Regiochemical Convergence in the Reaction of Heterosubstituted Allylic Carbanions via Allylic Aluminum and Boron "Ate" Complexes[1]

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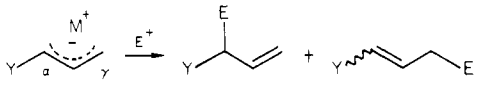
The regiochemistry in reactions of heterosubstituted allylic carbanions (1) is highly controlled via allylic aluminum or boron "ate" complexes which direct both carbonyl compounds and reactive halides to the α-position with high regioselectivity. For example, carbonyl compounds react with the oxygen- (3), sulfur- (12), selenium- (20), and silicon- (25) substituted allylic carbanions at the α-position via the ate complexes. Although the reactions of the ate complexes (2) with aldehydes generally produce a mixture of erythro and threo isomers, the aluminum ate complex of **3b** gives the erythro isomer (5) with very high stereoselectivity. This procedure is applied to the stereoselective synthesis of *exo*-brevicomin (9). With allylic halides, the oxygen- (**3a**) and sulfur- (12) substituted allylic carbanions again react at the α-position via the ate complexes. However, the coupling mode is entirely different; the α-α' coupling product (10) is obtained from **3a**, while the α-γ' coupling product (15) is produced from 12.

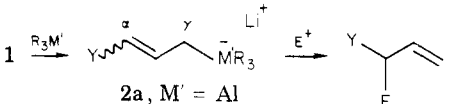
The question of regioselectivity in the reactions of 1-substituted allylic carbanions (1) with electrophiles, which give the α and γ products, has been of both theoretical and synthetic interest.[2] Such carbaions may serve as synthetic



1 α-product γ-product

Y = O, S, Se, N, P, B, Si, X, ...

equivalents to both carbonyl and homoenolate anions.[3] Regiochemical control of these ambident anions is crucial to the utility of these "reversed polarity" equivalents. The ratio of α to γ attack is dependent upon too many factors, including substituent atom (Y), counterion (M^+), solvent system, type of electrophiles (E^+), and steric effects. There seems to be as yet no general rule for predicting this regiochemistry.[4] We have been seeking a conceptually simple and synthetically useful method for controlling and predicting the regiochemistry. It appeared to us that trialkylaluminum or boron might react with 1 at the less substituted site (γ-position) regardless of the nature of substituent atom (Y) to produce the corresponding ate complex (2), and that the next step, carbon–carbon bond

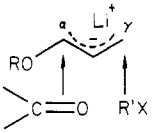


2a, M' = Al
2b, M' = B

formation, might take place at the α-position.[5] Consequently, we may be able to direct electrophiles to the α-position of 1 irrespective of substituents (Y). This proved to be practical as previously communicated;[1] triethylaluminum or trialkylboranes act as the regiocontrol element. We now report the full details of the previous work together with the stereochemical aspect of the reaction of 2 with aldehydes.[6]

Results and Discussion

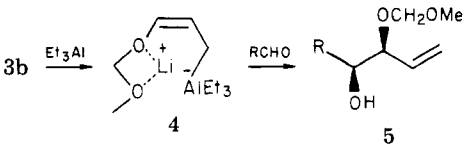
Oxygen-Substituted Allylic Carbanions (Y = O). The allyloxy carbanions (3) generally react with alkyl



3a, R = *i*-Pr
3b, R = $MeOCH_2$

halides at the γ position but react with carbonyl compounds at the α position.[7] Regiochemical convergence can be realized by using triethylaluminum and boron ate complexes of 3, and the results are summarized in Table I. Both carbonyl compounds and reactive halides go to the α position, while unfortunately a simple alkyl halide, such as *n*-butyl iodide or methyl iodide, does not react with the ate complex. The aluminum ate complex reacts more smoothly with carbonyl compounds than the corresponding boron ate complex, and generally the regioselectivity is extremely high (entries 1, 4, 6, 11–14).

Furthermore, stereochemical convergence can be realized in the reactions of **3b** (entries 11–14); the erythro isomer (5) is obtained stereoselectively.[8] The erythro/threo ratio



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(1) For preliminary reports on some aspects of the present study, see: (a) Yamamoto, Y.; Yatagai, H.; Maruyama, K. *J. Org. Chem.* **1980**, *45*, 195. (b) Yamamoto, Y.; Saito, Y.; Maruyama, K. *Tetrahedron Lett.* **1982**, *23*, 4597.

(2) For review articles, see: (a) Seebach, D.; Geiss, K.-H. "New Applications of Organometallic Reagents in Organic Synthesis"; Seyferth, D., Ed.; Elsevier: Amsterdam, 1976; p 1. (b) Ono, M. *J. Syn. Org. Chem. Jpn.* **1980**, *38*, 836. (c) Biellmann, J.-F.; Ducep, J.-B. *Org. React.* **1982**, *27*, 1.

(3) For example: Lever, Jr., O. W. *Tetrahedron* **1976**, *32*, 1943. Gröbel, B.-T.; Seebach, D. *Synthesis* **1977**, 357. Shono, T.; Nishiguchi, I.; Ohmizu, H. *J. Am. Chem. Soc.* **1977**, *99*, 5222. Trost, B. M.; Tamaru, Y. *Ibid.* **1977**, *99*, 3101. Nakamura, E.; Kuwajima, I. *Ibid.* **1977**, *99*, 5222. Evans, D. A.; Takacs, J. M.; Hurst, K. M. *Ibid.* **1979**, *101*, 371. A.-Chass, D.; Ehlinger, E.; Magnus, P. *J. Chem. Soc., Chem. Commun.* **1977**, 772.

(4) For a useful rule of thumb, see: Still, W. C.; Macdonald, T. L. *J. Org. Chem.* **1976**, *41*, 3620.

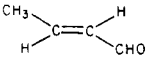
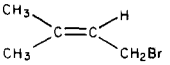
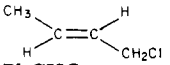
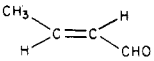
(5) This assumption is verified in the case of Y = C. Yamamoto, Y.; Yatagai, H.; Maruyama, K. *J. Am. Chem. Soc.* **1981**, *103*, 1969.

(6) We deal with allylic carbanions bearing a single heteroatom such as 1, and the reaction of allylic carbanions bearing two or more substituents will be reported in the future.

(7) (a) Evans, D. A.; Andrews, G. C.; Buckwalter, B. *J. Am. Chem. Soc.* **1974**, *96*, 5560. (b) Still, W. C.; Macdonald, T. L. *Ibid.* **1974**, *96*, 5561. (c) Still, W. C. *Tetrahedron Lett.* **1976**, 2115. (d) Hartmann, J.; Muthukrishnan, R.; Schlosser, M. *Helv. Chim. Acta* **1974**, *57*, 2261. (e) Trost, B. M.; Latimer, L. H. *J. Org. Chem.* **1977**, *42*, 3212. (f) Kozikowski, A. P.; Isobe, K. *Tetrahedron Lett.* **1979**, 833. (g) Hoppe, D.; Hanko, R.; Brönneke, A.; Lichtenberg, F. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 1024. (h) Hosomi, A.; Hashimoto, H.; Sakurai, H. *J. Org. Chem.* **1978**, *43*, 2251. (i) Kuwajima, I.; Kato, M. *J. Chem. Soc., Chem. Commun.* **1979**, 708. (j) Oopolzer, W.; Snowden, R. L.; Briner, P. H. *Helv. Chim. Acta* **1981**, *64*, 2022. (k) Yamaguchi, M.; Mukaiyama, T. *Chem. Lett.* **1982**, *237*.

0022-3263/84/1949-1096$01.50/0

Table I. Reaction of the Aluminum and Boron Ate Complexes of 3

entry	substituent (Y)	electrophile (E)	additive	ratio of products α:γ	total yield, %[a]
1	Me_2CHO (3a)	PhCHO	Et_3Al	>99:1	81
2			Et_3B	>99:1	80
3			none[b]	28:72	(95)
4			Et_3Al	~100:0	74
5			none	60:40	(90)
6			Et_3Al	~100:0	71
7			none	60:40	(74)
8			Bu_3B	81:19	66
9			none	40:60	(42)
10			Et_3Al	80:20	(80)
11	$MeOCH_2O$ (3b)	PhCHO	Et_3Al	~100:0	64
12		CH_3CH_2CHO	Et_3Al	~100:0	90
13		$CH_3(CH_2)_3CHO$	Et_3Al	~100:0	90
14			Et_3Al	~100:0	70

[a] Isolated yield (GLPC yield). [b] "None" indicates the normal reaction without the additive.

Table II. Reaction of the Aluminum and Boron Ate Complexes of 12

entry	electrophile (E)	additive	ratio of products α:γ	total yield, %[a]
1	$CH_3(CH_2)_2CHO$	Et_3Al	95:5	77
2		Et_3B	98:2	82
3		none[a]	43:57	(80)
4	$(CH_3)_2CHCHO$	Et_3Al	>99:1	75
5		Et_3B	94:6	75
6		none	44:56	(85)
7	$CH_3CH{=}CHCHO$	Et_3Al	94:6	77
8		none	35:65	(75)
9	PhCHO	Et_3B	98:2	82
10		*n*-Bu-9-BBN	>99:1	70
11		none	28:72	(80)
12		Et_3Al	92:8	77
13		Et_3B	72:28	80
14		none	42:58	(85)
15	$CH_3(CH_2)_5C(=O)CH_3$	Et_3Al	94:6	76
16		Et_3B	47:53	70
17		none	32:68	(78)
18	$PhC(=O)CH_3$	Et_3Al	95:5	74
19		Et_3B	45:55	(82)
20		none	29:71	(85)
21	$CH_3CH{=}CHCH_2Cl$	Et_3Al	~100:0 (76:24)[b]	78
22	$CH_3CH{=}CHCH_2Br$	Et_3Al	~100:0 (72:28)[b]	80
23	$CH_3CH{=}CHCH_2Cl$	*n*-Bu_3B	54:46 (51:3)[b] (15:31)[c]	(55)
24	$CH_3CH{=}CHCH_2Br$	*n*-Bu_3B	61:39 (59:2)[b] (18:21)[c]	(85)
25		*n*-Bu-9-BBN	~100:0 (100:0)[b]	77
26	$(CH_3)_2C{=}CHCH_2Cl$	*n*-Bu_3B	~100:0 (92:8)[b]	48
27		*n*-Bu-9-BBN	~100:0 (93:7)[b]	68
28	$(CH_3)_2C{=}CHCH_2Br$	*n*-Bu_3B	~100:0 (96:4)[b]	78
29		none	55:45 (0:100)[b] (10:90)[c]	70
30	$CH_2{=}CHCH_2Br$	*n*-Bu-9-BBN	89:11	52

[a] See footnotes to Table I. [b] (α-γ′:α-α′). [c] (γ-γ′:γ-α′).

from benzaldehyde is 92/8, and that from the other aldehydes is ~100/~0. A similar regio- and stereoselective condensation is also observed by Yamaguchi and Mukaiyama in the reaction of triethylaluminum até complex of lithiated 2-[2-allyloxy]benzimidazol.[7] On the other hand, the reactions of **3a** produce a mixture of threo and erythro isomers (entries 1 and 6); the ratio of two isomers is approximately 3.5:6.5.[9] Presumably, two oxygen atoms of **3b** strongly coordinate to lithium cation as depicted in **4**, so that the double bond is forced to take the cis geometry. Therefore, the erythro isomer is produced stereoselectively via a six-membered chair transition state.[10] Such coordination might be weakened or prevented in the ate complex derived from **3a**, owing to the steric effect of the isopropyl group and to a single oxygen atom. Conse-

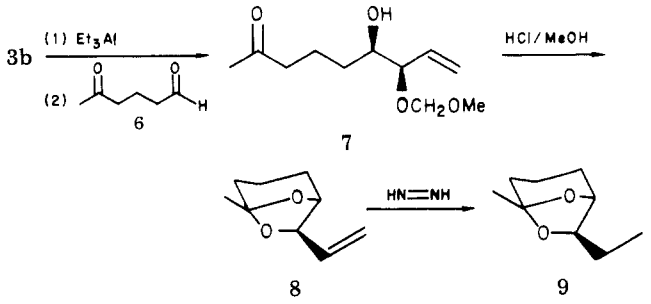
(8) Yamamoto, Y.; Saito, Y.; Maruyama, K. *Tetrahedron Lett.* **1982**, 4959.

(9) The ratio was determined by GLPC analysis, and it was assumed that the major isomer was erythro (see Experimental Section).

(10) For reviews on the transition state geometry in the reaction of allylic metal derivatives, see: (a) Bartlett, P. A. *Tetrahedron* **1980**, *36*, 2. (b) Yamamoto, Y.; Maruyama, K. *Heterocycles* **1982**, *18*, 357. (c) Hoffmann, R. W. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 555. (d) Pelter, A. *Chem. Soc. Rev.* **1982**, *11*, 191.

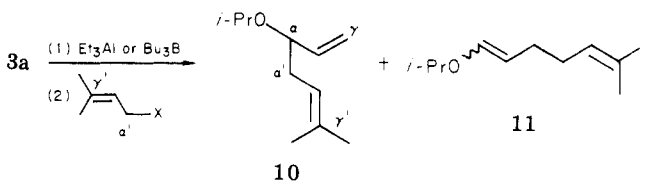
quently, the geometry of the double bond would not be homogeneous, resulting in loss of stereoselectivity.

We applied the regio- and stereochemical convergence via **3b** to the synthesis of *exo*-brevicomin (**9**).[11] Treatment of **3b** with Et_3Al at −78 °C, followed by the addition of the keto aldehyde (**6**) produced **7** in 82% yield (erythro/threo



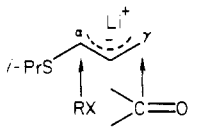
= 89/11). Treatment with aqueous HCl in methanol gave **8** in 90% yield. Reduction with diimide produced **9** in 65% yield.

In the α product derived from prenyl halides, exclusive coupling between the α position of **3a** and the α' position of prenyl halides is observed (**10**) (entries 8 and 10). On



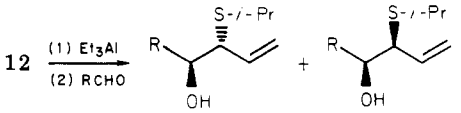
the contrary, the similar reaction via the lithium carbanion itself (**3a**) produces a mixture of regioisomers (**10** and **11**), presumably owing to the metal–halogen exchange.

Sulfur-Substituted Allylic Carbanion (Y = S). The (alkylthio)allyl carbanion (**12**) reacts with alkyl halides at the α position, but reacts with carbonyl compounds at the γ position.[12] Here again, the triethylaluminum or trialkylboron ate complexes of **12** react with carbonyl com-



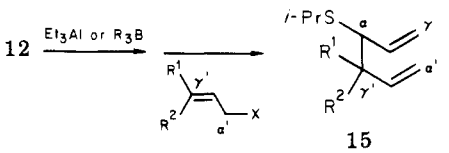
pounds and allylic halides at the α position. The results are summarized in Table II. In the reactions with carbonyl compounds, very high regioselectivity was achieved by using the aluminum method. On the other hand, the α regioselectivity decreases with ketones if the boron method is used (entries 13, 16, and 19). This difference appears largely steric in origin and appears to lie in the reaction step of the ate complex rather than its formation step. The longer C–Al bond should exert less steric hindrance and the more ionic nature of the C–Al bond should facilitate the condensation with carbonyl compounds.[13] Use of $^1/_2$ or $^2/_3$ equiv amounts of Et_3Al caused a marked decrease of the regioselectivity, and the use of excess amounts of the additive did not exert any significant influence upon the reaction course.

The stereoselectivity of the α adduct is low; a mixture of threo (**13**) and erythro (**14**) isomers is obtained in a ratio of 4.5:5.5. Presumably, the geometry of the double bond



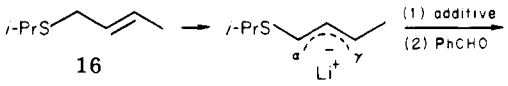
in the ate complex of **12** is not homogeneous. The cis geometry, as in **3b**, would not be expected because of the low coordination ability of sulfur atom toward lithium cation and the steric effect of the isopropyl group.

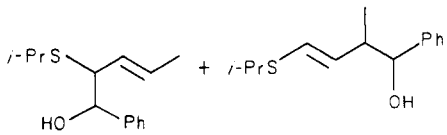
With allylic halides, the α–γ' coupling product (**15**) is



obtained either predominantly or exclusively (entries 21, 22, 25–28).[14] This regioselectivity is entirely different from that of the oxygen substituted ate complex in which the α–α' coupling product (**10**) is obtained. The reason is not clear at the present time. The reaction of the lithio anion gives a mixture of the α–α' and γ–α' coupling products (entry 29), and in any event the allylic halides react with the carbanion (**12**) at the α' position. The α–γ' selectivity via the ate complexes is higher with the *n*-Bu-9-BBN complex than with the triethylaluminum or with the tri-*n*-butylborane complex.

We also examined the applicability of our method to a chain elongation system (**16**). Unfortunately, neither the





additive	18	19	total yield, %
Et_3Al	44%	56%	65
Et_3B	59%	41%	58
none	8%	92%	70

aluminum nor the boron method could direct benzaldehyde to the α position with high regioselectivity. Since both the α and γ positions of **17** are secondary carbons,

(11) For the previous synthesis of racemic material: (a) Bellas, T. E.; Brownlee, R. G.; Silverstein, R. M. *Tetrahedron* **1969**, *25*, 5149. (b) Wasserman, H. H.; Barber, E. H. *J. Am. Chem. Soc.* **1969**, *91*, 3674. (c) Hoffmann, R. W.; Kemper, B. *Tetrahedron Lett.* **1982**, 845. (d) Wuts, P. G. M.; Bigelow, S. S. *Synth. Commun.* **1982**, 779. For the synthesis of chiral material: (e) Mori, K. *Tetrahedron* **1974**, *30*, 4223. (f) Sherk, A. E.; Fraser-Reid, B. *J. Org. Chem.* **1982**, *47*, 932. (g) Johnston, B. D.; Oehlschlager, A. C. *Ibid.* **1982**, *47*, 5384. (h) Masaki, Y.; Nagata, K.; Serizawa, Y.; Kaji, K. *Tetrahedron Lett.* **1982**, 5553. (i) Matteson, D. S.; Sadhu, K. M. *J. Am. Chem. Soc.* **1983**, *105*, 2077.

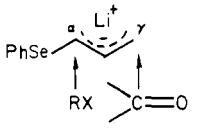
(12) (a) Biellmann, J.-F.; Ducep, J. B. *Tetrahedron Lett.* **1968**, 5629. (b) Oshima, H.; Yamamoto, H.; Nozaki, H. *J. Am. Chem. Soc.* **1973**, *95*, 7926. (c) Atlani, P. M.; Biellmann, J.-F.; Dube, S.; Vicens, J. J. *Tetrahedron Lett.* **1974**, 2665. (d) Torii, S.; Tanaka, H.; Tomotaki, Y. *Chem. Lett.* **1974**, 1541. (e) Geiss, K.; Seuring, B.; Pieter, R.; Seebach, D. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 479. (f) Evans, D. A.; Andrews, G. C. *Acc. Chem. Res.* **1974**, *7*, 147. (g) Taguchi, T.; Okamura, H.; Takei, H. *Chem. Lett.* **1975**, 853. (h) Cohen, T.; Bennett, D. A.; Mura, A. J. *J. Org. Chem.* **1976**, *41*, 2506. (i) Seebach, D.; Geiss, K. H.; Pohmakotr, M. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 437. (j) Pohmakotr, M.; Seebach, D. *Tetrahedron Lett.* **1979**, 2271. (k) Tanaka, K.; Terauchi, M.; Kaji, A. *Chem. Lett.* **1981**, 315. (l) Ikeda, Y.; Furuta, K.; Meguriya, N.; Ikeda, N.; Yamamoto, H. *J. Am. Chem. Soc.* **1982**, *104*, 7663.

(13) Negishi, E. *J. Organomet. Chem.* **1976**, *108*, 281.

(14) Yamamoto, Y.; Yatagai, H.; Maruyamam, K. *J. Chem. Soc., Chem. Commun.* **1979**, 157.

Et_3Al or Et_3B may coordinate to both positions at almost equal opportunity, resulting in loss of the regioselectivity.

Selenium-Substituted Allylic Carbanion (Y = Se). The lithio anion of allyl phenyl selenide generally reacts with carbonyl compounds at the γ position, while it reacts with alkyl halides at the α position.[15] The reversed regioselectivity is relized by using the triethylaluminum ate complexes and the results are summarized in Table III. With benzaldehyde and acetophenone, the degree of regiochemical convergence is not so high, presumably owing to the steric effect of the carbonyl group. Ordinary organic halides and trimethylsilyl chloride did not react with the aluminum ate complex of **20**.



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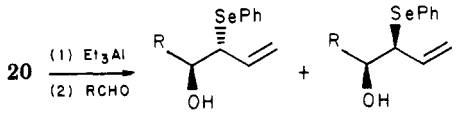
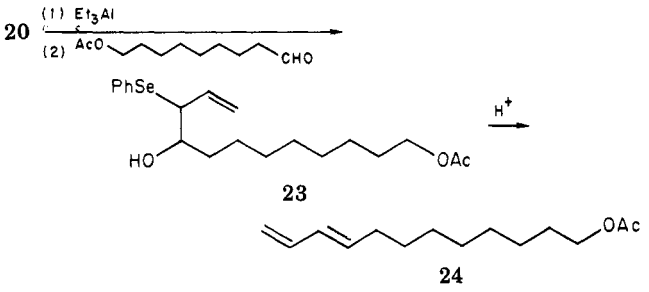
Concerning the stereoselectivity, the threo isomer (**21**)



21 **22**

is produced predominantly. The threo preference may be due to the trans geometry of the intermediate ate complex. The β-elimination reaction of β-hydroxy selenides using *p*-toluenesulfonic acid proceeds in a trans fashion;[16] the (*E*)-1,3-diene is obtained from **21** while the (*Z*)-1,3-diene is obtained from **22**. We applied this method to the synthesis of 9,11-dodecadien-1-yl acetate, a pheromone of *Diparopsis castanea*.[17] Treatment of the ate complex of **20** with 9-oxonon-1-yl acetate produced **23** in 70% yield.



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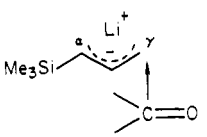
The β-elimination of **23** produced **24** in 77% yield; *E*:*Z* = 84:16. Interestingly, the maximum sex attraction occurs at the level of 88–93% *E* isomer, and not at the level of 100% *E* isomer.[18]

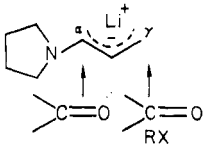
Silicon-Substituted Allylic Carbanion (Y = Si). The lithio anion of allyltrimethylsilane (**25**) usually reacts



25

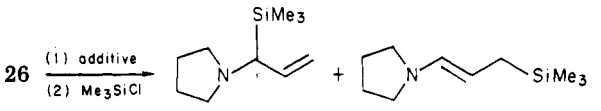
with carbonyl compounds at the γ position.[19] The γ selectivity can be converted to the α selectivity by changing the counterion to magnesium (II).[20] The aluminum method is again applicable to **25** and the results are summarized in Table III. Here again, the degree of the α selectivity decreases with benzaldehyde, and the γ product is obtained predominantly with acetophenone even when the aluminum ate complex is used. The stereoselectivity is low; a mixture of the erythro and threo isomers is produced in a ratio of 5.5:4.5.

Nitrogen-Substituted Allylic Carbanion (Y = N). The lithio anion (**26**) reacts with carbonyl compounds both



26

at the α and γ positions and generally the regioselectivity is quite low while it reacts with alkyl halides and trimethylsilyl chloride at the γ position.[21] Treatment of **26** with Et_3Al (or Et_3B) followed by the addition of Me_3SiCl gave the α adduct (**27**) along with small amounts of the γ adduct (**28**). Other alkyl halides such as methyl iodide



additive	27	28	total yield, %
Et_3Al	92%	8%	50
Et_3B	83%	17%	42
none	2% (5)[21]	98% (95)[21]	55

and *n*-butyl iodide did not react with the ate complexes of **26**. Furthermore, the reaction with carbonyl compounds resulted in a mixture of several products.

Experimental Section

General information concerning instrumentation and materials is described previously.[5] Organometallic reagents such as triethylaluminum, trialkylboranes, and alkyllithiums were purchased from Aldrich Chemical Co.

Oxygen-Substituted Allylic Carbanions. Allyl isopropyl ether was prepared by the Williamson ether synthesis from allyl bromide and sodium isopropoxide, bp 75–78 °C (lit.[22] 82–83 °C). 1-(Methoxymethoxy)-2-propene was prepared in a similar manner. To a solution of ether-washed sodium hydride (9.2 g of a 50% slurry in oil, 0.2 mol) suspended in 50 mL of dry THF was added 11.6 g (0.2 mol) of 2-propen-1-ol, and the resulting mixture was refluxed for 6 h. The solvent was removed under reduced pressure, and then the mixture was kept under nitrogen atmosphere. A solution of 16.1 g of chloromethyl methyl ether dissolved in 50 mL of dry ether was added. The resulting mixture was stirred for 12 h at room temperature and then poured into water overlaid with ether. The organic layer was separated and dried over anhydrous $MgSO_4$. The product was distilled at 80–85 °C to yield 19.3 g (95%) of the MOM allyl ether: ^1H NMR (CCl_4) δ 3.30 (s, 3), 3.90–4.10 (m, 2), 4.52 (s, 2), 4.92–5.38 (m, 2), 5.62–6.10 (m, 1).

Reactions of 3a. General Procedure. To a solution of 0.12 mL (1 mmol) of allyl isopropyl ether dissolved in 6 mL of dry ether

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Table III. Reaction of the Aluminum Ate Complexes of 20 and 25

carbanion	carbonyl compd	additive	ratio of products α(threo, erythro):γ	total yield, %[a]
20	CH_3CH_2CHO	Et_3Al	(81, 19)[b]:0	90
		none[a]	12[c]:88	91
	$(CH_3)_2CHCHO$	Et_3Al	(73, 27):0	74
		none	0:~100	64
	PhCHO	Et_3Al	(66, 12):22	79
		none	18:82	75
	$PhC(=O)CH_3$	Et_3Al	64:36	91
		none[d]	15:85	
25	$CH_3(CH_2)_2CHO$	Et_3Al	94:6	50
		none	10:90	55
	$(CH_3)_2CHCHO$	Et_3Al	(50, 35):15	50
		none	10:90	52
	PhCHO	Et_3Al	(43, 37):20	51
		none	17:83	(60)
	$PhC(=O)CH_3$	Et_3Al	24:76	55
		none	0:~100	(75)

[a] See footnotes to Table I. [b] The ratio of the threo to erythro isomer in the α adduct. [c] The ratio of threo/erythro was not determined. [d] The data from Reich, H. J. *J. Org. Chem.* 1975, *40*, 2570.

was added 1 equiv of *sec*-butyllithium in cyclohexane at −78 °C. The mixture was stirred for 30 min at −78 °C and then the additive (1 equiv of Et_3Al, Et_3B, or *n*-Bu_3B) was added. Subsequently, 1 equiv of the electrophile was added at −78 °C, and the resulting mixture was allowed to warm up to room temperature. The reaction was quenched at 0 °C by slow addition of water except for the case of using a borane derivative as an additive, in which the recovered borane was oxidized with H_2O_2–NaOH. The organic layer was separated, and the aqueous layer was extracted twice with ether. The combined organic layer was dried over anhydrous $MgSO_4$. The product ratio was determined by GLPC analysis (DC 550, 5%, 3 m) and/or ^1H NMR spectroscopy. Isolation of products was carried out by simple distillation through a Kugelrohr apparatus.

1-Phenyl-2-isopropoxy-3-butenol: bp 110–114 °C (2 mmHg); IR (CCl_4) 3560, 3480, 1635, 1600, 1120, 1040, 985, 920 cm^{-1}; MS, *m/e* (M^+) 206; ^1H NMR (CCl_4) of the erythro isomer δ 1.05 (dd, 6, *J* = 6.5 and 8.5 Hz), 3.20 (br s, 1), 3.40–3.90 (m, 2), 4.28 (d, 1, *J* = 8.0 Hz), 4.98 (dd, 1, *J* = 18.0 and 2.0 Hz), 5.02 (dd, 1, *J* = 10.0 and 2.0 Hz), 5.28–5.80 (m, 1), 7.20 (br s, 5); ^1H NMR of the threo isomer δ 1.04 (dd, 6, *J* = 6.5 and 8.5 Hz), 2.30 (br s, 1), 3.54 (septet, 1, *J* = 6.5 Hz), 3.83 (dd, 1, *J* = 4.0 and 7.0 Hz), 4.59 (d, 1, *J* = 4.0 Hz), 5.01 (dd, 1, *J* = 20.0 and 2.0 Hz), 5.06 (dd, 1, *J* = 7.0 and 2.0 Hz), 5.59 (ddd, 1, *J* = 7.0, 7.0, and 20.0 Hz), 7.19 (s, 5). Anal. ($C_{13}H_{18}O_2$) C, H. The structure determination of the erythro/threo isomer was based on the coupling constant of PhC*H*O (*J* = 8.0 Hz at 4.28 and *J* = 4.0 Hz at 4.59), since the hydrogen bond between two oxygen atoms presumably forces the compound to take a five membered cyclic structure and hence $J_{erythro} > J_{threo}$ of PhC*H*O is expected.[23]

1-(1-Isopropoxy-2-propen-1-yl)cyclohexanol: bp 110 °C (2 mmHg); IR (CCl_4) 3570, 1635, 1120, 1040, 990, 920 cm^{-1}; MS, *m/e* (M^+) 198; ^1H NMR (CCl_4) δ 1.07 (d, 3, *J* = 6 Hz), 1.09 (d, 3, *J* = 6 Hz), 1.50 (br s, 10), 1.92 (s, 1), 3.40 (d, 1, *J* = 8 Hz), 3.60 (quintet, 1, *J* = 6 Hz), 5.02–5.30 (m, 2), 5.58–5.94 (m, 1). Anal. ($C_{12}H_{22}O_2$) C, H.

3-Isopropoxy-4-hydroxy-1,5-heptadiene: bp 98–100 °C (2 mm Hg); IR (CCl_4) 3570, 1635, 1120, 1040, 990, 960, 920 cm^{-1}; MS, *m/e* (M^+) 170; ^1H NMR (CCl_4) δ 1.15 (d, 6, *J* = 6 Hz), 1.74 (d, 3, *J* = 5 Hz), 2.52 (br s, 1), 3.44–3.80 (m, 3), 5.10–5.28 (m, 2), 5.40–5.90 (m, 3). Anal. ($C_{10}H_{18}O_2$) C, H. Diastereomers could not be distinguished by the ^1H NMR spectra, but the GLPC analysis indicated two peaks in a ratio of 5:5 in the region of the α product. The minor γ products in the above reactions were not isolated, but the retention time in GLPC was compared with that of the products of the reference experiment (entries 3, 5, and 7).

3-Isopropoxy-6-methyl-1,5-heptadiene: bp 80–85 °C (2 mmHg); ^1H NMR (CCl_4) δ 1.07 (d, 3, *J* = 6 Hz), 1.09 (d, 3, *J* = 6 Hz), 1.62 (s, 3), 1.70 (s, 3), 2.14 (m, 2), 3.64 (m, 2), 5.02–5.22 (m, 2), 5.52–5.86 (m, 1); IR (CCl_4) 1640, 1125, 1060, 990, 920 cm^{-1}; MS, *m/e* (M^+) 168. Anal. ($C_{11}H_{20}O$) C, H.

1-Isopropoxy-6-methyl-1,5-heptadiene: bp 80–85 °C (2 mmHg); ^1H NMR (CCl_4) δ 1.11 (d, 6, *J* = 6 Hz), 1.60 (s, 3), 1.71 (s, 3), 1.90–2.10 (m, 4), 3.60 (m, 1), 5.16 (m, 2), 5.87 (d, 1, *J* = 6 Hz); IR (CCl_4) 1380, 1250, 1140, 860 cm^{-1}; MS, *m/e* (M^+) 168. Anal. ($C_{11}H_{20}O$) C, H. These regioisomers (**10** and **11**) were isolated through a preparative GLPC. The absence of other regioisomers, such as the α–γ′ and γ–γ′ coupling products, was revealed by the GLPC analysis of products from the reference experiment.

Reactions of 3b. General Procedure. To a solution of 0.11 mL of the MOM allyl ether dissolved in 5 mL of dry THF was added 1 equiv of *n*-butyllithium in hexane at −30 °C. The mixture was stirred for 1 h at this temperature and then 1 equiv of Et_3Al was added at −78 °C. Subsequently, 1 equiv of the aldehyde was added and the resulting mixture was allowed to warm up to room temperature. The workup was carried out as described above. The diastereomers were separated via a column of silica gel with hexane–ether (20:1) as an eluant.

1-Phenyl-2-(methoxymethoxy)-3-butenol: bp 110–115 °C (2 mmHg); IR (CCl_4) 3560, 1635, 1600, 1120, 1040, 985, 920 cm^{-1}; MS, *m/e* (M^+) 208; ^1H NMR ($CDCl_3$) of the erythro isomer δ 3.23 (s, 3), 3.60 (br s, 1), 4.06 (dd, 1, *J* = 7.0 and 7.0 Hz), 4.40–4.76 (m, 3), 5.08 (dd, 1, *J* = 19.0 and 3.0 Hz), 5.12 (dd, 1, *J* = 11.0 and 3.0 Hz), 5.58 (ddd, 1, *J* = 7.0, 11.0, and 19.0 Hz), 7.24 (s, 5); the ^1H NMR of the threo isomer δ 3.08 (s, 3), 3.60 (br s, 1), 3.80–4.20 (m, 1), 4.30–4.70 (m, 3), 4.96–5.28 (m, 2), 5.98–6.40 (m, 1), 7.24 (s, 5). Anal. ($C_{12}H_{16}O_3$) C, H. The threo isomer was isolated from the reaction of the Cp_2Zr derivative of **3b**.[8] The structure of both isomers was determined as follows. The MOM group was removed by treatment with HCl/MeOH under reflux, and the resulting diol was converted into the corresponding epoxide by the literature procedure.[24] The erythro isomer gave *cis*-1,2-epoxy-1-phenyl-3-butene, and the threo isomer produced the trans epoxide.[24]

***erythro*-4-Hydroxy-3-(methoxymethoxy)-1-hexene**: bp 90–95 °C (2 mmHg); ^1H NMR ($CDCl_3$) δ 0.95 (t, 3, *J* = 7.0 Hz), 1.40 (qd, 2, *J* = 7.0 and 8.0 Hz), 2.34 (br s, 1), 3.34 (s, 3), 3.75 (dd, 1, *J* = 7.0 and 7.0 Hz), 4.32–4.70 (m, 3), 5.20 (dd, 1, *J* = 15.5 and 3.0 Hz), 5.24 (dd, 1, *J* = 10.0 and 3.0 Hz), 5.40–5.80 (m, 1); IR (CCl_4) 3570, 1635, 1120, 1040, 990, 920 cm^{-1}; MS, *m/e* (M^+) 160. Anal. ($C_8H_{16}O_3$) C, H.

***erythro*-4-Hydroxy-3-(methoxymethoxy)-1-octene**: bp 95–98 °C (2 mmHg); ^1H NMR ($CDCl_3$) δ 0.80–1.80 (m, 9), 3.36 (s, 3), 3.50–3.80 (m, 2), 4.00 (br s, 1), 4.40–4.80 (m, 2), 5.30 (dd, 1, *J* = 16.0 and 1.0 Hz), 5.34 (dd, 1, *J* = 10.0 and 1.0 Hz), 5.66 (ddd, 1, *J* = 10.0, 10.0, and 16.0 Hz); IR (CCl_4) 3570, 1635, 1120, 1040, 99 0, 920 cm^{-1}; MS, *m/e* (M^+) 188. Anal. ($C_{10}H_{20}O_3$) C, H.

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(24) Paladini, J.-C.; Chuche, J. *Bull. Soc. Chim. Fr.* **1974**, 187.

***erythro*-4-Hydroxy-3-(methoxymethoxy)-1,5-heptadiene**: bp 90–95 °C (2 mmHg); ^{1}H NMR ($CDCl_3$) δ 1.80 (d, 3, J = 8.0 Hz), 3.14 (br s, 1), 3.35 (s, 3), 3.80–4.10 (m, 2), 4.40–4.70 (m, 2), 4.92–5.36 (m, 2), 5.36–6.20 (m, 3); IR (CCl_4) 3570, 1635, 1110, 1030, 990, 960, 915 cm^{-1}; MS, m/e (M^+) 172. Anal. ($C_9H_{16}O_3$) C, H. The threo isomers of the above three adducts were prepared through the Cp_2Zr derivative of **3b**[8] and subjected to GLPC analysis.

Synthesis of 9. The keto aldehyde **6** was prepared by the known method:[11c] ^{1}H NMR (CCl_4) δ 1.80 (septet, 2, J = 7.0 Hz), 2.04 (s, 3), 2.42 (t, 4, J = 7.0 Hz), 9.56 (br s, 1); IR (CCl_4) 1720, 1730 cm^{-1}. To a solution of 510 mg (5 mmol) of the MOM ether dissolved in 20 mL of dry THF was added 4.0 mL of *n*-butyllithium (1.26 M in hexane) at −30 °C. The mixture was stirred for 1 h at −30 °C, and 0.5 mL (6 mmol) of Et_3Al (15% solution in hexane) was added at −78 °C. Subsequently, 570 mg of **6** (5 mmol) was added at this temperature. After the usual workup procedure, the product was filtered through a short column of silica gel. ^{1}H NMR spectra indicated two singlet signals at δ 3.26 and 3.32 in a ratio of 11:89. Further purification via silica gel column chromatography using hexane–ether (20:1) as an eluant gave 0.886 g of **7** (82%): ^{1}H NMR (CCl_4) δ 1.00–1.80 (m, 4), 2.08 (s, 3), 2.40 (m, 2), 3.32 (s, 3), 3.50 (br s, 1), 3.84 (td, 1, J = 7.0 and 7.0 Hz), 4.40–4.74 (m, 3), 5.24 (dd, 1, J = 16.5 and 2.0 Hz), 5.28 (dd, 1, J = 7.0 and 2.0 Hz), 5.60 (ddd, 1, J = 7.0, 7.0, and 16.5 Hz). The material corresponding to δ 3.26 could not be isolated via the second chromatography. Without further purification, **7** (886 mg, 4.1 mmol) was treated with 3 mL of concentrated HCl in 20 mL of MeOH. The mixture was refluxed for 30 min, and the resulting mixture was poured into water overlaid with ether. The organic layer was separated, and the aqueous layer was extracted several times with ether. The combined organic layer was washed with aqueous Na_2CO_3 solution and dried over anhydrous $MgSO_4$. Purification through silica gel column chromatography gave 0.568 g of **8** (90%): ^{1}H NMR (CCl_4) δ 1.35 (s, 3), 1.40–1.90 (m, 6), 4.03 (br s, 1), 4.24 (d, 1, J = 6.5 Hz), 4.96 (ddd, 1, J = 9.5, 2.0, and 1.0 Hz), 5.08 (ddd, 1 J = 16.0, 2.0, and 1.0 Hz), 5.69 (ddd, 1, J = 16.0, 9.5, and 6.5 Hz); IR (CCl_4) 1380, 1185, 1170, 1115, 1100, 1040, 985, 920 cm^{-1}. To a solution of 1 g of KOO-C—N=N—COOK dissolved in 5 mL of CH_3CN was added a solution of 130 mg of **8** dissolved in 2 mL of CH_3CN at −20 °C, and then 0.2 mL of acetic acid was added at −20 °C. The mixture was stirred for 1 h at 0 °C. The resulting mixture was poured into water overlaid with ether. The organic layer was separated and the aqueous layer was extracted twice with ether. The combined organic layer was washed with aqueous Na_2CO_3 solution and dried over anhydrous $MgSO_4$. Evaporation of solvent and filtration through silica gel column chromatography gave 86 mg of **9** (65%): ^{1}H NMR (CCl_4)[11] δ 0.87 (t, 3, J = 7.0 Hz), 1.28 (s, 3), 1.10–2.00 (m, 8), 3.76 (t, 1, J = 6.0 Hz), 3.96 (br s, 1); MS, m/e (M^+) 156.

Sulfur-Substituted Allylic Carbanion. Allyl isopropyl sulfide was prepared from sodium isopropylmercaptide and allyl chloride.[12b] To a solution of 8.0 g (0.2 mol) of NaOH dissolved in methanol (100 mL) was added 15.2 g (0.2 mol) of 2-propanethiol at 0 °C. The mixture was stirred for 30 min, and then 15.3 g of allyl chloride was added. The resulting mixture was stirred for 1 h. Sodium chloride precipitated and was filtered off, and the mother liquor was concentrated. The mixture was poured into water overlaid with ether and the organic layer was separated, dried over $MgSO_4$, concentrated, and distilled: bp 120–122 °C, 90% (20.9 g); ^{1}H NMR (CCl_4) δ 1.23 (d, 6, J = 7 Hz), 2.80 (quintet, 1, J = 7 Hz), 3.10 (d, 2, J = 7 Hz), 4.92–5.12 (m, 2), 5.56–6.00 (m, 1).

Reactions of 12. General Procedure. To a solution of 0.13 mL (1 mmol) of allyl isopropyl sulfide dissolved in 3 mL of dry ether was added 1 equiv of *sec*-butyllithium at −78 °C. The mixture was stirred for 30 min at −30 °C, and 1 equiv of the additive was added at −78 °C. Subsequently, 1 equiv of the electrophile was added at −78 °C. The resulting mixture was allowed to warm up to room temperature and quenched with water at 0 °C, except for the case of using the borane derivative as an additive, in which the recovered borane was oxidized with NaO-H–H_2O_2. The organic layer was separated and the aqueous layer was extracted with ether. The combined organic layer was dried over $MgSO_4$, concentrated, and distilled. The product was analyzed by using ^{1}H NMR spectroscopy and GLPC (DC 550, 5%, 3m).

3-(Isopropylthio)-4-hydroxyheptene: bp 110–115 °C (2 mmHg); ^{1}H NMR (CCl_4) δ 0.94 (br s, 3), 1.24 (d, 3, J = 8 Hz), 1.26 (d, 3, J = 8 Hz), 1.44 (br s, 4), 2.24 and 2.48 (br s in a ratio of 1:1, 1), 2.84 (m, 1), 3.04–3.50 (m, 2), 4.96–5.20 (m, 2), 5.55–5.96 (m, 1); IR (CCl_4) 3480, 1625, 1460, 1380, 1240, 990, 910 cm^{-1}; MS, m/e (M^+) 188. Anal. ($C_{10}H_{20}OS$) C, H. The diastereoisomers were not separated, but the GLPC examination revealed that the ratio of the threo to erythro isomer was 1:1. This ratio corresponds to the area ratio of ^{1}H NMR signals at δ 2.24 and 2.48 and at δ 1.24 and 1.26.

3-(Isopropylthio)-4-hydroxy-5-methylhexene: bp 100–105 °C (2 mmHg); IR (CCl_4) 3480, 1630, 1460, 1385, 1240, 990, 910 cm^{-1}; MS, m/e (M^+) 188. Anal. ($C_{10}H_{20}OS$) C, H. Two diastereomers were separated via a column of silica gel with hexane–ether (20:1) as an eluant. GLPC examination revealed that the ratio of the threo to erythro isomers was 1:1. The erythro isomer ^{1}H NMR (CCl_4) δ 0.90 (dd, 6, J = 7.0 and 14.0 Hz), 1.25 (dd, 6, J = 7.0 and 2.0 Hz), 1.76 (m, 1), 2.15 (br s, 1), 2.80 (septet, 1, J = 7.0 Hz), 3.18 (m, 2), 4.96 (dd, 1, J = 16.0 and 2.0 Hz), 4.98 (dd, 1, J = 12.0 and 2.0 Hz), 5.62 (ddd, 1, J = 16.0, 12.0 and 5.0 Hz). The threo isomer ^{1}H NMR (CCl_4) δ 0.96 (dd, 6, J = 8.0 and 12.0 Hz), 1.26 (d, 6, J = 7.0 Hz), 1.84 (m, 1), 2.07 (br s, 1), 2.81 (septet, 1, J = 7.0 Hz), 3.27 (dd, 1, J = 5.0 and 9.0 Hz), 3.48 (dd, 1, J = 5.0 and 8.0 Hz), 5.08 (dd, 1, J = 16.0 and 2.0 Hz), 5.14 (dd, 1, J = 9.0 and 2.0 Hz), 5.76 (ddd, 1, J = 9.0, 9.0, and 16.0 Hz). The structure determination of both isomers was carried out by comparison with the product from the Sn–BF_3 reaction, which gave the erythro isomer selectively.[8]

3-(Isopropylthio)-4-hydroxy-1,5-heptadiene: bp 110 °C (2 mmHg); ^{1}H NMR (CCl_4) δ 1.28 (d, 6, J = 8.0 Hz), 1.73 (d, 3, J = 6.0 Hz), 2.16 (br s, 1), 2.84 (m, 1), 3.08–3.36 (m, 1), 3.84–4.08 (m, 1), 4.96–5.18 (m, 2), 5.44–5.92 (m, 3); IR (CCl_4) 3480, 1630, 1450, 1380, 1245, 985, 960, 910 cm^{-1}; MS, m/e (M^+) 186. Anal. ($C_{10}H_{18}OS$) C, H. The ratio of the diastereoisomers was not clear, since a sharp single peak appeared in GLPC.

1-Phenyl-2-(isopropylthio)-3-butenol: bp 120–125 °C (2 mmHg); IR (CCl_4) 3440, 1630, 1600, 1450, 1385, 1250, 990, 910 cm^{-1}; MS, m/e (M^+) 222. Anal. ($C_{13}H_{18}OS$) C, H. Two diastereomers were separated via a column of silica gel with hexane–ether (20:1) as an eluant. GLPC examination revealed that the ratio of the erythro to threo isomer was 6:4. The erythro isomer ^{1}H NMR (CCl_4) δ 1.25 (d, 6, J = 7.0 Hz), 2.76 (br s, 1), 2.79 (septet, 1, J = 7.0 Hz), 3.35 (dd, 1, J = 8.5 and 8.5 Hz), 4.42 (d, 1, J = 8.5 Hz), 4.86 (dd, 1, J = 18.0 and 1.2 Hz), 4.90 (dd, 1, J = 8.5 and 1.2 Hz), 5.60 (ddd, 1, J = 8.5, 8.5, and 18.0 Hz), 7.19 (s, 5). The threo isomer ^{1}H NMR (CCl_4) δ 1.20 (dd, 6, J = 6.5 and 3.5 Hz), 2.50 (br s, 1), 2.76 (septet, 1, J = 6.5 Hz), 3.45 (dd, 1, J = 8.5 and 4.5 Hz), 4.65 (d, 1, J = 4.5 Hz), 4.90 (dd, 1, J = 17.0 and 2.0 Hz), 5.02 (dd, 1, J = 10.0 and 2.0 Hz), 5.68 (ddd, 1, J = 8.5, 10.0, 17.0 Hz), 7.20 (s, 5). The structure of both isomers could be assumed from the coupling constant of PhC*H*O, J = 8.5 Hz at δ 4.42 and J = 4.5 at δ 4.65. To confirm this structure determination, both isomers were converted into the corresponding sulfoxides by treatment with $NaIO_4$ in CH_3CN. The erythro sulfoxide ^{1}H NMR (CCl_4) δ 1.20–1.40 (m, 6), 2.90 (septet, 1, J = 7.0 Hz), 3.40 (dd, 1, J = 9.0 and 9.0 Hz), 4.70–5.52 (m, 5), 7.20 (s, 5). The threo sulfoxide ^{1}H NMR (CCl_4) δ 1.10–1.40 (m, 6), 2.75 (septet, 1, J = 7.0 Hz), 3.08 (dd, 1, J = 5.0 and 5.0 Hz), 4.70–6.20 (m, 5), 7.24 (s, 5). Again, $J_{erythro}$ (9.0 Hz) > J_{threo} (5.0 Hz), owing to the hydrogen bonding between OH and S→O group, was observed at the signal of PhC*H*O.

1-[1-(Isopropylthio)-2-propen-1-yl]cyclohexanol: bp 130–135 °C (2 mmHg); ^{1}H NMR (CCl_4) δ 1.27 (d, 6, J = 7.0 Hz), 1.52 (br s, 10), 2.30 (br s, 1), 2.76 (quintet, 1, J = 7.0 Hz), 3.11 (d, 1, J = 9.0 Hz), 4.90–5.12 (m, 2), 5.64–6.00 (m, 1); IR (CCl_4) 3480, 1630, 1445, 1380, 1240, 1150, 1050, 990, 910 cm^{-1}; MS, m/e (M^+) 214. Anal. ($C_{12}H_{22}OS$) C, H.

3-(Isopropylthio)-4-hydroxy-4-methyldecene: bp 140 °C (2 mmHg); ^{1}H NMR (CCl_4) δ 0.90 (br s, 3), 1.06 and 1.16 in a ratio of 1:1 (s, totally 3), 1.23 (d, 6, J = 7.0 Hz), 1.28 (br s, 10), 2.75 (quintet, 1, J = 7.0 Hz), 3.13 and 3.17 in a ratio of 1:1 (d, totally 1, J = 10.0 and 9.0 Hz), 4.90–5.10 (m, 2), 5.60–5.94 (m, 1); IR (CCl_4) 3500, 1625, 1455, 1380, 1240, 1150, 1050, 990, 910 cm^{-1}; MS, m/e (M^+) 244. Anal. ($C_{14}H_{28}OS$) C, H. GLPC examination revealed

that the diastereoisomers were produced in a ratio of 1:1, and this ratio corresponded to the ratio of ^{1}H NMR signals at δ 1.06 and 1.16 and at δ 3.13 and 3.17.

3-(Isopropylthio)-4-hydroxy-4-phenylpentene: bp 135–140 °C (2 mmHg); ^{1}H NMR (CCl_4) δ 1.16 (d, 6, J = 7.0 Hz), 1.43 and 1.56 in a ratio of 7:3 (s, totally 3), 2.60 (quitet, 1, J = 7.0 Hz) 2.80 and 2.87 in a ratio of 3:7 (s, totallyt 1), 3.35 and 3.41 in a ratio of 3:7 (d, totally 1, J = 9.0 and 10.0 Hz), 4.80–5.04 (m, 2), 5.48–5.92 (m, 1), 7.12–7.40 (m, 5); IR (CCl_4) 3480, 1630, 1600, 1445, 1375, 1425, 1150, 990, 910 cm^{-1}; MS, m/e (M^+) 236. Anal. ($C_{14}H_{20}OS$) C, H. GLPC examination revealed that the diastereomer ratio was 7:3, which corresponded to the ratio of ^{1}H NMR signals at δ 1.43 and 1.56, δ 2.87 and 2.80, and δ 3.41 and 3.35. The γ adducts in the above seven reactions were not isolated, but the α/γ ratio was obtained by comparison with the products of the reference experiments (entries 3, 6, 8, 11, 14, 17, and 20).

3-(Isopropylthio)-4-methyl-1,5-hexadiene: bp 70–72 °C (20 mmHg); ^{1}H NMR (CCl_4) δ 1.09 (d, 3, J = 6.0 Hz), 1.23 (d, 6, J = 7.0 Hz), 2.22–2.48 (m, 1), 2.72 (quintet, 1, J = 7.0 Hz), 3.10 (dd, 1, J = 6.0 and 9.0 Hz), 4.86–5.10 (m, 4), 5.46–5.94 (m, 2); IR (CCl_4) 1635, 1250, 990, 910 cm^{-1}; MS, m/e (M^+) 170. Anal. ($C_{10}H_{18}S$) C, H.

3-(Isopropylthio)-1,5-heptadiene: bp 70–72 °C (20 mmHg); ^{1}H NMR (CCl_4) δ 1.21 (d, 3, J = 7.0 Hz), 1.23 (d, 3, J = 7.0 Hz), 1.68 (d, 3, J = 5 Hz), 2.24 (m, 2), 2.78 (quintet, 1, J = 7.0 Hz), 3.18 (quintet, 1, J = 7.0 Hz), 4.86–5.06 (m, 2), 5.36–5.80 (m, 3); IR (CCl_4) 1630, 1250, 990, 965, 910 cm^{-1}; MS, m/e (M^+) 170. Anal. ($C_{10}H_{18}S$) C, H.

1-(Isopropylthio)-4-methyl-1,5-hexadiene: bp 70–72 °C (20 mmHg); ^{1}H NMR (δ 1.04 (d, 3, J = 7.0 Hz), 1.32 (d, 3, J = 7.0 Hz), 1.35 (d, 3, J = 7.0 Hz), 2.10–2.20 (m, 3), 3.00 (quintet, 1, J = 7.0 Hz), 4.88–5.08 (m, 2), 5.80 (m, 1), 5.60 (dt, 1, J = 15.0 and 7.0 Hz), 6.05 (d, 1, J = 15.0 Hz); IR (CCl_4) 1640, 1615, 1250, 990, 945, 910 cm^{-1}; MS, m/e (M^+) 170. Anal. ($C_{10}H_{18}S$) C, H.

1-(Isopropylthio)-1,5-heptadiene: bp 70–72 °C (20 mmHg); ^{1}H NMR (CCl_4) δ 1.28 (d, 3, J = 7.0 Hz), 1.32 (d, 3, J = 7.0 Hz), 1.64 (d, 3, J = 4.0 Hz), 2.12 (br s, 4), 3.02 (quintet, 1, J = 7.0 Hz), 5.44 (m, 2), 5.70 (dt, 1, J = 15.0 and 7.0 Hz), 5.96 (d, 1, J = 15.0 Hz); IR (CCl_4) 1610, 1450, 1250, 965, 945 cm^{-1}; MS, m/e (M^+) 170. Anal. ($C_{10}H_{18}S$) C, H.

3-(Isopropylthio)-4,4-dimethyl-1,5-hexadiene: bp 75–80 °C (20 mmHg); ^{1}H NMR (CCl_4) δ 1.08 (s, 6), 1.20 (d, 6, J = 7.0 Hz), 2.63 (quintet, 1, J = 7.0 Hz), 2.89 (d, 1, J = 10.0 Hz), 4.76–5.00 (m, 4), 5.50–6.00 (m, 2); IR(CCl_4) 1630, 1460, 1410, 1380, 1365, 1250, 990, 910 cm^{-1}; MS, m/e (M^+) 184. Anal. ($C_{11}H_{20}S$) C, H.

3-(Isopropylthio)-6-methyl-1,5-heptadiene: bp 75–80 °C (20 mmHg); ^{1}H NMR (CCl_4) δ 1.20 (d, 3, J = 7.0 Hz), 1.22 (d, 3, J = 7.0 Hz), 1.62 (s, 3), 1.70 (s, 3), 2.12 (t, 2, J = 7.0 Hz), 2.74 (quintet, 1, J = 7.0 Hz), 2.96–3.28 (m, 1), 4.80–5.18 (m, 3), 5.40–5.80 (m, 1); IR (CCl_4) 1630, 1450, 1380, 1365, 1250, 990, 910 cm^{-1}; MS, m/e 184. Anal. ($C_{11}H_{20}S$) C, H.

1-(Isopropylthio)-4,4-dimethyl-1,5-hexadiene: bp 75–80 °C (20 mmHg); ^{1}H NMR (CCl_4) δ 1.00 (s, 6), 1.30 (d, 6, J = 7.0 Hz), 1.65 (d, 2, J = 8.0 Hz), 2.98 (quintet, 1, J = 7.0 Hz), 4.80–5.00 (m, 2), 5.50–5.85 (m, 2), 5.95 (d, 1, J = 15.0 Hz); IR (CCl_4) 1635, 1610, 990, 945, 910 cm^{-1}; MS, m/e (M^+) 184. Anal. ($C_{11}H_{20}S$) C, H.

1-(Isopropylthio)-6-methyl-1,5-heptadiene: bp 75–80 °C (20 mmHg); ^{1}H NMR (CCl_4) δ 1.18 (d, 3, J = 7.0 Hz), 1.22 (d, 3, J = 6.0 Hz), 1.60 (s, 3), 1.69 (s, 3), 2.08 (br s, 4), 2.80–3.12 (m, 1), 5.10 (m, 1), 5.50–5.80 (m, 1), 5.92 (d, 1, J = 15.0 Hz); IR (CCl_4) 1635, 1610, 945 cm^{-1}; MS, m/e (M^+) 184. Anal. ($C_{11}H_{20}S$) C, H.

3-(Isopropylthio)-1,5-hexadiene: 60–65 °C (20 mmHg); ^{1}H NMR (CCl_4) δ 1.20 (d, 3, J = 7.0 Hz), 1.22 (d, 3, J = 7.0 Hz), 2.28 (t, 2, J = 6.5 Hz), 2.74 (quintet, 1, J = 7.0 Hz), 3.20 (td, 1, J = 6.5 and 8.0 Hz), 4.80–5.08 (m, 4), 5.36–5.90 (m, 2); IR (CCl_4) 1640, 1460, 1420, 1385, 1370, 990, 910 cm^{-1}; MS, m/e (M^+) 156. Anal. ($C_9H_{16}S$) C, H.

1-(Isopropylthio)-1,5-hexadiene: bp 60–65 °C (20 mmHg); ^{1}H NMR (CCl_4) δ 1.27 (d, 3, J = 7.0 Hz), 1.29 (d, 3, J = 7.0 Hz), 1.17 (br s, 4), 2.80–3.08 (m, 1), 4.87–5.07 (m, 2), 5.40–5.90 (m, 2), 5.94 (d, 1, J = 15.0 Hz); IR (CCl_4) 1640, 1610, 1450, 1385, 1370, 990, 940, 910 cm^{-1}; MS, m/e (M^+) 156. Anal. ($C_9H_{16}S$) C, H. All these isomers were isolated through a preparative GLPC.

Reactions of 17. Sulfide **16** was prepared in a similar manner by using crotyl chloride instead of allyl chloride: bp 145–150 °C; ^{1}H NMR (CCl_4) δ of the trans isomer 1.16 (d, 6, J = 7.0 Hz), 2.64 (d, 3, J = 6.0 Hz), 2.56 (septet, 1, J = 7.0 Hz), 3.16 (d, 2, J = 8.0 Hz), 5.00–5.80 (m, 2); ^{1}H NMR of the cis isomer 1.20 (d, 6, J = 7.0 Hz), 2.70 (d, 3, J = 6.0 Hz), 2.56 (septet, 1, J = 7.0 Hz), 3.08 (d, 2, J = 6.0 Hz), 5.00–5.80 (m, 2). To a solution of 0.16 mL (1 mmol) of **16** dissolved in 10 mL of ether was added 1 equiv of *sec*-butyllithium at −78 °C. The mixture was allowed to warm to 0 °C, kept at this temperature for 10 min, and again cooled to −78 °C. The additive was added and subsequently benzaldehyde was added. The products were isolated via a column of silica gel.

18: bp 165–170 °C (1 mmHg); ^{1}H NMR (CCl_4) 1.20 (d, 3, J = 7.0 Hz), 1.23 (d, 3, J = 7.0 Hz), 1.70 (m, 3), 2.76 (m, 1), 2.80 (m, 1), 3.30 (m, 1), 4.42–4.50 (m, 1), 4.80 (m, 2); IR (CCl_4) 3440, 1630, 1600, 1450, 1385, 1250, 960 cm^{-1}; MS, m/e (M^+) 236. Anal. ($C_{14}H_{20}OS$) C, H. The stereoisomers were not separated.

19: bp 165–170 °C (1 mmHg); IR (CCl_4) 3480, 1635, 1600, 1450, 1385, 1250, 940 cm^{-1}; MS, m/e (M^+) 236; ^{1}H NMR ($CDCl_3$) of the erythro trans isomer δ 0.98 (d, 3, J = 6.5 Hz), 1.28 (d, 6, J = 7.0 Hz), 2.04 (br s, 1), 2.43 (m, 1), 2.90 (septet, 1, J = 7.0 Hz), 4.46 (d, 1, J = 5.5 Hz), 5.48 (dd, 1, J = 15.5 and 7.0 Hz), 5.80 (d, 1, J = 15.5 Hz), 7.20 (s, 5); ^{1}H NMR of the erythro cis isomer δ 0.91 (d, 3, J = 6.5 Hz), 1.29 (d, 6, J = 7.0 Hz), 2.00 (br s, 1), 2.43 (m, 1), 2.91 (septet, 1, J = 7.0 Hz), 4.56 (d, 1, J = 5.5 Hz), 5.44 (dd, 1, J = 9.5 and 9.0 Hz), 5.84 (d, 1, J = 9.5 Hz), 7.20 (s, 5); ^{1}H NMR of the threo trans isomer δ 0.88 (d, 3, J = 6.9 Hz), 1.24 (d, 6, J = 7.0 Hz), 1.84 (br s, 1), 2.43 (m, 1), 2.96 (septet, 1, J = 7.0 Hz), 4.26 (d, 1, J = 7.1 Hz), 5.52 (dd, 1, J = 15.8 and 8.4 Hz), 5.92 (d, 1, J = 15.8 Hz), 7.19 (s, 5); ^{1} H NMR of the threo cis isomer δ 0.84 (d, 3, J = 7.5 Hz), 1.26 (d, 6, J = 7.0 Hz), 1.72 (br s, 1), 2.40 (m, 1), 2.90 (septet, 1, J = 7.0 Hz), 4.33 (d, 1, J = 7.2 Hz), 5.43 (dd, 1, J = 9.1 and 9.1 Hz), 6.02 (d, 1, J = 9.1 Hz), 7.21 (s, 5). The stereochemistry of these isomers was determined by desulfurization using $(Ph_3P)_2NiCl_2/i$-PrMgCl,[25] which gave 1-phenyl-2-methyl-3-butenol. This butenol was compared with authentic samples.[26]

Selenium-Substituted Allyl Carbanion. 1-(Phenylseleno)-2-propene was prepared via the literature procedure.[27] To a solution of 31 g of diphenyl diselenide dissolved in 100 mL of ethanol was added 2.0 g of $NaBH_4$ at room temperature. The mixture was stirred for 30 min and 15.3 g of allyl chloride was added. Sodium chloride precipitated was filtered, and the mixture was concentrated. Ether (50 mL) was added and again the precipitate was filtered. Distillation gave the desired selenide in 95% yield: bp 115 °C (10 mmHg); ^{1}H NMR (CCl_4) δ 3.42 (d, 2, J = 7.5 Hz), 4.85 (dd, 1, J = 9.5 and 1.5 Hz), 4.86 (dd, 1, J = 18.0 and 1.5 Hz), 5.86 (ddd, 1, J = 7.5, 9.5, and 18.0 Hz), 7.00–7.20 (m, 3), 7.24–7.50 (m, 2); IR (CCl_4) 1635, 1580, 980, 910 cm^{-1}.

Reaction of 20. To a solution of 1.2 mmol of freshly prepared lithium diisopropylamide dissolved in 10 mL of THF was added 0.13 mL (1 mmol) of allyl phenyl selenide at −78 °C. The mixture was stirred for 30 min at −78 °C, and 1 equiv of Et_3Al was added. Subsequently, 1 equiv of the electrophile was added at −78 °C. The resulting mixture was allowed to warm to room temperature, and quenched with aqueous NH_4Cl solution at 0 °C. The same workup procedure as above was employed.

3-(Phenylseleno)-4-hydroxy-1-hexene: bp 90–95 °C (1 mmHg); IR(CCl_4) 3460, 1630, 1600, 990, 910 cm^{-1}; ^{1}H NMR (CCl_4) of the threo isomer **21** (R = Et) δ 0.95 (t, 3, J = 7.0 Hz), 1.55 (qd, 2, J = 7.0 and 7.0 Hz), 2.28 (br s, 1), 3.47 (dd, 1, J = 8.0 and 7.0 Hz), 3.59 (dd, 1, J = 8.0 and 8.0 Hz), 4.83 (dd, 1, J = 17.0 and 1.0 Hz), 4.88 (dd, 1, J = 8.0 and 1.0 Hz), 5.75 (ddd, 1, J = 8.0, 8.0, and 17.0 Hz), 7.20–7.60 (m, 5); ^{1}H NMR of the erythro isomer **22** (R = Et) δ 0.88 (t, 3, J = 7.0 Hz), 1.35 (qd, 2, J = 7.0 and 7.0 Hz), 2.07 (br s, 1), 3.40 (dd, 1, J = 4.0 and 7.0 Hz), 3.76 (dd, 1, J = 8.0 and 4.0 Hz), 4.95 (d, 1, J = 17.0 Hz), 4.99 (d, 1, J = 8.0 Hz), 5.87 (ddd, 1, J = 8.0, 8.0, and 17.0 Hz), 7.20–7.60 (m, 5). Anal. ($C_{12}H_{16}OSe$) C, H.

1-(Phenylseleno)-4-hydroxy-1-hexene: bp 90–95 °C (1 mmHg); IR (CCl_4) 3440, 1640, 1600 cm^{-1}; ^{1}H NMR δ 0.92 (t, 3, J = 7.0 Hz), 1.20–1.80 (m, 2), 1.86 (br s, 1), 2.24 (dd, 2, J = 6.0

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and 6.0 Hz), 3.20–3.70 (m, 1), 5.96 (td, 1, J = 6.0 and 10.0 Hz), 6.32 (d, 1, J = 10.0 Hz), 7.00–7.50 (m, 5). Anal. ($C_{12}H_{16}OSe$) C, H.

3-(Phenylseleno)-4-hydroxy-5-methyl-1-hexene: bp 105–110 °C (1 mmHg); IR (CCl_4) 3460, 1630, 1600, 990, 910 cm^{-1}; ^1H NMR (CCl_4) of the threo isomer **21** (R = *i*-Pr) δ 1.00 (d, 6, J = 7.0 Hz), 1.80 (d septet, 1, J = 5.0 and 7.0 Hz), 2.46 (br s, 1), 3.32 (dd, 1, J = 8.0 and 5.0 Hz), 3.64 (dd, 1, J = 8.0 and 10.0 Hz), 4.80 (d, 1, J = 17.0 Hz), 4.88 (d, 1, J = 10.0 Hz), 5.76 (ddd, 1, J = 10.0, 10.0, and 17.0 Hz), 7.20–7.80 (m, 5); ^1H NMR of the erythro isomer **22** (R = *i*-Pr) δ 0.88 (d, 6, J = 7.0 Hz), 1.60–2.00 (m, 1), 2.26 (br s, 1), 3.28 (dd, 1, J = 6.0 and 2.0 Hz), 3.92 (dd, 1, J = 10.0 and 2.0 Hz), 4.96 (d, 1, J = 17.0 Hz), 5.00 (d, 1, J = 10.0 Hz), 5.96 (ddd, 1, J = 10.0, 10.0, and 17.0 Hz), 7.20–7.80 (m, 5). Anal. ($C_{13}H_{18}OSe$) C, H.

1-(Phenylseleno)-4-hydroxy-5-methyl-1-hexene: bp 105–110 °C (1 mmHg); IR (CCl_4) 3440, 1640, 1600 cm^{-1}; ^1H NMR (CCl_4) δ 0.96 (d, 6, J = 8.0 Hz), 1.40 (br s, 1), 1.50–1.90 (m, 1), 2.28 (d, 2, J = 6.0 and 8.0 Hz), 3.20–3.65 (m, 1), 6.12 (td, 1, J = 8.0 and 8.0 Hz), 6.50 (d, 1, J = 8.0 Hz), 7.10–7.60 (m, 5). Anal. ($C_{13}H_{18}OSe$) C, H.

1-Phenyl-2-(phenylseleno)-3-buten-1-ol: bp 125–130 °C (0.1 mmHg); IR (CCl_4) 3460, 1630, 1600, 990, 910 cm^{-1}; ^1H NMR (CCl_4) of the threo isomer **21** (R = Ph) δ 3.10 (br s, 1), 3.80 (dd, 1, J = 8.0 and 10.0 Hz), 4.56 (d, 1, J = 8.0 Hz), 4.60 (dd, 1, J = 16.0 and 1.0 Hz), 4.75 (dd, 1, J = 10.0 and 1.0 Hz), 5.67 (ddd, 1, J = 10.0, 10.0, and 16.0 Hz), 7.10–7.60 (m, 10); ^1H NMR of the erythro isomer **22** (R = Ph) δ 3.35 (br s, 1), 3.92 (dd, 1, J = 6.0 and 10.0 Hz), 4.42 (d, 1, J = 6.0 Hz), 4.74 (dd, 1, J = 17.0 and 1.0 Hz), 4.88 (dd, 1, J = 10.0 and 1.0 Hz), 5.88 (ddd, 1, J = 10.0, 10.0, and 17.0 Hz), 7.10–7.60 (m, 10). Anal. ($C_{16}H_{16}OSe$) C, H.

1-Phenyl-4-(phenylseleno)-3-buten-1-ol: bp 125–130 °C (0.1 mmHg); IR (CCl_4) 3450, 1635, 1600 cm^{-1}; ^1H NMR (CCl_4) δ 1.90 (br s, 1), 2.52 (dd, 2, J = 7.0 and 7.0 Hz), 4.63 (t, 1, J = 7.0 Hz), 5.96 (td, 1, J = 7.0 and 14.0 Hz), 6.38 (d, 1, J = 14.0 Hz), 7.23 (s, 10). Anal. ($C_{16}H_{16}OSe$) C, H. The structure of diastereomers was determined by the β-elimination reaction.[16]

(*E*)-1-Phenyl-1,3-butadiene[28] from **21** (R =Ph): ^1H NMR (CCl_4) δ 5.10 (dd, 1, J = 10.4 and 1.8 Hz), 5.25 (dd, 1, J = 16.9 and 1.8 Hz), 6.50 (ddd, 1, J = 10.4, 10.9, and 16.9 Hz), 6.54 (d, 1, J = 15.9 Hz), 6.78 (dd, 1, J = 10.9 and 15.9 Hz), 7.00–7.20 (m, 5); IR (CCl_4) 1675, 1620, 1595, 1490, 990, 960, 900 cm^{-1}.

(*Z*)-1-Phenyl-1,3-butadiene[28] from **22** (R = Ph): ^1H NMR (CCl_4) δ 5.16 (dd, 1, J = 10.1 and 2.0 Hz), 5.28 (dd, 1, J = 16.8 and 2.0 Hz), 6.16 (dd, 1, J = 11.3 and 11.3 Hz), 6.42 (d, 1, J = 11.3 Hz), 6.82 (ddd, 1, J = 10.1, 11.3, and 16.8 Hz), 7.21 (s, 5); IR (CCl_4) 1645, 1600, 1580, 1495, 990, 960, 910 cm^{-1}. We are grateful to Professor Matteson for providing us with ^1H NMR spectra of (*E*)- and (*Z*)-1-phenyl-1,3-butadiene. It was very difficult to analyze very volatile 1,3-dienes derived from other diastereomers (R = Et and *i*-Pr), but the above result and the synthesis of **24** strongly supported their structures. The α/γ ratio from acetophenone was obtained by comparison with the products of Reich's condition (Table III, footnote d).

Synthesis of 24. 9-Oxonon-1-yl acetate was prepared by the literature procedure:[17c] ^1H NMR (CCl_4) δ 1.00–1.80 (m, 12 H), 1.98 (s, 3), 2.48 (td, 2, J = 8.0 and 1.0 Hz), 4.00 (t, 2, J = 6.0 Hz), 9.76 (br s, 1); IR (CCl_4) 2700, 1735, 1380, 1360, 1240 cm^{-1}. To a solution of 1.2 mmol of freshly prepared LDA dissolved in 10 mL of THF was added 197 mg (1 mmol) of allyl phenyl selenide at −78 °C. The mixture was stirred for 30 min at −78 °C, and 1.2 mmol of Et_3Al was added. Subsequently, 201 mg of the aldehyde was added. **23** was obtained in 70% yield: ^1H NMR (CCl_4) δ 1.10–1.76 (m, 14), 1.96 (s, 3), 2.00–2.44 (m, 2), 3.54 (td, 1, J = 8.0 and 2.0 Hz), 3.98 (t, 2, J = 6.0 Hz), 4.89 (dd, 1, J = 16.0 and 2.0 Hz), 4.96 (dd, 1, J = 10.0 and 2.0 Hz), 5.76 (td, 1, J = 10.0 and 16.0 Hz), 7.10–7.60 (m, 5); IR (CCl_4) 3640, 1735, 1240, 990, 910 cm^{-1}. To a solution of 239 mg (0.6 mmol) of **23** dissolved in 8 mL of *n*-pentane was added 192 mg (0.6 mmol) of *p*-toluenesulfonic acid. The mixture was refluxed for 7 h, quenched with aqueous $NaHCO_3$, and worked up as usual. **24** was obtained in 77% yield: ^1H NMR (CCl_4) δ 1.20–1.90 (m, 12), 2.00 (s, 3), 2.00–2.24 (m, 2), 4.02 (t, 2, J = 6.0 Hz), 4.80–6.54 (m, 5); IR (CCl_4) 1740, 1240, 965, 900 cm^{-1}; MS, m/e (M^+) 224. The structure of **24** was confirmed by comparison with the literature data[17d] and by the GLPC analysis of the corresponding epoxide which was obtained through MCPBA oxidation.[17c]

Silicon-Substituted Allylic Carbanion. Allyltrimethylsilane was prepared from Me_3SiCl and allylmagnesium chloride: bp 70–75 °C; ^1H NMR (CCl_4) δ −0.03 (s, 9), 1.48 (d, 2, J = 8.0 Hz), 4.64–4.92 (m, 2), 5.71 (tt, 1, J = 8.0 and 12.0 Hz).

Reaction of 25. 25 was generated by the method of Ehlinger and Magnus:[29] To a solution of 0.15 mL (1 mmol) of *N,N'*-tetramethylethylenediamine dissolved in 2 mL of THF was added 0.14 mL (1 mmol) of allyltrimethylsilane at −78 °C, and then 1 equiv of *sec*-butyllithium was added. The mixture was stirred at −30 °C for 30 min, and 1 equiv of Et_3Al was added. Subsequently, the carbonyl compounds (1 equiv) were added. A similar workup procedure was employed.

3-(Trimethylsilyl)-4-hydroxy-1-heptene: bp 80–85 °C (1 mmHg); IR (CCl_4) 3450, 1630, 990, 910 cm^{-1}; ^1H NMR (CCl_4) or the threo isomer δ 0.04 (s, 9), 0.92 (br s, 3), 1.20 (m, 4), 1.30 (br s, 1), 1.58 (dd, 1, J = 6.0 and 10.0 Hz), 3.56 (dt, 1, J = 10.0 and 6.0 Hz), 4.72 (dd, 1, J = 16.0, and 2.0 Hz), 4.86 (dd, 1, J = 10.0 and 2.0 Hz), 5.80 (ddd, 1, J = 10.0, 10.0, and 16.0 Hz). The erythro isomer could not be isolated. Anal. ($C_{10}H_{22}OSi$) C, H.

1-(Trimethylsilyl)-4-hydroxy-1-heptene: bp 80–85 °C (1 mmHg); ^1H NMR (CCl_4) δ 0.05 (s, 9), 0.90 (br s, 3), 1.40–1.50 (m, 4), 1.55 (br s, 1), 2.20 (dd, 2, J = 6.0 and 6.0 Hz), 3.35 (td, 1, J = 2.0 and 6.0 Hz), 5.67 (d, 1, J = 20.0 Hz), 6.05 (td, 1, J = 6.0 and 20.0 Hz).

3-(Trimethylsilyl)-4-hydroxy-5-methyl-1-hexene: bp 80 °C (1 mmHg); IR (CCl_4) 3450, 1630, 990, 910 cm^{-1}; ^1H NMR (CCl_4) of the threo isomer δ 0.04 (s, 9), 0.89 (dd, 6, J = 11.5 and 6.5 Hz), 1.20 (br s, 1), 1.48–1.96 (m, 2), 3.32 (dd, 1, J = 8.0 and 3.5 Hz), 4.84 (dd, 1, J = 17.5 and 2.0 Hz), 4.96 (dd, 1, J = 10.5 and 2.0 Hz), 5.85 (ddd, 1, J = 10.5, 10.5 and 17.5 Hz); ^1H NMR of the erythro isomer δ 0.06 (s, 9), 0.90 (dd, 6, J = 10.0 and 7.0 Hz), 1.30 (br s, 1), 1.48–1.96 (m, 2), 3.56 (dd, 1, J = 9.0 and 3.0 Hz), 4.72–5.04 (m, 2), 5.28–5.92 (m, 1). Anal. ($C_{10}H_{22}OSi$) C, H. The structure determination of the threo/erythro isomer was not unambiguous and was based on the result of the reaction of benzaldehyde.

1-(Trimethylsilyl)-4-hydroxy-5-methyl-1-hexene: bp 80–85 °C (1 mmHg); ^1H NMR (CCl_4) δ 0.05 (s, 9), 0.89 (d, 6, J = 8.0 Hz), 1.33 (br s, 1), 1.47–1.85 (m, 1), 2.21 (dd, 2, J = 6.0 and 6.0 Hz), 3.31 (td, 1, J = 6.0 and 2.0 Hz), 5.69 (d, 1, J = 20.0 Hz), 6.05 (td, 1, J = 6.0 and 20.0 Hz).

1-Phenyl-2-(trimethylsilyl)-3-buten-1-ol: bp 80–85 °C (0.1 mmHg); IR (CCl_4) 3460, 1630, 1600, 990, 910 cm^{-1}; ^1H NMR (CCl_4) of the threo isomer δ 0.09 (s, 9), 2.09 (dd, 1, J = 10.5 and 6.5 Hz), 2.20 (br s, 1), 4.96 (d, 1, J = 6.5 Hz), 5.01 (dd, 1, J = 16.5 and 2.0 Hz), 5.15 (dd, 1, J = 10.5 and 2.0 Hz), 6.01 (ddd, 1, J = 10.5, 10.5, and 16.5 Hz), 7.15 (s, 5); ^1H NMR of the erythro isomer δ 0.08 (s, 9), 1.88 (br s, 1), 2.09 (dd, 1, J = 9.0 and 10.0 Hz), 4.71 (dd, 1, J = 16.5 and 2.0 Hz), 4.73 (d, 1, J = 9.0 Hz), 4.83 (dd, 1, J = 10.0 and 2.0 Hz), 5.58 (ddd, 1, J = 10.0, and 10.0, and 16.5 Hz), 7.15 (s, 5). Anal. ($C_{13}H_{20}OSi$) C, H. These diastereomers were converted into the corresponding dienes by the method of Hudrlik.[30] The dienes thus obtained were compared with authentic samples.

1-Phenyl-4-(trimethylsilyl)-3-buten-1-ol: bp 80–85 °C (0.1 mmHg); ^1H NMR (CCl_4) δ 0.18 (s, 9), 1.88 (br s, 1), 2.58 (dd, 2, J = 6.0 and 6.0 Hz), 4.70 (t, 1, J = 6.0 Hz), 5.80 (d, 1, J = 20.0 Hz), 6.14 (td, 1, J = 6.0 and 20.0 Hz), 7.38 (s, 5).

3-(Trimethylsilyl)-2-phenyl-2-hydroxy-4-pentene: bp 90–95 °C (0.1 mmHg); IR (CCl_4) 3450, 1630, 1600, 990, 910 cm^{-1}; ^1H NMR (CCl_4) δ 0.14 and 0.24 in a ratio of 1:1 (s, totally 9), 1.68 and 1.72 in a ratio of 1:1 (s, totally 3), 1.90 and 1.95 in a ratio of 1:1 (s, totally 1), 2.00–2.20 (m, 1), 4.80–5.20 (m, 2), 5.50–6.00 (m, 1), 7.10–7.50 (m, 5). Anal. ($C_{14}H_{22}OSi$) C, H. The diastereomers were not separated.

1-(Trimethylsilyl)-4-phenyl-4-hydroxy-1-pentene: bp 90–95 °C (0.1 mmHg); ^1H NMR (CCl_4) δ 0.00 (s, 9), 1.48 (s, 3), 1.96 (br

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s, 1), 2.58 (d, 2, J = 6.0 Hz), 5.62 (d, 1, J = 20.0 Hz), 5.82 (td, 1, J = 6.0 and 20.0 Hz), 7.08–7.50 (m, 5).

Nitrogen-Substituted Allylic Carbanion. The carbanion **26** was generated by the method of Martin and DuPriest.[21] To a solution of 0.14 mL (1 mmol) of allylpyrrolidine dissolved in 3 mL of THF was added 1 equiv of *sec*-butyllithium at −78 °C. The resulting mixture was allowed to warm to −10 °C and ketp for 10 min at this temperature. The mixture was again cooled to −78 °C, and then 1 equiv of Et_3Al was added. Subsequently, 0.3 mL of Me_3SiCl was added, and the mixture was allowed to warm to room temperature. A similar workup procedure was employed.

(1-(Trimethylsilyl)-2-propen-1-yl)pyrrolidine: bp 140 °C (10 mmHg); IR (CCl_4) 1620, 900, 850, 830 cm^{-1}; ^1H NMR (CCl_4) δ 0.06 (s, 9), 1.70 (m, 4), 2.30–2.60 (m, 4), 2.44 (d, 1, J = 8.0 Hz), 4.80–5.04 (m, 2), 5.50–6.00 (m, 1). Anal. ($C_{10}H_{21}NSi$) C, H.

(3-(Trimethylsilyl)-1-propen-1-yl)pyrrolidine: bp 140 °C (10 mmHg); IR (CCl_4) 1640, 1360, 930, 850, 830 cm^{-1}; ^1H NMR (CCl_4) δ 0.02 (s, 9), 1.32 (d, 2, J = 8.0 Hz), 1.88 (m, 4), 2.93 (m, 2), 3.95 (td, 1, J = 8.0 and 14.0 Hz), 5.89 (d, 1, J = 14.0 Hz). Anal. ($C_{10}H_{21}NSi$) C, H.

Registry No. **3a**, 72520-12-8; **3b**, 88916-03-4; **5** (R = Ph), 82238-07-1; **5** (R = CH_3CH_2), 82238-09-3; **5** (R = $CH_3(CH_2)_3$), 85677-24-3; **5** (R = (*E*)-1-propenyl), 85677-25-4; **6**, 505-03-3; **7**, 85677-21-0; **8**, 82238-22-0; **9**, 60018-04-4; **12**, 72520-13-9; **13** (R = $CH_3(CH_2)_2$), 88915-90-6; **13** (R = $(CH_3)_2CH$), 88916-17-0; **13** (R = Ph), 85677-17-4; **14** (R = $CH_3(CH_2)_2$), 88916-16-9; **14** (R = $(CH_3)_2CH$), 85677-23-2; **14** (R = Ph), 85677-16-3; *cis*-**16**, 88915-94-0; *trans*-**16**, 88916-22-7; **17**, 88916-20-5; **18**, 88915-95-1; *erythro,trans*-**19**, 88915-96-2; *erythro,cis*-**19**, 88915-97-3; *threo,trans*-**19**, 88915-99-5; *threo,cis*-**19**, 88916-00-1; **20**, 74472-76-7; **21** (R = CH_3CH_2), 88916-06-7; **21** (R = $(CH_3)_2CH$), 88916-08-9; **21** (R = Ph), 88916-10-3; **22** (R = CH_3CH_2), 88916-07-8; **22** (R = $(CH_3)_2CH$), 88916-09-0; **22** (R = Ph), 88916-11-4; **23**, 85363-39-9; **24**, 50767-78-7; **25**, 67965-38-2; **26**, 88916-21-6; **27**, 88916-02-3; **28**, 88932-88-1; PhCHO, 100-52-7; $CH_3CH{=}CHCHO$, 123-73-9; $(CH_3)_2C{=}CHCH_2Cl$, 870-63-3; $(CH_3)_2C{=}CHCH_2Br$, 503-60-6; CH_3CH_2CHO, 123-38-6; $CH_3(CH_2)_3CHO$, 110-62-3; $CH_3(CH_2)_2CHO$, 123-72-8; $(CH_3)_2CHCHO$, 78-84-2; $CH_3(CH_2)_5C(O)CH_3$, 111-13-7; $PhC(O)CH_3$, 98-86-2; $CH_3CH{=}CHCH_2Cl$, 591-97-9; $CH_3CH{=}CHCH_2Br$, 4784-77-4; $CH_2{=}CHCH_2Br$, 106-95-6; Me_3SiCl, 75-77-4; Et_3Al, 97-93-8; Et_3B, 97-94-9; Bu_3B, 122-56-5; *n*-Bu-9-BBN, 23532-74-3; *erythro*-1-phenyl-2-isopropoxy-3-butenol, 85677-18-5; *threo*-1-phenyl-2-isopropoxy-3-butenol, 85677-19-6; 1-phenyl-4-isopropoxy-3-butenol, 72087-64-0; 1-(1-isopropoxy-2-propen-1-yl)cyclohexanol, 72087-65-1; 1-(3-isopropoxy-2-propen-1-yl)cyclohexanol, 88915-88-2; *erythro*-(*E*)-3-isopropoxy-4-hydroxy-1,5-heptadiene, 88915-89-3; *threo*-(*E*)-3-isopropoxy-4-hydroxy-1,5-heptadiene, 88916-23-8; 1-isopropoxy-4-hydroxy-1,5-heptadiene, 72087-67-3; 3-isopropoxy-6-methyl-1,5-heptadiene, 68060-20-8; 1-isopropoxy-6-methyl-1,5-heptadiene, 68060-21-9; *threo*-1-phenyl-2-(methoxymethoxy)-3-butenol, 85677-20-9; 1-(isopropylthio)-4-hydroxyheptene, 72087-68-4; 1-(isopropylthio)-4-hydroxy-5-methylhexene, 72087-69-5; 3-(isopropylthio)-4-hydroxy-1,5-heptadiene, 72087-72-0; 1-(isopropylthio)-4-hydroxy-1,5-heptadiene, 72087-73-1; 1-phenyl-4-(isopropylthio)-3-butenol, 88915-91-7; 1-[1-(isopropylthio)-2-propen-1-yl]cyclohexanol, 70600-06-5; 1-[3-(isopropylthio)-2-propen-1-yl]cyclohexanol, 70600-08-7; *erythro*-3-(isopropylthio)-4-hydroxy-4-methyldecene, 88915-92-8; *threo*-3-(isopropylthio)-4-hydroxy-4-methyldecene, 88916-18-1; 1-(isopropylthio)-4-hydroxy-4-methyldecene, 70624-57-6; *erythro*-3-(isopropylthio)-4-hydroxy-4-phenylpentene, 88915-93-9; *threo*-3-(isopropylthio)-4-hydroxy-4-phenylpentene, 88916-19-2; 1-(isopropylthio)-4-hydroxy-4-phenylpentene, 72087-71-9; 3-(isopropylthio)-4-methyl-1,5-hexadiene, 71535-38-1; 3-(isopropylthio)-1,5-heptadiene, 72087-74-2; 1-(isopropylthio)-4-methyl-1,5-hexadiene, 88915-98-4; 1-(isopropylthio)-1,5-heptadiene, 72087-75-3; 3-(isopropylthio)-4,4-dimethyl-1,5-hexadiene, 71535-36-9; 3-(isopropylthio)-6-methyl-1,5-heptadiene, 88916-01-2; 1-(isopropylthio)-4,4-dimethyl-1,5-hexadiene, 88916-04-5; 1-(isopropylthio)-6-methyl-1,5-hexadiene, 88916-05-6; 3-(isopropylthio)-1,5-hexadiene, 71535-37-0; 1-(isopropylthio)-1,5-hexadiene, 50996-70-8; 1-(phenylseleno)-4-hydroxy-1-hexene, 85363-35-5; 1-(phenylseleno)-4-hydroxy-5-methyl-1-hexene, 85363-36-6; 1-phenyl-4-(phenylseleno)-3-buten-1-ol, 85363-37-7; *threo*-4-phenyl-3-(phenylseleno)-1-penten-4-ol, 88916-12-5; 4-phenyl-1-(phenylseleno)-1-penten-4-ol, 85363-38-8; *threo*-3-(trimethylsilyl)-4-hydroxy-1-heptene, 88916-13-6; 1-(trimethylsilyl)-4-hydroxy-1-heptene, 88916-14-7; *threo*-3-(trimethylsilyl)-4-hydroxy-5-methyl-1-hexene, 88916-15-8; *erythro*-3-(trimethylsilyl)-4-hydroxy-5-methyl-1-hexene, 85125-25-3; 1-(trimethylsilyl)-4-hydroxy-5-methyl-1-hexene, 85363-31-1; *threo*-1-phenyl-2-(trimethylsilyl)-3-buten-1-ol, 85125-31-1; *erythro*-1-phenyl-2-(trimethylsilyl)-3-buten-1-ol, 85125-28-6; 1-phenyl-4-(trimethylsilyl)-3-buten-1-ol, 68724-62-9; *threo*-3-(trimethylsilyl)-2-phenyl-2-hydroxy-4-pentene, 85363-29-7; 1-(trimethylsilyl)-4-phenyl-4-hydroxy-1-pentene, 68724-59-4; (*E*)-1-phenyl-1,3-butadiene, 16939-57-4; (*Z*)-1-phenyl-1,3-butadiene, 31915-94-3; cyclohexanone, 25512-62-3; 9-oxonon-1-yl acetate, 29541-97-7; allyl isopropyl ether, 6140-80-3; MOM allyl ether, 62322-45-6; allyl isopropyl sulfide, 50996-72-0; 1-(phenylseleno)-2-propene, 14370-82-2; allyltrimethylsilane, 762-72-1; 1-allylpyrrolidine, 24420-11-9; allyl chloride, 107-05-1; 2-propanethiol, 75-33-2; diphenyl diselenide, 1666-13-3.