Pergamon

Tetrahedron Vol. 50, No. 45, pp. 12793-12810, 1994

0040-4020/94 $7.00+0.00

0040-4020(94)00855-8

Generation, Rearrangements and Some Synthetic Uses of Bishomoallyllithiums

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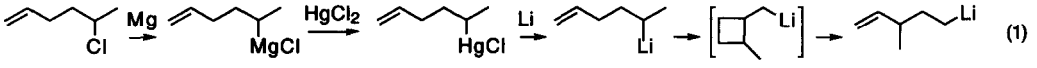
Abstract: A general preparative method for bishomoallyllithiums consists of reductive lithiation by 4,4'-di-*tert*-butylbiphenylide (LDBB) of bishomoallyl phenyl sulfides, which can be prepared by (1) thioacetalization of γ, δ-unsaturated ketones followed by replacing one of the phenylthio groups with an alkyl group or a hydrogen or (2) Wittig or Peterson olefination of γ-(phenylthio)ketones prepared in turn by conjugate addition of phenylthiomethyl cuprates to enones in the presence of chlorotrimethylsilane. Several of the secondary and tertiary bishomoallyllithiums rearrange to primary bishomoallyllithiums via cyclobutylcarbinyllithium intermediates. An oxyanionic group on a carbon atom adjacent to the lithium-bearing carbon atom has a remarkable accelerating effect on the ring closure to a 4-membered ring. Formylation of some bishomoallyllithiums affords the precursors of type-II intramolecular ene reactions, which generate six membered ring compounds when subjected to Lewis acid-catalyzed cyclization.

Reductive lithiation of phenyl thioethers with aromatic radical-anions[2] is a particularly versatile method of preparing organolithium compounds. The major reasons are the ready availability of the substrates and the fact that unlike the conventional method of organolithium production, electrophile removal, the more substituted organolithiums are produced more readily than the less substituted ones. Recently, we have reported the preparation and 1,2-vinyl rearrangements of secondary and tertiary homoallyllithiums (β-lithioalkenes) to less substituted homoallyllithiums.[3] Examples of such rearrangements leading to both ring contraction and expansion were demonstrated. Bishomoallyllithiums (γ-lithioalkenes) appear to be rare[4,5] and as far as we are aware, there is only one example in the literature of the related 1,3-rearrangement of one of these to a different bishomoallyllithium. The preparation of the seconday bishomoallyllithium and its rearrangement to a primary one was reported by Hill, Richey, and Rees as part of a mechanistic study (eq 1).[5]



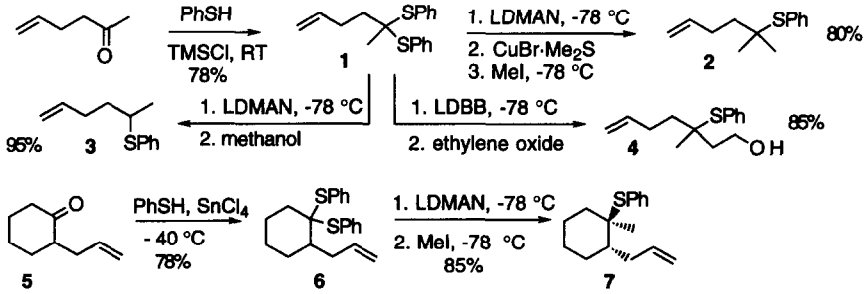
(1)

Tertiary bishomoallyllithiums, like tertiary organolithiums of any kind, are inaccessible by most preparative methods[6] and to our knowledge, have not been reported. We now present a general preparative method for bishomoallyllithiums using reductive lithiation with lithium 4,4'-di-*tert*-butylbiphenylide (LDBB)[7] of readily available bishomoallyl phenyl sulfides. It allows ready access even to secondary and tertiary bishomoallyllithiums which, in suitable cases, are capable of rearranging to primary bishomoallyllithiums. We also demonstrate the utility of bishomoallyllithiums for the preparation of the precursors of type-II intramolecular ene reactions.

RESULTS AND DISCUSSION

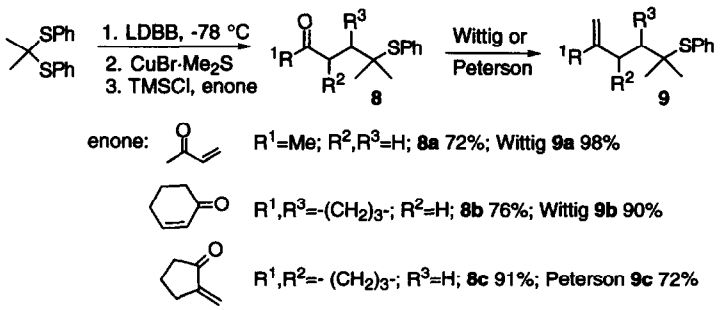
Preparation of Bishomoallyl Phenyl Sulfides

Two methods were used to prepare the precursors of bishomoallyllithiums. One (Scheme 1) is thioacetalization[8] of γ, δ-unsaturated ketones, available either commercially (hex-5-en-2-one) or by allylation of a ketone (2-allylcyclohexanone **5**[9]), followed by replacing one of the phenylthio groups with an alkyl group or hydrogen via reductive lithiation. In the presence of trimethylsilyl chloride (TMSCl) or stannic chloride, the carbonyl group can be thioacetalized by thiophenol without affecting the double bond. Treating the resulting bis(phenylthio)acetals with LDBB or lithium 1-(dimethylamino)naphthalenide[10] (LDMAN) affords α-lithiothioethers, which are treated with electrophiles directly or after being transformed into cuprates.[6] Sulfide **7** was formed stereoselectively. This may be due to the preference of the carbanion lone pair for the axial position, in which it can be most readily stabilized by hyperconjugation with the antiparallel S-phenyl bond.[11]



Scheme 1

The second method (Scheme 2) involves Wittig or Peterson olefination of γ-(phenylthio)ketones, which in turn are prepared[6b] by conjugate addition of phenylthiomethyl cuprates to enones in the presence of TMSCl.[12] Because of the presence of lithium thiophenoxide in the solution, this procedure leads directly to the desired "mixed" cuprate bearing a thiophenoxide group and allows full stoichiometric utilization of the organolithium species.[13] The thioacetal of acetone, 2,2-bis(phenylthio)propane, was treated with LDBB to form 2-(phenylthio)-2-lithiopropane, which was transformed to the corresponding mixed cuprate at -78 °C by adding cuprous bromide - dimethyl sulfide complex.[14] To the cuprate at -78 °C, TMSCl was added and then the enone. At the completion of the reaction, 5% aqueous NaOH and tetrabutylammonium hydroxide was added to hydrolyze the silyl enol ether that was generated by the 1,4-addition. Wittig reactions provided excellent yields for the methylenation of **8a** and **8b**, but in the case of cyclopentanone derivative **8c**, serious enolization occurred under the reaction conditions. However, the Johnson modification of the Peterson procedure[15] afforded a satisfactory yield.



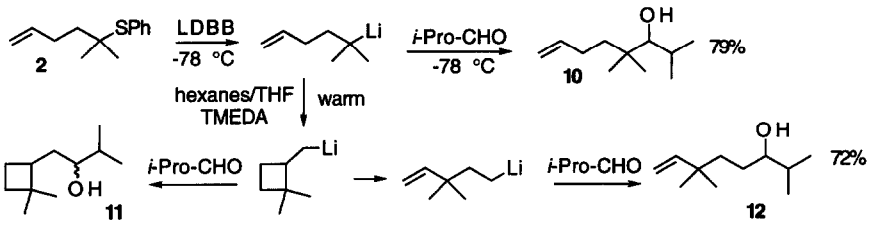
Scheme 2

Formation and Rearrangements of Bishomoallyllithiums

The bishomoallyllithiums were generated by reductive lithiation of bishomoallyl phenyl sulfides with LDBB. The solvent was usually THF and the temperature -78 °C. In cases that required warming to induce 1,3-vinyl rearrangements, a mixed solvent of THF and hexanes was used in order to decrease the degree of proton abstraction. In order to avoid precipitation of LDBB that occurs in this less polar solvent system at low temperature, a higher temperature (-50 °C) was used.

The large variety of successful 1,2-vinyl rearrangements of homoallyllithiums[3] led us to attempt 1,3-vinyl rearrangements of bishomoallyllithiums to less substituted ones. The similarity is that both involve small ring compounds, 3- and 4-membered rings, respectively, as intermediates. Saturated four-membered rings are known to be formed with greater difficulty than three-membered rings,[16] and hence 1,3-vinyl rearrangements of bishomoallyllithiums are expected to be, and in one case[4a] have been shown to be, slower than 1,2-vinyl rearrangements of homoallyllithiums. It was found in the case of homoallyllithiums that the addition of *N,N'*-tetramethylethylenediamine (TMEDA) to the THF reaction mixture accelerated the rearrangements[3] and that dilution of THF with hexanes retarded the competing proton abstraction from solvent.[3,17] These two techniques were applied to bishomoallyllithium rearrangements without modification.

5-Methyl-5-phenylthio-1-hexene (**2**) was reduced to the corresponding bishomoallyllithium with LDBB. At -78 °C, the tertiary organolithium could be detected by the formation in good yield of an aldehyde adduct (**10**). After the reductive lithiation reaction mixture had been warmed to -40 °C in the presence of TMEDA, three organolithiums, i.e., the unchanged tertiary organolithium, the cyclobutylcarbinyllithium intermediate, and the rearranged primary bishomoallyllithium, were detected in the mixture by their reactions with isobutyraldehyde (Table 1). The composition of the three organolithiums did not change appreciably when the reaction time was extended from 2 to 4 hours. Complete rearrangement occurred when the reaction mixture was warmed to -30 °C or higher.



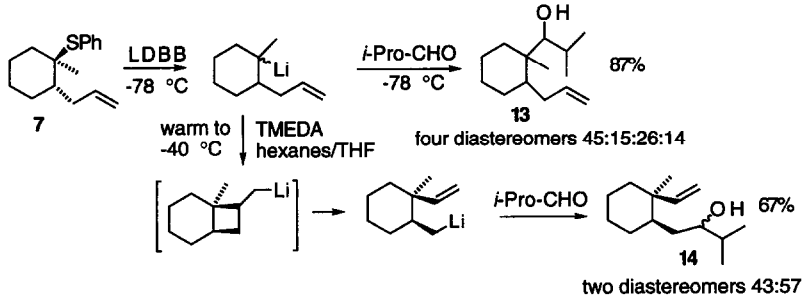
Scheme 3

Table I. Yields in Scheme 3

Temp.	Time	Solvent (THF : Hex)	TMEDA (equiv/Li^+)	Ratio[a] **10 : 11 : 12**	Total Yield %
-78 °C	10 min	1 : 0	0	100 : 0 : 0	79
-40 °C	2 hr	1 : 2	2	29 : 42 : 29	74
-40 °C	4 hr	1 : 2	2	29 : 49 : 22	not isolated
-30 °C	2 hr	1 : 2	2	0 : 0 : 100	72
0 °C	30 min	1 : 2	2	0 : 0 : 100	48

[a]according to capillary GC.

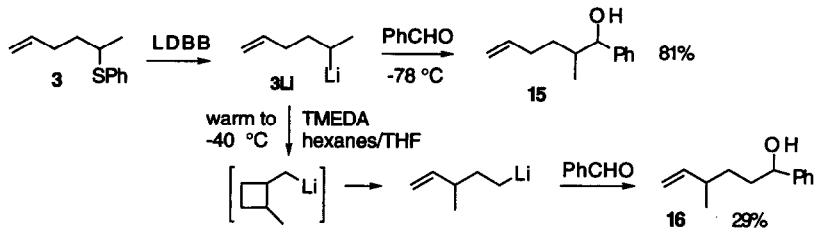
The rearrangement of 1-methyl-2-allylcyclohexyllithium (Scheme 4) was achieved with complete stereoselectively. Presumably, the stereochemistry of the rearranged product (alcohol **14**) is derived from that of the intermediate, in which the [4.2.0] bicyclooctane ring is produced in the *cis*-fused rather than in the more strained *trans*-fused configuration.



Scheme 4

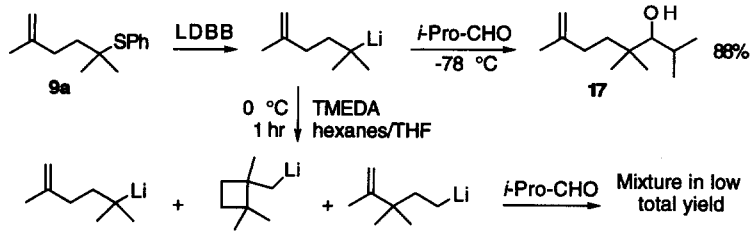
Like the tertiary bishomoallyllithiums described above, the secondary bishomoallyllithium **3Li**, previously prepared by a longer route (eq 1),[5] was formed efficiently as revealed by the high yield of **15** the product of its capture with benzaldehyde (Scheme 5). Also like its tertiary analogues, **3Li** rearranged completely to the primary organolithium under the same conditions used for the tertiary bishomoallyllithium rearrangements. However, the yield of the rearranged product **16**, formed by quenching the reaction with benzaldehyde, was significantly lower than that of the products derived from the rearrangements of tertiary

organolithiums. Presumably, the rate of ring closure of **3Li** is lower relative to the rate of solvent deprotonation than in the tertiary cases.



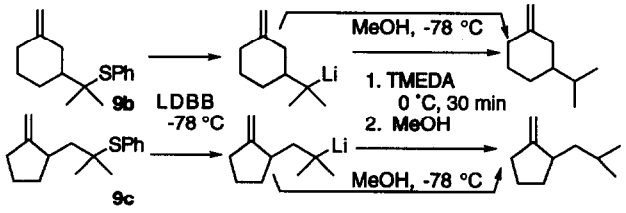
Scheme 5

A rearrangement in which the proximal terminus of the alkene function was disubstituted was also investigated (Scheme 6). With an extra methyl group on the proximal terminus of the double bond, a mixture was formed even after the reaction solution was allowed to remain at 0 °C for 1 hour and quenched with isobutyraldehyde. All of the peaks in the mixture had similar retention times and the same molecular weight as **17**, according to GC-MS, and they were thus presumably derived from the unrearranged, rearranged, and cyclobutylcarbinyl anions, although the total recovery was low presumably due to protonation by solvent during warm-up. No effort was made to resolve the products.



Scheme 6

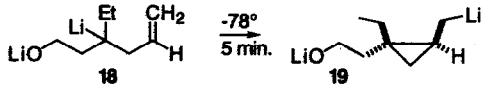
In the cases of **9b** and **9c**, there was no GC-MS evidence that any rearrangement of the tertiary organolithiums occurred when the reaction mixtures were allowed to remain at 0 °C for 30 minutes before the methanol quench (Scheme 7).



Scheme 7

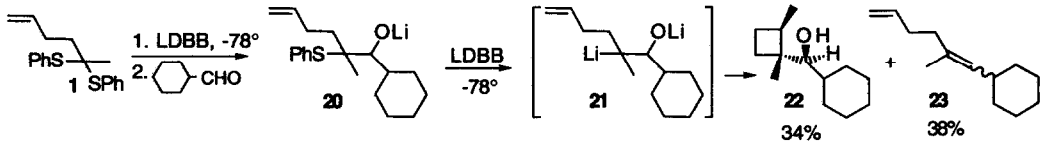
In the account of our study of the 1,2-vinyl rearrangement of homoallyllithiums,[3] we reported that **18** rearranged far more rapidly than homoallyllithiums lacking the oxyanionic function (eq 2) and that, unlike the

other cases, the cyclopropylcarbinyllithium **19** could be trapped successfully. There was no special accelerating effect when the lithium atom attached to oxygen was replaced by a methyl group. From the stereochemistry of the cyclopropane resulting from protonation, it was concluded that the CH_2Li group in **19** was in a trans relationship to the substituent bearing the oxyanionic group.



(2)

We have now uncovered closely analogous behavior in the rapid cyclization of **21**, a tertiary organolithium with an adjacent oxyanionic substituent. The production of **21** involved the addition of cyclohexanecarboxaldehyde to the reductive lithiation product of **1** followed by another reductive lithiation with LDBB at -78 °C (Scheme 8). The reaction solution was quenched with water after being allowed to warm to 0 °C. The crude mixture was analyzed by GC-MS and then separated by chromatography to provide 34% of cyclization product **22**, 38% of elimination product **23**, and ~10% of protonation product. A similar result was obtained when the reaction mixture was not allowed to warm, but was quenched at -78 °C after being stirred for 30 min. The β-elimination ($-Li_2O$) should be quite fast even at -78 °C and this elimination results in alkene **23**.[18] The rate of the cyclization, which provided 34% of **22**, must be comparable with that of the β-elimination and so is increased remarkably by the β-OLi group compared to the rearrangements in Schemes 3 and 4. The β-OLi group also significantly stabilizes the cyclobutylcarbinyllithium toward ring cleavage since ring opening did not occur even after the reaction mixture was allowed to warm to 0 °C. Based on NMR and capillary GC analysis, **22** was formed as a single diastereomer even though it has three chiral centers. The x-ray crystal structure of **22** (Figure 1) indicates that as in the case of **19** the CH_2Li group in the immediate precursor of **22** is oriented trans to the side chain bearing the oxyanionic group.



Scheme 8

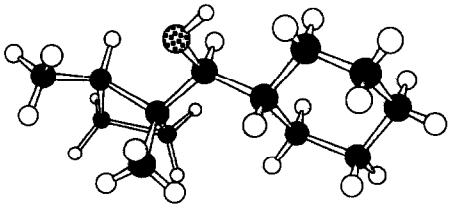


Figure 1. X-Ray crystal structure of **22**

In both **18** and **21**, the oxyanionic group is on a carbon atom separated by a chain of three-carbon atoms from the proximal vinyl carbon atom which becomes part of the newly formed ring. In **21**, there is one less methylene group in the chain bearing the oxyanionic function and one more in the chain separating the

lithium-bearing carbon atom from the vinyl group. The following explanation of the acceleration and the ring stereochemistry is analogous to that put forth for the cyclization of **18**.[3]

Computations by Houk and Schleyer[19] indicate that the addition of methyllithium to ethylene proceeds through a rather simple 4-center transition state and indeed a cis addition has been noted for the addition of phenyllithium to cyclopropene.[20] It is certainly reasonable to assume that the intramolecular addition of an alkyllithium to an alkene observed here proceeds in a similar fashion. Such a transition state has also been postulated by Grovenstein[21] 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 cyclopentylmethyllithiums.[22] Thus, in the conformation preceding ring closure, the carbon-lithium bond and the C-C double bond must become approximately parallel. In such conformations (e.g. Fig. 2), either the carbinol group (e.g. Fig. 2A) or the methyl substituent (e.g. Fig. 2B) on the lithium-bearing carbon atom can be close enough to the vinyl group to interact with it. That substituent that is pointing in the general direction of the alkene group is the one that ends up trans to the lithiomethyl group in the cyclobutane, assuming the above justified 4-center transition state for cyclization. The pronounced acceleration of the ring closure of **21** implies that in the transition state for cyclization the oxyanionic substituent interacts with the alkene linkage either indirectly, by "guiding" the alkyllithium into the alkene linkage,[23] as is thought to occur in additions of alkyllithiums to allylic alcoholate ions,[24] and/or directly, by polarizing the pi bond, as may be occurring in the addition of an alkyllithium to a homoallylic alcoholate.[25] Fig. 2 represents two conformers of one of the diastereomers of **21**. Only in conformer **21A** can the oxyanionic group interact with the alkene group. In this particular depiction of a possible precyclization conformer, both lithium atoms of the molecule are close enough to the distal terminus of the vinyl group that both could participate in polarizing the vinyl group. With regard to the right hand side of the molecule as drawn, a variety of conformations are possible in each diastereomer. In Fig. 2A, interchange of the positions of the cyclohexyl group and hydrogen atom attached to the carbinol carbon atom (leading to the other diastereomer) would cause severe steric compression that would become intolerable in the 4-center transition state. In fact, cyclization proceeding from **21A** yields the correct diastereomer of the cyclobutane that is actually produced; this can be taken as evidence for the participation of the oxyanionic group in the ring closure and lends credence to a precyclization conformation in which the oxyanionic substituent rather than the methyl group is pointing in the general direction of the alkene group as in **21A**. This finding does not give information about whether the carbon-lithium bond is pointing away or toward the vinyl group.

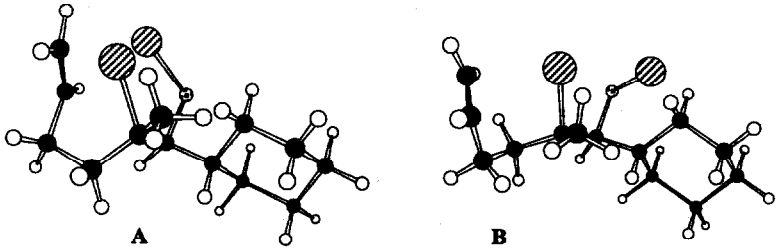
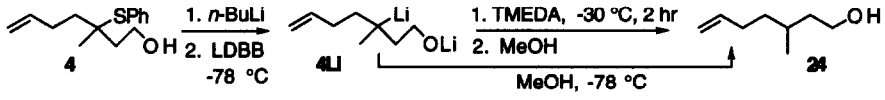


Figure 2. Possible precyclization conformers of **21**

In the earlier work on the 1,2-vinyl rearrangement of homoallyllithiums,[3] it was found that the homologue of **18** having one more methylene group in the chain bearing the oxyanionic group also displays the

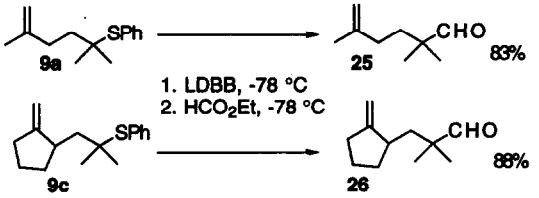
accelerating effect, although in that case the cyclopropyl intermediate can not be detected. In contrast, the OLi group in **4Li** (Scheme 9) *decreased* the rate of the cyclization. No rearrangement of **4Li** could be detected after it was allowed to remain at -30 °C for 2 hrs in the presence or absence of TMEDA. The reason for the retarding effect of the OLi group on the rearrangement in this specific case is not clear and the general role of oxyanionic groups in intramolecular additions of alkyllithiums to C-C double bonds still needs further investigation.



Scheme 9

Formylation of Bishomoallyllithiums and Ene Reactions of the Resulting Formylalkenes

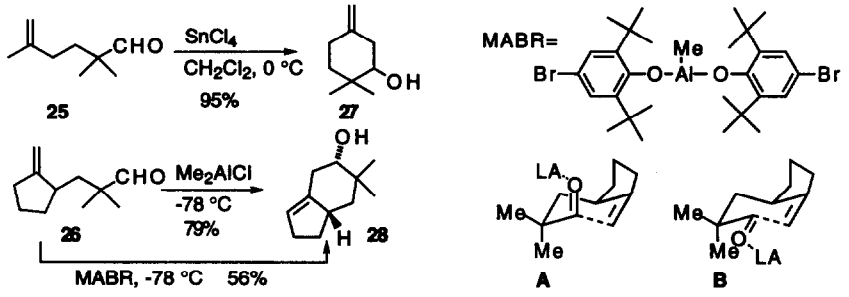
It has been shown that the acetals of primary, secondary, and tertiary β-[6a] and γ-lithioketones[6b] can be captured with a variety of electrophiles including acylating agents and enones (conjugate addition). It would be surprising if the organolithiums described here were incapable of such electrophile capture. One of the many uses that we envision for homoallyllithiums is acylation to produce substrates for intramolecular ene reactions.[26] Two examples are described. Tertiary bishomoallyllithiums react with ethyl formate[27] to give excellent yields of formylation product (Scheme 10).



Scheme 10

When the formylation products were submitted to Lewis acid catalyzed intramolecular ene reactions, 6-membered ring cyclization products were formed (Scheme 11). Stannic chloride was used as the Lewis acid in the cyclization of **25** and an excellent yield of **27** was obtained as reported by Andersen and coworkers.[28] However, when the same conditions were applied to the cyclization of **26**, a great deal of product isomerized to the more stable tetra-substituted alkene. Therefore, dimethyl aluminum chloride, which Snider[29] introduced for such reactions because it is both a Lewis acid and a Brönsted base, was used instead. Only about 5% of isomerization product was detected by capillary GC and a good yield of the ene reaction product **28** was obtained in the latter case. As expected from the stereochemistry of type-II intramolecular ene reactions catalyzed by small Lewis acids,[30] only cis isomer **28** was formed in the reactions catalyzed by both stannic chloride and dimethyl aluminum chloride. The assignment of the stereochemistry is based on its ^{1}H NMR spectrum; the proton attached to the carbinol carbon atom (C*H*OH) has a very small coupling constant (it appears as a singlet) with the adjacent CH_2, so it is in the equatorial orientation and the hydroxyl group is in the axial orientation, trans disposed to the bridge-H. What was not expected was that cis isomer **28** was still the only product, although in lower yield, when Yamamato's bulky Lewis acid MABR,[31] was used as the catalyst.

Yamamato had found that MABR reverses the stereochemistry in similar cases in which the gem-dimethyl group is absent. It is likely that, because of the gem-dimethyl group, transition state **B** is more crowded than **A**.



Scheme 11

CONCLUSIONS

Rare bishomoallyllithiums, including secondary and tertiary ones, are now readily available by reductive lithiation of bishomoallyl phenyl sulfides. Their 1,3-vinyl rearrangements via cyclobutylcarbinyllithiums are less facile than the corresponding 1,2-vinyl rearrangements of homoallyllithiums but a number of examples have been demonstrated. The cyclization to a 4-membered ring, which does not re-open to a less substituted bishomoallyllithium, is particularly facile in the case of a tertiary organolithium with a neighboring lithium oxyanion and the CH_2Li and carbinol groups in the product are trans disposed about the cyclobutane ring; a mechanistic rationale is provided. Finally, it has been shown that bishomoallyllithiums can be readily formylated in good yield to provide substrates for type-II intramolecular ene reactions that result, highly stereoselectively, in the production of alkylidenecyclohexanols.

EXPERIMENTAL

All reactions were carried out under an atmosphere of prepurified argon. All solvents were dried by using standard procedures and freshly distilled. A dry ice / methanol slush bath was used to generate -78 °C and an ice bath was used to obtain 0 °C. When a temperature of -78 °C was needed for an extended period of time, the FTS Systems, Inc Model TC-10 Flexi cool probe was used. Infrared spectra were recorded on a IBM IR / 32 or Mattson Cygnus 100 FTIR spectrometer. ^1H (300 MHz) and ^{13}C (75 MHz) NMR spectra were recorded either on a Brucker WH-300 or a Brucker AF-300 spectrometer. Two-dimensional NMR spectra were recorded on a Bruker AM-500 spectrometer. High resolution or CI mass spectra were recorded on a CH-5 double focusing Varian Mat mass spectrometer or on a VG 70-G mass spectrometer. Gas liquid chromatographic mass spectral (GC/MS) analyses of reaction mixtures were performed on a Hewlett Packard 5890 Series II gas chromatograph equipped with a 5970 mass selective detector. Capillary gas liquid chromatographic analyses were performed on a Hewlett-Packard 5890 gas chromatograph utilizing a 0.20 mm fused silica capillary column (Carbowax 20M) and a flame ionization detector. Thin layer chromatograms were developed on glass supported 250 μm silica gel GF plates (Analtech). Flash Chromatography was performed using 40 - 63 μm silica gel 60 (Merck). TLC plates were visualized using 7% phosphomolybdic acid in ethanol or 5% *p*-anisaldehyde in ethanol. Flash chromatography was performed using 40-60 μm silica gel 60 (E. Merck).

***5,5-Bis(phenylthio)-1-hexene* (1).** To a well-stirred solution of 5-hexen-2-one (4.90 g, 50.0 mmol) and thiophenol (12.1 g, 110 mmol) in chloroform, trimethylsilyl chloride (9.46 mL, 75.0 mmol) was added slowly over a period of 30 min at room temperature. After the mixture had been stirred for one hr at ambient, it was diluted with diethyl ether and washed with 5% aqueous NaOH until all of the thiophenol was removed (bleach test). The organic phase was dried over $MgSO_4$ and concentrated by rotary evaporation. A trace of the solvent and some low boiling impurities were removed under high vacuum to yield 11.7 g (78%) of the titled product as a yellow oil, which did not require further purification. ^{1}H NMR ($CDCl_3$): δ 7.65 - 7.31 (m, 10 H, Ph), 5.75 (m, 1 H, =CH), 5.05 - 4.93 (m, 2 H, $=CH_2$), 2.45 (m, 2 H, allylic), 1.79 (m, 2 H), 1.39 (s, 3 H, CH_3); CI MS using isobutane: $C_{18}H_{21}S_2$ $(M+1)^+$, 301.

***5-Methyl-5-phenylthio-1-hexene* (2).** To a solution of lithium dimethylaminonaphthalenide (LDMAN) (14.6 mmol) in THF (30 mL) at -78 °C, a solution of **1** (2.21 g, 7.30 mmol) in THF was added dropwise. At the end of addition, the dark green color of LDMAN turned to dark red. After 10 min of further stirring, cuprous bromide - dimethyl sulfide complex (1.95 g, 9.46 mmol) was added. The mixture was stirred at -78 °C for 3 hr to allow for the cuprate formation before iodomethane (1.35 g, 9.46 mmol) was added. After being stirred overnight, the mixture was warmed to room temperature and quenched by pouring it into 30 mL of saturated ammonium chloride solution and ether. The mixture was filtered though celite to remove the copper salts. The filtrate was poured into a separatory funnel and the aqueous layer was extracted with ether (3 x 30 mL). The combined organic layer was washed with 5% hydrochloric acid (to remove DMAN) and brine, and it was dried over anhydrous magnesium sulfate. The solvent was removed by rotary evaporation to give 1.50 g (98%) of the crude product which was purified by distillation, b. p. 90 °C / 0.02 torr, yield 1.22 g (80%), (colorless oil). ^{1}H NMR ($CDCl_3$): δ 7.53 - 7.29 (m, 5 H, Ph), 5.85 (m, 1 H, =CH), 5.07 - 4.93 (m, 2 H, $=CH_2$), 2.26 (m, 2 H, allylic), 1.53 (m, 2 H), 1.24 (s, 6 H, CH_3); ^{13}C NMR ($CDCl_3$): δ 138.4, 137.4, 132.1, 128.5, 128.3, 114.3, 48.8, 41.0, 29.1, 28.6; IR (neat, NaCl): 2974 (s), 2930 (s), 2864 (s), 1641 (s), 1473 (s), 1122 (s), 750 (s), 735 (s), 706 (s), 694 (s), 648 (m); HRMS: calc. for $C_{13}H_{18}S$ (M^+) 206.1129, found 206.1141.

***5-Phenylthio-1-hexene* (3).** LDMAN (26 mmol), freshly prepared at -55 °C in THF (60 mL), was cooled to -78 °C and treated with a solution of **1** (3.90 g, 13.0 mmol) in THF (10 mL). After the solution had been stirred for 10 min at -78 °C, one mL of methanol was added. The reaction mixture was allowed to warm to room temperature and 50 mL of water was added. The organic materials were extracted with ether (3 x 100 mL). The combined organic layer was washed with 5% HCl (2 x 150 mL) to remove DMAN and dried over $MgSO_4$. The solvent was removed under reduced pressure to give 2.37 g (95%) of the titled product as a yellow oil, which did not require further purification. ^{1}H NMR ($CDCl_3$): δ 7.41 - 7.20 (m, 5 H, Ph), 5.80 (m, 1 H, =CH), 5.07 - 4.96 (m, 2 H, $=CH_2$), 3.23 (m, 1 H, C*H*SPh), 2.23 (m, 2 H, allylic), 1.78 - 1.53 (m, 2 H), 1.28 (d, 3 H, J = 6.9 Hz, CH_3); ^{13}C NMR ($CDCl_3$): δ 137.8, 135.2, 132.0, 128.7, 126.6, 115.0, 42.6, 35.6, 31.1, 21.1. IR (neat, NaCl): 3074 (s), 2974 (s), 2924 (s), 1641 (m), 1479 (s), 1439 (s), 912 (s), 746 (s), 692 (s) cm^{-1}. HRMS: calc. for $C_{12}H_{16}S$ (M^+) 192.0973, found 192.0983.

***3-Methyl-3-phenylthio-6-hepten-1-ol* (4).** A solution of **1** (3.00 g, 10 mmol) in THF (10 mL) was added dropwise to a freshly prepared solution of lithium 4,4'-di-*tert*-butylbiphenylide (LDBB; 20 mmol) in THF (45 mL) at -78 °C. At the end of the addition, the dark blue color of LDBB turned to dark red. After the solution had been stirred for 10 min at -78 °C, a solution of ethylene oxide (1.3 g, 30 mmol) in THF (10 mL)

was added via syringe. After the mixture had been allowed to warm to room temperature, 50 mL of water was added. The reaction mixture was extracted with ether (3 x 100 mL) and the combined organic layer was dried over anhydrous $MgSO_4$. The solvent was removed by rotary evaporation. Flash chromatography gave recovered DBB and a mixture of the titled product and 2-phenylthioethanol. Distillation provided the titled product as a colorless oil, b. p. 130 °C / 0.05 torr, yield 2.00 g (85%). ^1H NMR ($CDCl_3$): δ 7.57 - 7.28 (m, 5 H, Ph), 5.87 - 5.74 (m, 1 H, =CH), 5.12 - 4.95 (m, 2 H, $=CH_2$), 3.99 - 3.88 (m, 2 H, CH_2OH), 2.36 - 2.22 (m, 2 H, allylic), 1.99 (s, 1 H, OH), 1.86 - 1.71 (m, 2 H), 1.63 - 1.51 (m, 2 H), 1.23 (s, 3 H, CH_3); HRMS: calc. for $C_{14}H_{20}OS$ (M^+) 236.1235, found 236.1225.

***1,1-Bis(phenylthio)-2-(3-propenyl)-cyclohexane* (6).** A 1.0 M solution of stannic chloride in methylene chloride (15 mL, 15 mmol) was added dropwise via syringe to a stirred solution of 2-(3-propenyl)-cyclohexanol **5**[9] (2.07 g, 15.0 mmol) and thiophenol (3.4 mL, 31 mmol) in dry dichloromethane (12 mL) at -40 °C. After being stirred at -40 °C for one hour, the reaction mixture was quenched with 20 mL of 15% sodium bicarbonate solution. The organic layer was diluted with ether and washed with 5% NaOH to remove all of the thiophenol (bleach test), then it was dried over anhydrous $MgSO_4$. The solvent was removed by rotary evaporation. Flash chromatography (pure hexanes) gave 3.86 g (76%) of the titled product. ^1H NMR ($CDCl_3$): δ 7.80 - 7.14 (m, 10 H, Ph), 5.78 (m, 1 H, =CH), 5.15 - 5.00 (m, 2 H, $=CH_2$), 3.47 (m, 1 H), 2.20 - 0.91(m, 10 H).

***E-1-Phenylthio-1-methyl-2-(3-propenyl)-cyclohexane* (7).** A solution of LDMAN (20 mmol) in THF (45 mL) was cooled to -78 °C and treated with a solution of **6** (3.40 g, 10.0 mmol) in THF (.10 mL). The dark green color of LDMAN turned to dark red. After 10 min of stirring, iodomethane (1.9 mL, 30 mmol) was added. The reaction mixture was stirred at -78 °C for 30 min before being quenched with 40 mL of water. The organic materials were extracted with ether (3 x 50 mL) and the combined organic layer was washed with 5% HCl (to remove DMAN,) brine, and dried over anhydrous $MgSO_4$. The solvent was removed by rotary evaporation. Distillation provided the titled product as a colorless oil, b. p. 115 °C / 0.2 torr, yield 2.10 g (85%). ^1H NMR ($CDCl_3$): δ 7.51 - 7.29 (m, 5 H, Ph), 5.72 (m, 1 H, =CH), 5.06 - 5.00 (m, 2 H, $=CH_2$), 3.03 (m, 1 H), 1.78 - 1.01 (m, 10 H), 1.18 (s, 3 H, CH_3); ^{13}C NMR ($CDCl_3$): δ 138.0, 131.4, 128.7, 128.4, 115.7, 54.3, 43.2, 40.7, 35.7, 27.8, 25.7, 23.3, 19.3; HRMS: calc. for $C_{16}H_{22}S$ (M^+) 246.1442, found 246.1450. In the 500 MHz NOESY spectrum, no NOE was observed between the methyl group (1.18) and the methine proton (3.03) in the cyclohexane ring.

5-Methyl-5-phenylthio-2-hexanone (8a). A solution of LDBB (31.5 mmol), freshly prepared in THF (70 mL) at 0 °C, was cooled to -78 °C and treated with 2,2-bis(phenylthio)propane (4.09 g, 15.7 mmol) in THF (15 mL). After the solution had been stirred for 10 min at -78 °C, copper bromide-dimethyl sulfide complex was quickly added under increased argon flow. The cuprate formation was ensured by stirring the reaction mixture at -78 °C for 3 hr. Trimethylsilyl chloride (3.0 mL, 23 mmol) was then added followed by the methyl vinyl ketone (1.7 mL, 21 mmol). The mixture was stirred at -78 °C overnight. Aqueous 5% sodium hydroxide solution (100 mL) and about 1 mL of tetrabutylammonium hydroxide were added and the mixture was allowed to warm to 0 °C. It was stirred at room temperature for about 45 min in order to hydrolyze all of the silyl enol ether to the ketone product. After the mixture had been filteried through celite to remove the copper salts, the organic materials were extracted by ether (3 x 100 mL) and the organic layer was dried over $MgSO_4$. The solvent was removed by rotary evaporation. Flash chromatography (5% AcOEt / hexanes) gave recovered DBB and the titled product as a yellow oil, 2.53 g (72%). ^1H NMR ($CDCl_3$): δ 7.49 - 7.29 (m, 5 H,

Ph), 2.72 (t, J = 8.1 Hz, 2 H, $COCH_2$), 2.19 (s, 3 H, $COCH_3$), 1.74 (t, J = 3.2 Hz, 2 H), 1.22 (s, 6 H, CH_3CSPh); HRMS: calc. for $C_{13}H_{18}OS$ (M^+) 222.1078, found 222.1099.

***3-[1-Methyl-1-(phenylthio)ethyl]-1-cyclohexanone* (8b).** The same procedure as that for **8a** was applied to **8b** except that 2-cyclohexen-1-one (1.2 mL, 12 mmol) was added to the cuprate instead of the methyl vinyl ketone. Flash chromatography (9% AcOEt / hexanes) provided the product as a pale yellow oil, 1.88 g (76%). ^1H NMR ($CDCl_3$): δ 7.51 - 7.28 (m, 5 H, Ph), 2.67 (m, 1 H), 2.40 - 2.10 (m, 5 H), 1.77 (m, 1 H), 1.62 - 1.50 (m, 2 H), 1.22 (s, 3 H, CH_3), 1.21 (s, 3 H, CH_3); HRMS: calc. for $C_{15}H_{20}OS$ (M^+) 248.1235, found 248.1244.

***2-[2-Methyl-2-(phenylthio)propyl]-1-cyclopentanone* (8c).** The same procedure was followed except that 2,2-bis(phenylthio)propane (2.60 g, 10.0 mmol) in THF (10 mL) was added to the LDBB solution and 2-methylenecyclopentanone[32] (700 mg, 7.30 mmol) was used. Flash chromatography (5% AcOEt / hexanes) provided the product as a pale yellow oil, 1.66 g (91% based on the enone). ^1H NMR ($CDCl_3$): δ 7.57 - 7.31 (m, 5 H, Ph), 2.56 - 1.30 (m, 9 H), 1.27 (s, 3 H, CH_3), 1.24 (s, 3 H, CH_3); ^{13}C NMR ($CDCl_3$): δ 220.8, 137.7, 131.7, 128.7, 128.5, 49.2, 47.0, 42.5, 37.2, 29.7, 29.2, 20.7; HRMS: calc. for $C_{15}H_{20}OS$ (M^+) 248.1235, found 248.1244.

***2,5-Dimethyl-5-phenylthio-1-hexene* (9a).** To a suspension of triphenylmethylphosphonium bromide (7.32 g, 20.5 mmol) in THF (70 mL) at 0 °C, *n*-butyllithium solution (1.55 M in hexanes, 11.8 mL, 18.2 mmol) was added dropwise. The mixture was stirred at 0 °C for 15 min; it was then cooled to -78 °C and **8a** (2.50 g, 11.4 mmol) in THF (10 mL) was added dropwise. After being stirred at -78 °C for 15 min, the reaction mixture was warmed to 0 °C, stirred for 30 min, and quenched with 1 mL of methanol. The mixture was poured into 250 mL of pentane and filtered through silica gel. The solvent was removed by rotary evaporation. Flash chromatography (hexanes) provided the titled product as a colorless oil, 2.47g (98%). ^1H NMR ($CDCl_3$): δ 7.53 - 7.32 (m, 5 H, Ph), 4.70 (s, 1 H, vinyl), 4.69 (s, 1 H, vinyl), 2.21 (m, 2 H, allylic), 1.74 (s, 3 H, allylic CH_3), 1.59 (m, 2 H), 1.25 (s, 6 H, CH_3); ^{13}C NMR ($CDCl_3$): δ 146.0, 137.6, 132.2, 128.7, 128.5, 109.7, 49.2, 40.3, 33.0, 28.8, 22.9; HRMS: calc. for $C_{14}H_{20}S$ (M^+) 220.1286, found 220.1260.

***1-Methylene-3-[1-methyl-1-(phenylthio)ethyl]cyclohexane* (9b).** The same procedure as that for **9a** was used except that **8b** (1.52 g, 6.12 mmol) was added to the ylide instead of **8a**. Flash chromatography (pure hexanes) provided the titled product as a colorless oil, 1.37 g (90%). ^1H NMR ($CDCl_3$): δ 7.53 - 7.30 (m, 5 H, Ph), 4.65 (s, 2 H, $=CH_2$), 2.64 (m, 2 H), 2.30 - 1.26 (m, 7 H), 1.22 (s, 3 H, CH_3), 1.21 (s, 3 H, CH_3); ^{13}C NMR ($CDCl_3$): δ 149.1, 137.7, 132.2, 128.5, 128.3, 107.6, 52.5, 48.2, 36.8, 34.9, 27.5, 27.4, 26.4, 26.2; HRMS: calc. for $C_{16}H_{22}S$ (M^+) 246.1442, found 246.1452.

***1-Methylene-2-[2-methyl-2-(phenylthio)propyl]cyclopentane* (9c).** To a slurry of anhydrous cerium trichloride (13.1 mmol) in THF (30 mL) at -78 °C, trimethylsilylmethyllithium solution (1.0 M in pentane, 11.25 mL, 11.2 mmol) was added dropwise via syringe with vigorous stirring. After the solution had been stirred for 30 min at -78 °C, **8c** (1.80 g, 7.25 mmol) in THF (5 mL) was added. The mixture was stirred at -78 °C overnight, warmed to room temperature and quenched with 5% HCl. The organic materials were extracted with ether (3 x 50 mL) and the combined organic layer was dried over $MgSO_4$. The solvent was removed by rotary evaporation and the residue was dissolved in acetonitrile (56 mL) and 49% hydrofluoric acid (2.5 mL). The reaction mixture was stirred at room temperature until the olefination was complete (about 30 min, TLC monitoring). 50 mL of 5% aqueous $NaHCO_3$ was then added, the organic

materials were extracted with pentane (3 x 50 mL) and the combined organic layer was dried over $MgSO_4$. Flash chromatography (pure hexanes) provided the titled product as a colorless oil, 1.30 g (73%). ^1H NMR ($CDCl_3$): δ 7.56-7.30 (m, 5 H, Ph), 4.90 (d, J = 1.7 Hz, 1 H, =CH), 4.74 (d, J = 2.0 Hz, 1 H, =CH), 2.60 (m, 1 H), 2.37 - 1.33 (m, 8 H), 1.30 (s, 3 H, CH_3), 1.29 (s, 3 H, CH_3); ^{13}C NMR ($CDCl_3$): δ 157.5, 137.7, 132.3, 128.6, 128.4, 104.4, 49.6, 47.9, 40.8, 35.8, 32.9, 30.2, 28.9, 24.5; CI MS using isobutane $C_{16}H_{23}S$ $(M+1)^+$ 247.

***2,4,4-Trimethyl-7-octen-3-ol* (10).** A solution of LDBB (2.00 mmol) in THF (6 mL) was cooled to -78 °C and treated with a solution of **2** (206 mg, 1.00 mmol) in THF (1 mL). The color of the reaction mixture changed from dark blue to dark red immediately at the end of the addition. After the solution had been stirred for 10 min at -78 °C, isobutyraldehyde (109 μL, 1.20 mmol) was added. The reaction mixture was stirred at -78 °C for 15 min, warmed to 0 °C and quenched with 5 mL of water The organic material was extracted with ether (3 x10 mL), the combined organic layer was dried over anhydrous $MgSO_4$, and the solvent was removed by rotary evaporation. Flash chromatography (3% AcOEt / hexanes) gave recovered DBB and the titled product as a pale yellow oil, 136 mg (79%). ^1H NMR ($CDCl_3$): δ 5.80 (m, 1 H, =CH), 5.04 - 4.90 (m, 2 H, $=CH_2$), 3.18 (d, J = 2.1 Hz, 1 H, C*H*OH), 1.99 (m, 2 H, allylic), 1.50-1.25 (m, 4 H), 1.01-0.90 (m, 12 H, CH_3); ^{13}C NMR ($CDCl_3$): δ 139.7, 113.9, 82.1, 39.1, 38.3, 28.4, 23.9, 23.8, 23.4, 16.8; IR (neat, NaCl): 3485 (m, br), 2963 (s), 2874 (s), 908 (m) cm^{-1}; CI MS using isobutane: $C_{11}H_{23}O$ $(M+1)^+$ 171.

***1-(2,2-Dimethylcyclobut-1-yl)-3-methyl-2-butanol* (11).** A solution of LDBB (1.43 mmol) in THF (3 mL) and hexanes (3 mL), prepared at 0 °C, was cooled to -50 °C and treated with **2** (147 mg, 0.715 mmol) in THF (1 mL). The color of the solution changed from dark blue to dark red immediately at the end of addition. *N,N,N',N'*-Tetramethylethylenediamine (TMEDA; 302 μL, 4.00 mmol) and hexanes (5 mL) were added before the mixture was warmed to -40 °C. After the mixture had been stirred for 2 hr at -40 °C, it was cooled to -78 °C and isobutyraldehyde (109 μL, 1.20 mmol) was added. The mixture was stirred at -78 °C for 15 min, warmed to 0 °C, and quenched with 5 mL of water. The organic materials were extracted with diethyl ether (3 x 10 mL). The combined organic layer was washed with 5% HCl (to remove TMEDA) and brine, and then dried over anhydrous $MgSO_4$. The solvents were removed by rotary evaporation. Flash chromatography (5% AcOEt / hexanes) gave recovered DBB, **10** (22 mg; 18%), 2,6,6-trimethyl-7-octen-3-ol (**12**; 31 mg; 25%) and the titled product (37 mg; 31%). Based on capillary GC, the ratio of the three compounds in the crude reaction mixture was: **10**:**11**:**12** = 29:42:29 and the two diastereomers of **11** were formed in the ratio 38 : 62. ^1H NMR ($CDCl_3$): δ 3.33 (m, 1 H, C*H*OH), 2.18 - 2.09 (m, 1 H), 2.00 - 1.85 (m, 1 H), 1.68 - 1.23 (m, 7 H), 1.06 - 0.88 (m, 12 H, CH_3); ^{13}C NMR ($CDCl_3$): δ 76.2, 74.4, 41.6, 41.0, 38.1, 37.6, 35.4, 35.0, 33.7, 33.2, 32.7, 30.7, 30.2, 29.8, 23.4, 22.5, 22.4, 22.2, 19.0, 18.9, 17.0, 17.0; IR: 3395.1(m, br), 2957 (s), 1005 (m) cm^{-1}; CI MS using ammonia: $C_{11}H_{26}NO$ $(M+NH_4)^+$ 188.

***2,6,6-Trimethyl-7-octen-3-ol* (12).** The same procedure was followed as that for **11** except that the reaction was allowed to warm to -30 °C instead of -40 °C for 2 hr and 0.8 mmol of **2** was used. Flash chromatography (5% AcOEt / hexanes) gave recovered DBB and the titled product as a pale yellow oil, 98 mg (72%). ^1H NMR ($CDCl_3$): δ 5.80 (dd, J=16.8 and 11.3 Hz, 1 H, =CH), 4.93 (two doublets, J=17.1 and 11.1 Hz, 2 H, $=CH_2$), 3.29 (m, 1 H, CHOH), 1.68 - 1.20 (m, 6 H), 1.00 (d, J = 7.0 Hz, 3 H, CH_3), 0.92 (s, 6 H, CH_3), 0.90 (d, J = 7.8 Hz, 3 H, CH_3); ^{13}C NMR ($CDCl_3$): δ 148.3, 110.6, 77.9, 38.8, 35.4, 30.8, 27.0, 26.8, 19.2, 17.0; IR (neat, NaCl): 3391 (m, br), 2959 (s), 2872 (s), 910 (s) cm^{-1}; CI MS using isobutane: $C_{11}H_{23}O$ $(M+1)^+$ 171.

***2-Methyl-1-(1-methyl-2-(2-propenyl)cyclohexyl)-1-propanol* (13).** The same procedure was followed as that for **10** except that **7** (206 mg, 0.830 mmol) was used instead of **2**. Flash chromatography (2.5% AcOEt / hexanes) gave recovered DBB and the titled product as a yellow oil, 149 mg (87%). Based on capillary GC, the four diastereomers were formed in the ratio 45:15:26:14. ^{1}H NMR ($CDCl_3$): δ 5.78 - 5.67(m, 1 H, =CH), 5.03 - 4.94 (m, 2 H, $=CH_2$), 3.48 - 3.36 (m, 1 H, C*H*OH), 2.33 - 1.07 (m, 11 H), 1.02 - 0.91 (m, 9 H); CI MS using butane: $C_{14}H_{27}O$ $(M+1)^+$ 211.

***Z-1-(2-ethenyl-2-methylcyclohex-1-yl)-3-methyl-2-butanol* (14).** The same procedure was followed as that for **11** except that **7** (192 mg, 0.780 mmol) was used instead of **2**. Flash chromatography (5% AcOEt / hexanes) gave the titled product as a pale yellow oil, 110 mg (67%). Based on capillary GC, only two diastereomers were formed in the ratio of 43 : 57. ^{1}H NMR ($CDCl_3$): δ 6.08 (m, 1 H, =CH), 5.08 - 4.95 (m, 2 H, $=CH_2$), 3.48 - 3.42 (m, 0.6 H, C*H*OH), 3.39 - 3.34 (m, 0.4 H, CHOH), 1.70 - 1.09 (m, 13 H), 1.04 (s, 1.2 H, CH_3), 1.02 (s, 1.8 H, CH_3), 1.00 - 0.82 (m, 6 H, CH_3); ^{13}C NMR ($CDCl_3$): δ 142.9, 112.8, 112.7, 76.5, 74.1, 44.3, 42.5, 39.8, 39.3, 36.0, 35.1, 34.5, 32.5, 29.3, 27.6, 27.0, 26.3, 22.2, 22.1, 19.4, 18.8, 17.6, 15.7; HRMS: calc. for $C_{14}H_{26}O$ 210.1984, found 210.2018; 125 MHz ^{13}C NMR with ^{1}H couplings combined with 500 MHz NOESY spectra revealed the chemical shift of the methinyl carbon atom on the cyclohexane ring in the ^{13}C NMR spectrum: δ 44.3 (major isomer) and δ 42.5 (minor isomer). Based on this result, the center of the chemical shift of the methinyl proton on the cyclohexane ring was found by ^{1}H, ^{13}C NMR - COSY spectrum: δ 1.23 (major) and δ 1.39 (minor). In the 500 MHz NOESY spectrum, strong NOE was observed between the methyl group attached to the ring (δ 1.02 major; δ 1.04 minor) and the methine proton in the cyclohexane ring (δ 1.23 major; δ 1.39 minor).

2-Methyl-1-phenyl-5-hexen-1-ol (15). The same procedure was followed as that for **10** except that **3** (144 mg, 0.750 mmol) was used and benzaldehyde (111 μL, 1.10 mmol, freshly distilled) was employed as the electrophile. Flash chromatography (3% AcOEt / hexanes) provided recovered DBB and the titled product as a pale yellow oil, 107.6 mg (81%). Based on ^{1}H NMR, the two diastereomers were formed in the ratio of 55 : 45. ^{1}H NMR ($CDCl_3$): δ 7.37 - 7.24 (m, 5 H, Ph), 5.82 (m, 1 H, =CH), 5.04 - 4.91 (m, 2 H, $=CH_2$), 4.57 (d, J = 5.6 Hz, 0.55 H, C*H*OH), 4.46 (d, J = 6.9 Hz, 0.45 H, C*H*OH), 2.32-1.12 (m, 6 H), 0.94 (d, J = 6.7 Hz, 1.65 H, CH_3), 0.78 (d, J = 6.7 Hz, 1.35 H, CH_3). ^{13}C NMR ($CDCl_3$): δ 153.7, 143.5, 139.0, 138.8, 128.1, 127.3, 127.1, 126.7, 126.4, 114.4, 114.3, 78.7, 77.8, 39.4, 32.1, 31.3, 31.2, 15.4, 14.2. IR (neat, NaCl): 3402 (m, br), 2928 (s), 1650 (m), 1490 (m), 702 (s) cm^{-1}; HRMS: calc. for $C_{13}H_{18}O$ (M^+) 190.1358, found 190.1353.

***4-Methyl-1-phenyl-5-hexen-1-ol* (16).** The same procedure was followed as that for **11** except that **3** (153 mg, 0.800 mmol) was added to LDBB and benzaldehyde (111 μL, 1.1 mmol) was used as the electrophile. Flash chromatography (3% AcOEt / hexanes) gave recovered DBB and the titled product, which was an approximately 1:1 mixture of diastereomers, as a pale yellow oil, 43.8 mg (29%). ^{1}H NMR ($CDCl_3$): δ 7.38 -7.24 (m, 5 H, Ph), 5.65 (m, 1 H, =CH), 5.00 - 4.89 (m, 2 H, $=CH_2$), 4.65 (m, 1 H, C*H*OH), 2.12-1.18 (m, 6 H), 0.99 (d, J = 6.7 Hz, 3 H, CH_3). ^{13}C NMR ($CDCl_3$): δ 144.9, 144.9, 144.4, 128.4, 127.5, 125.9, 112.9, 74.8, 74.7, 37.8, 37.8, 36.8, 32.7, 32.6, 20.3. IR (neat, NaCl): 3358 (m, br), 2928 (s), 1645 (m), 1454 (s), 910 (s), 700 (s) cm^{-1}. CI MS using ammonia: $C_{13}H_{18}O$ (M^+) 208.

***2,4,4,7-Tetramethyl-7-octen-3-ol* (17).** The same procedure was followed as that for **10** except that **9a** (225 mg, 1.01 mmol) instead of **2** was added to LDBB. Flash chromatography (3% AcOEt / hexanes) provided the titled product as a yellow oil, 167 mg, 88%. ^{1}H NMR ($CDCl_3$): δ 4.68 (s, 2 H, $=CH_2$), 3.19 (d,

J = 2.1 Hz, 1 H, C*H*OH), 1.96 (m, 2 H, allylic), 1.73 (s, 3 H, allylic CH_3), 1.55 - 1.18 (m, 4 H), 1.01 - 0.90 (m, 12 H, CH_3); ^{13}C NMR ($CDCl_3$): δ 146.7, 109.3, 82.0, 38.2, 37.8, 32.1, 28.4, 23.8, 23.8, 23.3, 22.7, 16.8. IR (neat, NaCl): 3481 (m, br), 2945 (s), 2797 (s), 1635 (m), 858 (s) cm^{-1}; CI using isobutane: $C_{12}H_{25}O$ $(M+1)^+$ 185.

***E-1-Cyclohexyl-1-(1,2-dimethylcyclobut-1-yl)methanol* (22) and *E,Z-1-Cyclohexyl-2-methyl-1,5-hexadiene* (23).** A solution of LDBB (2 mmol) in THF (6 mL), freshly prepared at 0 °C, was cooled to -78 °C and cannulated to a solution of **1** (300 mg, 1.00 mmol) in THF (3 mL) at -78 °C. The end of the addition was indicated when the dark blue color of of the LDBB solution did not disappear on contact with the solution. After the solution had been stirred for 10 min at -78 °C, cyclohexanecarboxaldehyde (230 μL, 1.05 mmol) was added via syringe. The reaction mixture was stirred at -78 °C for 30 min before another 2 mmol of LDBB was added via cannula. After being stirred at -78 °C for 30 min, the mixture was allowed to warm to 0 °C and it was quenched with 10 mL of water. The products were extracted with ether (3 x 15 mL) and the organic layer was dried over anhydrous $MgSO_4$. The solvents were removed under reduced pressure. Flash chromatography (pure pentane to 5% AcOEt / hexanes) provided **22** as a white solid, 67 mg (34%) and **23** as a colorless oil, 68 mg (38%). **22**: ^1H NMR ($CDCl_3$): δ 3.15 (d, J = 8.6 Hz, 1 H, C*H*OH), 2.24 (m, 1 H), 2.10 - 1.05 (m, 16 H), 1.00 (s, 3 H, CCH_3), 0.97 (d, J = 6.8Hz, 3 H, $CHCH_3$); ^{13}C NMR ($CDCl_3$): δ 86.1, 44.6, 41.3, 38.1, 31.4, 30.2, 29.3, 26.6, 26.3, 26.1, 25.0, 16.7, 13.1. HRMS: calc. for $C_{13}H_{24}O$ (M^+) 196.1827, found 196.1808; X-ray diffraction: Figure 1. **23**: Based on capillary GC, the *E* / *Z* isomers were formed in the ratio of 47 : 53. ^1H NMR ($CDCl_3$): δ 5.80 (m. 1 H, =CH), 5.05 -4.90 (m, 3 H, =CH and $=CH_2$), 2.18 - 2.00 (m, 5 H, allylic), 1.72 -1.49 (m, 4 H), 1.66 (d, J = 1.1 Hz, 1.59 H, CH_3), 1.60 (d, J = 1 Hz, 1.41 H, CH_3), 1.32 - 0.94 (m, 6 H); ^{13}C NMR ($CDCl_3$): δ 138.8, 132.5, 132.3, 131.4, 114.4, 114.2, 39.1, 37.0, 36.9, 33.7, 33.5, 32.7, 32.5, 31.6, 26.2, 23.4, 16.1. HRMS: calc. for $C_{13}H_{22}$ 178.1722, found 178.1723.

***3-Methyl-6-hepten-1-ol* (24).** 3-Methyl-3-phenylthio-6-hepten-1-ol (**4**, 236 mg, 1 mmol) was treated sequentially with a solution of *n*-BuLi (1.46 M in hexane, 0.72 mL, 1.05 mmol) and a solution of LDBB (~2 mmol) in THF at 0 °C. After 10 min of stirring at -78 °C, the mixture was quenched with 0.5 mL of methanol and allowed to warm to room temperature. Water (5 mL) was added and the mixture was extracted with ether (3 x 15 mL). The combined organic layer was dried over anhydrous $MgSO_4$ and concentrated. The product was isolated by flash chromatography as a pale yellow oil, 107 mg (85%). ^1H NMR ($CDCl_3$): δ 5.88 - 5.75 (m, 1 H, =CH), 5.05 - 4.92 (m, 2 H, $=CH_2$), 3.76 - 3.63 (m, 2 H, CH_2OH), 2.20 - 1.97 (m, 2 H, allylic), 1.68 - 1.53 (m, 2 H), 1.49 - 1.35 (m, 2 H), 1.30 (s, 1 H, OH), 1.25(m, 1 H), 0.93 (d, J = 6.5 Hz, 3 H, CH_3); ^{13}C NMR ($CDCl_3$): δ 139.0, 114.1, 60.7, 39.7, 36.2, 31.2, 29.0, 19.4. CI MS using isobutane $C_8H_{17}O$ $(M+1)^+$ 129.

When the above procedure was repeated except that the reaction mixture was warmed and stirred at -30 °C for 2 hr (with or without TMEDA being added) the same product (**24**) was found by ^1H NMR and ^{13}C NMR spectra after a methanolic quench.

***2,2,5-Trimethyl-5-hexenal* (25).** A solution of LDBB (1.36 mmol), freshly prepared in THF (6 mL) at 0 °C, was cooled to -78 °C and treated with **9a** (150 mg, 0.680 mmol) in THF (1 mL). The color of the solution changed from dark green to dark red immediately at the end of the addition. After being stirred for 15 min, the organolithium solution was cannulated to a precooled solution of ethyl formate (242 μL, 3.00 mmol) in 3 mL of THF (3 mL) at -78 °C. The mixture was stirred at -78 °C for 30 min before being quenched with 5 mL

of water. It was extracted with ether (3 x 10 mL) and the organic layer was dried over anhydrous $MgSO_4$. The solvent was removed by rotary evaporation. Flash chromatography (1% AcOEt / Hex) gave recovered DBB and the titled product as a pale yellow oil, 79 mg (83%). ^1H NMR: δ 9.47 (s, 1 H, CH=O), 4.72 (s, 1 H, vinyl), 4.69 (s, 1 H, vinyl), 1.94 - 1.89 (m, 2 H, allylic), 1.73 (s, 3 H, allylic CH_3), 1.67 - 1.59 (m, 2 H), 1.08 (s, 6 H, CH_3); the spectrum is identical to that reported.[28]

***2,2-Dimethyl-3-(2-methylenecyclopent-1-yl)propanal* (26).** The same procedure was followed as that for **25** except that **9c** (498 mg, 2.00 mmol) instead of **9a** was used. Flash chromatography (1% AcOEt / hexanes) provided 294 mg (88%) of the titled product as a colorless oil. ^1H NMR ($CDCl_3$): δ 9.50 (s, 1 H, O=CH), 4.89 (d, J = 2.0 Hz, 1 H, vinyl), 4.78 (d, J = 2.09 Hz, 1 H, vinyl), 2.42 -2.10 (m, 3 H, allylic), 1.90 - 1.14 (m, 6 H), 1.10 (s, 3 H, CH_3), 1.09 (s, 3 H, CH_3); ^{13}C NMR ($CDCl_3$): δ 205.5, 156.2, 104.4, 45.8, 42.6, 40.2, 34.4, 32.3, 24.0, 22.8, 20.6; IR (neat, NaCl): 2959 (s), 2869 (s), 1763 (m), 1756 (m), 1752 (s), 1729 (m), 1700 (m), 1697 (m), 1691 (m), 1685 (m), 1650 (m) cm^{-1}. HRMS: calc. for $C_{11}H18O$ 166.1357, found 166.1361.

***2,2-Dimethyl-5-methylidenecyclohexanol* (27).** To the solution of **25** (35 mg, 0.25 mmol) in dry dichloromethane (6 mL) at 0 °C, a stannic chloride solution (1.0 M in CH_2Cl_2, 250 μL, 0.250 mmol) was added dropwise. After 15 min stirring at 0 °C, the reaction mixture was treated with saturated ammonium chloride solution. The mixture was extracted with ether (3 x 10 mL), the combined organic layer was dried over Na_2SO_4, and the solvent was removed by rotary evaporation. Flash chromatography (5% AcOEt / hexanes) provided the titled product as a pale yellow oil, 34 mg (95%). ^1H NMR ($CDCl_3$): δ 4.74 (s, 1 H, vinyl), 4.69 (s, 1 H, vinyl), 3.38 (dd, J = 8.0 Hz and 3.9 Hz, 1 H, CHOH), 2.50 - 1.30 (m, 7 H), 1.00 (s, 3 H, CH_3), 0.95 (s, 3 H, CH_3); the spectrum is identical to that reported.

***trans-3,3a,4,5,6,7,-Hexahydro-5,5-dimethyl-2H-indene-6-ol* (28).**

Using dimethylaluminum chloride : To a solution of **26** (35 mg, 0.21 mmol) in dry CH_2Cl_2 (10 mL) at -78 °C, a solution of dimethylaluminum chloride (1.08 M in heptane, 200 μL, 0.210 mmol) was added dropwise. After being stirred at -78 °C for 10 min, the reaction mixture was quenched with a 5% solution of sodium bicarbonate and then allowed to warm to room temperature. The mixture was extracted with ether and the combined organic layer was dried over anhydrous Na_2SO_4. The solvent was removed by rotary evaporation. Flash chromatography (4% AcOEt / hexanes, silica gel was treated with 2% triethylamine) gave the titled product as colorless oil, 29 mg (79%). ^1H NMR ($CDCl_3$): δ 5.47 (s, 1 H, =CH), 3.44 (s, 1 H, C*H*OH), 2.55 (m, 1 H), 2.43 - 2.08 (m, 6 H), 1.54-1.02 (m, 3 H), 1.00 (s, 3 H, CH_3), 0.97(s, 3H, CH_3); ^{13}C NMR ($CDCl_3$): δ 141.1, 125.5, 75.4, 42.2, 41.2, 36.0, 32.9, 31.5, 30.8, 28.0, 24.5; IR (neat, NaCl): 3431 (m, br), 2925 (s), 2853 (s), 2335 (m) cm^{-1}; HRMS: calc. for $C_{11}H_{18}O$ (M^+) 166.1357, found 166.1324.

Using MABR: To a solution of 4-bromo-2, 6-di-*tert*-butylphenol (570 mg, 2 mmol) in dry dichloromethane (5 mL) at room temperature, trimethylaluminum (2 M in toluene 0.5 mL, 1 mmol) was added. Methane gas was evolved immediately. The resulting colorless solution was stirred at room temperature for 1 hr. The resulting MABR solution was cooled to -78 °C and **26** (83 mg, 0.50 mmol) in CH_2Cl_2 (2 mL) was added. The reaction mixture was stirred at -78 °C for 1 hr and warmed to -40 °C for 2 hr before 10 mL of saturated $NaHCO_3$ was added. The mixture was extracted with ether (3 x 15 mL), the combined organic layer was dried over Na_2SO_4, and the solvent was removed by rotary evaporation. Flash chromatography (3% AcOEt / hexanes) provided 47 mg (56%) of the product, which was the same compound as **28** according to ^1H and ^{13}C NMR spectra.

ACKNOWLEDGMENTS. We thank the National Science Foundation for financial support, Dr. Stephen Geib for the x-ray crystal analysis, Dr. Fu-Tyan Lin for performing the 2-dimensional NMR spectra, and Mr. Steven Norton for helpful suggestions and a heroic partial structure search of *Chemical Abstracts*.

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(*Received in USA* 8 *September* 1994; *accepted* 28 *September* 1994)