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Selective Condensation of [3-(Alkylthio)allyl]titanium Reagent with Carbonyl Compounds

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[3-(Ethylthio)allyl]titanium reagent generated easily from allyl ethyl sulfides condensed with aldehydes to give *erythro*-β-hydroxy sulfides in highly regio- and stereoselective manner. In contrast, crotyl ethyl sulfide reacted with aldehydes affording δ-hydroxy vinyl sulfide exclusively. The substitution pattern of the starting sulfide can have a pronounced effect on the selectivity in this condensation reaction. *erythro*-β-Hydroxy sulfide obtained was transformed stereoselectively to the *trans*-vinyloxirane or 1,3-alkadiene.

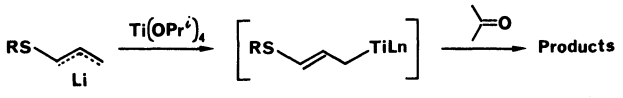
The role of the sulfur function in synthetic chemistry has become increasingly extensive.[1] In particular, the α-carbanion stabilized by sulfur contributed to the many important developments in sulfur utilizing synthetic chemistry.[2] Especially noteworthy is a large body of data relating to the reaction of sulfur-stabilized allylic carbanions.[2] The alkylthioallyl anion generated easily by treating the alkyl allyl sulfide with strong base can react with a variety of electrophiles to give synthetically useful intermediates. Efficient and useful methods for the extension of carbon chain by means of such reagents have recently been described.[3] Unsaturated β-hydroxy sulfide, which can be obtained in the reaction of alkylthioallyl anion with carbonyl compounds, has a potential utility as it can be easily converted to the alkenyloxiranes or 1,3-alkadienes. If it can be possible to obtain this olefinic β-hydroxy sulfide regio- and stereoselectively, the general route to stereochemically pure alkenyloxiranes or 1,3-alkadienes may be established. Previous investigators have attempted to optimize the stereoselectivity of the reaction. Consequently, the available methods afford only one substitution type of pure olefinic β-hydroxy sulfides after a rather tedious sequence in high yields.[2,3]

The major problem encountered in the reaction of allylic carbanions with carbonyl compounds is the one concerning the regio- (α/γ) and stereoselectivities (*erythro/threo*) of the reaction. Generally, it has been thought that the reactivity and the structure of the metallated carbanions are highly dependent on the countercation and solvents.[4] For example, it has been often observed that the lithio derivatives have shown little selectivity in some reactions, but the use of some other metals gave excellent results in the same reactions. In our continuous studies on the reaction of anionic species, we have confirmed the important role of metal countercation in the reaction. Among others, the organotitanium reagents have shown unusual results over a wide range of reactions.[5] This particular reactivity of the titanium reagents has not been fully understood,but it might be suggested that the rather tight nature of carbon–titanium bond and susceptibility to the steric demand are the origin of the selectivity. From this point of view, it may be meaningful to examine the ability of the [3-(alkylthio)allyl]titanium reagents for the selective reaction.

This paper deals with the reaction between a wide variety of [3-(alkylthio)allyl]titanium reagents and carbonyl compounds as a promising versatile synthetic method. Application of this methodology to the stereoselective syntheses of alkenyloxiranes and 1,3-alkadienes were also described.[6]

Results and Discussion

Regio- and Stereoselectivity. Easily prepared [3-(alkylthio)allyl]titanium reagent of type **1** from alkyl lithioallyl sulfide and titanium tetraisopropoxide was subjected to the reaction with carbonyl compounds. The major results of our findings are illustrated in Table 1. Several trends emerge from these data. First,



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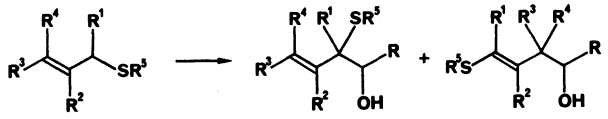
the substitution pattern of the starting sulfide can have a pronounced effect on α/γ ratio in the final condensation products. With unsubstituted allyl sulfides (R^1=R^2=R^3=R^4=H, entries 1—10), α-adducts were produced selectively with most of the aldehydes studied (the α % was about 95—99%). Even the aromatic aldehydes and ketones gave α-adduct with high regioselectivities.[7] On the other hand, a dramatic change in product distribution occurs when the condensation with aldehyde was carried out by using γ-substituted allyl sulfides (R^3 and/or R^4=Me, entries, 15, 16, and 19). In these cases, excellent γ-selectivity was observed. α- or β-Mono- and α,β-disubstituted allyl sulfides (R^1 and/or R^2=Me) were, however, showed a very high α-selectivities again. Furthermore, it is highly interesting that α,γ-disubstituted allyl sulfide (R^1=R^3=Me) gave the α-adduct almost exclusively (entry 18).

The second important trend that may be seen from the data in Table 1 is the exceedingly high *erythro* selectivity of the reaction. For example, [3-(phenylthio)allyl]titanium reagent generated from allyl phenyl sulfide reacted with cyclohexanecarbaldehyde at α-position to give *erythro*-β-hydroxy sulfide exclusively (entry 1). For the reaction with aromatic aldehyde and α,β-unsaturated aldehyde, the *erythro* selectivity was relatively low (entries 4, 5, and 10) compared with other saturated systems. This anomalous trend of unsaturated system was often observed in other similar type of reactions,[7] and may be due to an acyclic transition state or other electronic factors.[8] One electron transfer mechanism in the reaction of aromatic carbonyl compounds with some carbanion species was confirmed experimentally by Ashby.[8a] If such was

TABLE 1. REGIO- AND STEREOSELECTIVITIES[a]

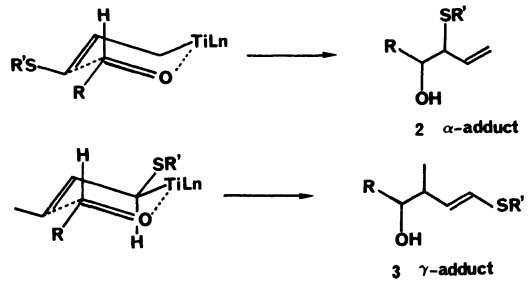


Entry	Sulfide					Carbonyl compd[b]	Product,[c] Yield/%	
	R^1	R^2	R^3	R^4	R^5		α-Adduct (*erythro/threo*)[d]	γ-Adduct
1	H	H	H	H	Ph	A	99(>30:1)	<1
2	H	H	H	H	Et	A	99(>30:1)	<1
3	H	H	H	H	Et	B	87(>30:1)	5
4	H	H	H	H	Et	C	93(9:1)	3
5	H	H	H	H	Et	D	94(6:1)	2
6	H	H	H	H	Et	E	90[e]	7
7	H	H	H	H	Et	F	95(>30:1)	5
8	H	H	H	H	*t*-Bu	A	93(>30:1)	2
9	H	H	H	H	*t*-Bu	B	90(>30:1)	<1
10	H	H	H	H	*t*-Bu	D	99(9:1)	<1
11	CH_3	H	H	H	Ph	A	99(>30:1)	<1
12	CH_3	H	H	H	Et	A	70(>30:1)	<1
13	H	CH_3	H	H	Ph	A	96(>30:1)	4
14	H	CH_3	H	H	Et	A	98(>30:1)	2
15	H	H	CH_3	H	Ph	A	2	98
16	H	H	CH_3	H	Et	A	<1	93
17	CH_3	CH_3	H	H	Ph	A	83(>30:1)[f]	<1
18	CH_3	H	CH_3	H	Ph	A	85(>30:1)[f]	4
19	H	H	CH_3	CH_3	Ph	A	<1	99

a) All reactions were performed on a 2—3 mmol scale with the same experimental procedure as described in the text. b) Freshly distilled prior to use. A: Cyclohexanecarbaldehyde; B: Hexanal; C: 2-Hexenal; D: Benzaldehyde; E: 4-*t*-Butylcyclohexanone; F: Acetophenone. c) Isolated pure product. d) Unless otherwise specified, stereochemical assignments were based on conversion to the corresponding oxiranes. *erythro/threo* Ratio was determined by GLC analyses of the α adduct and/or the corresponding oxirane. e) The major product (97%) was found to be the structure having an axial hydroxyl group. f) Structure determination was not unambiguous but was based on (1) extrapolation from the other examples and (2) the characteristic features of NMR spectrum which were almost identical with those of entry 11 and different from those of the *threo* isomer.

the case, it was surprising that aromatic ketone revealed an exceedingly high *erythro* selectivity (entry 7).

It should be noted that the *erythro* stereoselectivity was not affected by the α and/or β branching of the starting sulfides. In addition, these regio- and stereoselectivities were not affected by the difference in another groups (R^5) on the sulfides. The corresponding [3-(alkylthio)allyl]lithium or other similar organometallic species are totally unsatisfactory reagents[3] for such rigorously regio- and stereoselective transformations. For example, [1-methyl-1-(phenylthio)allyl]lithium (see entry 11 of Table 1) gave 33% yield of the α-adduct (*erythro/threo*=61:39) and 62% yield of the γ-adduct. Analogously, [2-methyl-1-(phenylthio)allyl]lithium (see entry 13 of Table 1) produced 26% yield of the α-adduct (*erythro/threo*=52:48) and 73% yield of the γ-adduct.



2 α-adduct

3 γ-adduct

The possible explanation of these observation is as follows. It is generally assumed that the addition of the allylic organometallics to the carbonyl takes place through an allylic rearrangement of the organometallics by a chelate transition state (Fig. 1).[9] From this point of view, the structural feature of organometallic species may considerably influence on the regioselectivity of the reaction. Thus, the metal site in the organometallic reagents may be the cotrolling factor of the regioselectivity. It is very useful to know the structure of the organometallic reagents for the estimation of the course of the reactions, but it is, of course, not an easy task. In this case, our efforts to confirm the structure (metal site) of the anionic species by a physical technics gave, hitherto, unsuccessful results. Consequently, the only method for an understanding of the selectivity of this reaction is to examine the product distributions. If one can accept the assumption of the allylic rearrangement mechanism, the alkylthioallyl anion which has a countercation at the γ-position should give the α-adduct, and in contrast, that with cation at α-position to sulfur affords γ-adduct (see Fig. 1). In conclusion, the metal site of the alkylthioallyl anion can be rationalized as follows; (1) for unsubstituted allyl sulfide (entries 1—10), titanium moiety is attached at γ-position to sulfur; (2) γ-substituted allyl sulfide (entries 15, 16, and 19) has, in contrast, the titanium

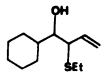
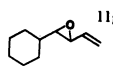
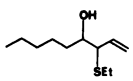
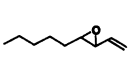
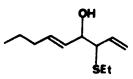
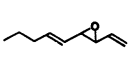
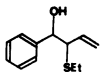
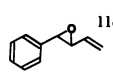
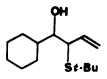
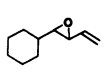
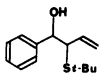
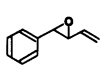
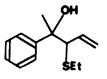
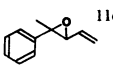
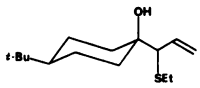
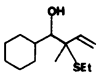
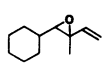
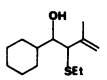
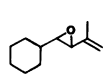
metal at its α-position; (3) α- or β-mono- and α,β-disubstituted allyl sulfides are metallated at γ-position again; (4) α,γ-disubstituted allyl sulfide (entry 18) is metallated at γ-position with remarkably high selectivity. Thus, the metallation (titanation) of the alkyl allyl sulfide is very sensitive to the substitution pattern of the starting allyl sulfide. If these trends are owing to the steric factor between the titanium metal and geminal substituent, the complete selectivity for the crotyl sulfide metallation is very surprising.

Next noticeable results is the high *erythro* selectivity of the reaction. The predominant formation of *erythro*-β-hydroxy sulfide (α-adduct) was explicable by considering the transition state structure for an allylic rearrangement mechanism stated above (see Fig. 1). As shown in Fig. 1, a six-membered ring transition state in which both R'S and R groups are equatorial is more favorable, and *erythro* product is thus formed. Apparently, it should be expected that the large substituents at α-position of the allyl sulfide reduce the stereoselectivity as a result of the disordering of the sulfide stereochemistry in the transition state (axial-equatorial).

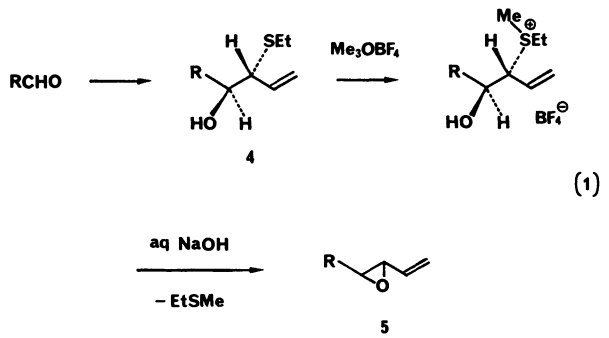
The Synthesis of Alkenyl Oxiranes and Dienes. As the general trends of the reaction of [3-(alkylthio)allyl]-titanium reagents with carbonyl compounds became clear, our attention turned to the synthetic applications of this reaction. Thus, the well-known procedure to desulfurize β-hydroxy sulfides *via* sulfonium salt formation followed by base-catalyzed cyclization[10] converts this reaction into a new stereoselective entry to alkenyloxirane synthesis.[11]

A few examples of this transformation were summarized in Table 2.

Table 2. Stereoselective synthesis of alkenyloxiranes[a]

Entry	Hydroxy Sulfide	Oxirane	*cis*:*trans*[b]	Yield/%	^{1}H NMR δ[i]
1		 11g)	c)	96	2.95 (dd, *J*=2, 5.5 Hz, 1H), 2.43 (br, 1H)[j]
2			96:4	86	2.88 (dd, *J*=2, 5.5 Hz, 1H), 2.61 (br, 1H)[k]
3			88:12[d]	97	3.2 (d, *J*=6.2 Hz, 2H)[l]
4		 11c, j)	86:14	94	3.15 (dd, *J*=2, 6 Hz, 1H), 3.55 (d, *J*=2 Hz, 1H)[m]
5			c)	83	
6			90:10	62	
7		 11e, g)	98:2[e]	95	3.25 (d, *J*=5.5 Hz, 1H), 1.63 (s, 3H, Me)
8		 11b, h)	f)	93	3.04 (d, *J*=5.5 Hz, 1H)
9			c), g)	82[h]	1.33 (s, 3H, Me), 2.17 (br, 1H)
10			93:7[d]	94	2.98 (d, *J*=2 Hz, 1H), 2.5 (br, 1H)[n]

a) All reaction were performed on a 0.5 mmol scale. b) Unless otherwise specified, stereochemical assignments were based on the NMR analyses of the oxiranes. *cis*/*trans* Ratio was determined by GLC and/or NMR analyses. c) Not determined. Two isomers were not separated on GLC, but pure *trans* isomer was confirmed by NMR analysis. d) Determined by NMR analysis. e) This product was transformed to the saturated oxirane, and spectrally identified by comparison with an authentic specimen prepared independently. f) The stereochemical assignment was based on the method of Trost. The equatorial/axial ratio was 96:4 (GLC). The major isomer was the one depicted in Table. g) Stereochemical assignment was based on NMR analysis of the saturated oxirane derived from the corresponding saturated hydroxy sulfide. The saturated oxirane was >95% pure *trans* by GLC analysis (trace amount of *cis* isomer was detected). h) It should be noted that the usual reaction conditions gave none of the desired product in this case (see text). The same reaction proceeds but in very low yield with use of the corresponding phenylthio derivatives. i) Measured in $CDCl_3$. j) *cis*-Isomer: ^{1}H NMR δ=3.20 (dd, *J*=5, 6 Hz, 1H), 2.58 (br, 1H). k) *cis*-Isomer: ^{1}H δ=3.19 (dd, *J*=5, 6 Hz, 1H). l) *cis*-Isomer: ^{1}H NMR δ=3.47 (m, 2H). m) *cis*-Isomer: ^{1}H NMR δ=4.03 (d, *J*=4 Hz, 1H). n) *cis*-Isomer: ^{1}H NMR δ=3.18 (d, *J*=4 Hz, 1H).

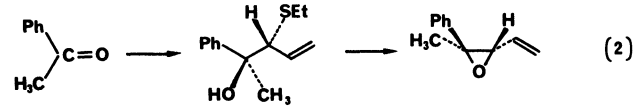


(1)

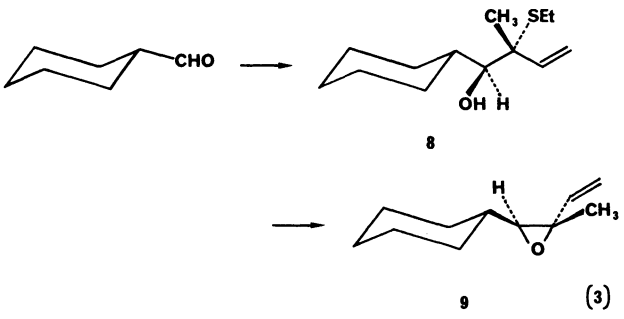
This desulfurization reaction is known to proceed *via* anti attack of oxide ion to sulfonium carbon in complete stereospecific manner. Thus, the *erythro*-β-hydroxy sulfides should be converted to *trans*-oxiranes. Actually, *trans*-oxirane was obtained as a major isomer and the isomer ratios (*trans/cis*) were parallel to those of the β-hydroxy sulfide (*erythro/threo*).

It should be noted that the efficiency of this transformation highly depends on steric factors, especially on the size of alkyl substituents on sulfur atom. Thus, the phenylthio and *t*-butylthio derivatives resulted in lower yield of oxirane than the corresponding ethylthio compound (see entries 1 and 5, 4 and 6 in Table 2). The same reaction in entry 10 but with the use of the phenylthio derivatives proceeds with fairly low yield.

The significant feature of this method can be seen for the preparation of trisubstituted oxiranes, for which there exists no stereoselective methodology (entries 7—9). Thus, two types of trisubstituted oxiranes can be prepared stereoselectively by this method in compliance with the appropriate choice of the starting materials (Eqs. 2 and 3).

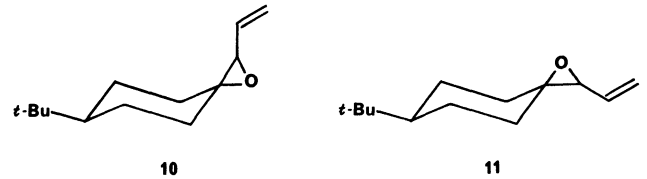


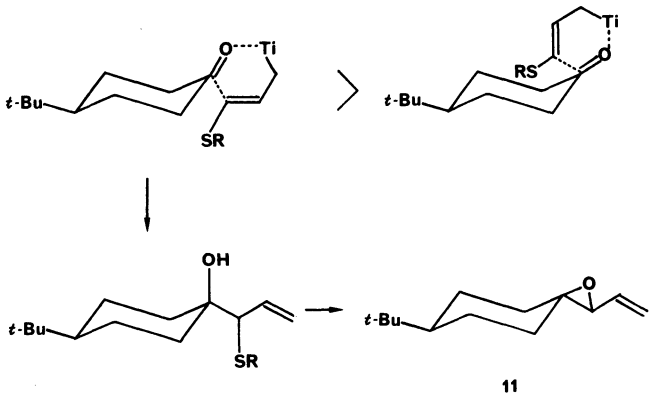
(2)



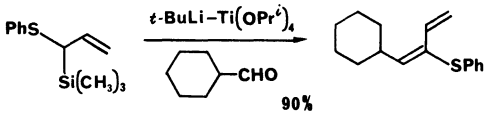
(3)

Another type of stereoselection is also observed in entry 8 of Table 2. It was known that the diphenylsulfonium allylide reacted with 4-*t*-butylcyclohexanone to give two isomeric vinyloxiranes **10** and **11** in a ratio of 1:4.[11b] In comparison with this data, it can be stated that the equatorial attack selectivity of the [3-(alkylthio)ally]titanium reagent is exceedingly high (96%).

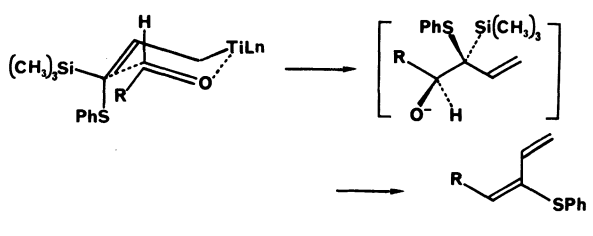




We next chose to examine the related reaction system in which the alkyl substituent was replaced by the silyl group. As mentioned in the preceeding section, the α-substituent of the starting allyl sulfides induce the α regioselectivity of the product and may give the significant influence on the *erythro* selectivity of the reaction. The silyl substituent in place of alkyl group may be expected to function in the same way. The silyl group when positioned at α to sulfur has the potential of Peterson elimination[12] following α-selective addition to carbonyl compounds so as to produce 2-(alkylthio)-1,3-alkadiene, an intriguing structure as a Diels-Alder component. Thus the metallation of **12**,[3g,13] metal exchange with titanium tetraisopropoxide as usual manner, and condensation with cyclohexanecarbaldehyde followed by elimination of Me_3SiO^- afforded the (*E*)-sulfide **13** (*E*/*Z*=10:1).[14]

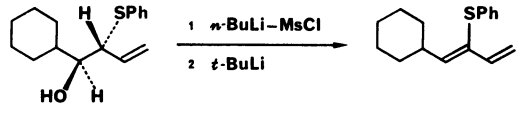


The formation of the elimination product is indicative of the α-selective addition of this reagent to carbonyl. As the syn elimination of the Me_3SiO^- in Peterson reaction gains general acceptance,[12] the product (*E*)-dienyl sulfide **13** must result from the α-*erythro*-selective carbonyl addition of the reagent. Although the other possible explanation is the α-*threo*-selective carbonyl addition followed by anti elimination, the α-*erythro*-selective reaction mechanism seems to be more likely since the similar syn elimination of Me_3SiO^- using titanium tetraisopropoxide was observed previously[15] and since allyltrimethylsilane on treatment with *t*-BuLi-Ti(OPr^i)$_4$ followed by cyclohexanecarbaldehyde gave the (*Z*)-diene selectively.[16]

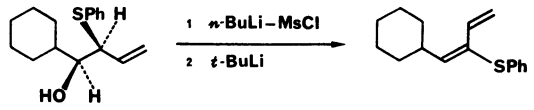


It should be noted that the reverse positioning (equatorial→axial) of the sulfur group in transition state is essential for the *erythro* selective addition of this reagent (Fig. 2). The direction of two substituents, phenylthio and trimethylsilyl group, in transition state may be determined by the thermodynamic requirement (relative stability between the possible transition states). Thus, the large trimethylsilyl group should have the equatorial position.

Further interesting results were obtained from the direct dehydration from the sulfide **14** (entry 1 of Table 1). Sequential treatment of the *erythro*-β-hydroxy sulfide **14** in THF first with butyllithium, then methanesulfonyl chloride and finally two equivalents of *t*-butyllithium produced the (*Z*)-sulfide **15** stereospectifically. This reaction is highly stereospecific. Thus,



14 **15**



16 **13**

the corresponding *threo* isomer **16**, obtained from the [3-(phenylthio)allyl]lithium and aldehyde followed by chromatographic separation, gave the (*E*)-isomer **13** exclusively under the same reaction conditions. Thus the remarkable syn elimination of MsOH should be concluded. The mechanistic details of this reaction will be published elsewhere.

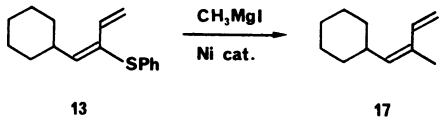
For the confirmation of the stereochemistry of the dienes, the sulfides **13** and **15** were converted to the corresponding sulfoxides through $NaIO_4$ oxidation. The large downfield shift (ΔH_1 shift=6.38 ppm) of the resonances of HC=CS(O)Ph of the product derived from **13** in the presence of Eu(fod)$_3$ (0.4 equiv) is expected from its *E* configuration. On the other hand, the (*Z*)-isomer revealed a small downfield shift (1.29 ppm) under the same conditions. The model experiment of (*E*)- and (*Z*)-2-cyclohexylvinyl phenyl sulfoxides gave a supporting result for this characteristic shift of absorption spectra (Table 3).

Table 3. ^{1}H NMR Parameters of vinyl sulfoxides[a)]

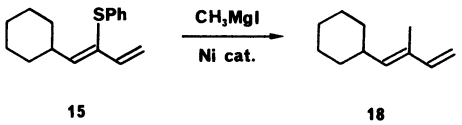
R	δH_a	δH_b	δH_e[b)]	ΔH[c)]
H	6.42		11.02	4.60
CH=CH$_2$	6.22		12.60	6.38
H		~5.8	7.13	~1.3
CH=CH$_2$		5.98	7.27	1.29

a) Chemical shifts are reported in parts per million downfield from the internal TMS reference. b) δH_E shows the chemical shift of H_a or H_b in the presence of 0.4 equiv of Eu(fod)$_3$. c) $\Delta H=\delta H_E-\delta H_a$ (or δH_b).

Exposure of these sulfides **13** and **15** to methylation conditions with MeMgI under Ni catalyst[17] led to dienes **17** and **18**, respectively with rigorous stereospecificities.



13 **17**



15 **18**

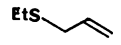
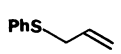
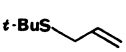
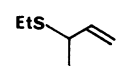
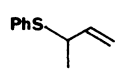
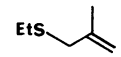
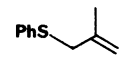
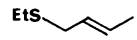
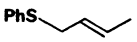
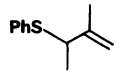
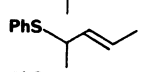
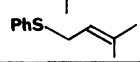
Experimental

General. ^{1}H NMR spectra were taken on a JNM-PMX 60 spectrometer. The chemical shifts are reported as parts per million relative to TMS as the internal standard. The infrared spectra were recorded on a Hitachi 260-10 spectrometer in CCl_4 solution unless otherwise stated. The isomeric ratio of the products was determined by gas-liquid phase chromatography (GLC) using a Hitachi Model 163 and 164 instruments equipped with a flame ionization detector using nitrogen as carrier gas. For TLC analysis throughout this work, Merck precoated TLC plates (silica gel 60 GF_{254}, 0.25 mm, or silica gel 60 HF_{254} silanized, 0.25 mm) were used. The products were purified by preparative column chromatography on silica gel E. Merck Art. 9385, or silanized silica gel E. Merck Art. 7719. Microanalyses were accomplished at the Institute of Applied Organic Chemistry, Faculty of Engineering, Nagoya University. Unless otherwise specified, all reactions were carried out under an atmosphere of dry argon. In experiments requiring dry solvents, ether and tetrahydrofuran (THF) were distilled from sodium-benzophenone. Benzene, hexane, and toluene were dried over sodium metal. Dichloromethane was dried over 4A molecular sieves. Other commercially supplied materials were used as received.

Preparation of Allyl Sulfides. Method A:[18] To a mixture of thiol (0.15 mol) and sodium methoxide (0.17 mol) in methanol (200 ml) was added allyl bromide (0.15 mol) at 0 °C, and the mixture was stirred at 0 °C for 1 h and 25 °C overnight. The resulting mixture was poured into 2 mol dm^{-3} sodium hydroxide and the product was extracted with ether. The organic layer was washed with brine, dried, and freed of solvent. Distillation of the residue gave desired allyl sulfide. Method B: To a solution of alkyl allyl sulfide (48 mmol) dissolved in THF (50 ml) was added *t*-butyllithium in pentane (48 mmol) dropwise at −78 °C, and the resulted solution was stirred for 10 min at the same temperature and 30 min at 0 °C leading to complete lithiation. Then, the mixture was cooled to −78 °C again and methyl iodide (60 mmol) was added to this solution. After stirring for 10 min at −78 °C and 10 min at 0 °C, and further 20 min at 25 °C, the resulting mixture was poured into 2 mol dm^{-3} hydrochloric acid. The product was extracted with ether, and the combined organic layer was dried and freed of solvent. Distillation of the residue gave desired allyl sulfide.

Preparation of Phenyl 1-(Trimethylsilyl)allyl Sulfide.[13] To a solution of allyl phenyl sulfide (15 g, 100 mmol) in THF

TABLE 4. PREPARATION OF ALLYL SULFIDES[a]

Sulfides	Method[b]	Yield(%)	Bp(°C)/mmHg	^{1}H NMR δ[c]
	A	72	110—115/760	1.20(t, 7Hz, 3H), 2.41(q, 7Hz, 2H), 3.06(d, 6.5Hz, 2H), 4.8—5.3(m, 2H), 5.75(ddt, 6.5, 9, and 18Hz, 1H).[3b,19a]
	A	84	110—111/23	3.43(d, 6.5Hz, 2H), 4.98(dd, 1 and 10Hz, 1H), 5.02(dd, 1 and 18Hz, 1H), 5.83(ddt, 6.5, 10, and 18Hz, 1H).[18]
	A	66[d]	58—60/37	1.30(s, 9H), 3.11(d, 7Hz, 2H), 4.80—5.27(m, 2H), 5.80(ddt, 7, 9.5, and 17Hz, 1H).[20]
	B	70	124—125/760	1.19(t, 7Hz, 3H), 1.28(d, 7Hz, 3H), 2.36(q, 7Hz, 2H), 3.23(dt, 7 and 7Hz, 1H), 4.87(dd, 1 and 16Hz, 1H), 4.92(dd, 1 and 10Hz, 1H), 5.33—5.92(m, 1H).[19c]
	B	79	e)	1.35(d, 7Hz, 3H), 3.68(dt, 7 and 7Hz, 1H), 4.87(dd, 1 and 16Hz, 1H), 4.88(dd, 1 and 10Hz, 1H), 5.4—6.07(m, 1H), 7.20(m, 5H).[18]
	A	83	36—37/19	1.18(t, 7Hz, 3H), 1.78(s, 3H), 2.34(q, 7Hz, 2H), 3.0(s, 2H), 4.72(s, 2H).[19b]
	A	89	113—115/18	1.83(s, 3H), 3.42(s, 2H), 4.74(s, 2H), 7.17(m, 5H).[2a,21]
	A	87[f]	42—47/19	1.19(t, 7Hz, 3H), 1.70(m, 3H), 2.38(q, 7Hz, 2H), 2.99(m, 2H), 5.42(m, 2H).[19b]
	A	96[g]	119—122/20	1.64(d, 3.5Hz, 3H), 3.41(m, 2H), 5.46(m, 2H), 7.14(s, 5H).[18,21]
	B	78	118—122/19	1.38(d, 7Hz, 3H), 1.82(s, 3H), 3.68(q, 7Hz, 1H), 4.62(s, 2H), 7.18(m, 5H).[22]
	B	72[h]	130—132/26	1.32(d, 7Hz, 3H), 1.58(d, 5Hz, 3H), 3.59(dt, 7 and 7Hz, 1H), 5.31(m, 2H), 7.17(m, 5H).[21]
	A	90	133—139/23	1.56(s, 3H), 1.69(s, 3H), 3.42(d, 7.5Hz, 2H), 5.24(t, 7.5Hz, 1H), 4.16(m, 5H).[23]

a) The reactions were performed on 50—250 mmol scale. b) Method A: Thiol-sodium methoxide-allyl bromide; Method B: Allyl sulfide-*t*-butyllithium-methyl iodide. c) ^{1}H NMR spectrum were measured in CCl_4 solution. d) This product was contaminated with *ca.* 15% of diallyl sulfide, which could not be separated. The mixture was used for the reaction. e) Purified by silica-gel column chromatography (hexane, R_f=0.24). A small amount of the regioismer, 1-butenyl phenyl sulfide, was also produced as a side product, but it could be separated out by column chromatography (hexane, R_f=0.35). f) This contains *ca.* 8% of the *Z*-isomer. g) This contains *ca.* 4% of the *Z*-isomer and 5% of the regioisomer, 1-methylallyl phenyl sulfide. They could be separated out by repeated fractional distillation. h) This contains *ca.* 10% of *Z*-isomer.

(200 ml) was added *t*-butyllithium in pentane (2.0 mol dm^{-3} solution, 50 ml, 100 mmol) at −78 °C. The solution was stirred at 0 °C for 30 min, and then cooled to −78 °C again. Titanium tetraisopropoxide[24] (32.7 ml, 110 mmol) was added to the mixture and the resulting solution was stirred for 10 min at the same temperature. To this solution was added chlorotrimethylsilane (12.7 ml, 100 mmol) at −78 °C, and stirring was continued for 10 min at −78 °C and 1 h at 0 °C. The reaction mixture was poured into 2 mol dm^{-3} hydrochloric acid and the product was extracted with ether. The combined organic layer was dried and concentrated.[25] Fractional distillation of the residue gave phenyl 1-(trimethylsilyl)-allyl sulfide (14.6 g, 66%). Bp 73—74 °C (0.9 mmHg†); ^{1}H NMR (CCl_4) δ=0.13 (s, 9H), 3.12 (d, *J*=8.5 Hz, 1H), 4.86 (dd, *J*=1 and 8.5 Hz, 1H), 4.88 (dd, *J*=1 and 17 Hz, 1H), 5.72 (dt, *J*=8.5 and 17 Hz, 1H).

Reaction of [3-(Alkylthio)allyl]titanium Reagents with Carbonyl Compounds. The following experimental procedure provides details of typical reaction conditions. To a solution of allyl phenyl sulfide (0.36 g, 2.4 mmol) in THF (8 ml) was added butyllithium[26] in hexane (1.6 mol dm^{-3} solution, 1.5 ml, 2.4 mmol) dropwise at −78 °C, and the orange mixture was stirred at 0 °C for 30 min. Titanium tetraisopropoxide (0.71 ml, 2.4 mmol) was added to the solution at −78 °C, and the resulting solution was stirred for 10 min. Cyclohexanecarbaldehyde (0.24 ml, 2.0 mmol) was added over a period of 5 min at −78 °C, and the mixture was stirred at −78 °C for 10 min and then at 0 °C for 1 h. Then the mixture was poured into 2 mol dm^{-3} hydrochrolic acid and the product was extracted with ether. The organic layer was dried and concentrated. Chromatography of the residue on silica-gel column[27] (4:1 hexane-ether) gave *erythro*-1-cyclohexyl-2-phenylthio-3-buten-1-ol (0.52 g, 99%).[28] GLC analysis of the product revealed the isomeric ratio of >30:1 (*erythro*: *threo*). Stereochemical assignments of the sulfide-carbonyl adducts were based on conversion to the corresponding oxiranes.

erythro-*1-Cyclohexyl-2-phenylthio-3-buten-1-ol*: R_f=0.30 (4:1 hexane-ether); ^{1}H NMR (CCl_4) δ=0.55—2.3 (m, 11H), 2.17 (d, *J*=3 Hz, 1H), 3.30 (m, 1H), 3.73 (dd, *J*=4 and 8.5 Hz, 1H), 4.96 (dd, *J*=2 and 16.5 Hz, 1H), 5.04 (dd, *J*=2 and 10 Hz, 1H), 5.83 (ddd, *J*=8.5, 10, and 16.5 Hz, 1H), 7.2 (m, 5H); IR 3550, 3090, 2930, 2860, 1645, 1450 cm^{-1}; Found: C, 73.20; H, 8.47%. Calcd for $C_{16}H_{22}OS$: C, 73.23; H, 8.45%.

erythro-*1-Cyclohexyl-2-ethylthio-3-buten-1-ol*: R_f=0.38 (2:1 hexane-ether); ^{1}H NMR (CCl_4) δ=1.22 (t, *J*=7 Hz, 3H), 0.83—2.17 (m, 12H), 2.42 (q, *J*=7 Hz, 2H), 3.33 (m, 2H), 5.00 (dd, *J*=2 and 18 Hz, 1H), 5.10 (dd, *J*=2 and 8 Hz, 1H), 5.42—6.08 (m, 1H); IR 3550, 3090, 2920, 2850, 1640, 1450 cm^{-1}; Found: C, 66.95; H, 10.30%. Calcd for $C_{12}H_{22}OS$: C, 67.23; H, 10.35%.

erythro-*3-Ethylthio-1-nonen-4-ol*: R_f=0.31 (2:1 hexane-ether); ^{1}H NMR (CCl_4) δ=0.73—1.73 (m, 14H), 1.85 (m, 1H), 2.41 (q, *J*=7 Hz, 2H), 3.15 (dd, *J*=4.2 and 8 Hz, 1H), 3.50 (m, 1H), 4.98 (dd, *J*=2 and 16 Hz, 1H), 5.05 (dd, *J*=2 and 9 Hz, 1H), 5.37—

† 1 mmHg≈133.322 Pa.

6.00 (m, 1H); IR 3500, 3090, 2950, 2860, 1635, 1450 cm^{-1}; Found: C, 65.60; H, 10.73%. Calcd for $C_{11}H_{22}OS$: C, 65.29; H, 10.96%.

erythro-*3-Ethylthio-1,5-nonadien-4-ol*: R_f=0.30 (2:1 hexane–ether); ^{1}H NMR (CCl_4) δ=0.71—1.79 (m, 8H), 1.80—2.21 (m, 3H), 2.42 (q, J=7 Hz, 2H), 3.18 (dd, J=5 and 8.5 Hz, 1H), 3.99 (m, 1H), 4.99 (dd, J=2 and 17 Hz, 1H), 5.05 (dd, J=2 and 9 Hz, 1H), 5.36—5.96 (m, 3H); IR 3500, 3070, 2950, 2860, 1635, 1450 cm^{-1}; MS m/z: 200 (M^+).

erythro-*2-Ethylthio-1-phenyl-3-buten-1-ol*: R_f=0.38 (2:1 hexane–ether); ^{1}H NMR (CCl_4) δ=1.19 (t, J=7 Hz, 3H), 2.18—2.67 (m, 3H), 3.38 (dd, J=5 and 9 Hz, 1H), 4.58—5.17 (m, 3H), 5.33—6.00 (m, 1H); IR 3460, 3070, 2970, 2930, 1640, 1450 cm^{-1}; Found: C, 69.49; H, 7.63%. Calcd for $C_{12}H_{16}OS$: C, 69.18; H, 7.74%.

4-t-Butyl-1-[1-(ethylthio)allyl]cyclohexanol: R_f=0.45 (2:1 hexane–ether); ^{1}H NMR (CCl_4) δ=0.85 (s, 9H), 1.03—1.82 (m, 12H), 1.87 (br s, 1H), 2.43 (q, J=7 Hz, 2H), 2.98 (d, J=10 Hz, 1H), 4.95 (dd, J=3 and 18 Hz, 1H), 5.02 (dd, J=3 and 9 Hz, 1H), 5.38—5.97 (m, 1H); IR 3520, 2950, 1630, 1440 cm^{-1}; MS m/z: 256 (M^+).

erythro-*3-Ethylthio-2-phenyl-4-penten-2-ol*: R_f=0.33 (4:1 hexane–ether); ^{1}H NMR (CCl_4) δ=1.17 (t, J=7 Hz, 3H), 1.60 (s, 3H), 2.34 (q, J=7 Hz, 2H), 2.70 (s, 1H), 3.35 (d, J=10 Hz, 1H), 4.87 (dd, J=2 and 18 Hz, 1H), 4.95 (dd, J=2 and 9.5 Hz, 1H), 5.68 (ddd, J=9.5, 10, and 18 Hz, 1H), 7.23 (m, 5H); IR 3500, 3060, 2980, 2880, 1640, 1450 cm^{-1}; MS m/z: 222 (M^+).

erythro-*1-Cyclohexyl-2-(t-butylthio)-3-buten-1-ol*: ^{1}H NMR (CCl_4) δ=0.7—2.12 (m, 12H), 1.32 (s, 9H), 3.03—3.37 (m, 1H), 3.43 (dd, J=4 and 9 Hz, 1H), 4.87—5.28 (m, 2H), 5.87 (ddd, J=9, 9, and 18 Hz, 1H); IR 3400, 2930, 1635, 1450 cm^{-1}; MS m/z: 242 (M^+).

erythro-*1-Phenyl-2-(t-butylthio)-3-buten-1-ol*: ^{1}H NMR (CCl_4) δ=1.28 (s, 9H), 2.52 (m, 1H), 3.46 (dd, J=4.5 and 8.5 Hz, 1H), 4.53—5.12 (m, 3H), 5.65 (ddd, J=8.5, 8.5, and 17 Hz, 1H), 7.10 (s, 5H); IR 3400, 3070, 2970, 1640, 1450 cm^{-1}; MS m/z: 236 (M^+).

erythro-*3-(t-Butylthio)-1-nonen-4-ol*: ^{1}H NMR (CCl_4) δ=0.7—1.62 (m, 11H), 1.32 (s, 9H), 2.42 (br d, J=7 Hz, 1H), 3.35 (dd, J=4 and 8 Hz, 1H), 3.53 (m, 1H), 5.05 (dd, J=2 and 10 Hz, 1H), 5.17 (dd, J=2 and 17 Hz, 1H), 5.90 (ddd, J=8, 10, and 17 Hz, 1H); IR 3530, 3090, 2960, 2860, 1640, 1460 cm^{-1}; MS m/z: 230 (M^+).

erythro-*1-Cyclohexyl-2-methyl-2-phenylthio-3-buten-1-ol*: R_f= 0.39 (4:1 hexane–ether); ^{1}H NMR (CCl_4) δ=1.29 (s, 3H), 0.66—1.99 (m, 11H), 2.52 (br s, 1H), 3.25 (br s, 1H), 4.83 (dd, J=1 and 17 Hz, 1H), 5.01 (dd, J=1 and 11 Hz, 1H), 6.21 (dd, J=11 and 17 Hz, 1H), 7.26 (m, 5H); IR 3620, 3090, 2930, 2850, 1640, 1450 cm^{-1}; Found: C, 74.12; H, 8.81%. Calcd for $C_{17}H_{24}OS$: C, 73.86; H, 8.75%.

erythro-*1-Cyclohexyl-2-ethylthio-2-methyl-3-buten-1-ol*: R_f= 0.33 (4:1 hexane–ether); ^{1}H NMR (CCl_4) δ=1.18 (t, J=7 Hz, 3H), 1.39 (s, 3H), 0.8—1.97 (m, 11H), 2.13—2.57 (m, 3H), 3.23 (br d, J=4.5 Hz, 1H), 4.97 (dd, J=2 and 17 Hz, 1H), 5.07 (dd, J=2 and 10 Hz, 1H), 6.08 (dd, J=10 and 17 Hz, 1H); IR 3480, 3080, 2920, 2850, 1635, 1450 cm^{-1}; Found: C, 68.11; H, 10.60%. Calcd for $C_{13}H_{24}OS$: C, 68.37; H, 10.59%.

erythro-*1-Cyclohexyl-3-methyl-2-phenylthio-3-buten-1-ol*: R_f= 0.23 (8:1 hexane–ether); ^{1}H NMR (CCl_4) δ=0.87—2.2 (m, 12H), 1.82 (s, 3H), 3.2—3.53 (m, 1H), 3.62 (d, J=7 Hz, 1H), 4.75 (m, 2H), 7.17 (m, 5H); IR 3600, 3090, 2940, 2860, 1650, 1600, 1450 cm^{-1}; Found: C, 73.95; H, 8.78%. Calcd for $C_{17}H_{24}OS$: C, 73.86; H, 8.75%.

erythro-*1-Cyclohexyl-2-ethylthio-3-methyl-3-buten-1-ol*: R_f= 0.35 (8:1 hexane–ethyl acetate); ^{1}H NMR (CCl_4) δ=1.20 (t, J=7 Hz, 3H), 1.80 (s, 3H), 1.0—2.0 (m, 12H), 2.33 (q, J=7 Hz, 2H), 3.27 (br s, 2H), 4.83 (m, 2H); IR 3500, 3080, 2940, 2860, 1650, 1450 cm^{-1}; Found: C, 68.47; H, 10.67%. Calcd for $C_{13}H_{24}OS$: C, 68.37; H, 10.59%.

1-Cyclohexyl-2-methyl-4-phenylthio-3-buten-1-ol: R_f=0.20 (8:1 hexane–ether); ^{1}H NMR (CCl_4) δ=1.06 (d, J=7 Hz, 3H), 0.67—2.0 (m, 12H), 2.45 (m, 1H), 3.03 (br s, 1H), 5.63—6.33 (m, 2H), 7.18 (br s, 5H); IR 3500, 3080, 2930, 2850, 1590, 1450 cm^{-1}; Found: C, 73.91; H, 8.76%. Calcd for $C_{17}H_{24}OS$: C, 73.86; H, 8.75%.

1-Cyclohexyl-4-ethylthio-2-methyl-3-buten-1-ol: R_f=0.22 (8:1 hexane–ethyl acetate); ^{1}H NMR (CCl_4) δ=1.07 (t, J=7 Hz, 3H), 1.34 (d, J=7 Hz, 3H), 0.83—2.11 (m, 12H), 2.44 (m, 1H), 2.63 (q, J=7 Hz, 2H), 3.00 (m, 1H), 5.38 (dd, J=8 and 15 Hz, 1H), 5.92 (d, J=15 Hz, 1H); IR 3550, 2920, 2840, 1440, 980, 970 cm^{-1}; Found: C, 68.54; H, 10.65%. Calcd for $C_{13}H_{24}OS$: C, 68.37; H, 10.59%.

erythro-*1-Cyclohexyl-2,3-dimethyl-2-phenylthio-3-buten-1-ol*: R_f=0.36 (4:1 hexane–ether); ^{1}H NMR (CCl_4) δ=1.25 (s, 3H), 0.75—2.0 (m, 11H), 2.03 (s, 3H), 2.12 (s, 1H), 3.41 (br m, 1H), 4.80 (br s, 1H), 4.90 (br s, 1H), 7.25 (m, 5H); IR 3600, 3500, 3080, 2920, 2850, 1635, 1450 cm^{-1}; Found: C, 74.45; H, 9.06%. Calcd for $C_{18}H_{26}OS$: C, 74.43; H, 9.02%.

erythro-*1-Cyclohexyl-2-methyl-2-phenylthio-3-penten-1-ol*: R_f= 0.39 (4:1 hexane–ether); ^{1}H NMR (CCl_4) δ=1.28, (s, 3H), 1.65 (d, J=6 Hz, 3H), 0.75—1.83 (m, 11H), 2.52 (d, J=2 Hz, 1H), 3.17 (d, J=2 Hz, 1H), 5.23 (dq, J=6 and 16 Hz, 1H), 5.83 (d, J=16 Hz, 1H), 7.27 (m, 5H); IR 3540, 3080, 2930, 2850, 1450, 975 cm^{-1}; Found: C, 74.23; H, 8.98%. Calcd for $C_{18}H_{26}OS$: C, 74.43; H, 9.02%.

1-Cyclohexyl-2,2-dimethyl-4-phenylthio-3-buten-1-ol: R_f=0.25 (4:1 hexane–ether); ^{1}H NMR (CCl_4) δ=1.08 (s, 6H), 0.86—1.94 (m, 12H), 3.01 (s, 1H), 5.97 (s, 2H), 7.14 (s, 5H); IR 3650, 3080, 2930, 2850, 1590, 1480, 1450, 1100, 970 cm^{-1}; Found: C, 74.63; H, 9.07%. Calcd for $C_{18}H_{26}OS$: C, 74.43; H, 9.02%.

Synthesis of Vinyloxiranes.[10] *The following experimental procedure is typical for the conversion of β-hydroxy sulfides to oxiranes*: To a suspension of trimethyloxonium tetrafluoroborate (0.54 mmol) in dichloromethane (2 ml) was added β-hydroxy sulfide (0.50 mmol) dissolved in dichloromethane (2 ml) at 0 °C, and the mixture was stirred at 0—25 °C until all the sulfide had been consumed (TLC assay). Then, 0.5 mol dm^{-3} sodium hydroxide solution (5 ml) was added to the mixture at 0 °C, and the resulting two phases mixture was efficiently stirred for 1—12 h at 25 °C. The reaction mixture was poured into water and the product was extracted with ether. The combined organic layer was dried and concentrated. Chromatography of the residual oil on silica-gel column (20:1 hexane–ether) gave the pure vinyloxirane.[29] 4-Cyclohexyl-3,4-epoxy-3-methyl-1-butene (entry 9 in Table 2) could not be prepared by this typical procedure, but was efficiently formed by treating the sulfonium salt obtained as above with butyllithium (1 equiv) at −78 °C.

The *trans*-oxirane was generally characterized by a coupling constant between the vicinal oxirane hydrogenes of ≈2 Hz[11] observed in the ^{1}H NMR spectrum. On the other hand, the *cis*-oxirane was characterized by a coupling constant of ≈4 Hz.[11]

The stereochemistry of 3,4-epoxy-4-phenyl-1-pentene was determined as follows. To a solution of propyltriphenylphosphonium bromide (1.55 g, 4 mmol) in THF (10 ml) was added butyllithium in hexane (1.6 mol dm^{-3}, 2.5 ml, 4 mmol) at 0 °C, and the mixture was stirred for 30 min at the same temperature. Acetophenone (0.47 ml, 4 mmol) dissolved in THF (1 ml) was added to the solution and the resulting mixture was stirred for 2 h at 0 °C and 0.5 h at 25 °C. Then, the reaction mixture was poured into water and the product was extracted with ether. The combined organic layer was dried and evaporated. Chromatography of the residual oil on silica-gel column (hexane) gave 2-phenyl-2-pentene (530 mg, 91%). NMR analysis of this product revealed an isomeric ratio of *ca.* 7:3 (*Z*:*E*).[30] ^{1}H NMR (CCl_4) δ=0.57—1.41 (m), 1.98 (s, 3H), 1.67—2.44 (m, 2H), 5.31 (br t, J=6.5 Hz, *Z*-isomer), 5.61 (br

t, J=7 Hz, *E*-isomer), 7.04 (m, 5H). To a solution of *m*-chloroperbenzoic acid (271 mg, 1.1 mmol) in dichloromethane (4 ml) was added 2-phenyl-2-pentene (150 mg, 1.0 mmol) dissolved in dichloromethane (2 ml) at 0 °C. The mixture was stirred for 1 h at 0 °C, and then poured into aqueous sodium sulfite solution. The product was extracted with ether and washed with aqueous sodium hydrogencarbonate. The combined organic layer was dried and concentrated. Chromatography of the residue on silica-gel column gave the isomeric mixture of 2,3-epoxy-2-phenylpentane (156 mg, 96%). GLC analysis of this product revealed the isomeric ratio of 28:72 (*trans*:*cis*). ^{1}H NMR (CCl_4) δ=0.67—1.35 (m, 5H), 1.56 (s, 3H), 2.58 (t, J=6 Hz, *trans* isomer), 2.80 (t, J=5.8 Hz, *cis* isomer), 7.13 (s, 5H). NMR spectrum and GLC behaviour of the major isomer of this product was in complete agreement with the product derived from the sulfide-carbonyl adduct by the following sequence: (1) Reduction of double bond by H_2NNH_2–H_2O_2–$CuSO_4$ in aquous ethanol at 0—25 °C (60%); (2) Epoxidation by the general method described in text (90%).

3-Ethylthio-2-phenyl-2-pentanol: ^{1}H NMR (CCl_4) δ=0.77—1.43 (m, 8H), 1.58 (s, 3H), 2.1—2.77 (m, 4H), 7.22 (m, 5H).

trans-*2,3-Epoxy-2-phenylpentane*: ^{1}H NMR (CCl_4) δ=0.83—1.33 (m, 5H), 1.56 (s, 3H), 2.58 (t, J=6 Hz, 1H), 7.12 (s, 5H); MS *m/z*: 162 (M^+).

The stereochemistry of 4-cyclohexyl-3,4-epoxy-3-methyl-1-butene was determined as follows. To a solution of propyltriphenylphosphonium bromide (1.93 g, 5.0 mmol) in THF (15 ml) was added butyllithium in hexane (1.6 mol dm^{-3} solution, 3.13 ml, 5.0 mmol) at 0 °C, and the mixture was stirred for 1 h at the same temperature. Methyl iodide (0.31 ml, 5.0 mmol) was added to the mixture and the solution was stirred for 1 h at 0 °C. To the resulting dark brown solution was added butyllithium in hexane (3.13 ml, 5.0 mmol) at 0 °C. After stirring for 1 h, cyclohexanecarbaldehyde (0.61 ml, 5.0 mmol) was added to the solution at 0 °C and stirring was continued for 1 h. The reaction mixture was poured into water and the product was extracted with ether. The combined organic layer was dried and concentrated. Chromatography of the residual oil on silica-gel column (pentane) gave 1-cyclohexyl-2-methyl-1-butene (0.52 g, 69%). GLC analysis of this product revealed an isomeric ratio of *ca.* 1.3:1 (*E*:*Z*). ^{1}H NMR ($CDCl_3$) δ=1.00 (t, J=7 Hz), 1.60 (d, J=1.5 Hz, *E*-isomer), 1.67 (d, J=1.8 Hz, *Z*-isomer), 0.67—2.33 (m), 4.95 (br d, J=8 Hz, 1H). To a solution of *m*-chloroperbenzoic acid (271 mg, 1.1 mmol) in dichloromethane (4 ml) was added 1-cyclohexyl-2-methyl-1-butene (152 mg, 1.0 mmol) dissolved in dichloromethane (2 ml) at 0 °C. The mixture was stirred for 1 h at 0 °C, and then poured into aqueous sodium sulfite solution. The product was extracted with ether and washed with aqueous sodium hydrogencarbonate. The combined organic layer was dried and concentrated. Chromatography of the residue on silica-gel column gave the isomeric mixture of 1-cyclohexyl-1,2-epoxy-2-methylbutane (162 mg, 96%). ^{1}H NMR ($CDCl_3$) δ=1.27 (s, *trans*-isomer), 1.29 (s, *cis*-isomer), 0.67—2.11 (m), 2.41 (br, 1H). GLC analysis of this product showed an isomeric ratio of *ca.* 1.4:1 (*trans*:*cis*).[31] The major isomer (*trans*) was spectrally and chromatographically in complete agreement with the product derived from the sulfide-carbonyl adduct by the following sequence: (1) Reduction of the double bond by H_2NNH_2–H_2O_2–$CuSO_4$ in aqueous ethanol at 0—25 °C (44%); (2) Epoxidation by usual manner (89%).

1-Cyclohexyl-2-ethylthio-2-methyl-1-butanol: ^{1}H NMR ($CDCl_3$) δ=1.08 (t, J=7 Hz), 1.24 (s, 3H), 0.67—2.02 (m), 2.32 (m, 1H), 2.43 (q, J=7 Hz, 2H), 3.09 (br d, J=4 Hz, 1H).

1-Cyclohexyl-1,2-epoxy-2-methylbutane: ^{1}H NMR (CCl_4) δ=1.17 (s, 3H),[32] 0.67—2.08 (m, 16H), 2.18 (br, 1H); ($CDCl_3$) δ=1.26 (s, 3H), 0.67—2.08 (m, 16H), 2.39 (br, 1H); MS *m/z*: 168 (M^+). GLC analysis of this product showed a >95% purity of *trans* isomer.

Reaction of Metallated 4 with Cyclohexanecarbaldehyde. To a solution of phenyl 1-(trimethylsilyl)allyl sulfide (445 mg, 2.0 mmol) in THF (5 ml) was added *t*-butyllithium in pentane (2.0 mol dm^{-3} solution, 1.0 ml, 2.0 mmol) at −78 °C, and the mixture was stirred at 0 °C for 1 h. Titanium tetraisopropoxide (0.65 ml, 2.2 mmol) was added to the solution at −78 °C, and the resulting mixture was stirred for 10 min. Cyclohexanecarbaldehyde (0.24 ml, 2.0 mmol) was added at −78 °C and the solution was stirred for 10 min at −78 °C and 1 h at 0 °C, and further 1 h at 25 °C. Then the mixture was poured into 2 mol dm^{-3} hydrochloric acid and the product was extracted with ether. The organic layer was dried and concentrated. Chromatography of the residue on silanized silica-gel column (hexane) gave (*E*)-1-cyclohexyl-2-phenylthio-1,3-butadiene (440 mg, 90%). GLC analysis of the product revealed the *E*/*Z* ratio of 10:1. R_f=0.59 (hexane, silanized silica gel); ^{1}H NMR (CCl_4) δ=0.41—1.91 (m, 10 H), 2.57 (br, 1H), 5.11 (ddd, J=1, 1, and 10.4 Hz, 1H), 5.61 (dd, J=1 and 17 Hz, 1H), 5.99 (br d, J=9.6 Hz, 1H), 6.64 (dd, J=10.4 and 17 Hz, 1H), 7.03 (br s, 5H); IR 3080, 3020, 2940, 2870, 1633, 1590, 1485, 1460, 1450, 1040, 986, 928, 910 cm^{-1}; MS *m/z*: 244 (M^+).

Dehydration of 1-Cyclohexyl-2-phenylthio-3-buten-1-ol. To a solution of *erythro*-1-cyclohexyl-2-phenylthio-3-buten-1-ol (525 mg, 2.0 mmol) in THF (8 ml) was added butyllithium in hexane (1.6 mol dm^{-3} solution, 1.25 ml, 2.0 mmol) at 0 °C. Methanesulfonyl chloride (0.155 ml, 2.0 mmol) was added to the mixture and stirring was continued for 1 h at 0 °C. Then, the resulting mixture was cooled to −78 °C and treated with *t*-butyllithium in pentane (2.0 mol dm^{-3} solution, 2.0 ml, 4.0 mmol). After stirring for 2 h at 0 °C, the mixture was poured into ice-cooled 2 mol dm^{-3} hydrochloric acid and the product was extracted with ether. The organic layer was dried and concentrated to give oily product. Chromatography of the crude product on silica-gel column (hexane) gave(*Z*)-1-cyclohexyl-2-phenylthio-1,3-butadiene (318 mg, 65%). R_f=0.31 (hexane); ^{1}H NMR (CCl_4) δ=0.72—1.97 (m, 10H), 2.82 (br m, 1H), 4.94 (dd, J=1 and 10 Hz, 1H), 5.42 (dd, J=1 and 16.4 Hz, 1H), 6.01 (d, J=9 Hz, 1H), 6.28 (dd, J=10 and 16.4 Hz, 1H); IR 3080, 3020, 2940, 2870, 1635, 1595, 1482, 1455, 1450, 1035, 990, 918, 908 cm^{-1}; MS *m/z*: 244 (M^+).

The corresponding *E*-isomer was prepared by this method from the *threo*-1-cyclohexyl-2-phenylthio-3-buten-1-ol. The NMR spectrum and GLC behaviour of this compound were complete agreement with the product from the reaction of metallated **4** with aldehyde.

NMR Analysis of Vinyl Sulfoxides. (*E*)- and (*Z*)-1-cyclohexyl-2-phenylsulfinyl-1,3-butadiene were prepared by the oxidation of the corresponding sulfides with sodium periodate (excess, in MeOH–H_2O, 2:1).

(E)-1-Cyclohexyl-2-phenylsulfinyl-1,3-butadiene: ^{1}H NMR (CCl_4) δ=0.9—2.07 (m, 10H), 2.42 (br m, 1H), 5.17 (dd, J=1.5 and 11 Hz, 1H), 5.36 (dd, J=1.5 and 17.5 Hz, 1H), 6.22 (d, J=9.5 Hz, 1H), 6.25 (dd, J=11 and 17.5 Hz, 1H), 7.34 (m, 5H).

(Z)-1-cyclohexyl-2-phenylsulfinyl-1,3-butadiene: ^{1}H NMR (CCl_4) δ=0.82—2.08 (m, 10H), 3.07 (br m, 1H), 4.99 (dd, J=2 and 10.4 Hz, 1H), 5.37 (dd, J=2 and 18 Hz, 1H), 5.98 (d, J=10 Hz, 1H), 6.14 (dd, J=10.4 and 18 Hz, 1H), 7.41 (br s, 5H).

(*E*)- and (*Z*)-2-cyclohexylvinyl phenyl sulfoxide were prepared by the following sequence: (1) Condensation of cyclohexanecarbaldehyde with phenyl lithio(trimethylsilyl)-methyl sulfide (1 equiv) in THF; (2) Separation of (*E*) and (*Z*)-2-cyclohexylvinyl phenyl sulfide by silica-gel column chromatography (hexane); (3) Oxidation with sodium periodate (5 equiv, in MeOH–H_2O, 2:1).

(E)-2-Cyclohexylvinyl Phenyl Sulfoxide: ^{1}H NMR (CCl_4) δ=0.78—2.36 (m, 11H), 6.00 (d, J=15.5 Hz, 1H), 6.42 (dd, J=5.5 and 15.5 Hz, 1H), 7.41 (m, 5H).

(Z)-2-Cyclohexylvinyl Phenyl Sulfoxide: ^{1}H NMR (CCl_4) δ= 0.72—2.13 (m, 10H), 2.97 (br, 1H), 5.8 (m, 2H), 7.43 (m, 5H).

NMR spectra of the mixture of vinyl sulfoxides (0.50 mmol) and shift reagent, tris(6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionato)europium (0.20 mmol), in carbon tetrachloride (0.70 ml) were taken (see Table 3).

Synthesis of 1-Cyclohexyl-2-methyl-1,3-butadiene. To a mixture of 1-cyclohexyl-2-phenylthio-1,3-butadiene (244 mg, 1.0 mmol) and [$NiCl_2(PPh_3)_2$] (65 mg, 0.1 mmol) in benzene (10 ml) was added methylmagnesium iodide in ether (5.0 mmol) which was prepared from magnesium (300 mg, 12 mmol) and methyl iodide (0.25 ml, 4 mmol) in ether (10 ml). After the removal of ether from the reaction system, the mixture was heated for 2 h under reflux. The resulting mixture was poured into 2 mol dm^{-3} hydrochloric acid and the product was extracted with ether. The organic layer was washed with 1 mol dm^{-3} sodium hydroxide, and then brine. The combined organic layer was dried and concentrated. Chromatography of the residue on silica-gel column (hexane) gave 1-cyclohexyl-2-methyl-1,3-butadiene. (*E*)-1-Cyclohexyl-2-methyl-1,3-butadiene: 70% yield; R_f=0.6 (hexane); ^{1}H NMR (CCl_4) δ=1.71 (d, J=1.5 Hz, 3H), 0.64—1.98 (m, 10H), 2.29 (br m, 1H), 4.72—5.39 (m, 3H), 6.24 (dd, J=10.8 and 17.6 Hz, 1H); IR 2920, 1780, 1640, 1610, 1440, 990, 890 cm^{-1}; MS *m/z*: 150 (M^+).

(Z)-1-Cyclohexyl-2-methyl-1,3-butadiene: 78% yield; R_f=0.58 (hexane); ^{1}H NMR (CCl_4) δ=1.76 (s, 3H), 0.6—2.02 (m, 10H) 2.33 (br m, 1H), 4.76—5.37 (m, 3H), 6.65 (dd, J=10.4 and 17.6 Hz, 1H); IR 2920, 1800, 1645, 1595, 1440, 990, 900 cm^{-1}; MS *m/z*: 150 (M^+).

References

1) General review, for example: B. M. Trost and L. S. Melvin, Jr., "Sulfur Ylides," Academic Press, New York (1975).

2) For a general reviews, see: a) D. A. Evans and G. C. Andrews, *Acc. Chem. Res.*, **7**, 147 (1974); b) B-T. Gröbel and D. Seebach, *Synthesis*, **1977**, 357; c) S. Warren, *Acc. Chem. Res.*, **11**, 401 (1978); d) H. J. Reich, *ibid.*, **12**, 22 (1979); e) E. Negishi, "Organometallics in Organic Synthesis," Wiley, New York (1980), Vol. 1; f) J. F. Biellman and J. B. Ducey, *Org. React.* **27**, 1 (1982).

3) a) T. Hayashi, N. Fujita, T. Oishi, and T. Takeshima, *Tetrahedron Lett.*, **21**, 303 (1980); b) R. W. Hoffmann and B. Kemper, *Tetrahedron Lett.*, **21**, 4883 (1980); c) Y. Yamamoto, H. Yatagai, and K. Maruyama, *J. Org. Chem.*, **45**, 195 (1980); d) M. R. Bin, R. K Haynes, T. L. Houston, and W. R. Jackson, *Tetrahedron Lett.*, **21**, 573 (1980); e) Y. Yamamoto, Y. Saito, and K. Maruyama, *Tetrahedron Lett.*, **23**, 4959 (1982); f) H. Baba, T. Hayashi, and T. Oishi *Chem. Pharm. Bull.*, **30**, 3852 (1982); g) K. S. Kyler, M. A. Netzel. S. Arseniyadis, and D. S. Watt, *J. Org. Chem.*, **48**, 383 (1983).

4) S. A. Shevekev, *Russ. Chem. Rev. (Engl. Transl.)*, **39**, 844 (1970); L. M. Jackman and B. C. Lange, *Tetrahedron*, **33**, 2737 (1977); P. W. K. Lau and T. H. Chan, *Tetrahedron Lett.*, **1978**, 2383; see also, D. Seebach and K.-H. Geiss, "New Application of Organometallic Reagents in Organic Chemistry," Elsevier, Amsterdam (1976), p. 22.

5) M. Ishiguro, N. Ikeda, and H. Yamamoto, *J. Org. Chem.*, **47**, 2227 (1982); K. Furuta, M. Ishiguro, R. Haruta, N. Ikeda, and H. Yamamoto, *Bull. Chem. Soc. Jpn.*, **57**, 2777 (1984). For some recent synthetic methods using organotitanium reagents, see: M. T. Reetz, in "Topics in Current Chemistry," Springer, Berlin (1982), pp. 1—54; B. Weidmann and D. Seebach, *Angew. Chem., Int. Ed. Engl.*, **22**, 31 (1983); D. Seebach, B. Weidmann, and L. Widler, in "Modern Synthetic Methods 1983," ed by R. Scheffold, Wiley, New York and Salle/Sauerländer, Aarau (1983), pp. 217—353.

6) For preliminary accounts of the present work, see: Y. Ikeda, K. Furuta, N. Meguriya, N. Ikeda, and H. Yamamoto, *J. Am. Chem. Soc.*, **104**, 7663 (1982), **105**, 3745 (1983).

7) The anomalous behaviour of benzaldehyde has been observed elsewhere; see Ref. 5.

8) a) E. C. Ashby and A. B. Goel, *J. Am. Chem. Soc.*, **103**, 4983 (1981); b) S. Murata, M. Suzuki, and R. Noyori, *J. Am. Chem. Soc.*, **102**, 3248 (1980).

9) M. Saniere-Karila, M. L. Capmau, and W. Chodkiewicz, *Bull. Soc. Chim. Fr.*, **1973**, 3371; E. Favre and M. Gaudemar, *J. Organomet. Chem.*, **92**, 17 (1975).

10) J. R. Shanklin, C. R. Johnson, J. Ollinger, and R. M. Coates, *J. Am. Chem. Soc.*, **95**, 3429 (1973); S. Kano, T. Yokomatsu, and S, Shibuya, *J. Chem. Soc., Chem. Commun.*, **1978**, 785.

11) Recent efforts for the preparation of disubstituted oxiranes: a) G. G. Lyle and L. K. Keefer, *J. Org. Chem.*, **31**, 3921 (1966); b) R. W. La Rochelle, B. M. Trost, and L. Krepski, *J. Org. Chem.*, **36**, 1126 (1971); c) J.-C. Paladini and J. Chuche, *Bull. Soc. Chim. Fr.*, **1974**, 187; d) D. Van Ende and A. Krief, *Tetrahedron Lett.*, **1976**, 457; e) D. Seebach, K.-H. Geiss, and M. Pohmakotr, *Angew. Chem. Int. Ed. Engl.*, **15**, 437 (1976); f) M. Yamaguchi and T. Mukaiyama, *Chem. Lett.*, **1979**, 1279; g) M. Ochiai and E. Fujita, *Tetrahedron Lett.*, **21**, 4369 (1980); h) W. C. Still and V. J. Novack, *J. Am. Chem. Soc.*, **103**, 1283 (1981); i) M. Yamaguchi and T. Mukaiyama, *Chem. Lett.*, **1982**, 237; j) J. Auge and S. David, *Tetrahedron Lett.*, **24**, 4009 (1983); k) J. B. Ousset, C. Mioskowski, and G. Solladie, *Tetrahedron Lett.*, **24**, 4419 (1983).

12) For a general review, see: T.-H. Chan, *Acc. Chem. Res.*, **10**, 442 (1977); see also: A. W. P. Jarvie, *Organomet. Chem. Rev. Sect. A*, **6**, 153 (1970); For stereoselective olefination using Peterson reaction, see: Y. Yamakado, M. Ishiguro, N. Ikeda, and H. Yamamoto, *J. Am. Chem. Soc.*, **103**, 5568 (1981).

13) K. Hiroi and L.-M. Chen, *J. Chem. Soc., Chem. Commun.*, **1981**, 377; K. S. Kyler and D. S. Watt, *J. Am. Chem. Soc.*, **105**, 619 (1983).

14) The *E*-isomer was slowly isomerized to the *Z*-isomer at 25 °C.

15) R. Haruta, M. Ishiguro, K. Furuta, A. Mori, N. Ikeda, and H. Yamamoto, *Chem. Lett.*, **1982**, 1093.

16) Our unpublished results. See also: F. Sato, Y. Suzuki, and M. Sato, *Tetrahedron Lett.*, **23**, 4589 (1982); M. T. Reetz and B. Wenderoth, *ibid.*, **23**, 5259 (1982).

17) H. Okamura, M. Miura, and H. Takei, *Tetrahedron Lett.*, **1979**, 43; E. Wenkert, T. W. Ferreira, and E. L. Michelotti, *J. Chem. Soc., Chem. Commun.*, **1979**, 637.

18) C. D. Hurd and H. Greengard, *J. Am. Chem. Soc.*, **52**, 3356 (1930); A. C. Cope, D. E. Morrison, and L. Field, *J. Am. Chem. Soc.*, **72**, 59 (1950); W. E. Parham, and S. H. Groen, *J. Org. Chem.*, **30**, 728 (1965); H. Kwart and E. R. Evans, *J. Org. Chem.*, **31**, 413 (1966).

19) a) L. Brandsma, *Rec. Trav. Chim. Pays-Bas*, **89**, 593 (1970); b) W. Ando, S. Kondo, K. Nakayama, K. Ichibori, H. Kohoda, H. Yamato, I. Imai, S. Nakaido, and T. Migita, *J. Am. Chem. Soc.*, **94**, 3870 (1972); c) T. Kubota, S. Miyashita, T. Kitazume, and N. Ishikawa, *J. Org. Chem.*, **45**, 5052 (1980).

20) D. S. Tarbell and W. E. Lovett, *J. Am. Chem. Soc.*, **78**, 2259 (1956); C. C. Price and W. H. Snyder, *J. Org. Chem.*, **27**, 4639 (1962).

21) J. F. Biellmann, J. B. Ducep, and J. Vicens, *Tetrahedron*, **32**, 1801 (1976).

22) P. Brownbridge and S. Warren, *J. Chem. Soc., Chem. Commun.*, **1975**, 820; *J. Chem. Soc., Perkin Trans. 1*, **1977**, 1131.

23) P. M. Atlani, J. F. Biellmann, S. Dube, and J. J. Vicens, *Tetrahedron Lett.*, **1974**, 2665, see also 2f.

24) Lithio reagent gave a mixture of regioisomers, which were difficult to separate.

25) This compounds may undergo thioallylic rearrangement

to give phenyl 3-(trimethylsilyl)allyl sulfide. Addition of 2,6-di-*t*-butyl-4-methylphenol can effectively prevent the rearrangement.

26) Deprotonation of allyl phenyl sulfide could be accomplished with butyllithium without any difficulties. In contrast, *s*- or *t*-butyllithium was required for alkyl allyl sulfide. *t*-Butyllithium recommended for the generation of 1-alkylallyl phenyl sulfide anion.

27) For prevention of thioallylic rearrangement of the produced phenyl sulfides, small amount of hydroquinone or 2,6-di-*t*-butyl-4-methylphenol was added during the workup and chromatographic operations.

28) Trace amount of regioisomer, 1-cyclohexyl-4-phenylthio-3-buten-1-ol, was also formed. This was isolated by column chromatography (R_f=0.15, 4:1 hexane–ether).

29) This reaction is highly stereospecific. Thus, the corresponding *cis*-isomers were prepared under the same reaction conditions from the *threo*-β-hydroxy sulfides, which were obtained from the reaction of [3-(alkylthio)allyl]lithium reagents followed by separation by column chromatography.

30) I. Gosney and A. G. Rowley, in "Organophosphorus Reagents in Organic Synthesis," ed by J. I. G. Cadogan, Academic Press, New York (1979), pp. 17—153.

31) The latter peak (long retention time) was assigned to the *trans*-isomer (carbowax, N_2 carrier).

32) The corresponding *cis*-isomer has an absorption at 1.19 ppm. See: W. S. Johnson, T.-T. Li, D. J. Faulkner, and S. F. Cammpell, *J. Am. Chem. Soc.*, **90**, 6225 (1968).

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