold, C. K.; Thorpe, J. F. *J. Chem. Soc., Chem. Commun.* **1915**, *107*, 1080–1106. Ingold, C. K. *J. Chem. Soc., Chem. Commun.* **1921**, *119*, 305–329. Kon, G. A. R.; Stevenson, A.; Thorpe, J. F. *J. Chem. Soc., Chem. Commun.* **1922**, *1922*, 650–665. Allinger, N. L.; Zalkow, V. G. *J. Org. Chem.* **1960**, *25*, 701–706.

Table I. Rearrangements of Hydrocarbon Homoallyllithiums

RLi	rearr condns[b]	alcohols, %[a] U	R	yield
6aLi	−78 °C, 5 min	100	0	74
	−40 °C, 2 h	0	100	70
8aLi	−78 °C, 5 min	100	0	89
	−30 °C, 2 h	0[c]	100[c]	85
6bLi	−78 °C, 5 min	100	0	78
	−78 °C, 1 h			
	−40 °C, 15 min	40	60	60
		59[d]	41[d]	e
		3[c]	97[c]	e
	−40 °C, 2 h	0	100	68
	0 °C, 15 min	0	100	44
8lLi	−78 °C, 5 min	100	0	87
	−40 °C, 2 h	0	100	70
8bLi	−78 °C, 5 min	99	1	80
	−78 °C, 1 h			
	−40 °C, 15 min	4	96	79
8cLi	−78 °C, 5 min	100	0	82
		91[c]	9[c]	e
6cLi	−78 °C, 1 h			
	−40 °C, 15 min	100	0	67
	−20 °C, 2 h	0[c]	100[c]	42
	−40 °C, 3 h	0[f]	100[f]	73
7aLi	−78 °C, 5 min	100	0	95
	0 °C, 30 min	3[f]	97[f]	62
7bLi	−78 °C, 5 min	100	0	86
	−15 °C, 1.5 h	5[f]	95[f]	64
7dLi	−78 °C, 5 min	100	0	82
	−50 °C – −20°C 1.25 h	0[f]	100[f]	75

[a] Reaction products of the homoallyllithiums with isobutyraldehyde. [b] Reductive lithiations with LDBB in THF performed at −78 °C unless otherwise indicated. [c] 2 equiv of TMEDA per equivalent of Li added. [d] 1.5 equiv of *n*-PrOLi added. [e] GC ratio. [f] Hexanes–THF–TMEDA 62:31:7 (2 equiv of TMEDA per equivalent of Li ion), reductive lithiation performed at the rearrangement temperature.

which the two geminal methyl groups would stabilize the cyclopropane intermediate.[6] This effect is presumably responsible for the increase in rearrangement rate of the diethyl system **8bLi** as compared to the dimethyl system **6bLi**. Thus, in our case, the greater rearrangement rate for the secondary homoallyllithium **6aLi** over the tertiary one, **6bLi**, can not be accounted for in an obvious manner at present. Other factors that lead to uncertainty in interpretation are the effect of the unknown state of aggregation of these species and of the presence of lithium thiophenoxide.

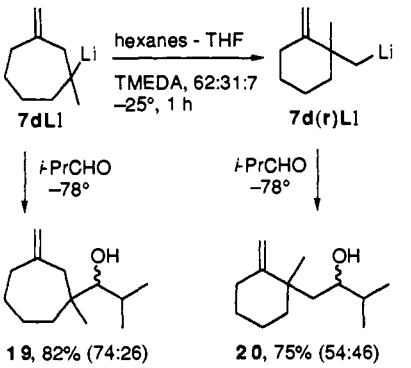
The results of the rearrangements of **6bLi** and **8cLi** reveal the important practical conclusion that the addition of tetramethylethylenediamine (TMEDA) to the THF reaction mixture causes a significant acceleration of the rearrangement. Maercker has also reported that the rearrangement of a homoallyllithium is facilitated by TMEDA,[11] and Bailey has reported that the rate of 5-membered ring formation of a lithioalkene is enhanced by this reagent as well.[21] As has been pointed out recently,[22] it is hazardous to attribute an explanation to such acceleration.

As mentioned briefly above, disubstitution at the proximal terminus of the alkene significantly decreases the rate of the rearrangement (as seen by comparing the rearrangements of **6bLi** and **6cLi**). This is consistent with an increase in steric crowding in the transition state for ring closure overriding any stabilization of this transition state due to the Thorpe–Ingold effect. One result is that higher temperatures were required in order to effect

(21) For a discussion and references to 5-membered ring formation, see: Bailey, W. F.; Khanolkar, A. D.; Gavaskar, K.; Ovaska, T. V.; Rossi, K.; Thiel, Y.; Wiberg, K. B. *J. Am. Chem. Soc.* **1991**, *113*, 5720–5727.

(22) Collum, D. B. *Acc. Chem. Res.* **1992**, *25*, 448–454.

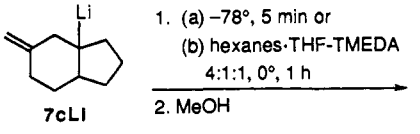
Scheme VI



rearrangement in systems with such a substitution pattern. However, as indicated in several entries in the table, higher temperatures during the rearrangements invariably caused decreases in the yield of recovered material. It is likely that competing proton removal by the carbanionic carbon atom is responsible for these reduced yields, and in a number of cases, the hydrocarbon generated by such proton removal was detected by gas chromatography–mass spectrometry. Extensive optimization studies indicated that this problem could be alleviated by diluting the reaction medium with hexanes (Rychnovsky[23] has found that the presence of hexanes greatly decreases the propensity of α-lithio ethers to remove protons from THF) and adding 2 equiv of TMEDA per equivalent of lithium ions.

Such conditions made it possible to induce some ring contractions. Thus, the tertiary organolithium **7dLi**, which could be captured in high yield by isobutyraldehyde, underwent rather efficient ring contraction to **7d(r)Li** which was trapped by the same aldehyde as in Scheme VI. Ring contractions of the 6-membered analogs **7aLi** and **7bLi** were more sluggish, requiring higher temperatures and giving somewhat lower yields of methylenecyclopentanes (Table I). It is quite reasonable to attribute this difference to the more strained [3.1.0] bicyclic intermediate in these latter cases as compared to the [4.1.0] intermediates in the former.

A similar ring contraction, of **7cLi**, followed by protonation by means of methanol, led mainly to diquinane **21** (eq 6). In this ring contraction, 4 equiv of TMEDA per equivalent of Li ion was used; the greater concentration of TMEDA led to somewhat better results than those obtained with the lower concentrations used in Table I. In this case, the rearranged organolithium could not be trapped efficiently with isobutyraldehyde. It is likely that the rigidly crowded rearranged neopentyl-type organolithium either deprotonates the solvent before the electrophile is added or the neopentyl-type organolithium deprotonates the α-position of the aldehyde more rapidly than it adds to its carbonyl group.

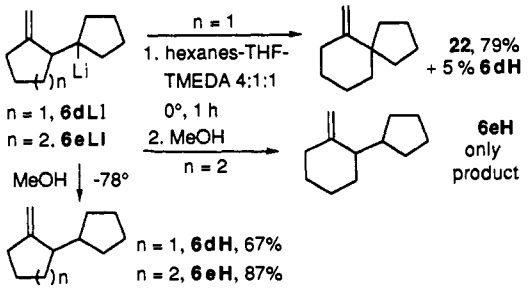


(6)

A *ring expansion* from a 5- to a 6-membered ring was also possible in the case of **6dLi** (Scheme VII). However, the analogous 6- to 7-ring expansion of **6eLi** was not successful. Presumably, the optimal size of the 6-membered ring is largely responsible for

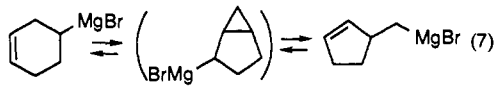
(23) Rychnovsky, S. D. *J. Org. Chem.* **1989**, *54*, 4982–84.

Scheme VII

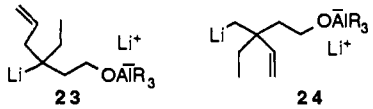


this difference. Once again the crowded, rearranged carbanionic precursor of **22** underwent protonation before quenching and thus could not be efficiently captured by isobutyraldehyde.

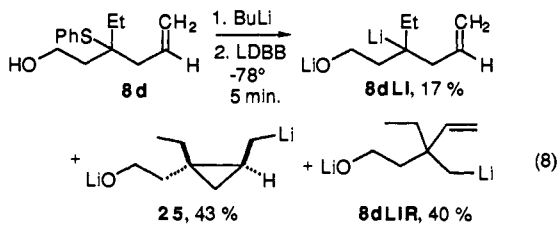
These are the first ring contractions or expansions of homoallyllithiums. Maercker has detected a reversible ring contraction of a homoallylic Grignard reagent at 80 °C by NMR spectroscopy (eq 7).[24] The equilibrium strongly favored the primary Grignard reagent.



A major impetus for the current work was the discovery that the tertiary organolithium **23**, generated by reductive cleavage of an oxetane in the presence of tri-*n*-propylaluminum, underwent an extremely rapid rearrangement to **24** at −70 °C.[25] By



comparison with other 1,2-vinyl rearrangements of tertiary homoallyllithiums in Table I, it is clear that the rearrangement of **23** is greatly accelerated. On the presumption that the oxygen-bearing side chain was responsible for this acceleration, the analog **8dLi** of **23** was prepared by reductive lithiation of **8d** at −78 °C and treated within 5 min with isobutyraldehyde. The results (eq 8) indicate that the carbanion–oxyanion displays a high rate of rearrangement regardless of which Lewis acid is coordinated with the oxyanion. After 5 min at −78 °C, only 17% of **8dLi** remains unrearranged. This case is quite unusual in that the intermediate (cyclopropylcarbinyl)lithium can be trapped, indicating that the rate of cyclopropane formation from the tertiary homoallyllithium **8dLi** is comparable to the rate of opening of the (cyclopropylcarbinyl)lithium to the primary homoallyllithium. Maercker has reported that the organolithium derived from treatment of 4-chloro-3,3,4,4-tetramethyl-1-butene with lithium exists at equilibrium almost completely in the ring closed, (cyclopropylcarbinyl)lithium form; as suggested by Maercker, the Thorpe–Ingold effect is probably responsible in that case.[6] However, in the present case, the open chain primary homoallyllithium is the stable form of the anion since it is virtually the only anion that can be trapped after the mixture is allowed to warm to −40 °C (Table II).



(8)

(24) Maercker, A.; Geuss, R. *Chem. Ber.* **1973**, *106*, 773–797.
(25) Mudryk, B.; Cohen, T. *J. Org. Chem.* **1991**, *56*, 5760–5761.

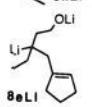
These results and others on related systems are summarized in Table II. The most important result is that for **8fLi** in which it is found that there is no special accelerating effect on the rearrangement when the OLi group is replaced by methoxyl. The special effect is displayed by the homologue **8gLi** of **8dLi**, but in that case hardly any of the (cyclopropylcarbinyl)lithium can be detected. A surprising result is that the oxyanionic secondary homoallyllithium **8hLi** rearranges far slower than the tertiary analog **8dLi** and even slower than the secondary homoallyllithium **6aLi** lacking the oxyanionic side chain; a possible explanation is discussed below. The addition of external oxyanion in the form of lithium *n*-propoxide slightly decreased the rate of 1,2-vinyl migration in **6bLi** (Table I); an analogous reduction in rate had been reported by Maercker in the rate of rearrangement of a homoallyllithium.[11] Finally, it is seen that even the oxyanionic side chain is insufficient to cause rearrangement of **8eLi**, the analog of **8dLi** in which the carbon–carbon double-bond group is trisubstituted.

The first explanation of these results to present itself involved intramolecular complexation of the oxyanion with the lithium ion of the organolithium; such lithium bonding[26] is thought to play a role in many directed lithiations.[27] Intuitively, such an interaction would seem to imply that the lithiomethyl group and the chain bearing the oxyanionic group would be disposed cis to each other in the cyclopropane intermediate. However, NOESY studies of the protonation product **29** of **25** established that the methyl and ethanol side chains are in fact trans disposed. Interactions were evident between the protons of the methyl group of **29** that is attached to the cyclopropane ring and those of the other methyl group as well as one of the protons of the methylene moiety of the ethyl group. None were displayed between this methyl group and any of the protons on the hydroxyethyl chain. Independent evidence was also obtained. Reductive cleavage of the oxetane[25,28] **27** with LDMAN followed by quenching of the resulting dianion with water yielded **28** contaminated with 6% of the *Z*-isomer and about 2% of the terminal olefin resulting from attack of the proton at the most substituted terminus of the dianion (Scheme VIII). Once again, the stereochemistry of **28** was determined by NOESY experiments. There was magnetic interaction between the protons of the allylic methyl group and both classes of those of the ethyl group but none between the methyl protons and those of the hydroxyethyl group. Cyclopropanation of **28**, using the diethylzinc modification[29] of the Simmons–Smith reaction, yielded **29** which was identical to the protonation product of **25**. The unlikely possibility that the OLi group, with the attendant THF ligands about the Li ion, was so large that it created a Thorpe–Ingold effect surpassing that of any other substituent that we have tried was tested by replacing that group with a *tert*-butyl group. However, the special accelerating effect was absent for the rearrangement of **6kLi** (penultimate entry, Table II).

Although counterintuitive, a fairly simple explanation for the trans relationship of the lithiomethyl and the oxyanionic substituent on the cyclopropane intermediate is revealed by molecular modeling. Computations by Houk and Schleyer[30] indicate that the addition of methyllithium to ethylene proceeds through a rather simple 4-center transition state. Furthermore, phenyl-

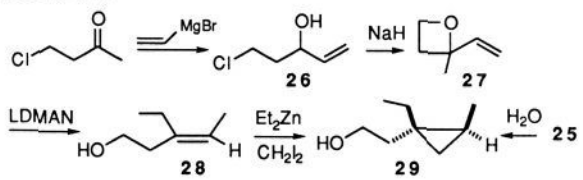
(26) Sannigrahi, A. B.; Kar, T.; Niyogi, B. G.; Hobza, P.; Schleyer, P. R. *Chem. Rev.* **1990**, *90*, 1061–1076.
(27) Klumpp, G. W. *Recl. Trav. Chim. Pays-Bas* **1986**, *105*, 1–21.
(28) Mudryk, B.; Cohen, T. *J. Org. Chem.* **1989**, *54*, 5657–59. Mudryk, B.; Cohen, T. *J. Am. Chem. Soc.* **1991**, *113*, 1866–1867.
(29) Furukawa, J.; Kawabata, N.; Nishimura, J. *Tetrahedron* **1968**, *24*, 53–58. Miyano, S.; Hashimoto, H. *J. Chem. Soc., Chem. Commun.* **1971**, 1418–19. Miyano, S.; Matsumoto, Y.; Hashimoto, H. *J. Chem. Soc., Chem. Commun.* **1975**, 364–65.
(30) Houk, K. N.; Rondan, N. G.; Schleyer, P. R.; Kaufmann, E.; Clark, T. *J. Am. Chem. Soc.* **1985**, *107*, 2821–23.

Table II. Rearrangements of Homoallyllithiums Containing an Oxygen Function

RLi	condtns[a]	alcohols, %[b] U	C	R	yield
 8dLi	–78 °C, 5 min –78 °C, 1 h	17	43	40	75
	–40 °C, 15 min	0	1	99	68
 8hLi	–78 °C, 1 h –40 °C, 15 min	75	0	25	55
	0 °C, 15 min	4	0	96	51
 8gLi	–78 °C, 5 min	37	<1	63	74
 8fLi	–78 °C, 5 min	100	0	0	88
 8kLi	–78 °C, 5 *min*	97	0	3	75
 8eLi	0 °C, 30 min[c]	100	0	0	90

[a] Reductive lithiations were performed at –78 °C with LDBB in THF. [b] Reaction products of the homoallyllithiums with isobutyraldehyde. U, from unrearranged organolithium; C, from (cyclopropylcarbinyl)lithium; R, from rearranged organolithium. [c] THF–hexanes 1:2.

Scheme VIII



lithium has been found to add in a cis fashion to cyclopropene.[31] It is certainly reasonable to assume that the intramolecular addition of an alkyllithium to an alkene observed here proceeds in a similar fashion. Indeed, such a transition state has also been postulated by Grovenstein[10b] in order to account for the stereochemistry of an anionic, 1,2-vinyl rearrangement; a cis addition has also been postulated for the cyclization of certain lithioalkenes to (cyclopentylmethyl)lithiums.[21] Thus, in the conformation preceding ring closure, the carbon–lithium bond and the C–C double bond must become approximately parallel. In such a conformation (e.g., Figure 1), one of the substituents (A) on the original lithium-bearing carbon atom is pointing in the general direction of the alkene group and the other (B) is pointing away. The latter is the one that ends up cis to the lithiomethyl group in the cyclopropane. The pronounced acceleration of the ring closure implies that in the transition state for ring closure, the oxyanionic substituent interacts with the alkene linkage either indirectly, by "guiding" the alkyllithium into the alkene linkage,[32] as is thought to occur in additions of alkyllithiums to allylic alcoholate ions,[27] or directly, by polarizing the π bond, as may be occurring in the addition of an alkyllithium to a homoallylic alcoholate.[33] The former, and in this case apparently more likely, situation is depicted in Figure 1; chelation between the oxygen atom and the lithium attached to the tertiary carbon atom would generate a 5-membered ring that could remain intact until the transition state for transfer of the lithium ion between its carbon partners is approached. If, on the other hand, the oxyanionic

(31) Welch, J. G.; Magid, R. M. *J. Am. Chem. Soc.* **1967**, *89*, 5300–5301.
(32) The coordination of the oxyanion with the lithium may have the effect electronically and/or sterically of promoting desolvation of the lithium, presumably a prerequisite for its interaction with the π bond.
(33) Richey, H. G.; Wilkins, C. W.; Benison, R. M. *J. Org. Chem.* **1980**, *45*, 5042–5047.

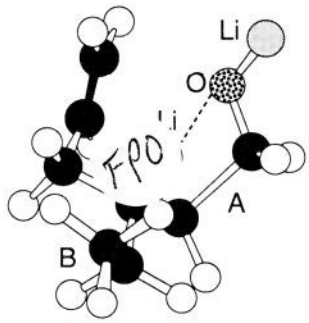


Figure 1.

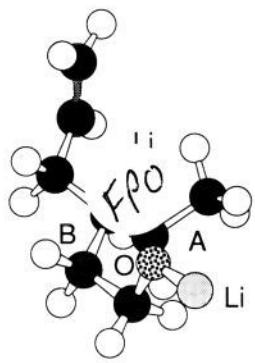


Figure 2.

side chain were to occupy site B (Figure 2), interaction with the alkene linkage can not occur; stabilization due to lithium bonding would be at least partially lost in approaching the transition state for ring closure. Thus, it is probable that regardless of the precise mode of interaction, the oxyanion-bearing chain must occupy substituent site A and will therefore be trans to the lithiomethyl group in the cyclopropane.

If lithium bonding does indeed occur in the transition state for conversion of **8dLi** to the cyclopropane **25**, it is not surprising that the homologous **8gLi** also displays the accelerating effect. Lithium bonding proceeding from **8gLi** involves a 6-membered ring which is only slightly less favorable than a 5-membered ring in heteroatom-directed lithiations and carbolithiations.[27]

This analysis also allows a rationalization for fact that the secondary homoallyllithium **8hLi** rearranges far slower than the tertiary analog **8dLi**, the opposite of the situation in the system in which the oxyanionic group is absent (see above). In the conformations shown in Figures 1 and 2, the substituents that occupy site A both experience repulsive steric interactions with the allyl group. In the analogous molecules in which there is a hydrogen atom in place of the ethyl group, the analog of the configuration shown in Figure 2 would experience far less of such steric repulsion. Thus, the steric disadvantage of the analog of the conformation shown in Figure 1 may be great enough to offset the advantage that would be gained by participation in the ring closure of the oxyanionic group.

The present ring closure appears to be unique among heteroatom-assisted carbolithiations of alkenes. As indicated by models, bonding in the (cyclopropylmethyl)lithium **25** between the oxyanion and the lithium ion associated with carbon is virtually impossible. In all other reported cases of heteroatom-assisted carbolithiation, such a lithium bond is possible and believed to occur.[27] Indeed, such bonding has been cited as a criterion for predicting heteroatom assistance to carbolithiation.[27] Thus, this criterion apparently is not completely general.

These are apparently the first cases of oxyanionic acceleration of carbanionic ring closures, and it raises the question as to whether a strategically placed lithium alkoxide group will accelerate and control the stereochemistry of intramolecular additions of

alkyllithiums to alkenes to form larger size rings as well. It has been reported that allylic and homoallylic ether functions influence the stereochemistry of (cyclopentylmethyl)lithium formation in the ring closure of a lithioalkene, but yields were modest, and no acceleration was indicated.[34]

Experimental Section

General. Tetrahydrofuran (THF) was distilled over sodium benzophenone ketyl. Hexanes and *N,N,N',N'*-tetramethylethylenediamine (TMEDA) were distilled before use and stored above molecular sieves. NMR spectra were recorded at 300 or 500 MHz in $CDCl_3$ unless otherwise stated. Chemical shifts are reported in δ and J values in hertz. Multiplicities are given as s (singlet), d (doublet), t (triplet), q (quartet), h (heptet), m (multiplet), and br (broad). Low resolution and high resolution mass spectra were obtained in the electron impact mode at 70 eV. All reaction mixtures were preliminarly analyzed by thin layer chromtography with 0.25-mm silica gel plates, by gas chromatography (Hewlett Packard 5890 A equipped with the fused silica capillary column 0.25 mm × 30 m), and by the GC mass spectrometry (OV-3 column). The products from the small scale experiments were isolated by radial chromatography (Harrison chromatotron 7924 equipped with a 4-mm plate) or by flash chromatography (silica gel 230–400 mesh). In larger scale experiments, the products were isolated and purified by vacuum distillation or by crystallization.

Starting Materials. Method A. The following enals and enones were commercially available: crotonaldehyde, 3-methyl-2-butenal, mesityl oxide, 3-methyl-2-cyclohexen-1-one (all Aldrich), and 2-cyclopentylidenecyclopentanone (TCI America). They were distilled immediately before use. 3-*n*-Butyl-2-cyclohexen-1-one was prepared in 79% yield by addition of *n*-BuLi to 3-ethoxy-2-cyclohexen-1-one (Aldrich) followed by hydrolysis,[35] bp 70–72 °C/0.1 Torr: ^{1}H NMR 0.91 (t, J = 7.3 Hz, 3 H), 1.29–1.39 (m, 2 H), 1.43–1.51 (m, 2 H), 1.93–2.02 (m, 2 H), 2.21 (t, J = 7.5 Hz, 2 H), 2.28 (t, J = 5.9 Hz, 2 H), 2.35 (t, J = 6.7 Hz, 2 H), 5.87 (d, J = 0.9 Hz, 1 H). 3-Methyl-2-cyclohepten-1-one was prepared by the addition of MeLi to 2-cyclohepten-1-one (Aldrich) in Et_2O followed by the PCC allylic oxidative transposition (50% overall) in analogy to the procedure by Dauben,[36] bp 109–111 °C/20 Torr: ^{1}H NMR 1.77–1.83 (m, 4 H), 1.96 (s, 3 H), 2.42 (m, 2 H), 2.58 (m, 2 H), 5.93 (s, 1 H). Bicyclo[4.3.0]-1-nonen-3-one was obtained by the Robinson annulation procedure from 4-(1-cyclopenten-1-yl)morpholine and methyl vinyl ketone[37] (~60%), bp 89–96 °C/1.4 Torr. The crude product of 85% purity (GC, NMR) was used for the next steps.

Addition of Thiophenol to Enals and Enones. General Procedure. Thiophenol (0.10 mol), triethylamine (0.005 mol), and THF (10–15 mL) were placed under argon in a dry 100-mL 3-necked round bottomed flask equipped with a magnetic stirrer, thermometer, and argon inlet. An enal or enone (0.10 mol) was added slowly at 0 °C and the temperature increased to 10–30 °C. The reaction mixture was stirred at room temperature, and the reaction progress was monitored by TLC. In the case of the more sterically crowded enones, two or more equivalents of thiophenol were used and reactions were conducted without solvent. The crude mixture was dissolved in ether (100 mL), and the solution was washed extensively with a 5% NaOH solution, then washed with water, and dried with anhydrous $MgSO_4$. After the solvents had been removed by rotary evaporation, the acyclic (phenylthio) aldehydes and (phenylthio) ketones (80–100% yield) were pure enough for the next steps. The cyclic products were purified by vacuum distillation or by crystallization: 3-methyl-3-(phenylthio)cyclohexanone (70%), bp 120–125 °C/0.1 Torr: ^{1}H NMR 1.28 (s, 3 H), 1.85–2.0 (m, 3 H), 2.15–2.35 (m) and 2.32 (d, J = 14.2 Hz, AB system) (4 H), 2.50 (d, J = 14.2 Hz, AB system, 1 H), 7.32–7.38 (m, 3 H), 7.49–7.54 (m, 2 H). 3-*n*-Butyl-3-(phenylthio)-cyclohexanone (60%): bp 135–138 °C/0.1 Torr; ^{1}H NMR 0.92 (t, J = 7.3 Hz, 3 H), 1.23–1.30 (m, 2 H), 1.32–1.47 (m, 3 H), 1.55–1.65 (m, 1 H), 1.81–1.89 (m, 3 H), 2.12–2.40 (m), and 2.32 (d, J = 14.3 Hz, AB system) (4 H) 2.45 (d, J = 14.3 Hz, AB system, 1 H), 7.29–7.38 (m, 3 H), 7.46–7.50 (m, 2 H). 3-Methyl-3-(phenylthio)cycloheptanone (75%): bp 123–126 °C/0.1 Torr; ^{1}H NMR 1.30 (s, 3 H), 1.75–1.95 (m, 5 H), 2.1–2.4 (m, 4 H), 2.54 (d, J = 14.4 Hz, 1 H), 7.30–7.36 (m, 3 H), 7.45–7.52 (m, 2 H). *cis*-1-(Phenylthio)bicyclo[4.3.0]nonan-3-one (90%): mp 58–60 °C; ^{1}H NMR 1.45–1.57 (m, 2 H), 1.63–1.75 (m, 2 H), 1.85–1.95 (m, 1 H), 2.00–2.25 (m, 4 H), 2.30–2.35 (m, 2 H), 2.43 (d, J = 15.3 Hz, AB system, 1 H), 2.58 (d, J = 15.3 Hz, AB system, 1 H), 7.33–7.40 (m, 3 H), 7.47–7.51 (m, 2 H); ^{13}C NMR 22.8, 26.6, 31.5, 37.0, 40.2, 44.0, 48.3, 58.4, 128.7, 129.1, 131.5, 137.3, 210.7. 2-(1'-(Phenylthio)cyclopent-1'-yl)cyclopentanone (60%): ^{1}H NMR 1.6–2.15 (m, 13 H), 2.2–2.35 (m, 2 H), 2.59 (dd, J = 4.6 and 11.6, 1 H), 2.83–2.91 (m, 1 H), 7.30–7.38 (m, 3 H), 7.48–7.52 (m, 2 H).

Preparation of Homoallyl Phenyl Sulfides 6 and 7 from 3-(Phenylthio) Aldehydes and 3-(Phenylthio) Ketones by the Wittig Reaction.[38] *n*-Butyllithium (9.5 mL of a 1.55 M hexane solution, 14.7 mmol) was added dropwise to a suspension of methyltriphenylphosphonium bromide (5.7 g, 16 mmol) in THF (50 mL) at 0 °C under argon. After 20 min of stirring at 0 °C, the mixture was cooled to −78 °C, and a solution of phenylthio carbonyl compound (10 mmol) in THF (5 mL) was added dropwise. The mixture was stirred for 15 min at −78 °C, warmed to 0 °C, quenched with methanol (1 mL), and poured into pentane (200 mL). The solids were removed by slow filtration through silica gel, and the solvents were removed by rotary evaporation. The crude homoallyl phenyl sulfides were purified by flash chromatography (hexanes). **4-(Phenylthio)-1-pentene (6a)**: 80%; ^{1}H NMR 1.27 (d, J = 6.9 Hz, 3 H), 2.23 (dt, J = 14.2 and 7.1 Hz, 1 H), 2.40 (dt, J = 14.2 and 7.1 Hz, 1 H), 3.22–3.34 (m, 1 H), 5.05–5.11 (m, 2 H), 5.77–5.90 (m, 1 H), 7.19–7.32 (m, 3 H), 7.41 (d, J = 7.0 Hz, 2 H).

4-Methyl-4-(phenylthio)-1-pentene (6b): 76%; ^{1}H NMR 1.23 (s, 6 H), 2.25 (d, J = 7.2 Hz, 2 H), 5.07 (d, J = 17.1 Hz) and 5.11 (d, J = 10.0 Hz) (2 H), 5.96 (ddt, J = 10.0, 17.1, and 7.2 Hz, 1 H), 7.30–7.37 (m, 3 H), 7.51–7.55 (m, 2 H).

2,4-Dimethyl-4-(phenylthio)-1-pentene (6c): 81%; ^{1}H NMR 1.28 (s, 6 H), 1.85 (s, 3 H), 2.34 (s, 2 H), 4.75 (s, 1 H), 4.93 (s, 1 H), 7.33–7.37 (m, 3 H), 7.53–7.57 (m, 2 H).

1-Methylene-2-[1'-(phenylthio)cyclopent-1'-yl]cyclopentane (6d): 87%; ^{1}H NMR 1.35–1.50 (m, 1 H), 1.55–1.95 (m, 10 H), 1.98–2.10 (m, 1 H), 2.32–2.40 (m, 2 H), 2.72 (t, J = 7.1 Hz, 1 H), 5.03 (s, 1 H), 5.06 (s, 1 H), 7.23–7.36 (m, 3 H), 7.49–7.58 (m, 2 H); ^{13}C NMR 24.0, 24.7, 31.4, 36.2, 36.6, 50.5, 65.9, 109.2, 128.4, 128.5, 133.6, 136.9, 153.2.

1-Methylene-3-methyl-3-(phenylthio)cyclohexane (7a): 80%; ^{1}H NMR 1.22 (s, 3 H), 1.53–1.64 (m, 2 H), 1.67–1.74 (m, 1 H), 1.82–1.89 (m, 1 H), 2.11 (t, J = 6.1 Hz, 2 H), 2.19 (d, J = 13.3 Hz, AB system, 1 H), 2.27 (d, J = 13.3 Hz, AB system, 1 H), 4.67 (s, 1 H), 4.77 (s, 1 H), 7.30–7.38 (m, 3 H), 7.52–7.56 (m, 2 H); ^{13}C NMR 23.4, 27.1, 34.1, 37.6, 47.3, 50.5, 109.9, 128.4, 128.7, 131.6, 137.8, 145.7.

3-*n*-Butyl-1-methylene-3-(phenylthio)cyclohexane (7b): 90%; ^{1}H NMR 0.93 (t, J = 7.3 Hz, 3 H), 1.2–1.65 (m, 9 H), 1.80–1.91 (m, 1 H), 2.10 (t, J = 6.1 Hz, 2 H), 2.19 (d, J = 13.4 Hz, AB system, 1 H), 2.31 (d, J = 13.4 Hz, 1 H), 4.64 (s, 1 H), 4.76 (s, 1 H), 7.28–7.40 (m, 3 H), 7.47–7.53 (m, 2 H).

***cis*-3-Methylene-1-(phenylthio)bicyclo[4.3.0]nonane (7c)**: 95%; ^{1}H NMR 1.32–1.45 (m, 1 H), 1.50–1.57 (m, 1 H), 1.65–2.00 (m, 5 H), 2.06–2.20 (m, 2 H), 2.37 (d and d, J = 12.2 Hz, center of an AB system, 2 H), 4.63 (s, 1 H), 4.76 (s, 1 H), 7.33–7.38 (m, 3 H), 7.51–7.56 (m, 2 H); ^{13}C NMR 20.7, 28.3, 29.0, 31.3, 35.6, 42.0, 42.9, 60.7, 109.2, 128.2, 128.3, 132.2, 137.0, 145.4.

3-Methyl-1-methylene-3-(phenylthio)cycloheptane (7d): 76%; ^{1}H NMR 1.23 (s, 3 H), 1.45–1.8 (m, 6 H), 2.32 (t, J = 6.5 Hz) and 2.35 (d, J = 13.3 Hz, AB system) (3 H), 2.49 (d, J = 13.3 Hz, AB system, 1 H), 4.76 (s, 1 H), 4.85 (s, 1 H), 7.33–7.38 (m, 3 H), 7.52–7.56 (m, 2 H); ^{13}C NMR 23.8, 28.4, 37.0, 41.8, 48.2, 51.8, 114.2, 128.5, 128.7, 132.3, 137.8, 146.1.

Method B. 1-[(Trimethylsilyl)oxy]cyclohexene was commercially available. 1,1-Bis(phenylthio)cyclopentane was prepared as in method C.

Coupling of the Cyclohexanone Silyl Enol Ether with Bis(phenylthio)-cyclopentane in the Presence of Tin Tetrachloride. The reaction was conducted similarly to the Reetz's procedure[14] employing a diphenyl dithioacetal instead of a dialkyl dithioacetal and using longer reaction time (5 h instead of 45 min). 2-(1'-(Phenylthio)cyclopent-1'-yl)-cyclohexanone (82%): ^{1}H NMR 1.6–2.15 (m, 13 H), 2.2–2.35 (m, 2 H), 2.59 (dd, J = 4.6 and 11.6 Hz, 1 H), 2.83–2.91 (m, 1 H), 7.30–7.38 (m, 3 H), 7.48–7.52 (m, 2 H).

Addition of [(Trimethylsilyl)methyl]cerium Dichloride to the β-(Phenylthio) Ketones. Elimination of Trimethylsilanol. The β-(phenylthio) ketone was subjected to the Johnson modification of the Peterson's

(34) Smith, M. J.; Wilson, S. E. *Tetrahedron Lett.* **1981**, *22*, 4615–4618.
(35) A modified procedure of Eschenmoser, A.; Schreiber, J.; Julia, S. A. *Helv. Chim. Acta* **1953**, *36*, 482–488.
(36) Dauben, W. G.; Michno, D. M. *J. Org. Chem.* **1977**, *42*, 682–685.
(37) Aumiller, J. C.; Whittle, J. *J. Org. Chem.* **1976**, *41*, 2955–2959.
(38) A modified procedure of Plamondon, L.; Wuest, J. D. *J. Org. Chem.* **1991**, *56*, 2066.

olefination procedure.[13] The intermediate β-trimethylsilyl alcohol was not purified before treatment with aqueous hydrofluoric acid in acetonitrile.

1-Methylene-2-[1′-(phenylthio)cyclopent-1′-yl]cyclohexane (6e): 85% overall; ^{1}H NMR 1.4–2.05 (m, 15 H), 2.18 (dd, J = 4.0 and 9.1 Hz, 1 H), 2.29 (dt, J = 13.0 and 4.8 Hz, 1 H), 4.84 (s, 1 H), 4.93 (s, 1 H), 7.28–7.36 (m, 3 H), 7.51–7.55 (m, 2 H).

Method C. 1,1-Bis(phenylthio)propane, 1,1-bis(phenylthio)pentane, 3,3-bis(phenylthio)pentane, and 1,1-bis(phenylthio)cyclohexane were prepared by bubbling dry HCl gas through a mixture (or through a methylene chloride solution) of thiophenol (2 equiv) and an aldehyde or ketone (1 equiv) for a few minutes at 0 °C under argon until the temperature stopped rising (usually at 15–25 °C).[39] After the ethereal workup, the crude diphenyl dithioacetals were purified by vacuum distillation or crystallization, yield 76–95%. 4,4-Bis(phenylthio)-1-butene was prepared by the allylation of lithiobis(phenylthio)methane (generated from bis(phenylthio)methane and n-BuLi in THF at 0 °C) with allyl bromide. The product (88% yield) was isolated by vacuum distillation, bp 136–140 °C/0.1 Torr: ^{1}H NMR 2.62 (t, J = 6.7 Hz, 2 H), 4.45 (t, J = 6.5 Hz, 1 H), 5.09–5.18 (m, 2 H), 5.99 (ddt, J = 10.3, 17.1, and 6.8 Hz, 1 H), 7.28–7.38 (m, 6 H), 7.42–7.50 (m, 4 H). 3,3-Bis(phenylthio)-1-propanol (70%) was obtained by an analogous procedure using an excess (~5 equiv) of ethylene oxide, bp 180–185 °C/0.1 Torr: ^{1}H NMR 1.72 (s, 1 H), 2.10 (q, J = 6.3 Hz, 2 H), 3.90 (t, J = 5.8 Hz, 2 H), 4.65 (t, J = 7.0 Hz, 1 H), 7.28–7.36 (m, 6 H), 7.47–7.51 (m, 4 H).

Allylation of Diphenyl Dithioacetals. General Procedure.[40] n-Butyllithium (26.3 mL of a 1.6 M hexane solution, 0.042 mol) was added to freshly distilled TMEDA (5.1 g, 0.044 mol) at 0 °C under argon. After 15 min, the efficiency stirred solution was cooled to −70 to −60 °C, and the diphenyl dithioacetal (0.040 mol) in THF (10 mL) was added dropwise. A yellow orange precipitate formed, and THF (30 mL) was added. The mixture was warmed briefly to 0 °C whereupon the solid dissolved, and it was cooled again to −40 °C. Freshly distilled allyl bromide or 3-bromocyclopentene[41] was added dropwise at −40 to −20 °C, and the mixture was stirred for 1 h at room temperature. After the reaction had been quenched with a saturated NH_4Cl solution and after ethereal workup, the crude diphenyl dithioacetals were purified by vacuum distillation. 4,4-Bis(phenylthio)-1-hexene (82%): bp 155–160 °C/0.1 Torr; ^{1}H NMR 1.09 (t, J = 7.3 Hz, 3 H), 1.66 (q, J = 7.3 Hz, 2 H), 2.41 (d, J = 6.7 Hz, 2 H), 5.06 (dd, J = 1.6 and 17.1 Hz, 1 H), 5.15 (dd, J = 1.0 and 10.4 Hz, 1 H), 6.11 (ddt, J = 10.4, 17.1, and 6.7 Hz), 7.30–7.40 (m, 6 H), 7.67–7.73 (m, 4 H). 4,4-Bis(phenylthio)-1-octene (75%): bp 165–170 °C/0.1 Torr; ^{1}H NMR 0.86 (t, J = 7.3 Hz, 3 H), 1.16–1.24 (m, 2 H), 1.59–1.63 (m, 4 H), 2.41 (d, J = 6.7 Hz, 2 H), 5.04 (dd, J = 1.3 and 17.1 Hz, 2 H), 5.15 (d, J = 10.2 Hz, 1 H), 7.28–7.41 (m, 6 H), 7.67–7.71 (m, 4 H). 1,1-Bis(phenylthio)-1-(2-cyclopenten-1-yl)propane (70%): bp 180–190 °C/0.1 Torr; ^{1}H NMR 1.07 (t, J = 7.5 Hz, 3 H), 1.55–1.63 (m, 2 H), 1.92–2.05 (m, 1 H), 2.07–2.20 (m, 1 H), 2.27–2.38 (m, 1 H), 2.44–2.56 (m, 1 H), 3.26–3.33 (m, 1 H), 5.70–5.75 (m, 1 H), 5.82–5.88 (m, 1 H), 7.25–7.37 (m, 6 H), 7.55–7.60.

Preparation of Tertiary and Secondary Homoallyl Phenyl Sulfides by the Reductive Lithiation–Cuprate Formation–Alkylation Sequence. General Procedure. A solution of a diphenyl dithioacetal (0.020 mol) in THF (5 mL) was added dropwise to a preformed solution of lithium 4,4′-di-*tert*-butylbiphenylide[16] (LDBB) (0.044 mol) or lithium (*N*,*N*-dimethylamino)naphthalenide[1,4b] (LDMAN) (0.044 mol) in THF (130 mL) at −78 °C. The dark-blue (LDBB) or dark-green (LDMAN) color of the solution turned to a dark-red color at the end of the addition. Ethyl iodide (0.050 mol, 2.5 equiv), ethylene oxide (0.080 mol, a solution in THF, 4 equiv) or oxetane (0.080 mol, 4 equiv) and BF_3 etherate (0.080 mol, 4 equiv) were added. The mixture was stirred for 15 min at −78 °C, warmed to room temperature, and quenched with water. The organic material was extracted with ether (2 × 100 mL); in LDMAN reactions the organic layer was washed with 5% HCl (2 × 50 mL) to remove DMAN. The organic phase was dried with anhydrous $MgSO_4$. After rotary evaporation of the solvents for reactions involving LDBB, methanol (100 mL) was added, and the precipitated DBB was filtered off (85–90% DBB could be separated by this way). The crude reaction mixtures contained mainly the desired homoallyl phenyl sulfides and the products of thiophenoxide reactions with electrophiles, which were separated by vacuum distillation or by flash chromatography.

4-Ethyl-4-(phenylthio)-1-hexene (8b): 71%; bp 73–76 °C/0.1 Torr; ^{1}H NMR 1.00 (t, J = 7.3 Hz, 6 H), 1.42 (q, J = 7.3 Hz, 4 H), 2.17 (d, J = 6.9 Hz, 2 H), 5.06–5.16 (m, 2 H), 6.03 (ddt, J = 10.6, 17.4, and 6.9 Hz, 1 H), 7.27–7.38 (m, 3 H), 7.48–7.55 (m, 2 H).

4-Ethyl-4-(phenylthio)-1-octene (8c): 77%; bp 80–82 °C/0.1 Torr; ^{1}H NMR 0.92 (t, J = 7.3 Hz, 3 H), 1.00 (t, J = 7.3 Hz, 3 H), 1.22–1.50 (m, 8 H), 2.17 (d, J = 7.0 Hz, 2 H), 5.05–5.14 (m, 2 H), 6.03 (ddt, J = 10.4, 17.3, and 7.0 Hz, 1 H), 7.27–7.35 (m, 3 H), 7.47–7.51 (m, 2 H).

3-Ethyl-3-(phenylthio)-5-hexen-1-ol (8d): 70%; bp 135–138 °C/0.1 Torr; ^{1}H NMR 1.01 (t, J = 7.3 Hz, 3 H), 1.47 (q, J = 7.3 Hz, 2 H), 1.73 (t, J = 6.9 Hz, 2 H), 2.01 (br s, 1 H), 2.21 (dd, J = 1.0 and 7.2 Hz, 2 H), 3.93 (t, J = 6.9 Hz, 2 H), 5.07–5.16 (m, 2 H), 5.98 (ddt, J = 10.4, 17.2, and 7.2 Hz, 1 H), 7.29–7.37 (m, 3 H), 7.53–7.56 (m, 2 H).

3-(2-Cyclopenten-1-yl)-3-(phenylthio)-1-pentanol (8e): 75% (2 diastereoisomers, 60:40); bp 96–98 °C/0.1 Torr; ^{1}H NMR (C_6D_6) 0.88–0.96 (m, 3 H), 1.23 (br s, 1 H), 1.40–1.50 (m, 2 H), 1.70–1.86 (m, 4 H), 2.05–2.18 (m, 1 H), 2.20–2.30 (m, 1 H), 2.86–2.94 (m, 1 H), 3.65–3.80 (m, 2 H), 5.61–5.67 (m, 1 H), 5.71–5.75 (m) and 5.78–5.83 (m) (1 H), 6.98–7.03 (m, 3 H), 7.57–7.62 (m, 2 H).

4-Ethyl-6-methoxy-4-(phenylthio)-1-hexene (8f) was prepared from the lithium salt of **8d** and MeI in THF–HMPA (2 equiv) at 0 °C: yield 87%; ^{1}H NMR 1.01 (t, J = 7.3 Hz, 3 H), 1.44 (q, J = 7.3 Hz, 2 H), 1.71 (t, J = 7.4 Hz, 2 H), 2.19 (dd, J = 1.0 and 7.1 Hz, 2 H), 3.35 (s, 3 H), 3.65 (td, J = 7.9 and 2.7 Hz, 2 H), 5.07–5.15 (m, 2 H), 6.01 (ddt, J = 10.4, 17.2, and 7.1 Hz, 1 H), 7.28–7.36 (m, 3 H), 7.47–7.51 (m, 2 H).

4-Ethyl-4-(phenylthio)-6-hepten-1-ol (8g): 55%; ^{1}H NMR 1.00 (t, J = 7.3 Hz, 3 H), 1.39–1.47 (m, 4 H), 1.56 (s, 1 H), 1.72–1.83 (m, 2 H), 2.18 (d, J = 7.0 Hz, 2 H), 3.62 (t, J = 6.5 Hz, 2 H), 5.07–5.14 (m, 2 H), 6.01 (ddt, J = 10.4, 17.3, and 7.0 Hz, 1 H), 7.26–7.35 (m, 3 H), 7.47–7.51 (m, 2 H).

3-(Phenylthio)-5-hexen-1-ol (8h): 65%; ^{1}H NMR 1.69–1.80 (m, 1 H), 1.81 (s, 1 H), 1.89–2.00 (m, 1 H), 2.32–2.46 (m, 2 H), 3.32–3.39 (m, 1 H), 3.78–3.93 (m, 2 H), 5.07–5.13 (m, 2 H), 5.81–5.96 (m, 1 H), 7.27–7.39 (m, 3 H), 7.43–7.48 (m, 2 H).

In the preparation of **8a**, **8i**, **8j**, and **8k** (Scheme II, eq 5) the corresponding α-(phenylthio)organolithium compounds were transformed into their cuprates by stirring with cuprous bromide–dimethyl sulfide (1.3 equiv) for 3 h at −78 °C before the allylation reaction. After the mixture had been stirred overnight at −78 °C, it was warmed to room temperature and poured into a saturated NH_4Cl solution and ether. Stirring was continued for 1–2 h, the solids were removed by filtration, and the ether layer was washed with a saturated NH_4Cl solution and a 5% HCl solution (to remove DMAN) and dried with anhydrous $MgSO_4$. The solvents were removed by rotary evaporation, and the products (slightly contaminated with allyl phenyl sulfide or 3-(phenylthio)-cyclopentene) were purified by distillation.

4-(Phenylthio)-1,6-heptadiene (8a): 66%; bp 137–140 °C/10 Torr; ^{1}H NMR 2.36 (td, J = 6.9 and 0.9 Hz, 4 H), 3.23 (p, J = 6.5 Hz, 1 H), 5.05–5.13 (m, 4 H), 5.81–5.96 (m, 2 H), 7.27–7.33 (m, 3 H), 7.39–7.44 (m, 2 H).

1-(Phenylthio)-1-(2-propenyl)cyclohexane (8i): 75%; bp 96–98 °C/0.1 Torr; ^{1}H NMR 1.28–1.39 (m, 1 H), 1.44–1.65 (m, 7 H), 1.75–1.87 (m, 2 H), 2.20 (d, J = 7.0 Hz, 2 H), 5.04–5.16 (m, 2 H), 6.10 (ddt, J = 10.2, 17.1, and 7.0 Hz, 1 H), 7.27–7.40 (m, 3 H), 7.49–7.53 (m, 2 H).

3-[1′-(Phenylthio)cyclopenten-1′-yl]cyclopentene (8j): 75%; ^{1}H NMR 1.55–1.70 (m, 6 H), 1.75–1.90 (m, 3 H), 1.98–2.10 (m, 1 H), 2.25–2.45 (m, 2 H), 3.00–3.07 (m, 1 H), 5.76–5.80 (m, 1 H), 5.83–5.87 (m, 1 H), 7.28–7.34 (m, 3 H), 7.53–7.57 (m, 2 H).

4-Ethyl-4-(phenylthio)-1-octene (8k): 70%; ^{1}H NMR 0.88 (s, 9 H), 1.00 (t, J = 7.3 Hz, 3 H), 1.25–1.44 (m, 6 H), 2.15 (d, J = 7.0 Hz, 2 H), 5.06–5.15 (m, 2 H), 6.05 (ddt, J = 10.3, 17.0, and 7.0 Hz, 1 H), 7.26–7.37 (m, 3 H), 7.48–7.52 (m, 2 H).

Generation of Tertiary and Secondary Homoallyllithiums and Their Reactions with Electrophiles. General Procedure. A homoallyl phenyl sulfide (1.5 mmol) in THF (0.5 mL) was added dropwise to a preformed solution of LDBB (3.3 mmol) in THF (12 mL) at −78 °C or in hexanes–THF (2:1) at −40 °C. The color of the solution changed immediately from a dark-blue to a dark-red after all the sulfide was added. The homoallyllithiums generated at −78 °C (all but **8dLi** and **8gLi** did not undergo the rearrangement) were immediately treated at −78 °C with methanol (0.1 mL), isobutyraldehyde (1.5 mmol), or carbon dioxide (by bubbling dry CO_2 gas through the solution). 4-Lithio-1,6-heptadiene (**8aLi**) was transformed into its cuprate by stirring with CuBr–Me_2S (1.8 mmol) for 3 h at −78 °C, and the mixture was treated with trimethylsilyl chloride (1.7 mmol) and 2-cyclopenten-1-one (1.3 mmol), consecutively. In the rearrangement experiments, TMEDA (2–8 equiv) was added when

(39) Trost, B. M.; Lavoie, A. C. *J. Am. Chem. Soc.* **1983**, *105*, 5075–5090.
(40) A modified procedure by Ager was employed. See: Ager, D. J. *Tetrahedron Lett.* **1980**, *21*, 4763–4766. When the exact procedure was followed (alkylation at 0 °C), a considerable elimination of thiophenol from the starting material was observed.
(41) Hatch, L. F.; Bachman, G. *Chem. Ber.* **1964**, 132–139.

necessary; the solution was warmed to the desired temperature using the cold probe (−40 to −15 °C) or the ice bath (0 °C), stirred at the elevated temperature for 15 min to 3 h, cooled again to −78 °C, and quenched with the electrophile. In the cuprate reaction, CuBr–Me_2S (1.3 equiv) was added at −78 °C, and the mixture was stirred for 3 h before quenching. In all experiments, the mixture was stirred at −78 °C for 15–60 min after quenching and warmed to 0 °C, and water (6 mL) was added. The organic material was extracted with ether (2 × 15 mL), the organic layer was dried with anhydrous $MgSO_4$, and the solvents were rotary evaporated. In the cuprate reactions, a saturated NH_4Cl solution (15 mL) was added, the mixture was stirred for 1 h, and the solids were filtered off. In the carbonation experiments, the mixture was quenched with 5% HCl. After ether extraction, the carboxylic acids were transferred to water by 2 × 25 mL washings with 5% NaOH; the water layer was acidified again and extracted with ether (2 × 25 mL). All products were isolated by radial chromatography or by flash chromatography (eluent system in parentheses, isomer ratios were established by GC).

1-(1′-Hydroxy-2′-methylpropyl)-1-(2″-propenyl)cyclohexane (9): 87% (2.5% EtOAc/hexanes); ^{1}H NMR 0.93 (d, J = 6.8 Hz, 3 H), 0.99 (d, J = 6.8 Hz, 3 H), 1.2–1.3 (m, 1 H), 1.34 (d, J = 7.1 Hz, 1 H), 1.35–1.60 (m, 9 H), 2.01 (hd, J = 6.8 and 2.0 Hz, 1 H), 2.14 (dd, J = 7.1 and 14.4 Hz, 1 H), 2.35 (dd, J = 7.8 and 14.4 Hz, 1 H), 3.27 (dd, J = 2.0 and 7.1 Hz, 1 H), 5.02–5.10 (m, 2 H), 5.82–5.97 (m, 1 H); ^{13}C NMR 17.2, 18.3, 21.9, 22.0, 26.4, 34.4, 37.4, 39.0, 72.5, 113.5, 147.6; HRMS calcd for $C_{13}H_{22}$ (M^+ − 18) 178.1721, found 178.1722.

1-Ethenyl-1-(2′-hydroxy-3′-methylbutyl)cyclohexane (10): 70% (2.5% EtOAc/hexanes); ^{1}H NMR 0.867 (d, J = 6.9 Hz) and 0.880 (d, J = 6.9 Hz) (6 H), 1.3–1.65 (m, 12 H), 1.68–1.75 (m, 1 H), 1.80 (d, J = 3.3 Hz, 1 H), 3.50–3.56 (m, 1 H), 5.07 (dd, J = 1.2 and 17.9 Hz, 1 H), 5.17 (dd, J = 1.2 and 11.0 Hz, 1 H), 5.79 (dd, J = 11.0 and 17.9 Hz, 1 H); HRMS calcd for $C_{13}H_{22}$ (M^+ − 18) 178.1721, found 178.1721.

1-(2′-Propenyl)cyclohexanecarboxylic acid (11): 75% (EtOAc); ^{1}H NMR 1.2–1.6 (m, 8 H), 2.04 (d, J = 13.0 Hz, 2 H), 2.28 (d, J = 7.4 Hz, 2 H), 5.02–5.08 (m, 2 H), 5.68–5.83 (m, 1 H), ~11.6 (br s, 1 H); ^{13}C NMR 23.1, 25.7, 33.4, 44.4, 47.2, 117.9, 133.3, 183.6.

(1′-Ethenylcyclohex-1′-yl)acetic acid (12): 68% (EtOAc); ^{1}H NMR 1.30–1.55 (m, 8 H), 1.65–1.72 (m, 2 H), 2.35 (s, 2 H), 5.04 (dd, J = 0.9 and 17.7 Hz, 1 H), 5.08 (dd, J = 0.7 and 11.0 Hz, 1 H), 5.80 (dd, J = 11.0 and 17.7 Hz, 1 H), ~11.5 (br s, 1 H); ^{13}C NMR 22.1, 26.1, 35.6, 39.2, 45.8, 60.5, 113.6, 144.6, 178.4.

Iodolactonization reactions were conducted according to the procedure of Bartlett,[42] and the crude products were purified by radial chromatography.

3-(Iodomethyl)-2-oxaspiro[4.5]decan-1-one (13): 90% (6% EtOAc/hexanes); ^{1}H NMR 1.2–1.4 (m, 3 H), 1.5–1.85 (m, 8 H), 2.52 (dd, J = 6.5 and 13.1 Hz, 1 H), 3.26 (dd, J = 7.4 and 10.2 Hz, 1 H), 3.42 (dd, J = 4.6 and 10.2 Hz, 1 H), 4.38–4.48 (m, 1 H); ^{13}C NMR 8.1, 21.7, 21.8, 24.9, 31.8, 33.7, 39.5, 45.2, 75.1, 180.3; HRMS calcd for $C_{10}H_{15}O_2I$ (M^+) 294.0119, found 294.0118.

1-(Iodomethyl)-2-oxaspiro[4.5]decan-3-one (14): 93% (10% EtOAc/hexanes); ^{1}H NMR 1.2–1.7 (m, 10 H), 2.37 (d, J = 17.4 Hz, 1 H), 2.65 (d, J = 17.4 Hz, 1 H), 3.19 (dd, J = 9.0 and 11.0 Hz, 1 H), 3.37 (dd, J = 3.7 and 11.0 Hz, 1 H), 4.34 (dd, J = 3.7 and 9.0 Hz, 1 H); ^{13}C NMR 1.1, 22.2, 22.8, 25.5, 29.2, 35.7, 39.6, 43.8, 88.0, 174.5; HRMS calcd for $C_{10}H_{15}O_2I$ (M^+) 294.0119, found 294.0119.

2-Methyl-4-(2-propenyl)-6-hepten-3-ol (15): 89% (4% EtOAc/hexanes); ^{1}H NMR 0.89 (d, J = 6.8 Hz, 3 H), 0.95 (d, J = 6.8 Hz, 3 H), 1.43 (s, 1 H), 1.66–1.74 (m, 1 H), 1.75–1.87 (m, 1 H), 2.05 (dd, J = 8.3 and 14.2 Hz, 1 H), 2.11–2.18 (m, 2 H), 2.23–2.33 (m, 1 H), 3.23 (dd, J = 4.7 and 6.9 Hz, 1 H), 5.00–5.10 (m, 4 H), 5.71–5.93 (m, 2 H); ^{13}C NMR 18.0, 19.6, 30.6, 32.6, 34.9, 39.9, 78.2, 116.1, 116.4, 137.1, 137.7; HRMS calcd for $C_{11}H_{18}$ (M^+ − 18) 150.1408, found 150.1406.

5-Ethenyl-2-methyl-7-octen-3-ol (16): 85% (4% EtOAc/hexanes) (isomer ratio, 60:40); ^{1}H NMR 0.887 (d, J = 6.8 Hz) and 0.893 (d, J = 6.8 Hz) (6 H), 1.3–1.7 (m, 4 H), 2.03–2.38 (m, 3 H), 3.37 (ddd, J = 2.4, 5.3, and 7.7 Hz) and 3.48 (dt, J = 8.8 and 4.1 Hz) (1 H), 4.97–5.09 (m, 4 H), 5.49–5.62 (m) and 5.67–5.82 (m) (2 H); ^{13}C NMR 16.7, 17.5, 18.7, 18.9, 33.3, 34.2, 38.6, 38.8, 39.3, 40.3, 40.5, 41.7, 74.0, 75.1, 114.6, 115.3, 115.9, 116.2, 136.5, 136.8, 142.2, 143.4; HRMS calcd for $C_{11}H_{18}$-(M^+ − 18) 150.1408, found 150.1408.

3-[1′-(2″-Propenyl)-3′-butenyl]cyclopentanone (17): 77% (5% EtOAc/hexanes); ^{1}H NMR 1.48–1.58 (m, 2 H), 1.85 (dd, J = 11.6 and 17.6 Hz, 1 H), 2.0–2.45 (m, 9 H), 5.01–5.10 (m, 4 H), 5.71–5.84 (m, 2 H); ^{13}C NMR 27.5, 34.5, 35.4, 38.7, 39.9, 42.5, 43.3, 116.5, 135.9, 136.0, 218.7; HRMS calcd for $C_{12}H_{18}O$ (M^+) 178.1358, found 178.13593.

3-(2′-Ethenyl-4′-pentenyl)cyclopentanone (18): 57% (4% EtOAc/hexanes) (isomer ratio, ~50:50); ^{1}H NMR 1.4–1.55 (m, 3 H), 1.76 (dt, J = 18.3 and 10.3 Hz, 1 H), 2.05–2.43 (m, 8 H), 4.95–5.05 (m, 4 H), 5.51–5.61 (m, 1 H), 5.69–5.79 (m, 1 H); ^{13}C NMR 29.0, 30.0, 34.65, 34.75, 38.3, 38.5, 39.8, 39.9, 40.1, 40.3, 42.0, 42.6, 44.6, 45.7, 114.78, 114.84, 116.0, 136.4, 141.8, 142.0, 219.3; HRMS calcd for $C_{12}H_{18}O$ (M^+) 178.1358, found 178.1358.

2,4-Dimethyl-6-hepten-3-ol: 74% (4% AcOEt/hexanes) (isomer ratio, 53:47); ^{1}H NMR (C_6D_6, both isomers) 0.70–0.91 (m, 9 H), 1.50–1.65 (m) and 1.54 (s) (2 H), 1.82–1.96 (m, 1 H), 2.08 (dt, J = 13.4 and 6.5 Hz) and 2.32–2.40 (m) (1 H), 2.84 (dd, J = 5.0 and 6.7 Hz) and 2.91 (dd, J = 3.8 and 7.6 Hz) (1 H), 4.92–5.08 (m, 2 H), 5.64–5.82 (m, 1 H); ^{13}C NMR 12.6, 15.9, 16.2, 18.7, 19.3, 20.1, 30.0, 31.0, 31.9, 35.8, 36.5, 38.8, 79.6, 80.5, 115.9, 137.5, 137.7; HRMS calcd for C_9H_{16} (M^+ − 18) 124.1252, found 124.1252.

2,5-Dimethyl-6-hepten-3-ol: 70% (4% EtOAc/hexanes) (isomer ratio, 54:46); ^{1}H NMR (C_6D_6, both isomers) 0.79–1.00 (m, 9 H), 1.12–1.48 (m, 4 H), 2.28 (dt, J = 14.1 and 7.0 Hz) and 2.38–2.42 (m) (1 H), 3.23–3.30 (m, 1 H), 4.86–5.03 (m, 2 H), 5.56 (ddd, J = 8.3, 10.0, and 17.3 Hz) and 5.72 (ddd, J = 7.6, 10.0, and 17.3 Hz) (1 H); irradiation of the dt at 2.28 resulted in the change of the ddd at 5.72 to a dd (J = 10.0 and 17.3 Hz) whereas irradiation of the m at 2.38–2.42 transformed the ddd at 5.56 into a dd (J = 10.0 and 17.3 Hz); ^{13}C NMR 17.0, 17.3, 18.6, 18.8, 21.4, 22.6, 33.6, 34.0, 34.9, 35.3, 40.9, 41.0, 74.1, 74.7, 112.5, 113.4, 144.2, 145.4; HRMS calcd for $C_9H_{18}O$ (M^+) 142.1358, found 142.1357.

2,4,4-Trimethyl-6-hepten-3-ol: 78% (2% EtOAc/hexanes); ^{1}H NMR 0.90 (s), 0.92 (d, J = 6.9 Hz) and 0.92 (s) (9 H), 0.99 (d, J = 6.9 Hz, 3 H), 1.42 (s, 1 H), 1.96 (hd, J = 6.9 and 2.2 Hz) and 2.00 (dd, J = 7.3 and 13.4 Hz, A part of the ABX system) (2 H), 2.14 (dd, J = 7.6 and 13.4 Hz, B part of the ABX system, 1 H), 3.17 (d, J = 2.2 Hz, 1 H), 5.00–5.09 (m, 2 H), 5.80–5.95 (m, X part of the ABX system, 1 H); ^{13}C NMR 16.8 (q), 23.4 (q), 23.7 (q), 23.8 (q), 28.5 (d), 38.9 (s), 45.0 (t), 82.0 (d), 117.1 (t), 135.7 (d); HRMS calcd for $C_{10}H_{18}$ (M^+ − 18) 138.1408, found 138.1408.

2,5,5-Trimethyl-6-hepten-3-ol: 68% (2.5% EtOAc/hexanes); ^{1}H NMR 0.875 (d, J = 6.8 Hz) and 0.89 (d, J = 6.8 Hz) (6 H), 1.05 (s) and 1.07 (s) (6 H), 1.43 (d, J = 5.6 Hz, 2 H), 1.53–1.65 (m, 1 H), 1.67 (d, J = 3.5 Hz, 1 H), 3.45–3.51 (m, 1 H), 4.98 (d, J = 10.7 Hz, 1 H), 5.01 (d, J = 17.6 Hz, 1 H), 5.93 (dd, J = 10.7 and 17.6 Hz, 1 H); HRMS calcd for $C_{10}H_{20}O$ (M^+) 156.1514, found 156.1513.

4,4-Diethyl-2-methyl-6-hepten-3-ol: 80% (2% EtOAc/hexanes); ^{1}H NMR 0.85 (t, J = 7.5 Hz, 3 H), 0.95 (d, J = 6.8 Hz) and 0.99 (d, J = 6.8 Hz) (6 H), 1.26–1.50 (m, 5 H), 1.98 (hd, J = 2.0 and 6.8 Hz, 1 H), 2.08 (dd, J = 7.1 and 14.2 Hz, A part of the ABX system) and 2.18 (dd, J = 7.8 and 14.2 Hz, B part of the ABX system) (2 H), 3.33 (d, J = 1.8 and 7.0 Hz, 1 H), 4.98–5.12 (m, 2 H), 5.96 (ddd, J = 7.4, 10.2, and 17.3 Hz, X part of the ABX system, 1 H); ^{13}C NMR 8.25 (q), 8.31 (q), 17.1 (q), 24.1 (t), 26.6 (t), 28.0 (d), 39.2 (t), 43.5 (s), 81.2 (d), 116.4 (t), 136.7 (d); HRMS calcd for $C_{10}H_{19}O$ (M^+ − 29) 155.1436, found 155.1434.

5,5-Diethyl-2-methyl-6-hepten-3-ol: 79% (2% EtOAc/hexanes); ^{1}H NMR 0.72–0.80 (m, 6 H), 0.885 (d, J = 6.8 Hz) and 0.895 (d, J = 6.8 Hz) (6 H), 1.26–1.63 (m, 7 H), 1.80 (d, J = 3.0 Hz, 1 H), 3.46–3.52 (m, 1 H), 5.01 (d, J = 17.8 Hz, 1 H), 5.13 (d, J = 11.0 Hz, 1 H), 5.80 (dd, J = 11.0 and 17.8 Hz, 1 H); HRMS calcd for $C_{12}H_{22}$ (M^+ − 18) 166.1721, found 166.1720.

4-Ethyl-2-methyl-4-(2-propenyl)-3-octanol: 82% (2% EtOAc/hexanes) (2 isomers); ^{1}H NMR 0.82–1.01 (m, 12 H), 1.2–1.5 (m, 9 H), 1.97 (hd, J = 6.9 and 1.9 Hz, 1 H), 2.05–2.25 (m, 2 H), 3.32 (d, J = 7.0 Hz, 1 H), 5.00–5.11 (m, 2 H), 5.88–6.03 (m, 1 H); ^{13}C NMR 8.35, 8.40, 14.2, 17.1, 23.8, 24.1, 25.9, 26.0, 27.1, 27.2, 28.0, 34.4, 39.6, 39.7, 43.6, 81.4, 116.5, 136.7; HRMS calcd for $C_{14}H_{26}$ (M^+ − 18) 194.2034, found 194.2034.

2,4,4,6-Tetramethyl-6-hepten-3-ol: 67% (3% EtOAc/hexanes); ^{1}H NMR 0.915 (d, J = 6.9 Hz), 0.93 (s) and 0.945 (s) (9 H), 0.99 (d, J = 6.9 Hz, 3 H), 1.48 (d, J = 6.0 Hz, 1 H), 1.80 (s, 3 H), 1.93–2.00 (m) and 1.98 (d, J = 12.8 Hz, A part of an AB system) (2 H), 2.12 (d, J = 12.8 Hz, B part of an AB system, 1 H), 3.19 (dd, J = 2.0 and 6.0 Hz, 1 H), 4.70 (d, J = 1.3 Hz, 1 H), 4.86 (d, J = 1.3 Hz, 1 H); HRMS calcd for $C_{10}H_{17}$ (M^+ − 18 − 15) 137.1330, found 137.1332.

2,5,5,6-Tetramethyl-6-hepten-3-ol: 73% (3% EtOAc/hexanes); ^{1}H NMR 0.896 (d, J = 6.8 Hz) and 0.901 (d, J = 6.8 Hz) (6 H), 1.10 (s, 3 H), 1.13 (s, 3 H), 1.40 (dd, J = 1.5 and 14.5 Hz, 1 H), 1.55–1.62 (m) and 1.62 (dd, J = 9.6 and 14.5 Hz) (2 H), 1.80 (d, J = 0.7 Hz, 3 H),

(42) Bartlett, P. A.; Myerson, J. *J. Org. Chem.* **1979**, *44*, 1625–1627.

1.88 (br s, 1 H), 3.47 (ddd, J = 1.5, 4.9, and 9.6 Hz, 1 H), 4.84 (s) and 4.86 (s) (2 H); ^{13}C NMR 17.3, 18.6, 19.8, 26.7, 29.0, 34.4, 38.2, 44.6, 73.8, 110.4, 153.8; HRMS calcd for $C_{10}H_{20}O$ (M^+ − 15) 155.1436, found 155.1436.

3-(1′-Hydroxy-2′-methylpropyl)-3-methyl-1-methylenecyclohexane: 95% (3% EtOAc/hexanes) (isomer ratio, 70:30); major isomer ^{1}H NMR 0.85 (s, 3 H), 0.93 (d, J = 6.8 Hz, 3 H), 1.01 (d, J = 6.8 Hz, 3 H), 1.37 (br s, 1 H), 1.45–1.65 (m, 4 H), 1.86 (d, J = 13.0 Hz, 1 H), 1.94–2.05 (m, 2 H), 2.16–2.22 (m) and 2.18 (d, J = 13.0 Hz) (2 H), 3.19 (d, J = 1.9 Hz, 1 H), 4.59 (s, 1 H), 4.70 (s, 1 H); ^{13}C NMR 16.9, 19.8, 22.9, 23.9, 28.1, 33.8, 34.9, 40.8, 44.3, 82.6, 108.9, 147.4; HRMS calcd for $C_{12}H_{22}O$ (M^+) 182.1671, found 182.1670; minor isomer ^{1}H NMR 0.86 (s, 3 H), 0.917 (d, J = 6.8 Hz, 3 H), 1.01 (d, J = 6.8 Hz, 3 H), 1.38 (br s, 1 H), 1.45–1.68 (m, 4 H), 1.9–2.22 (m, 5 H), 3.21 (s, 1 H), 4.61 (s, 1 H), 4.70 (s, 1 H); ^{13}C NMR 16.6, 19.2, 23.0, 28.0, 34.5, 34.8, 40.5, 44.4, 82.1, 109.1, 147.1.

2-(2′-Hydroxy-3′-methylbutyl)-2-methyl-1-methylenecyclopentane: 62% (3% EtOAc/hexanes) (isomer ratio, 50:50); ^{1}H NMR 0.87–0.93 (m, 6 H), 1.08 (s) and 1.13 (s) (3 H), 1.45–1.90 (m, 8 H), 2.40–2.50 (m, 2 H), 3.51–3.60 (m, 1 H), 4.83 (s, 1 H), 4.91 (s) and 4.96 (s) (1 H); ^{13}C NMR 17.2, 18.41, 18.47, 21.4, 22.7, 26.2, 29.1, 32.9, 34.1, 34.6, 34.7, 39.1, 40.7, 44.1, 44.4, 44.6, 73.9, 74.0, 104.4, 104.5, 162.0, 162.5; HRMS calcd for $C_{11}H_{17}$ (M^+ − 18 − 15) 149.1330, found 149.1331.

3-*n*-Butyl-3-(1′-hydroxy-2′-methylpropyl)-1-methylenecyclohexane: 86% (2.5% EtOAc/hexanes) (isomer ratio, 62:38); ^{1}H NMR 0.88–0.95 (m, 6 H), 0.99–1.06 (m, 3 H), 1.1–1.7 (m, 11 H), 1.9–2.05 (m, 3 H), 2.15–2.23 (m, 2 H), 3.27 (d, J = 7.9 Hz) and 3.34 (d, J = 6.0 Hz) (1 H), 4.58 (s) and 4.61 (s) (1 H), 4.70 (s, 1 H); ^{13}C NMR 14.1, 16.9, 17.0, 22.5, 22.7, 23.7, 23.9, 25.3, 27.8, 30.3, 31.1, 32.4, 32.7, 34.7, 40.6, 41.4, 42.6, 42.7, 79.6, 79.8, 108.7, 109.1, 147.4, 147.6; HRMS calcd for $C_{15}H_{28}O$ (M^+) 224.2140, found 224.2138.

2-*n*-Butyl-2-(2′-hydroxy-2′-methylbutyl)-1-methylenecyclopentane: 64% (2% EtOAc/hexanes) (isomer ratio, 53:47); ^{1}H NMR 0.85–0.92 (m, 9 H), 1.15–1.7 (m, 13 H), 2.07 (br s, 1 H), 2.33–2.58 (m, 2 H), 3.52–3.59 (m, 1 H), 4.809 (s) and 4.815 (s) (1 H), 4.97 (s) and 5.04 (s) (1 H); ^{13}C NMR 14.1, 17.19, 17.24, 18.4, 18.5, 21.6, 23.1, 23.5, 23.6,26.5, 26.8, 33.4, 34.6, 34.7, 34.8, 36.5, 37.8, 38.1, 41.5, 42.2, 43.0, 47.2, 47.6, 73.4, 73.8, 104.8, 105.1, 161.2, 161.4; HRMS calcd for $C_{15}H_{28}O$ (M^+) 224.2140, found 224.2138.

3-(1′-Hydroxy-2′-methylpropyl)-3-methyl-1-methylenecycloheptane (19): 82% (2.5% EtOAc/hexanes) (isomer ratio, 74:26); major isomer ^{1}H NMR 0.88 (s, 3 H), 0.93 (d, J = 6.8 Hz, 3 H), 1.02 (d, J = 6.8 Hz, 3 H), 1.21–1.33 (m, 2 H), 1.36–1.73 (m, 5 H), 1.95–2.05 (m), and 2.04 (d, J = 13.3 Hz) (2 H), 2.22 (d, J = 13.3 Hz) and 2.15–2.21 (m) (3 H), 3.26 (d, J = 1.5 Hz, 1 H), 4.70 (s, 1 H), 4.81 (s, 1 H); characteristic signals for the minor isomer, 1.97 (d, J = 13.2 Hz, 1 H), 2.37 (d, J = 13.2 Hz, 1 H), 3.29 (d, J = 2.0 Hz, 1 H), 4.73 (s, 1 H), 4.81 (s, 1 H); ^{13}C NMR (both isomers) 16.8, 22.3, 22.5, 23.2, 23.6, 24.0, 28.3, 28.6, 28.8, 37.3, 37.5, 37.9, 39.0, 41.3, 44.9, 45.1, 81.2, 82.4, 113.1, 148.0, 148.2; HRMS calcd for $C_{13}H_{24}O$ (M^+) 196.1827, found 196.1826.

2-(2′-Hydroxy-3′-methylbutyl)-2-methyl-1-methylenecyclohexane (20): 75% (1–3% EtOAc/hexanes) (isomer ratio, 54:46); major isomer ^{1}H NMR 0.886 (d, J = 6.8 Hz) and 0.909 (d, J = 6.8 Hz) (6 H), 1.17 (s, 3 H), 1.20–1.39 (m, 4 H), 1.52–1.66 (m, 4 H), 1.70–1.78 (m, 1 H), 1.90 (dd, J = 1.0 and 14.7 Hz, 1 H), 2.02–2.21 (m, 2 H), 3.38 (ddd, J = 1.6, 4.5, and 8.7 Hz, 1 H), 4.70 (s, 1 H), 4.77 (s, 1 H); ^{13}C NMR 17.0 (q), 18.6 (q), 22.2 (t), 27.0 (q), 28.6 (t), 33.4 (t), 35.1 (d), 39.1 (s), 41.1 (t), 41.6 (t), 73.8 (d), 107.5 (t), 155.1 (s); HRMS calcd for $C_{12}H_{21}O$ (M^+ − 15) 181.1592, found 181.1592; minor isomer ^{1}H NMR 0.905 (d, J = 6.8 Hz) and 0.910 (d, J = 6.8 Hz) (6 H), 1.12 (s, 3 H), 1.17 (dd, J = 1.0 and 14.3 Hz, 1 H), 1.22–1.36 (m, 3 H), 1.50–1.72 (m, 3 H), 1.79–1.85 (m, 1 H), 2.1 (br s) and 2.11 (dd, J = 9.8 and 14.3 Hz) (2 H), 2.19–2.26 (m, 1 H), 2.42 (td, J = 4.7 and 13.3 Hz, 1 H), 3.56 (ddd, J = 1.0, 5.3, and 9.8 Hz, 1 H), 4.81 (s) and 4.84 (s) (2 H); ^{13}C NMR 17.6, 18.6, 21.8, 26.1, 28.6, 33.5, 34.3, 38.7, 41.8, 42.6, 73.6, 108.0, 157.6.

***cis*-1-Methyl-2-methylenebicyclo[3.3.0]octane (21)**: 44% (pentane); ^{1}H NMR 1.13 (s, 3 H), 1.25–1.85 (m, 7 H), 2.0–2.1 (m, 2 H), 2.3–2.5 (m, 2 H), 4.73 (d, J = 1.2 Hz, 1 H), 4.81 (d, J = 1.4 Hz, 1 H); ^{13}C NMR 22.4, 26.1, 28.0, 33.5, 33.9, 42.1 (t), 51.9 (d), 53.1 (s), 102.7 (t), 163.1 (s); HRMS calcd for $C_{10}H_{16}$ (M^+) 136.1252, found 136.1254.

***cis*-3-Methylenebicyclo[4.3.0]nonane (*cis*-7cH)**: 81% (pentane) (cis/trans isomer ratio, 95:5); ^{1}H NMR 1.0–1.2 (m, 5 H), 1.6–1.8 (m, 5 H), 1.9–2.1 (m, 2 H), 2.30–2.37 (m, 1 H), 2.48 (d, J = 12.4 Hz, 1 H), 4.65 (s, 2 H), ^{13}C NMR 22.5 (t), 30.6 (t), 31.1 (t), 32.2 (t), 35.1 (t), 40.8 (t), 46.4 (d), 48.0 (d), 107.9 (t), 149.8 (s); minor *trans* isomer ^{13}C NMR 14.2, 29.0, 29.1, 30.3, 32.7, 36.4, 39.0, 41.3, 107.7, 148.4; HRMS calcd for $C_{10}H_{16}$ (M^+) 136.1252, found 136.1252.

6-Methylene[4.5]spirodecane (22): 79% (pentane); ^{1}H NMR 1.38–1.48 (m, 4 H), 1.52–1.63 (m, 8 H), 1.70–1.80 (m, 2 H), 2.18 (t, J = 5.7 Hz, 2 H), 4.60 (d, J = 1.9 Hz) and 4.63 (t, J = 0.9 Hz) (2 H); ^{13}C NMR 23.7 (t), 23.9 (t), 28.9 (t), 34.6 (t), 36.5 (t), 39.7 (t), 49.2 (s), 104.3 (t), 155.5 (s); HRMS calcd for $C_{11}H_{18}$ (M^+) 150.1408, found 150.1408.

2-Cyclopentyl-1-methylenecyclopentane (6dH): 67% (pentane); ^{1}H NMR 1.1–1.95 (m, 13 H), 2.20–2.35 (m, 3 H), 4.83 (d, J = 1.6 Hz) and 4.86 (d, J = 1.6 Hz) (2 H); ^{13}C NMR 24.3 (t), 25.3 (t), 25.5 (t), 30.0 (t), 30.7 (t), 31.7 (t), 33.7 (t), 43.5 (d), 48.9 (d), 104.8 (t), 156.4 (s); HRMS calcd for $C_{11}H_{18}$ (M^+) 150.1408; found 150.1408.

2-Cyclopentyl-1-methylenecyclohexane (6eH): 87% (pentane); ^{1}H NMR 1.05–1.15 (m, 2 H), 1.4–1.7 (m, 11 H), 1.75–1.90 (m, 2 H), 2.0–2.2 (m, 3 H), 4.57 (d, J = 2.4 Hz) and 4.61 (d, J = 1.2 Hz) (2 H); ^{13}C NMR 22.9 (t), 25.4 (t), 25.7 (t), 28.9 (t), 31.1 (t), 31.7 (t), 31.9 (t), 33.7 (t), 39.9 (d), 50.2 (d), 106.4 (t), 153.0 (s); HRMS calcd for $C_{12}H_{20}$ (M^+) 164.1565, found 164.1565.

3-Ethyl-5-methyl-3-(2-propenyl)-1,4-hexanediol: 13% (25% EtOAc/hexanes) (isomer ratio, 50:50); ^{1}H NMR 0.825 (t, J = 7.5) and 0.831 (t, J = 7.5 Hz) (3 H), 0.95–1.01 (m, 6 H), 1.32–1.52 (m, 3 H), 1.79 (ddd, J = 5.1, 8.8, and 14.6 Hz, 1 H), 1.90–2.20 (m, 2 H), 2.22–2.27 (m, 1 H), 3.28 (s, 1 H), 3.6 (br s) and 3.6–3.8 (m) (4 H), 5.00–5.12 (m, 2 H), 5.70–5.86 (m, 1 H); HRMS calcd for $C_{12}H_{22}O$ (M^+ − 18) 182.1671, found 182.1671.

3-Ethenyl-3-ethyl-6-methyl-1,5-heptanediol: 68% (25% EtOAc/hexanes) (isomer ratio, 50:50); isomer A ^{1}H NMR 0.76 (J = 7.5 Hz, 3 H), 0.91 (t, J = 6.5 Hz, 6 H), 1.3–1.65 (m, 6 H), 1.93 (dq, J = 7.1 and 14.2 Hz, 1 H), 2.54 (s, 2 H), 3.57 (ddd, J = 1.8, 4.5, and 6.3 Hz, 1 H), 3.67 (t, J = 6.3 Hz, 2 H), 4.99 (d, J = 17.7 Hz, 1 H), 5.13 (d, J = 11.0 Hz, 1 H), 5.66 (dd, J = 11.0 and 17.7 Hz, 1 H); isomer B ^{1}H NMR 0.76 (t, J = 7.4 Hz, 3 H), 0.87 (t, J = 6.5 Hz, 6 H), 1.3–1.44 (m, 2 H), 1.50–1.68 (m, 4 H), 1.89 (dq, J = 14.5 and 7.3 Hz, 1 H), 2.73 (s, 2 H), 3.49 (dd, J = 4.5 and 8.8 Hz, 1 H), 3.71 (t, J = 6.4 Hz, 2 H), 4.98 (d, J = 17.8 Hz, 1 H), 5.11 (d, J = 11.0 Hz, 1 H), 5.65 (dd, J = 11.0 and 17.8 Hz, 1 H); ^{13}C NMR 8.0, 17.0, 18.4, 29.2, 34.9, 35.6, 41.3, 42.3, 59.0, 73.2, 113.3, 147.4; HRMS calcd for $C_{12}H_{22}O$ (M^+ − 18) 182.1671, found 182.1672.

***trans*-1-Ethyl-1-(2-hydroxyethyl)-2-(2-hydroxy-3-methylbutyl)cyclopropane**: 30% (25% EtOAc/hexanes) (isomer ratio, 66:34); ^{1}H NMR −0.06 (t, J = 4.9 Hz) and 0.09 (t, J = 4.6 Hz) (1 H), 0.44 (dd, J = 4.2 and 8.7 Hz) and 0.50 (dd, J = 3.9 and 8.5 Hz) (1 H), 0.56–0.68 (m, 1 H), 0.86–0.93 (m, 9 H), 1.2–1.45 (m, 4 H), 1.55–1.75 (m, 3 H), 1.95 (br s, 2 H), 3.41–3.47 (m, 1 H), 3.66–3.82 (m, 2 H); ^{13}C NMR 10.6, 10.7, 14.1, 17.1, 17.3, 17.4, 18.8, 19.0, 20.1, 21.0, 22.3, 30.4, 30.5, 31.6, 32.7, 32.8, 33.3, 33.4, 33.5, 60.8, 61.1, 77.4, 77.6; HRMS calcd for $C_{12}H_{22}O$ (M^+ − 18) 182.1671, found 182.1673.

5-Methyl-3-(2-propenyl)-1,4-hexanediol: 41% (50% EtOAc/hexanes) (isomer ratio, 60:40); ^{1}H NMR 0.876 (d, J = 6.8 Hz), 0.885 (d, J = 6.8 Hz), 0.950 (d, J = 6.8 Hz) and 0.969 (d, J = 6.8 Hz) (6 H), 1.6–1.85 (m, 4 H), 2.05–2.27 (m, 2 H), 2.6 (br s, 2 H), 3.17 (dd, J = 4.9 and 7.0 Hz) and 3.23 (dd, J = 3.3 and 8.1 Hz) (1 H), 3.54–3.62 (m) and 3.65–3.77 (m) (2 H), 5.00–5.09 (m, 2 H), 5.71–5.83 (m, 1 H); ^{13}C NMR 18.1, 19.4, 19.5, 30.7, 30.8, 31.0, 31.6, 33.4, 35.4, 37.8, 38.2, 59.3, 59.7, 78.3, 79.2, 116.1, 116.4, 137.0, 137.7; HRMS calcd for $C_{10}H_{18}O$ (M^+ − 18) 154.1358, found 154.1357.

3-Ethenyl-6-methyl-1,5-heptanediol: 50% (50% EtOAc/hexanes) (isomer ratio, 57:43); isomer A ^{1}H NMR 0.89 (d, J = 6.8 Hz, 6 H), 1.3–1.5 (m, 2 H), 1.55–1.65 (m, 2 H), 1.98 (br s, 1 H), 2.39–2.52 (m, 1 H), 3.38 (ddd, J = 2.4, 5.1, and 7.6 Hz, 1 H), 3.57–3.74 (m, 2 H), 5.02–5.12 (m, 2 H), 5.55 (dt, J = 17.1 and 9.6 Hz, 1 H); isomer B ^{1}H NMR 0.885 (d, J = 6.7 Hz) and 0.90 (d, J = 6.8 Hz) (6 H), 1.38–1.51 (m, 3 H), 1.61–1.80 (m, 2 H), 2.06 (br s, 2 H), 2.30–2.40 (m, 1 H), 3.48 (dt, J = 4.3 and 8.3 Hz, 1 H), 3.59–3.70 (m, 2 H), 5.02 (dd, J = 1.5 and 10.1 Hz, 1 H), 5.08 (d, J = 17.2 Hz, 1 H), 5.70 (dt, J = 17.2 and 9.6 Hz, 1 H); ^{13}C NMR 17.0, 18.9, 33.4, 36.9, 38.6, 39.8, 60.8, 74.7, 114.9, 143.5; HRMS calcd for $C_{10}H_{18}O$ (M^+ − 18) 154.1358, found 154.1358.

4-Ethyl-6-methyl-4-(2-propenyl)-1,5-heptanediol: 27% (20–40% EtOAc/hexanes) (2 isomers); ^{1}H NMR 0.82–0.90 (m, 3 H), 0.93–0.99 (m, 6 H), 1.2–1.65 (m, 8 H), 1.94–2.02 (m, 1 H), 2.07–2.23 (m, 2 H), 3.34 (s, 1 H), 3.58–3.68 (m, 2 H), 5.00–5.13 (m, 2 H), 5.88–6.03 (m, 1 H).

4-Ethenyl-4-ethyl-7-methyl-1,6-octanediol: 47% (20–40% EtOAc/hexanes) (2 isomers); ^{1}H NMR 0.78 (t, J = 7.4 Hz, 3 H), 0.886 (d, J = 6.8 Hz) and 0.898 (d, J = 6.8 Hz) (6 H), 1.35–1.65 (m, 9 H), 1.98 (s, 2 H), 3.50 (q, J = 5.0 Hz, 1 H), 3.56–3.72 (m, 2 H), 5.02 (d, J =

17.8 Hz, 1 H), 5.14 (d, J = 10.9 Hz, 1 H), 5.74 (dd, J = 10.9 and 17.8 Hz, 1 H); HRMS calcd for $C_{13}H_{24}O$ ($M^+ - 18$) 196.1827, found 196.1925.

4-Ethyl-4-(2-methoxyethyl)-2-methyl-6-hepten-3-ol: 88% (10% EtOAc/hexanes) (2 isomers); ^{1}H NMR 0.83 (t, J = 7.5 Hz, 3 H), 0.934 (d, J =6.8 Hz) and 0.939 (d, J = 6.8 Hz) (3 H), 0.995 (d, J = 6.8 Hz, 3 H), 1.30–1.55 (m, 3 H), 1.73–1.85 (m, 1 H), 1.88–1.98 (m, 1 H), 2.05 (dd, J = 7.2 and 14.3 Hz) and 2.17 (dd, J = 7.9 and 14.3 Hz) (1 H), 2.22 (d, J = 7.9 Hz, 1 H), 3.20 (d, J = 8.2 Hz, 1 H), 3.34 (s, 3 H), 3.38–3.55 (m, 3 H), 5.01–5.10 (m, 2 H), 5.72–5.89 (m, 1 H); ^{13}C NMR 7.8, 8.1, 17.4, 24.1, 24.2, 26.4, 26.4, 27.7, 28.0, 34.2, 34.4, 38.3, 39.5, 43.4, 43.6, 58.6, 69.16, 69.23, 79.5,m 79.7, 117.2, 135.2, 135.3; HRMS calcd for $C_{13}H_{24}O$ ($M^+ - 18$) 196.1827, found 196.1827.

4-Ethyl-4-(2-propenyl)-2,7,7-trimethyl-3-octanol: (75%) (2% EtOAc/hexane) (2 isomers) ^{1}H NMR 0.82–0.90 (m, 12 H), 0.97 (d, J = 6.8 Hz, 3 H), 1.01 (d, J = 6.8 Hz, 3 H), 1.05–1.55 (m, 7 H), 2.00 (hd, J = 6.8 and 1.9 Hz, 1 H), 2.05–2.23 (m, 2 H), 3.33 (s, 1 H), 5.01–5.12 (m, 2 H), 5.89–6.05 (m, 1 H); ^{13}C NMR 8.3, 8.4, 17.2, 24.1, 27.0, 27.2, 28.0, 28.5, 28.7, 29.4, 30.4, 37.0, 39.5, 39.7, 43.3, 81.5, 81.6, 116.5, 136.7; HRMS calcd for $C_{16}H_{30}$ ($M^+ - 18$) 222.2347, found 222.2348.

3-(1′-Ethyl-3′-hydroxypropyl)cyclopentene: 8% EtOAc/hexanes) (isomer ratio, ~50:50); ^{1}H NMR 0.88 (t, J = 7.5 Hz) and 0.89 (t, J = 7.5 Hz) (3 H), 1.25–1.60 (m, 7 H), 1.88–2.01 (m, 1 H), 2.25–2.35 (m, 2 H), 2.76–2.86 (m, 1 H), 5.60–5.66 (m, 1 H), 5.72–5.77 (m, 1 H); ^{13}C NMR 11.4, 11.6, 24.0, 24.6, 26.1, 26.7, 32.3, 33.9, 34.4, 40.1, 40.4, 48.3, 48.5, 61.6, 61.7, 131.0, 131.1, 133.4, 133.7; HRMS calcd for $C_{10}H_{18}O$ (M^+) 154.1358, found 154.1357.

***trans*-1-Ethyl-1-(2-hydroxyethyl)-2-methylcyclopropane. 2-Ethenyl-2-ethyloxetane (27).** A solution of 5-chloro-3-ethyl-1-penten-3-ol (**26**) (prepared from the commercial 1-chloro-3-pentanone and vinylmagnesium bromide in ether/THF at 0 °C) (1.98 g, 13 mmol) in dry dimethyl sulfoxide (1.5 mL) was added dropwise to a suspension of sodium hydride in ether at room temperature under argon. After 2 h of stirring, the mixture was carefully quenched with water. The crude oxetane was extracted with ether (2 × 25 mL), and the ether layer was washed with water (2 × 50 mL) and dried. Ether was distilled off under normal pressure followed by the product, bp 115–120 °C, 75% yield: ^{1}H NMR 0.90 (t, J = 7.4 Hz, 3 H), 1.70–1.81 (m, 2 H), 2.39–2.57 (m, 2 H), 4.47 (t, J = 7.7 Hz, 2 H), 5.19 (dd, J = 1.8 and 10.8 Hz, 1 H), 5.36 (dd, J = 17.1 Hz, 1 H), 5.92 (dd, J = 10.8 and 17.1 Hz, 1 H).

(*E*)-3-Ethyl-3-penten-1-ol (28). 2-Ethenyl-2-ethyloxetane (1.01 g, 9 mmol) was added dropwise to a preformed LDMAN (20 mmol) solution in THF (50 mL) at −78 °C. The mixture was warmed to 0 °C, stirred at 0 °C for 15 min, and quenched with water. The product was extracted with ether (2 × 25 mL), and the organic layer was washed with 5% HCl (2 × 25 mL) and dried with anhydrous $MgSO_4$. The GC analysis showed three isomeric alcohols in the ratio 89:8:3. After rotary evaporation of ether, radial chromatography separation gave the major alcohol (92% pure) in the first two fractions. **28**: ^{1}H NMR[43] 1.01 (t, J = 7.4 Hz, 3 H), 1.48 (br s, 1 H), 1.64 (d, J = 6.9 Hz, 3 H), 2.03 (dq, J = 1.1 and 7.4 Hz, 2 H), 2.36 (t, J = 6.8 Hz, 2 H), 3.67 (t, J = 6.8 Hz, 2 H), 5.41 (q, J = 6.9 Hz, 1 H); ^{13}C NMR 12.8 (q), 13.3 (q), 29.7 (t), 33.2 (t), 60.8 (t), 120.2 (d), 137.6 (s). The 500 MHz NOESY spectrum revealed a weak NOE for the methyl groups.

***trans*-1-Ethyl-1-(2-hydroxyethyl)-2-methylcyclopropane (29).** The modified Simmons–Smith cyclopropanation procedure[29] was applied; yield 72%. GC retention time, mass spectrum, and ^{1}H NMR of the product matched those obtained in the homoallyl rearrangement reaction involving the phenylthio alcohol **8d**. **29**: ^{1}H NMR 0.08 (t, J = 4.7 Hz, 1 H), 0.41 (dd, J = 4.1 Hz and 8.5 Hz, 1 H), 0.52–0.58 (m, 1 H), 0.89 (t, J = 7.3 Hz, 3 H), 1.07 (d, J = 6.3 Hz, 3 H), 1.13 (dq, J = 14.2 and 7.3 Hz, 1 H), 1.27 (dq, J = 7.3 and 7.3 Hz, 1 H), 1.50–1.70 (m) and 1.59 (s) (3 H), 3.75 (t, J = 7.5 Hz, 2 H). In the 500 MHz NOESY spectrum, a strong NOE was observed for both methyl groups (0.89, t and 1.07 d) and for the methyl d and for each methylene proton from the ethyl group (1.13, dq and 1.27, dq); ^{13}C NMR 10.5, 14.0, 17.1, 19.0, 21.7, 23.2, 30.5, 32.4, 60.8.

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Supplementary Material Available: ^{1}H NMR spectra of compounds **9**, **14**, **20**, **22**, **29**, 2,5,5-trimethyl-6-hepten-3-ol, the reaction products of **6b(r)Li** with isobutyraldehyde, **10**, and **16**, the ^{13}C NMR spectra of all of these except the last three, and the NOESY spectrum of **29** (14 pages). Ordering formation is given on any current masthead page.

(43) Koyama, T.; Sato, A.; Ogura, K.; Shuichi, S. *J. Am. Chem. Soc.* **1980**, *102*, 3614–3618. The ^{1}H NMR spectra for both *E* and *Z* are reported. However, no explanation of their assignment is given.