Tetrahedron Vol. 40, No. 18, pp 3481 to 3490, 1984
Printed in the U.S.A.

0040-4020/84 $3.00 + .00
Pergamon Press Ltd.

FACILE FUNCTIONALIZATION OF THE ISOPROPYLIDENE TERMINUS OF ACYCLIC MONOTERPENES BY WAY OF BENZENESULFENYL CHLORIDE ADDITION

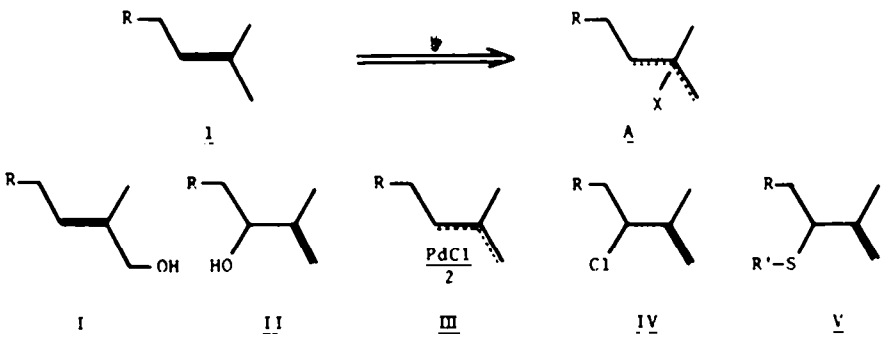
YUKIO MASAKI,* KINJI HASHIMOTO and KENJI KAJI
Gifu College of Pharmacy, 5-6-1 Mitahora Higashi, Gifu 502, Japan

(*Received in Japan* 21 *November* 1983)

Abstract—Highly site- and regioselective terminal functionalizations of acyclic monoterpenes **1** via benzenesulfenyl chloride addition followed by hydrolysis assisted by silica gel, dehydrochlorination under neutral or weakly basic condition, or dehydrochlorination by strongly basic treatment respectively providing β-hydroxy sulfides **3**, terminal methallylic sulfides **4**, or vinylsulfides **5** are developed. Conversion of **4** to terminal *trans*-allylic alcohols **10** via sulfoxides **9** by the Evans procedure is also described.

Since Cornforth synthesis of squalene in 1959,[1] a vast array of the stereo-selective and specific synthetic methods for trisubstituted olefins have been developed[2] because many naturally occurring compounds of this class exhibit significant biological activities. In addition to the importance of trisubstituted olefins with distinct geometry (*E* or *Z*) as the primary building blocks for natural product synthesis,[3] those involve also considerable synthetic potentials in further elaborations, for example, C-C bond formation involved in biomimetic polyolefin cyclization[4] and pericyclic reactions such as Claisen rearrangement,[5] and oxygen functionalization via epoxidation[6] with excellent stereochemical control. In the field of polyisoprenoid synthesis, one of the most versatile strategies has been the utilization of easily accessible natural or synthetic isoprenoids **1** such as prenyl alcohol, linalool, myrcene, geraniol, nerol, and farnesol which contain inherently trisubstituted olefinic portions in the molecule, as building blocks. Introduction of the framework of the isoprenoid building blocks into the target molecules requires at first highly site-, regio-, and stereoselective modifications of the former. The potential utility of terminally functionalized olefins of type **A** has received much attentions from the viewpoint of C–C bond formation with highly geometric and positional control.[3] A number of methods have been reported for the synthesis of such olefins **A** by direct functionalization of easily accessible isoprenoids **1** which contain the isopropylidene terminus in the molecule.[7] Thus, terminal *trans*-allylic alcohols of type **I** have been obtained by oxidation of **1** using stoichiometric or catalytic amounts of SeO_2,[7e] terminal methallylic alcohols of type **II** via photosensitized oxygenation[7b] or epoxidation,[7c] π-allyl palladium complexes of type **III** by direct metallation with $PdCl_2$,[7d] and allylic chlorides of type **IV** by treatment with chlorinating reagents[7e] or by electrochemical method,[7f] respectively. Direct conversion of **1** into allylic sulfides of type **V** and the corresponding sulfoxides also appeared in the limited cases via the ene reaction of olefins **1** with a thioacetone derivative or benzenesulfinyl chloride.[7g] Among these terminally functionalized isoprenoids, the allylic sulfides of type **V** have attracted particular synthetic interests because they bring about various types of reactions leading to construction of trisubstituted olefinic linkages: [2,3]sigmatropic rearrangement via the sulfoxides,[8a] α-sulfenyl carbanions,[8b] or sulfonium ylides;[8c] [3,3]sigmatropic rearrangement;[9] nucleophilic substitution via the sulfoxides or sulfones in regio- and stereoselective S_N2' fashion.[10] In our synthetic projects of physiologically active polyisoprenoids,[11] e.g. vitamin(s) K, ubiquinones, and insect pheromones, we required a facile and large-scale operative method for transformation of acyclic isoprenoids **1** into terminal methallylic sulfides **V**.

Addition of sulfenyl halides to alkenes has been a familiar and much studied reaction[12] in which the reaction mechanism and regio- and stereochemistry have been extensively investigated. Several aspects concerning the chemistry of adducts, which usually are obtained quantitatively as regioisomeric mixture, and utilization of adducts in organic synthesis have been reported.[13] Among the limited examples[14] of



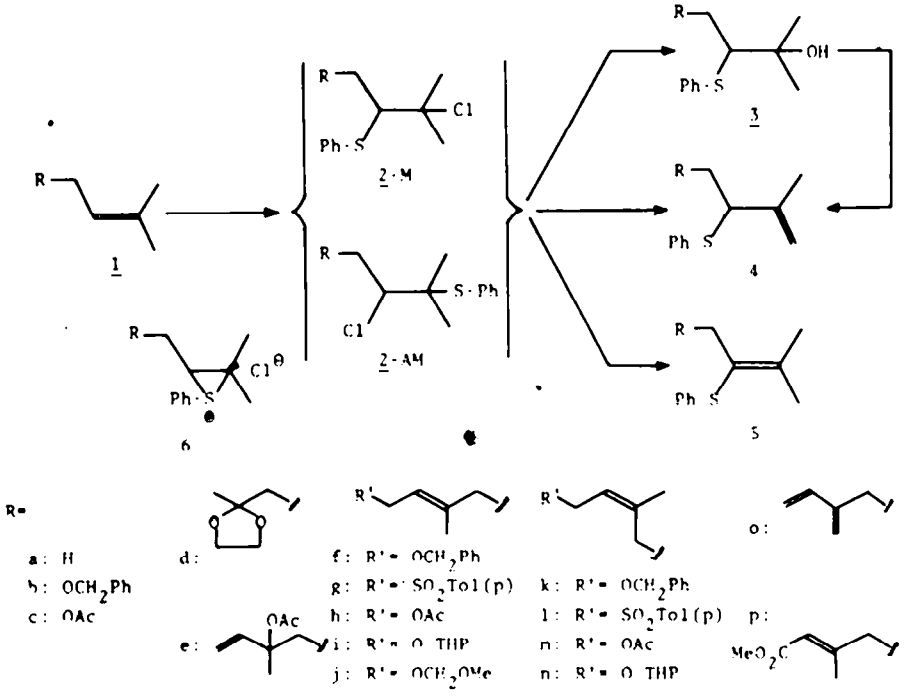
1 A I II III IV V

addition reaction of trisubstituted olefins with sulfenyl halide, Mustafaeva reported that methyl geranate **1p** underwent cyclization on treatment with benzenesulfenyl chloride (PhSCl) in nitromethane in the presence of $AgBF_4$ via the intermediate PhSCl-terminal trisubstituted olefin adduct **2p** or the episulfonium ion **6p**[14e] (Scheme 1). Taking account of the general preference of the terminal isopropylidene group over the other trisubstituted olefinic portions of linear polyisoprenoids in the reactions with electrophiles such as bromonium ion liberated from 2,4,4,6-tetrabromocyclohexa-2,5-dienone[15a] or N-bromosuccinimide[15b] as well as of Mustafaeva's results, we intended to investigate the chemistry of the sulfenyl halide-trisubstituted olefin adducts and also to develop a new terminal functionalization of isoprenoids utilizing sulfenyl halide addition.[16]

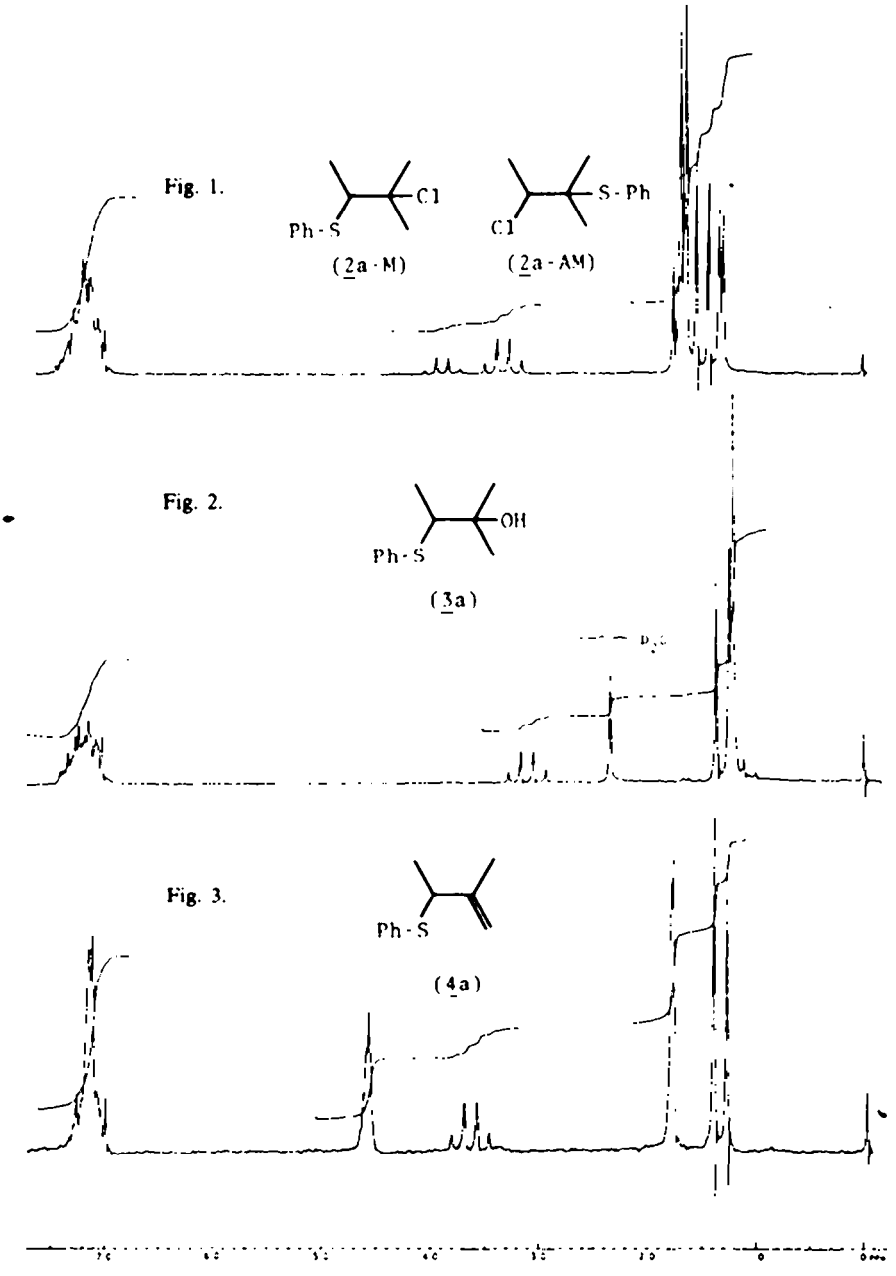
Here we disclose the full details of the preliminary results concerning the functionalization of the isopropylidene terminus of isoprenoids **1**, particularly of acyclic monoterpenes[16a] to lead site- and regioselectively to terminal methallylic sulfides V by utilizing addition reaction of various monoterpenes **1** with benzenesulfenyl chloride[12b] (PhSCl), and also to provide terminal *trans*-allylic alcohols I.

METHODS AND RESULTS

In the preliminary experiment, the addition reaction of 2-methyl-2-butene **1a**, the simplest trisubstituted olefin, with PhSCl and the chemical behavior of the adduct **2a** were studied (Scheme 1). Dropwise addition of an equivalent of PhSCl into a solution of **1a** in CH_2Cl_2 at $-20°$ resulted with instantaneous discharging of the orange color of PhSCl in quantitative production of adduct **2a** as a regioisomeric mixture. As shown in Fig. 1, for the Markovnikov adduct **2a**-M the two diastereotopic Me signals attached to the C bearing Cl and a doublet corresponding to the Me group attached to the C bearing SPh appeared respectively at δ 1.66, 1.70, and 1.50 (J = 7.0 Hz), and the methine proton at δ 3.35 as a quartet (J = 7.0 Hz). For the anti-Markovnikov adduct **2a**-AM, two diastereotopic Me signal attached to the C bearing SPh, a doublet corresponding to the Me group attached to the C bearing Cl, and the methine proton respectively at δ 1.30, 1.34, 1.73, and 3.91 in NMR. Charging of the adduct **2a** on a silica gel column followed by elution with hexane–Et_2O gave a totally changed single product which was assigned to be β-hydroxy sulfide **3a** (94%) by spectral analysis (Fig. 2). A six-protons singlet at δ 1.23 ($\underline{Me_2}C(OH)$), a doublet at δ 1.32 ($\underline{Me}CH(SPh)$), a $\underline{D_2O}$-quenchable one proton singlet at $\underline{2}.33$, and a quartet at δ 3.11 (MeC$\underline{H}$(SPh)) supported the assignment. The hydrolysis observed is supposed to be caused by the adherent water on silica gel. Upon warming the adduct **2a** in turn with dimethylformamide (DMF) in the presence of triethylamine (Et_3N) (excess) at 60° for 20 hr afforded regiospecifically in 73% yield terminal methallylic sulfide **4a**, structure of which was confirmed by mass and NMR analyses: M$^+$ *m/e* 178, a doublet at δ 1.35 ($\underline{Me}CH(SPh)$), vinylic Me at δ 1.80 and terminal methy$\underline{l}$ene at δ 4.58 respectively as broad singlets ($\underline{H_2}C{=}C(Me)$), and a quartet at δ 3.65 (MeC$\underline{H}$(SPh)) (Fig. 3). In the dehydrochlorination of the adduct **2a**, selection of basicity of conditions was crucial because under strongly basic condition with t-BuOK (1.2 equiv) in dimethylsulfoxide (DMSO)[17] (20°, 20 hr), **2a** afforded vinylsulfide **5a** in 75% yield. The fact that the regioisomeric mixture of adducts **2a** afforded the single regioisomeric product **3a**, **4a**, or **5a** in the reactions mentioned above is understandable on the basis of intermediacy of episulfonium ion **6a**.[12] The allylic sulfide **4a** was also obtained by treatment of the



Scheme 1.



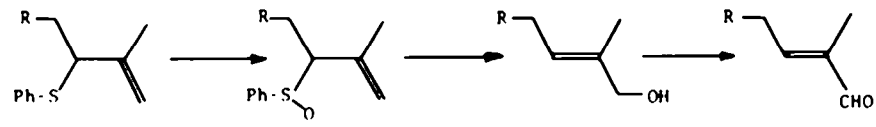
Figs. 1 3. ^{1}H-NMR spectra of compounds (**2a**), (**3a**) and (**4a**) derived from a trisubstituted olefin (**1a**)

β-hydroxy sulfide **3a** with (+)-10-camphorsulfonic acid (CSA) (catalytic) in benzene at 50° for 3 days in 73% yield. The β-hydroxy sulfide **3a** also underwent dehydration on treatment with catalytic amount of *p*-toluenesulfonic acid (*p*-TsOH) in benzene[17] under reflux for 1 hr to give in this case the rearranged allylic sulfide **7** in 92% yield which was interpreted to be formed via **4a** by acid-catalyzed 1,3-rearrangement,[18] and whose structure was confirmed by identification with that derived from tiglic acid **8** via *E*-2-methyl-2-buten-1-ol (**10a**)[19] (Scheme 2).

Transformation of allylic sulfides of type V to allylic alcohols of type I is much more general and efficient.[20] As shown in Scheme 2, oxidation of **4a** with $NaIO_4$ in aqueous MeOH followed by subjection of the intermediate sulfoxide **9a** to the Evans procedure[20] ($(MeO)_3P$, MeOH, 20°, 2 days) led in 79% yield to stereospecific formation of *trans*-allylic alcohol **10a** which was identified with that derived from tiglic acid **8**.

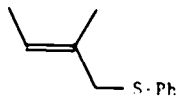
Now we have a set of procedures for structural modification of trisubstituted olefins **1** via benzenesulfenyl chloride addition in hand. Application of the regio- and stereospecific functionalization of trisubstituted olefins described above to acyclic monoterpenes which contain the additional olefinic bond(s) as well as the isopropylidene terminus in the molecule and many of which are commercially and synthetically available, is very attractive for synthesis of terminally functionalized isoprenoids which have broad spectrum for terpenoid synthesis.

Treatment of geranylbenzyl ether **1f** with an equiv-

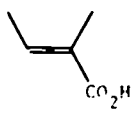


4 9 10 11

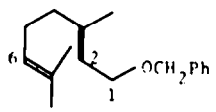
Scheme 2.



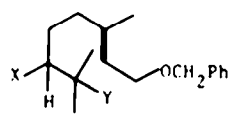
7



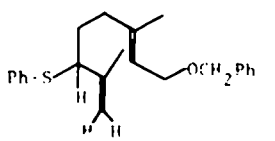
8



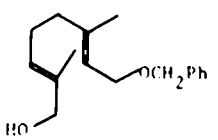
1f



2f-M X=S-Ph, Y=Cl
2f-AM X=Cl, Y=S-Ph
3f X=S-Ph, Y=OH



4f



10f

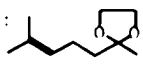
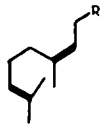
alent of PhSCl in CH_2Cl_2 at $-20°$ led instantaneously to quantitative formation of a pair of regioisomeric mixture of adducts **2f**. Expectedly, NMR analysis of **2f** confirmed that Δ^2-*E*-double bond was intact: the olefinic proton attached to C(2) at δ 5.37 (bt) and the methylene protons to C(1) at δ 3.94 (d) were observed, and instead of the C(6)-olefinic proton signal at δ 5.00 (br) found in the starting material **1f** a pair of broad doublets at δ 3.20 and 3.70 (each J = 10.0 Hz) assignable to the C(6)-methine proton of the anti-Markovnikov **2f**-AM and the Markovnikov adduct **2f**-M respectively appeared. The adduct **2f** was warmed at 60° in DMF with Et_3N under the identical condition in the case of **2a** to give the single terminal methallylic sulfide **4f** in 88% yield, whose structure was verified by spectral analysis (NMR: δ 3.47 (1H, t, =C–CH(SPh)–CH_2), 4.50, 4.60 (each 1H, bs, H_2C=C)). Contrastingly to the recent observation by Weiler[14a] that the terminal adduct of methyl 7-methyl-3-oxo-6-octenoate (**1** R=CH_2C(O)CH_2CO_2Me) with PhSCl cyclized by refluxing with silica gel in CH_2Cl_2 to afford cyclohexyl derivative, the adduct **2f** underwent hydrolysis by simple passing through a silica gel column similarly to the case of **2a** to furnish β-hydroxy sulfide **3f** in 68% yield. The structure of **3f** was verified by NMR analysis: δ 1.16, 1.23 (two singlets of 3H, (Me_2C(OH)), 2.91 (one proton double doublets, =C(OH)–CH(SPh)–CH_2). The terminal methallylic sulfide **4f** was also obtained by warming the β-hydroxy sulfide **3f** with catalytic amount of CSA in benzene at 40–50° for 2 days in 80% yield. More detailed examination of the reaction conditions for conversions of adduct **2f** to allylic sulfide **4f** and to β-hydroxy sulfide **3f**, and of **3f**–**4f** was made and the following conditions proved effective: for the conversion of **2f**–**4f**, warming in DMF without Et_3N at 60–80° for 20 hr (86%) or heating in toluene in the presence of Et_3N (excess) at 120° for 20 hr (74%); for **2f** to **3f**, stirring in aqueous acetonitrile[21] (H_2O:CH_3CN = 1:5) at 20° for 16 hr (59%); and for **3f** to **4f**, warming at 40–50° in benzene with *p*-TsOH (catalytic) for 4–6 hr (77%). Submitting the adduct **2f** to the strongly basic condition (t-BuOK, DMF, 20°, 15 hr) gave vinylsulfide **5f** in 63% yield.

The versatility of the method for the terminal functionalization mentioned above was demonstrated on the various isoprenoids and acyclic monoterpenes including protected OH groups, ketal function **1d**, conjugated 1,3-diene system **1o**, and α, β-unsaturated ester group **1p**, and results are summarized in Table 1. With isoprenoids which contain acid-labile OH protecting groups such as tetrahydropyranyl (THP) and methoxymethyl (MM), ketal function, and conjugated 1,3-diene system, basic conditions were necessary for dehydrochlorination of the corresponding adducts **2** providing allylic sulfides **4** and the silica gel treatment of such adducts **2** was not effective for preparation of β-hydroxy sulfides **3**, which were obtained alternatively in moderate yields by stirring **2** in aqueous CH_3CN.

In analogy with the simple allylic sulfide **4a**, consecutive treatments of **4f** with oxidizing reagent such as $NaIO_4$ in aqueous MeOH (20°, 16 hr), 30% H_2O_2 in AcOH (20°, 16 hr), or *m*-chloroperbenzoic acid in CH_2Cl_2 (0°, 1 hr) converting to sulfoxide **9f** and then with $(MeO)_3P$ in MeOH (20°, 2 days) gave the terminal *trans*-allylic alcohol **10f** in 87% yield (76% overall yield from **1f**). The structure and stereochemistry of the alcohol **10f** were confirmed by identification with that obtained directly from **1f** (33%) by the known procedure (SeO_2),[7a] and by NMR analysis of the *trans*-α,β-unsaturated aldehyde **11f** (δ 6.33 (1H, t, olefinic β-proton), 9.30 (1H, s, aldehyde proton)) derived from **10f** by active manganese dioxide (MnO_2) oxidation.† This conversion was general for the other sulfides **4** in high yields as summarized in Table 1.

†No aldehyde proton signal corresponding to *cis*-α, β-unsaturated aldehyde, which generally appears at δ 9.95–10.20, was observed. For NMR spectra of various β-substituted α-methyl-acroleins see: G. Büchi and H. Wüest, *J. Org. Chem.* **34**, 1122 (1969) and refs cited; A. F. Thomas, *J. Chem. Soc.* Chem. Commun. 1657 (1968); K. C. Chan, R. A. Jewell, W. H. Nutting and H. Rapoport, *J. Org. Chem.* **33**, 3382 (1968) and refs cited. It is familiar that oxidation of allylic alcohols with active MnO_2 generally gives α, β-unsaturated aldehydes or ketones without isomerization across the double bond: A. J. Fatiadi, *Synthesis* 65 (1976).

Table 1. Transformation of isoprenoids (1) to terminal β-hydroxy sulfides (3), terminal methallylic sulfides (4), vinyl sulfides (5), and terminal trans-allylic alcohols (10) via benzenesulfenyl chloride addition

Isoprenoid (1)	R[*1]	% Yield[*2] Terminal β-Hydroxy Sulfide (3)	% Yield Terminal Methallylic Sulfide (4) Obtained by Dehydrochlorination[*3] of Adduct (2)	% Yield Terminal Methallylic Sulfide (4) Obtained by Dehydration[*4] of (3)	% Yield Vinyl Sulfide (5)	% Yield[*5] Terminal Trans-Allylic Alcohol (10)
 Prenyl	a: H	94 (A)	75 (A)	73 (A)	75	79 (59)
	b: O-Bzl	61 (B)	89 (A)	·	48	86 (77)
	c: O-Ac	—[*6]	77 (A)	····	-	87 (67)
d: 		—[*7]	74 (A)	—	·	81 (60)
e: Linalyl Acetate		68 (B)	86 (A)	·	—	79 (68)
 Geranyl	f: O-Bzl	68 (A)	88 (A), 86 (B)	80 (A)	63	87 (76)
	g: SO_2Tol	79 (A)	74 (A), 77 (B)	85 (B)	—	92 (68)
	h: O-Ac	74 (A)	73 (A), 74 (B)	73 (B)	--	79 (58)
	i: O-THP	46 (B)	89 (A)	—	—	89 (79)
	j: O-MM	-[*7]	76 (A)	·	69	72 (55)
 Neryl	k: O-Bzl	65 (A)	84 (A)	79 (A)	65	95 (80)
	l: SO_2Tol	84 (A)	70 (C)	98 (B)	-	86 (70)
	m: O-Ac	85 (A)	74 (C)	68 (A)	—	75 (55)
	n: O-THP	—[*7]	86 (A)	—	—	85 (73)
o: Myrcene		55 (B)	68 (A)	—	--	69 (47)
p: Methyl Geranate		·	83 (A)	--	--	72 (60)

*1 Bzl: benzyl, Tol: p-tolyl, Ac: acetyl, THP: tetrahydropyranyl, MM: methoxy methyl

*2 Conditions, A: silica gel column; B: aqueous CH_3CN (see experimental).

*3 Conditions, A: DMF/Et_3N/60 °C/20 hr; B: DMF/60 °C/20 hr; C: toluene/Et_3N/reflux/20 hr (see experimental).

*4 Conditions, A: CSA/benzene/50 °C/2-3 days; B: p-TsOH/benzene/45 °C/6 hr (see experimental).

*5 Yields from 4 are listed and the values shown in parentheses represent overall yields from the starting isoprenoids (1).

*6 Unless otherwise noted, the empty columns in the table mean that the corresponding transformations have not been tried.

*7 Hydrolysis of each adduct (2) was tried by the procedure A but gave a trace amount of the corresponding β-hydroxy sulfide (3) with decomposed materials.

CONCLUSION

The overall synthetic sequence of the present terminal functionalization of isoprenoids 1 involves: (1) addition of an equivalent amount of PhSCl to isoprenoids to make adducts 2; (2) formation of terminal methallylic sulfides 4 by direct dehydrochlorination of adducts 2 or by way of hydrolysis of 2 providing β-hydroxy sulfides 3 and dehydration catalyzed by acid; (3) dehydrochlorination of 2 with strong base affording vinylsulfides 5; and (4) application of the Evans procedure to 4 to lead to terminal *trans*-allylic alcohols 10. It is worth noting that the terminal isopropylidene group of various monoterpenes 1 studied underwent highly siteselective addition of PhSCl to give a mixture of a pair of regioisomers 2-M and 2-AM, purification and separation of which were not necessary for the requisite transformations to β-hydroxy sulfides 3, allylic sulfides 4, and vinylsulfides 5. The present method offers not only a direct modification of isopropylidene terminus of monoterpenes 1 to terminal allylic sulfides 4 but also a useful alternative route to terminal *trans*-allylic alcohols 10.

EXPERIMENTAL

General. Proton NMR spectra were obtained in CCl_4 with a Hitachi R-20B (60 MHz) instrument, chemical shifts are reported in δ units, parts per million (ppm) down field from

tetrametylsilane (Me_4Si) as internal standard, and coupling constants are reported in hertz (Hz). IR spectra were recorded in $CHCl_3$ using a Jasco IRA-1 spectrometer and are reported in cm $^{-1}$. Mass spectra (MS) were obtained on a JMS-D300 instrument at an ionizing potential of 70 eV and data are reported as *m/e*. Column chromatography was performed by using Wakogel C-200 (100–200 mesh) silica gel and the materials were eluted with hexane-Et_2O solvent system. TLC was performed by using Wakogel B-5F silica gel by developing with hexane–Et_2O solvent system. Solvents used in reactions were distilled before use: CH_2Cl_2 over P_2O_5; DMF, DMSO, CH_3CN, pyridine, benzene, and toluene over CaH_2; Et_2O and DME over $LiAlH_4$; MeOH and EtOH with Na. Unless otherwise noted, reaction mixture was usually worked up by extracting with Et_2O, washing with 5% $NaHCO_3$, if necessary, and water or saturated brine, drying over $MgSO_4$, and then solvent was evaporated *in vacuo* to give crude products which were separated and purified by column chromatography on silica gel.

Materials. Starting material isoprenoids, **1a**, 2 - methyl - 2 - hepten - 6 - one, prenyl bromide, **1e**, geraniol, nerol, and **1o** were all purchased from Tokyo Kasei (TIC) Co., Ltd. Benzenesulfenyl chloride (PhSCl) was prepared according to the lit[26] from diphenyldisulfide and sulfuryl chloride in the presence of pyridine in CH_2Cl_2 and distilled (b.p. 55°/5 mmHg).

Compounds, **1c**,[22] **1d**,[23] **1f**,[24] **1g**,[25] **1h**,[26] **1i**,[27] **1k**,[28] **1l**,[25] **1m**,[26] and **1p**[29] were prepared according to the literature procedures, respectively.

Compound **1b** was prepared from prenyl bromide and benzyl alcohol (NaH/DME/20°/18 hr) by usual manner and distilled: b.p. 83–86°/5 mmHg; ^{1}H-NMR 1.62, 1.74 (each 3H, s, Me_2C–), 3.88 (2H, d, J = 6.5, –$CHCH_2O$), 4.39 (2H, s, OCH_2Ph), 5.30 (1H, bt, J = 6.5, =$CHCH_2O$), 7.23 (5H, s, arom-H). (Found: C, 81.92; H, 9.03. Calc for $C_{12}H_{16}O$: C, 81.77; H, 9.15%).

Compound **1j** was prepared from geraniol and methoxymethyl chloride (NaH/DME/20°/20 hr) and distilled: b.p. 122–126°/25 mmHg; ^{1}H-NMR 1.59 (3H, s, MeC=), 1.66 (6H, s, 2 MeC=), 1.90–2.20 (4H, br, CH_2CH_2), 3.30 (3H, s, OMe), 3.95 (2H, d, J = 7.0, –$CHCH_2O$), 4.48 (2H, s, OCH_2O), 4.85 5.20 (1H, br, HC=), 5.26 (1H, bt, J = 7.0, –$CHCH_2O$). (Found: C, 72.49; H, 11.20. Calc for $C_{12}H_{22}O_2$: C, 72.68; H, 11.18%). Compound **1n** was prepared from nerol and dihydropyran in the presence of catalytic amount of $POCl_3$ (CH_2Cl_2/0°/1 hr) and distilled: b.p. 70–75°/1 mmHg; ^{1}H-NMR 1.30–1.70 (6H, br, $(CH_2)_3$), 1.60, 1.67, 1.73 (each 3H, s, 3 MeC=), 1.90–2.17 (4H, br, CH_2CH_2), 3.20–4.10 (4H, m, 2 CH_2O), 4.53 (1H, bs, OCHO), 4.90–5.20 (1H, br, HC=), 5.28 (1H, bt, J = 7.0, HC=). (Found: C, 75.63; H, 10.85. Calc for $C_{15}H_{26}O_2$: C, 75.58; H, 11.00%).

Addition reaction of gem-dimethyl olefins (**1**) *with benzenesulfenyl chloride* (PhSCl)

General procedure. To a soln of **1** (1.0 mmol) in CH_2Cl_2 (3 ml) was added dropwise under N_2 a soln of PhSCl (145 mg, 1.0 mmol) in CH_2Cl_2 (0.5 ml) at −20° over 5 min. After 10 min stirring, the mixture was concentrated to give a crude adduct (**2**) as oil, which was usually subjected to the next reactions without purification. The ^{1}H-NMR spectrum of the simplest representative adduct **2a** was shown in Fig. 1.

Preparation of β-hydroxy sulfide (**3**) *from* PhSCl-*olefin adduct* (**2**)

General procedure. Method A. A crude adduct **2** (1.0 mmol) in hexane containing least amount of Et_2O to dissolve was run through a silica gel column (25–30 g) followed by elution with hexane–Et_2O mixed solvent system to give pure **3** as oil.

Method B. A crude adduct **2** (1 mmol) was stirred in aqueous CH_3CN (CH_3CN/H_2O = 5/1) (5 ml) at 20° for 16 hr. The usual work-up of the mixture and product isolation by column chromatography gave pure **3**.

Some physical data of β-hydroxy sulfides (**3a–3o**), *whose yields are listed in Table* 1

Compound **3a** (R–H): ^{1}H-NMR 1.23 (6H, s, $Me_2C(OH)$), 1.32 (3H, d, J = 7.0, MeCH(SPh)), 2.33 (1H, s, OH), 3.11 (1H, q, J = 7.0, MeCH(SPh)), 7.00–7.45 (5H, m, arom-H) (Fig. 2); IR 3480, 1590; MS 196 (M$^+$, 76%), 137 (100%). (Found: C, 67.03; H, 8.14. Calc for $C_{11}H_{16}OS$: C, 67.32; H, 8.22%).

Compound **3b** (R=O−CH_2Ph): ^{1}H-NMR 1.24, 1.29 (each 3H, s, $Me_2C(OH)$), 3.14 (1H, s, OH), 3.20 (1H, dd, J = 7.5, 5.0, CH(SPh)), 3.71, 3.74 (each 1H, d, J = 5.0, 7.5, $OCH_2CH(SPh)$), 4.45 (2H, s, $PhCH_2O$), 7.10–7.50 (10H, m, arom-H); IR 3450, 1590. (Found: C, 71.39; H, 7.37. Calc for $C_{18}H_{22}O_2S$: C, 71.49; H, 7.33%).

Compound **3e**: ^{1}H-NMR 1.19, 1.23 (each 3H, s, $Me_2C(OH)$), 1.48 (3H, s, MeC(OAc)), 1.50–2.50 (4H, m, CH_2CH_2), 1.91 (3H, s, $MeCO_2$), 2.46 (1H, s, OH), 2.90 (1H, dd, J = 11.0, 3.0, CH(SPh)), 4.90–5.30 (2H, m, CH=CH_2), 5.66 6.20 (1H, dd, J = 17.5, 9.5, CH=CH_2), 7.10–7.55 (5H, m, arom-H); IR 3460, 1730, 1590. (Found: C, 66.81; H, 8.00. Calc. for $C_{18}H_{26}O_3S$: C, 67.06; H, 8.13%).

Compound **3f** (R'–O–CH_2Ph): ^{1}H-NMR 1.16, 1.23 (each 3H, s, $Me_2C(OH)$), 1.55 (3H, bs, MeC=), 2.91 (1H, dd, J = 10.5, 2.5, CH(SPh)), 3.80 (2H, d, J = 6.5, =$CHCH_2O$), 4.30 (2H, s, OCH_2Ph), 5.11 (1H, bt, J = 6.5, =$CHCH_2O$), 7.00 7.45 (10H, m, arom-H); IR 3450, 1590. (Found: C, 74.34; H, 8.19. Calc for $C_{23}H_{30}O_2S$: C, 74.56; H, 8.16%).

Compound **3g** (R'=SO_2Tol): ^{1}H-NMR 1.20 (6H, s, $Me_2C(OH)$), 1.44 (3H, bs, MeC=), 1.80–2.30 (4H, m, CH_2CH_2), 2.25 (1H, s, OH), 2.42 (3H, s, MePh), 2.95 (1H, dd, J = 10.0, 2.5, CH(SPh)), 3.56 (2H, d, J = 8.0, =$CHCH_2SO_2$), 5.01 (1H, bt, J = 8.0, =$CHCH_2SO_2$), 7.00-7.70 (9H, m, arom-H); IR 3480, 1600, 1590; MS 418 (M$^+$, 4%), 204 (100%). (Found: C, 66.25; H, 7.46. Calc for $C_{23}H_{30}O_3S_2$: C, 66.01; H, 7.23%).

Compound **3h** (R'–OAc): ^{1}H-NMR 1.19, 1.24 (each 3H, s, $Me_2C(OH)$), 1.65 (3H, bs, MeC=), 1.94 (3H, s, $MeCO_2$), 1.85 2.35 (4H, m, CH_2CH_2), 2.39 (1H, s, OH), 2.90 (1H, dd, J = 11.0, 2.5, CH(SPh)), 4.36 (2H, d, J = 7.5, –$CHCH_2OAc$), 5.08 (1H, bt, J = 7.5, =$CHCH_2OAc$), 7.00–7.45 (5H, m, arom-H); IR 3480, 1730, 1590; MS 322 (M$^+$, 3%), 136 (100%). (Found: C, 66.87; H, 8.18. Calc for $C_{18}H_{26}O_3S$: C, 67.06; H, 8.13%).

Compound **3i** (R'–O–THP): ^{1}H-NMR 1.19, 1.25 (each 3H, s, $Me_2C(OH)$), 1.62 (3H, bs, MeC=), 1.35–2.55 (10H, m, methylene-H), 2.35 (1H, s, OH), 2.95 (1H, dd, J = 11.0, 3.0, CH(SPh)), 3.20 4.10 (4H, m, 2 OCH_2), 4.51 (1H, bs, OCHO), 5.19 (1H, bt, J = 7.0, =$CHCH_2O$), 7.10–7.55 (5H, m, arom-H); IR 3450, 1590. (Found: C, 69.04; H, 8.96. Calc for $C_{21}H_{32}O_3S$: C, 69.20; H, 8.85%).

Compound **3k** (R'–O–CH_2Ph): ^{1}H-NMR 1.14, 1.21 (each 3H, s, $Me_2C(OH)$), 1.70 (3H, bs, MeC=), 2.18 (1H, s, OH), 1.45-2.40 (4H, m, CH_2CH_2), 2.85 (1H, dd, J = 11.0, 3.0, CH(SPh)), 3.77 (2H, d, J = 6.5, –$CHCH_2O$), 4.29 (2H, s, OCH_2Ph), 5.29 (1H, bt, J = 6.5, =$CHCH_2O$), 7.00–7.45 (10H, m, arom-H); IR 3460, 1590. (Found: C, 74.28; H, 8.14. Calc for $C_{23}H_{30}O_2S$: C, 74.56; H, 8.16%).

Compound **3l** (R'–SO_2Tol): ^{1}H-NMR 1.15, 1.19 (each 3H, s, $Me_2C(OH)$), 1.69 (3H, bs, MeC=), 1.55–2.10 (4H, m, CH_2CH_2), 2.37 (3H, s, MePh), 2.80 (1H, dd, J = 10.0, 2.5, CH(SPh)), 3.49 (2H, d, J = 8.0, –$CHCH_2SO_2$), 3.55 (1H, br, OH), 5.05 (1H, bt, J = 8.0, =$CHCH_2SO_2$), 7.00–7.63 (9H, m, arom-H); IR 3480, 1600, 1590; MS 418 (M$^+$, 1%), 204 (100%). (Found: C, 65.87; H, 7.28. Calc for $C_{23}H_{30}O_3S_2$: C, 66.01; H, 7.23%).

Compound **3m** (R'–OAc): ^{1}H-NMR 1.20, 1.28 (each 3H, s, $Me_2C(OH)$), 1.73 (3H, s, MeC=), 1.93 (3H, s, $MeCO_2$), 1.58–2.30 (4H, m, CH_2CH_2), 2.92 (1H, dd, J = 11.0, 3.0, CH(SPh)), 4.36 (2H, d, J = 7.5, –$CHCH_2OAc$), 5.24 (1H, bt, J = 7.5, =$CHCH_2OAc$), 7.00–7.55 (5H, m, arom-H); IR 3480, 1730, 1590; MS 322 (M$^+$, 21%), 234 (100%). (Found: C, 67.18; H, 8.07. Calc for $C_{18}H_{26}O_3S$: C, 67.06; H, 8.13%).

Compound **3o**: ^{1}H-NMR 1.16, 1.23 (each 3H, $Me_2C(OH)$), 1.40–2.75 (4H, m, CH_2CH_2), 2.31 (1H, s, OH),

2.98 (1H, dd, J = 11.0, 3.0, CH(SPh)), 4.80–5.30 (4H, m, 2 CH_2=), 6.03–6.54 (1H, dd, J = 18.0, 11.0, CH=CH_2), 7.10–7.55 (5H, m, arom-H); IR 3400, 1595, 1590; MS 262 (M⁺, 56%), 136 (100%). (Found: C, 73.28; H, 8.52. Calc for $C_{16}H_{22}OS$: C, 73.25, H, 8.45%).

Preparation of terminal methallylic sulfide (**4**)

General procedure. From β-hydroxy sulfide (**3**). *Method A.* A mixture of **3** (1.0 mmol) and CSA (46 mg, 0.2 mmol) in benzene (15 ml) was warmed at 50° for 2–3 days in the dark. The usual work-up of the mixture and product isolation by column chromatography gave pure terminal methallylic sulfide **4** as oil.

Method B. A mixture of **3** (1.0 mmol) and *p*-TsOH·H_2O (38 mg, 0.2 mmol) in benzene (15 ml) was warmed at 45° for 6 hr in the dark to give **4** as oil.

From PhSCl-*olefin adduct* **2**. *Method A.* A mixture of **2** (1.0 mmol) and Et_3N (505 mg, 5.0 mmol) in DMF (10 ml) was warmed at 60° for 20 hr. The usual work-up of the mixture and product isolation by column chromatography gave pure **4** as oil.

Method B. A soln of **2** (1.0 mmol) in DMF (10 ml) was warmed at 60° for 20 hr to give **4**.

Method C. A mixture of **2** (1.0 mmol) and Et_3N (505 mg, 5.0 mmol) in toluene (10 ml) was heated under reflux for 20 hr to give **4**.

Some physical data of terminal methallylic sulfides (**4a–4p**), *whose yields are listed in Table* 1

Compound **4a** (R = H)[30]: ^{1}H-NMR 1.35 (3H, d, J = 8.0, MeCH(SPh)), 1.80 (3H, bs, MeC=), 3.65 (1H, q, J = 8.0, MeCH(SPh)), 4.58 (2H, bs, CH_2=), 7.00–7.40 (5H, m, arom-H) (Fig. 3); IR 1640, 1590; MS 178 (M⁺, 40%), 110 (100%).

Compound **4b** (R = O CH_2Ph): ^{1}H-NMR 1.81 (3H, bs, MeC=), 3.40–3.90 (3H, m, CH(SPh)CH_2O), 4.40 (2H, s, OCH_2Ph), 4.72, 4.77 (each 1H, bs, CH_2=), 6.95–7.45 (10H, m, arom-H); IR 1640, 1590. (Found: C, 76.16; H, 7.31. Calc for $C_{18}H_{20}OS$: C, 76.03; H, 7.09%).

Compound **4c** (R = OAc): ^{1}H-NMR 1.85 (3H, bs, MeC=), 1.90 (3H, s, $MeCO_2$), 3.68–3.92 (1H, dd, J = 8.5, 6.0, CH(SPh)CH_2OAc), 4.16–4.29 (2H, 2 d, J = 8.5, 6.0, CH(SPh)CH_2OAc), 4.74, 4.82 (each 1H, bs, CH_2=), 7.10–7.55 (5H, m, arom-H); IR 1730, 1635, 1590. (Found: C, 66.21; H, 6.73. Calc for $C_{13}H_{16}O_2S$: C, 66.08; H, 6.83%).

Compound **4d**: ^{1}H-NMR 1.25 (3H, s, $MeC(O)_2$), 1.78 (3H, s, MeC=), 3.40–3.63 (1H, m, CH(SPh)), 3.84 (4H, s, OCH_2CH_2O), 4.56, 4.67 (each 1H, bs, CH_2=), 7.07–7.40 (5H, m, arom-H); IR 1640, 1590. (Found: C, 69.31; H, 7.92. Calc for $C_{16}H_{22}O_2S$: C, 69.04; H, 7.97%).

Compound **4e**: ^{1}H-NMR 1.48 (3H, s, MeC(OAc)), 1.73 (3H, s, MeC=), 1.90 (3H, s, $MeCO_2$), 3.44 (1H, t, J = 6.5, CH(SPh)), 4.52, 4.64 (each 1H, bs, CH_2=), 4.88–5.22 (2H, m, CH CH_2), 5.63–6.10 (1H, dd, J = 18.0, 10.0, CH=CH_2), 7.03–7.34 (5H, m, arom-H); IR 1730, 1640, 1590. (Found: C, 70.91; H, 7.90. Calc for $C_{18}H_{24}O_2S$: C, 71.02; H, 7.95%).

Compound **4f** (R = O–CH_2Ph): ^{1}H-NMR 1.77, 1.59 (each 3H, bs, 2MeC=), 3.47 (1H, t, J = 7.0, CH(SPh)), 3.88 (2H, d, J = 7.0, =CHCH_2O), 4.35 (2H, s, OCH_2Ph), 4.50, 4.60 (each 1H, bs, CH_2=), 5.30 (1H, bt, J = 7.0, =CHCH$_2$O), 6.97–7.28 (10H, m, arom-H); IR 1635, 1595. (Found: C, 78.23; H, 8.20. Calc for $C_{23}H_{28}OS$: C, 78.37; H, 8.01%).

Compound **4g** (R = SO_2Tol): ^{1}H-NMR 1.39, 1.70 (each 3H, bs, 2 MeC=), 1.75–2.23 (4H, m, CH_2CH_2), 2.41 (3H, s, MePh), 3.50 (1H, t, J = 7.0, CH(SPh)), 3.61 (2H, d, J = 7.5, CHCH_2SO_2), 4.55, 4.64 (each 1H, bs, CH_2=), 5.10 (1H, bt, J = 7.5, =CHCH$_2SO_2$), 7.05–7.72 (9H, m, arom-H); IR 1640, 1600, 1590. (Found: C, 69.73; H, 6.93. Calc for $C_{23}H_{28}O_2S_2$: C, 69.98; H, 7.05%).

Compound **4h** (R = OAc): ^{1}H-NMR 1.69, 1.77 (each 3H, s, 2 MeC=), 1.94 (3H, s, $MeCO_2$), 1.80–2.30 (4H, m, CH_2CH_2), 3.44 (1H, t, J = 7.0, CH(SPh)), 4.44 (2H, d, J = 7.0, CHCH_2OAc), 4.50, 4.62 (each 1H, bs, CH_2=), 5.28 (1H, bt, J = 7.0, =CHCH$_2$OAc), 7.00–7.35 (5H, m, arom-H); IR 1730, 1635, 1580. (Found: C, 71.04; H, 8.08. Calc for $C_{18}H_{24}O_2S$: C, 71.02; H, 7.95%).

Compound **4i** (R = O-THP): ^{1}H-NMR 1.68, 1.80 (each 3H, s, 2 MeC=), 4.55 (1H, bs, OCHO), 4.55, 4.67 (each 1H, bs, CH_2=), 5.32 (1H, bt, J = 7.0, =CHCH$_2$O), 7.07–7.40 (5H, m, arom-H); IR 1640, 1590. (Found: C, 72.63; H, 8.99. Calc for $C_{21}H_{30}O_2S$: C, 72.80; H, 8.73%).

Compound **4j** (R = OCH_2OMe): ^{1}H-NMR 1.67, 1.78 (each 3H, s, 2 MeC=), 3.28 (3H, s, OMe), 3.50 (1H, t, J = 7.0, CH(SPh)), 3.96 (2H, d, J = 7.0, =CHCH_2O), 4.48 (2H, s, OCH_2O), 4.55, 4.67 (each 1H, bs, CH_2=), 5.30 (1H, bt, J = 7.0, =CHCH$_2$O), 7.06–7.40 (5H, m, arom-H); IR 1635, 1590. (Found: C, 70.71; H, 8.39. Calc for $C_{18}H_{26}O_2S$: C, 70.56; H, 8.55%).

Compound **4k** (R = O CH_2Ph): ^{1}H-NMR 1.72 (6H, s, 2 MeC=), 3.40 (1H, t, J = 7.0, CH(SPh)), 3.85 (2H, d, J = 7.5, CHCH_2O), 4.35 (2H, s, OCH_2Ph), 4.48, 4.58 (each 1H, bs, CH_2=), 5.30 (1H, bt, J = 7.5, =CHCH$_2$O), 6.97–7.28 (10H, bs, arom-H); IR 1640, 1590. (Found: C, 78.32; H, 7.92. Calc for $C_{23}H_{28}OS$: C, 78.37; H, 8.01%).

Compound **4l** (R = SO_2Tol): ^{1}H-NMR 1.70 (6H, s, 2 MeC=), 1.50–2.02 (4H, m, CH_2CH_2), 2.38 (3H, s, MePh), 3.33 (1H, t, J = 6.5, CH(SPh)), 3.60 (2H, d, J = 7.5, CHCH_2SO_2), 4.47, 4.60 (each 1H, bs, CH_2=), 5.11 (1H, bt, J = 7.5, =CHCH$_2SO_2$), 7.00–7.70 (9H, m, arom-H); IR 1640, 1600, 1590; MS 400 (M⁺, 6%), 245 (100%). (Found: C, 70.01; H, 7.15. Calc for $C_{23}H_{28}O_2S_2$: C, 69.98; H, 7.05%).

Compound **4m** (R = OAc): ^{1}H-NMR 1.72, 1.79 (each 3H, bs, 2 MeC=), 1.93 (3H, s, $MeCO_2$), 1.80–2.32 (4H, m, CH_2CH_2), 3.45 (1H, t, J = 7.0, CH(SPh)), 4.42 (2H, d, J = 7.0, =CHCH_2OAc), 4.51, 4.67 (each 1H, bs, CH_2=), 5.26 (1H, bt, J = 7.0, =CHCH$_2$OAc), 7.00–7.35 (5H, m, arom-H); IR 1730, 1635, 1590. (Found: C, 70.95; H, 8.01. Calc for $C_{18}H_{24}O_2S$: C, 71.02; H, 7.95%).

Compound **4n** (R = O-THP): ^{1}H-NMR 1.75, 1.79 (each 3H, bs, 2 MeC=), 4.55 (1H, bs, OCHO), 4.55, 4.68 (each 1H, bs, CH_2=), 5.30 (1H, bt, J = 7.0, =CHCH$_2$O), 7.06–7.40 (5H, m, arom-H); IR 1640, 1590. (Found: C, 72.91; H, 8.70. Calc for $C_{21}H_{30}O_2S$: C, 72.80; H, 8.73%).

Compound **4o**: ^{1}H-NMR 1.79 (3H, bs, MeC=), 1.70–2.50 (4H, m, CH_2CH_2), 3.53 (1H, t, J = 7.0, CH(SPh)), 4.57, 4.67 (each 1H, bs, CH_2=), 4.96 (2H, bs, CH_2=), 5.30 (2H, m, CH=CH_2), 6.06–6.35 (1H, dd, J = 18.0, 11.0, CH CH_2), 7.05–7.33 (5H, br, arom-H); IR 1635, 1595, 1500; MS 244 (M⁺, 6%), 134 (100%). (Found: C, 78.55; H, 8.42. Calc for $C_{16}H_{20}S$: C, 78.65; H, 8.25%).

Compound **4p**: ^{1}H-NMR 1.89 (3H, bs, MeC=), 2.13 (3H, d, J = 1.5, MeC CCO_2), 1.57–2.68 (4H, m, CH_2CH_2), 3.49 (1H, t, J = 7.0, CH(SPh)), 3.62 (3H, s, MeO_2C), 4.60, 4.72 (each 1H, bs, CH_2=), 5.62 (1H, bs, $CHCO_2$), 7.11–7.40 (5H, m, arom-H); IR 1705, 1630, 1595. (Found: C, 70.13; H, 7.68. Calc for $C_{17}H_{22}O_2S$: C, 70.32; H, 7.64%).

Preparation of vinylsulfide (**5**) *from* PhSCl-*olefin adduct* (**2**) *General procedure.* A soln of **2** (1.0 mmol) in DMSO (1.0 ml) was added dropwise into a mixture of t-BuOK (168 mg, 1.5 mmol) and DMSO (4 ml) at 20° and the mixture was stirred for 16 hr at 20°. The usual work-up of the mixture and product isolation by column chromatography gave pure **5** as oil.

Some physical data of vinylsulfides (**5a–5k**), *whose yields are listed in Table* 1

Compound **5a** (R = H)[31]: ^{1}H-NMR 1.90 (6H, bs, 2 MeC=), 2.02 (3H, bs, MeC=), 6.90–7.20 (5H, m, arom-H); IR 1630, 1585.

Compound **5b** (R = O CH_2Ph): ^{1}H-NMR 1.95, 2.03 (each 3H, s, Me_2C=), 4.05 (2H, s, CCH_2O), 4.35 (2H, s, OCH_2Ph), 7.13 (5H, bs, S-Ph), 7.17 (5H, s, CH_2Ph); IR 1620, 1580. (Found: C, 76.11; H, 7.01. Calc for $C_{18}H_{20}OS$: C, 76.03; H, 7.09%).

Compound **5f** (R = O–CH_2Ph): ^{1}H-NMR 1.55, 1.90, 2.00 (each 3H, s, MeC=, Me_2C=), 3.85 (2H, d, J = 6.5, CHCH_2O), 4.36 (2H, s, OCH_2Ph), 5.26 (1H, bt, J = 6.5,

$CHCH_2O$), 7.11, 7.21 (each 5H, s, S–Ph and CH_2Ph); IR 1650, 1620, 1580. (Found: C, 78.20; H, 8.15. Calc for $C_{21}H_{28}OS$: C, 78.37; H, 8.01%).

Compound **5j** (R'=OCH_2OMe): ^{1}H-NMR 1.60, 1.91, 2.02 (each 3H, s, MeC , Me_2C–), 2.10–2.35 (4H, m, CH_2CH_2), 3.27 (3H, s, OMe), 3.92 (2H, d, J = 7.0, $CHCH_2O$), 4.45 (2H, s, OCH_2O), 5.23 (1H, bt, J = 7.0, =$CHCH_2O$), 7.13 (5H, s, S–Ph); IR 1660, 1620, 1580. (Found: C, 70.79; H, 8.46. Calc for $C_{18}H_{26}O_2S$: C, 70.56; H, 8.55%).

Compound **5k** (R' O–CH_2Ph): ^{1}H-NMR 1.66, 1.82, 1.98 (each 3H, s, MeC–, Me_2C), 2.10–2.30 (4H, br, CH_2CH_2), 3.83 (2H, d, J = 7.0, $CHCH_2O$), 4.33 (2H, s, OCH_2Ph), 5.27 (1H, bt, J = 7.0, =$CHCH_2O$), 7.10, 7.21 (each 5H, s, S–Ph and CH_2Ph); IR 1640, 1620, 1585. (Found: C, 78.45; H, 8.22. Calc for $C_{21}H_{28}OS$: C, 78.37; H, 8.01%).

Preparation of E-2 - *methyl* - 1 - *phenylthio* - 2 - *butene* (**7**)[30]

From 2 - *hydroxy* - 2 - *methyl* - 3 - *phenylthiobutane* (**3a**). A mixture of **3a** (50 mg) and *p*-T$_s$OH·H_2O (5 mg) in benzene (2 ml) was refluxed for 1 hr. The usual work-up of the mixture and product isolation by column chromatography gave pure **7** as oil (42 mg, 92%). ^{1}H-NMR 1.51 (3H, d, J = 7.0, $MeCH$=), 1.71 (3H, s, MeC(SPh)=), 3.43 (2H, bs, $PhSCH_2C$=), 5.25 (1H, bq, J = 7.0, $MeCH$=), 7.04–7.55 (5H, br, arom-H); IR 1660, 1590. The sulfide **7** was identified by ^{1}H-NMR and IR comparisons with that prepared from tiglic acid (**8**) via *E*-2-methyl-2-buten-1-ol (**10a**) as described below.

From E - 2 - *methyl* - 2 - *buten* - 1 - *ol* (**10a**). The *E*-alcohol (**10a**),[19] prepared from **8**, was brominated according to the lit[19] with PBr_3. A mixture of the bromide (75 mg, 0.5 mmol) and PhSNa (100 mg, 0.75 mmol) in DMF (2.0 ml) was stirred at 20° for 16 hr. The usual work-up of the mixture and product isolation gave pure **7** as oil (70 mg, 78%).

Transformation of terminal methallylic sulfide (**4**) *to terminal* trans-*allylic alcohol* (**10**) *via the sulfoxide* (**9**)

(i) *General procedure for oxidation of* **4** *furnishing the sulfoxide* (**9**). *Method A*: A mixture of **4** (1.0 mmol) and $NaIO_4$ (258 mg, 1.2 mmol) in 50% aqueous MeOH (20 ml) was stirred at 20° for 20 hr. After concentration of the mixture to a half volume *in vacuo*, the residue was extracted with CH_2Cl_2, washed with water, dried, and evaporated to give crude **9**, which could be easily purified by column chromatography but usually without purification was subjected to the Evans' condition[20] to lead to terminal *trans*-allylic alcohol (**10**).

Method B. To a soln of **4** (1.0 mmol) in AcOH (5 ml) was added dropwise 30% H_2O_2 (100 μl) at 20°, and the mixture was stirred at 20° for 20 hr. The mixture was extracted with CH_2Cl_2, washed successively with water, 5% $NaHCO_3$, and then water, dried, and evaporated to give crude **9**.

Method C. To a soln of **4** (1.0 mmol) in CH_2Cl_2 (4 ml) was added dropwise a soln of *m*-chloroperbenzoic acid (net 80%) (240 mg, 1.1 mmol) in CH_2Cl_2 (5 ml) at 0°, and the mixture was stirred at 0° for 0.5 hr. The mixture was diluted with CH_2Cl_2 and worked up by usual mannner to give crude **9**.

(ii) *General procedure for* [2,3]*sigmatropic rearrangement of sulfoxide* (**9**) *affording terminal* trans-*allylic alcohol* (**10**) *under the Evans' conditon*.[20] A mixture of **9** (1.0 mmol) and $(MeO)_3P$ (248 mg, 2.0 mmol) in MeOH (8 ml) was stirred at 20° for 2 days under N_2. The usual workup of the mixture and product isolation by column chromatography gave pure **10** as oil.

Some physical data of terminal trans-*allylic alcohols* (**10a–10p**), *whose yields are listed in Table* 1

Compound **10a** (R–H)[19]: ^{1}H-NMR 1.50–1.67 (6H, overlapped bs and bd, MeC CHMe), 2.42 (1H, s, OH), 3.83 (2H, s, –CCH_2OH), 5.20–5.55 (1H, m, $MeCH$); IR 3580, 3440, 1660.

Compound **10b** (R=O–CH_2Ph): ^{1}H-NMR 1.59 (3H, s, MeC), 3.40 (1H, s, OH), 3.85 (2H, s, CCH_2OH), 3.96 (2H, d, J = 7.0, –$CHCH_2O$), 4.43 (2H, s, OCH_2Ph), 5.55 (1H, bt, J = 7.0, –$CHCH_2O$), 7.24 (5H, s, arom-H); IR 3560, 3300, 1660, 1500. (Found: C, 75.14; H, 8.25. Calc for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39%).

Compound **10c** (R=OAc)[32]: ^{1}H-NMR 1.69 (3H, s, MeC=), 1.99 (3H, s, $MeCO_2$), 3.35 (1H, s, OH), 3.89 (2H, s, –CCH_2OH), 4.53 (2H, d, J = 7.5, =$CHCH_2OAc$), 5.50 (1H, t, J = 7.5, =$CHCH_2OAc$); IR 3580, 3430, 1730, 1660.

Compound **10d**[33]: ^{1}H-NMR 1.23 (3H, s, $MeC(O)_2$), 1.60 (3H, s, MeC–), 3.84 (6H, s, –CCH_2OH and OCH_2CH_2O), 5.31 (1H, bt, J = 7.0, CH); IR 3580, 3460.

Compound **10e**[34]: ^{1}H-NMR 1.50 (3H, s, $MeC(OAc)$), 1.60 (3H, bs, MeC), 1.94 (3H, s, $MeCO_2$), 2.42 (1H, s, OH), 3.83 (2H, s, CCH_2OH), 4.90–5.24 (2H, m, CH–CH_2), 5.10–5.40 (1H, br, HC=), 5.68–6.15 (1H, dd, J = 18.0, 10.0, CH–CH_2); IR 3580, 3460, 1730.

Compound **10f** (R'–O–CH_2Ph)[24,35]: ^{1}H-NMR 1.63 (6H, bs, 2 MeC–), 1.95–2.20 (4H, m, CH_2CH_2), 2.60 (1H, s, OH), 3.84 (2H, s, CCH_2OH), 3.90 (2H, d, J = 7.5, –$CHCH_2O$), 4.40 (2H, s, OCH_2Ph), 5.30 (2H, br, 2 HC=), 7.20 (5H, s, arom-H); IR 3580, 3400, 1660, 1500. (Found: C, 78.13; H, 9.26. Calc for $C_{13}H_{24}O_2$: C, 78.42; H, 9.29%).

Compound **10g** (R' SO_2Tol)[25,36]: ^{1}H-NMR 1.40, 1.60 (each 3H, bs, 2 MeC), 1.90–2.20 (4H, m, CH_2CH_2), 2.42 (3H, s, MePH), 2.55 (1H, s, OH), 3.64 (2H, d, J = 8.0, –$CHCH_2SO_2$), 3.85 (2H, s, =CCH_2OH), 5.09 (1H, bt, J = 8.0 =$CHCH_2SO_2$), 5.24 (1H, br, HC=), 7.10–7.70 (4H, A_2B_2q, J = 8.0, arom-H); IR 3800, 3500 1660, 1600; MS 308 (M$^+$, 10%), 93 (100%). (Found: C, 65.97; H, 7.88. Calc for $C_{13}H_{24}O_4S$: C, 66.21; H, 7.85%).

Compound **10h** (R' OAc)[36]: ^{1}H-NMR 1.62, 1.70 (each 3H, bs, 2 MeC–), 1.95–2.20 (4H, m, CH_2CH_2), 1.98 (3H, s, $MeCO_2$), 2.45 (1H, s, OH), 3.83 (2H, s, =CCH_2OH), 4.46 (2H, d, J = 7.0, $CHCH_2OAc$), 5.28 (2H, bt, J = 7.0, HC= and –$CHCH_2OAc$); IR 3580, 3430, 1720, 1660.

Compound **10i** (R'–O–THP)[33a]: ^{1}H-NMR 1.65 (6H, s, 2 MeC–), 1.35–1.75 (6H, br, $(CH_2)_3$), 2.00–2.20 (4H, br, CH_2CH_2), 2.15 (1H, s, OH), 3.83 (2H, bs, –CCH_2OH), 4.53 (1H, bs, OCHO), 5.28 (2H, bt, J = 6.5, 2 CH=); IR 3580, 3440, 1660.

Compound **10j** (R' OCH_2OMe): ^{1}H-NMR 1.65 (6H, bs, 2 MeC), 2.00–2.25 (4H, br, CH_2CH_2), 2.60 (1H, s, OH), 3.30 (3H, s, OMe), 3.83 (2H, s, –CCH_2OH), 3.96 (2H, d, J = 7.0, $CHCH_2O$), 4.48 (2H, s, OCH_2O), 5.25 (2H, bt, J = 7.0, 2 HC–); IR 3580, 3450, 1655. (Found: C, 67.45; H, 10.32. Calc for $C_{12}H_{22}O_3$: C, 67.25; H, 10.35%).

Compound **10k** (R'=O–CH_2Ph): ^{1}H-NMR 1.58, 1.73 (each 3H, bs, 2 MeC–), 2.00–2.20 (4H, br, CH_2CH_2), 2.17 (1H, bs, OH), 3.79 (2H, s, –CCH_2OH), 3.85 (2H, d, J = 7.0, –$CHCH_2O$), 4.40 (2H, s, OCH_2Ph), 5.16–5.47 (2H, br, 2 CH), 7.23 (5H, s, arom-H); IR 3580, 3450, 1660, 1500. (Found: C, 78.68; H, 9.15. Calc for $C_{17}H_{24}O_2$: C, 78.42; H, 9.29%).

Compound **10l** (R' SO_2Tol): ^{1}H-NMR 1.58, 1.73 (each 3H, bs, 2 MeC–), 1.80–2.20 (4H, br, CH_2CH_2), 2.43 (3H, s, MePh), 2.48 (1H, s, OH), 3.66 (2H, d, J = 7.5, $CHCH_2SO_2$), 3.81 (2H, s, =CCH_2OH), 5.08 (1H, bt, J = 7.5, $CHCH_2SO_2$), 5.20 (1H, br, CH), 7.10–7.70 (4H, A_2B_2q, J = 8.5, arom-H); IR 3500, 3440, 1660, 1600; MS 308 (M$^+$, 7%), 134 (100%). (Found: C, 66.28, H, 7.91. Calc for $C_{13}H_{24}O_4S$: C, 66.21; H, 7.85%).

Compound **10m** (R' OAc): ^{1}H-NMR 1.60, 1.73 (each 3H, bs, 2 MeC–), 1.95 (3H, s, $MeCO_2$), 1.90–2.20 (4H, br, CH_2CH_2), 2.33 (1H, s, OH), 3.80 (2H, s, CCH_2OH), 4.40 (2H, d, J = 7.5, $CHCH_2OAc$), 5.24 (2H, bt, J = 7.5, 2 CH); IR 3570, 3400, 1730, 1660. (Found: C, 67.83; H, 9.46. Calc for $C_{13}H_{20}O_3$: C, 67.89; H, 9.50%).

Compound **10n** (R' O–THP): ^{1}H-NMR 1.63, 1.75 (each 3H, bs, 2 MeC), 1.40–1.65 (6H, br, $(CH_2)_3$), 2.05–2.17 (4H, br, CH_2CH_2), 2.13 (1H, s, OH), 3.81 (2H, s, –CCH_2OH), 4.50 (1H, bs, OCHO), 5.25 (2H, bt, J = 7.0, 2 CH); IR 3580, 3440, 1655. (Found: C, 70.98; H, 10.12. Calc for $C_{13}H_{26}O_3$: C, 70.83; H, 10.30%).

Compound **10o**[37]: ^{1}H-NMR 1.63 (3H, s, MeC–), 2.15–2.28

(4H, br, CH_2CH_2), 1.38 (1H, s, OH), 3.87 (2H, bs, $-CCH_2OH$), 4.94 (2H, bs, CH_2=), 4.90–5.35 (2H, m, $CH-CH_2$), 6.07–6.56 (1H, dd, J = 18.0, 11.0, CH=CH_2); IR 3580, 3440, 1600.

Compound **10p**: ^{1}H-NMR 1.64 (3H, s, MeC=), 2.13 (3H, d, J = 2.0, MeC=$CHCO_2$), 1.57–2.68 (4H, br, CH_2CH_2), 2.85 (1H, s, OH), 3.66 (3H, s, MeO_2C), 3.93 (2H, s, $-CCH_2OH$), 5.20–5.50 (1H, br, CH=), 5.67 (1H, s, $-CHCO_2$); IR 3550, 3400, 1705, 1640.

Oxidation of terminal trans*-allylic alcohol* (**10**) *with active* MnO_2 *providing* E-α,β*-unsaturated aldehyde* (**11**)

General procedure. A mixture of **10** (1.0 mmol) and active MnO_2 (4 g) in $CHCl_3$ (25 ml) was stirred at 20° for 24 hr. The mixture was diluted with Et_2O and filtered. Evaporation of the solvent and column chromatography of the residue gave pure **11** as oil. All the aldehydes (**11f–11m**) obtained showed the IR absorptions at 1640 and 1680 cm^{-1} associated with the system C=C–CHO, and exhibited the aldehyde proton signal in the region of 9.25–9.30 ppm as singlet and β-olefinic proton in 6.31–6.35 as broad triplet in ^{1}H-NMR.

Some physical data of E-α,β-unsaturated aldehydes (**11f 11m**)

Compound **11f** (R′=O-CH_2Ph) (65%): ^{1}H-NMR 1.65, 1.73 (each 3H, s, 2 MeC=), 2.10–2.55 (4H, m, CH_2CH_2), 3.95 (2H, d, J = 7.0, $-CHCH_2O$), 4.41 (2H, s, OCH_2Ph), 5.37 (1H, bt, J = 7.0, $-CHCH_2O$), 6.33 (1H, bt, J = 7.0, CH=CCHO), 7.28 (5H, s, arom-H), 9.30 (1H, s, CHO); IR 1680, 1640, 1500.

Compound **11g** (R′=SO_2Tol) (61%): ^{1}H-NMR 1.48, 1.69 (each 3H, s, 2 MeC=), 2.10–2.50 (4H, m, CH_2CH_2), 2.46 (3H, s, MePh), 3.66 (2H, d, J = 8.0, $-CHCH_2SO_2$), 5.15 (1H, bt, J = 7.0, $CHCH_2SO_2$), 6.30 (1H, bt, J = 7.0, CH=CCHO), 7.17–7.75 (4H, A_2B_2q, J = 8.5, arom-H), 9.28 (1H, s, CHO); IR 1680, 1640, 1600, 1490.

Compound **11h** (R′=OAc)[36] (66%): ^{1}H-NMR 1.75 (6H, s, 2 MeC=), 1.99 (3H, s, $MeCO_2$), 2.15–2.60 (4H, m, CH_2CH_2), 4.48 (2H, d, J = 7.0, $CHCH_2OAc$), 5.31 (1H, bt, J = 7.0, $CHCH_2OAc$), 6.34 (1H, bt, J = 7.0, CH=CCHO), 9.30 (1H, s, CHO); IR 1730, 1680, 1640.

Compound **11i** (R′=SO_2Tol) (67%): ^{1}H-NMR 1.67, 1.77 (each 3H, s, 2 MeC=), 1.90–2.40 (4H, m, CH_2CH_2), 2.43 (3H, s, MePh), 3.66 (2H, d, J = 8.0, $CHCH_2SO_2$), 5.15 (1H, bt, J = 8.0, $-CHCH_2SO_2$), 6.30 (1H, bt, J = 7.0, CH=CCHO), 7.18–7.75 (4H, A_2B_2q, J = 8.5, arom-H), 9.24 (1H, s, CHO); IR 1680, 1640, 1600, 1595.

Compound **11m** (R′=OAc) (59%): ^{1}H-NMR 1.71, 1.79 (each 3H, s, 2 MeC=), 1.98 (3H, s, $MeCO_2$), 2.15–2.55 (4H, m, CH_2CH_2), 4.46 (2H, d, J = 7.0, $CHCH_2OAc$), 5.36 (1H, bt, J = 7.0, $CHCH_2OAc$), 6.35 (1H, bt, J = 7.0, CH=CCHO), 9.30 (1H, s, CHO); IR 1730, 1680, 1640.

Acknowledgement The authors are grateful to Dr. S. Terao, Central Research Division of Takeda Chemical Ind. Ltd., for helpful discussions.

REFERENCES

[1] J. W. Cornforth, R. H. Cornforth and K. K. Mathew, *J. Chem. Soc.* 2539 (1959).

[2] J. Reucroft and P. G. Sammes, *Quart. Rev.* **25**, 135 (1971). D. J. Faulkner, *Synthesis* 175 (1971). A. Marfat, P. R. McGuirk, R. Kramer and P. Helquist, *J. Am. Chem. Soc.* **99**, 253 (1977) and Refs. cited.

[3] A. F. Thomas, C. H. Heathcock, J. W. ApSimon and J. W. Hooper, *The Total Synthesis of Natural Products* (Edited by J. ApSimon), Vol. 2. Wiley, New York (1973); P. M. Savu and J. A. Katzenellenbogen, *J. Org. Chem.* **46**, 239 (1981) and Refs. cited.

[4] E. E. van Tamelen, *Acc. Chem. Res.* **8**, 152 (1975); W. S. Johnson, *Angew. Chem.* Int. Ed. Engl. **15**, 9 (1976).

[5] A. F. Thomas, *J. Am. Chem. Soc.* **91**, 3281 (1969); G. Frater, *Helv. Chim. Acta* **58**, 442 (1975); *Chimia* **29**, 528 (1975).

[6] T. Katsuki and K. B. Sharpless, *J. Am. Chem. Soc.* **102**, 5974 (1982) and Refs. cited.

[7] N. Rabjohn, *Organic Reactions*, Vol. 24, p. 261. Wiley, New York (1976). M. A. Umbreit and K. B. Sharpless, *J. Am. Chem. Soc.* **99**, 5526 (1977). F. W. Sum and L. Weiler, *Ibid.* **101**, 4401 (1979); [b] R. W. Denney and A. Nickon, *Organic Reactions*, Vol. 20, p. 133. Wiley, New York (1973). K. Kondo and M. Matsumoto, *Tetrahedron Letters*. 391 (1976); [c] S. Terao, M. Shiraishi and K. Kato, *Synthesis* 467 (1979) and Refs. cited; [d] B. M. Trost and L. Weber, *J. Org. Chem.* **40**, 3617 (1975). B. M. Trost, L. Weber, P. Strege, T. J. Fullerton and T. J. Dietsche, *J. Am. Chem. Soc.* **100**, 3407, 3416 and 3426 (1978); [e] W. Sato, N. Ikeda and H. Yamamoto, *Chem. Letters* 141 (1982) and Refs. cited. J. Garapon, J. Weil and B. Sillion, *C. R. Acad. Sci.* Ser. C, **290**, 207 (1980); [f] S. Torii, K. Uneyama, T. Nakai and T. Yasuda, *Tetrahedron Letters* **22**, 2291 (1981); [g] B. B. Snider and L. Füzesi, *Ibid.* 877 (1978). B. B. Snider, *J. Org. Chem.* **46**, 3155 (1981).

[8] [a] D. A. Evans and G. C. Andrews, *Acc. Chem. Res.* **7**, 147 (1974); [b] J. E. Baldwin and N. R. Tzodikov, *J. Org. Chem.* **42**, 1878 (1977); [c] P. A. Grieco, D. Boxler and K. Hiroi, *Ibid.* **38**, 2572 (1973).

[9] H. Takahashi, K. Oshima, H. Yamamoto and H. Nozaki, *J. Am. Chem. Soc.* **95**, 5803 (1973). T. Nakai, H. Shiono and M. Okawara, *Chem. Letters* 249 (1975).

[10] Y. Masaki, K. Sakuma and K. Kaji, *J. Chem. Soc.* Chem. Commun. 434 (1980) and Refs. cited.

[11] R. H. Thomson, *Naturally Occurring Quinones* 2nd Edn. Academic Press, New York (1971). S. Patai, *The Chemistry of the Quinoid Compounds*, Parts 1 and 2. Wiley, New York (1974). K. Mori, *The Total Synthesis of Natural Products* (Edited by J. ApSimon), Vol. 4, p. 1. Wiley, New York (1981).

[12] [a] J. P. Marino, *Topics in Sulfur Chemistry* (Edited by A. Senning), Vol. 1, p. 1. Georg Thieme, Stuttgart (1976). F. Freeman, *Chem. Rev.* **75**, 439 (1975). G. A. Jones and C. J. M. Stirling, *J. Chem. Soc.* Perkin II 385 (1983). [b] W. H. Mueller and P. E. Butler, *J. Am. Chem. Soc.* **90**, 2075 (1968).

[13] A. J. Havlik and N. Kharasch, *Ibid.* **78**, 1207 (1956). K. Toyoshima, T. Okuyama and T. Fueno, *J. Org. Chem.* **43**, 2789 (1978). P. B. Hopkins and P. J. Fuchs, *Ibid.* **43**, 1208 (1978). D. A. Evans, C. A. Bryan and C. L. Sims, *J. Am. Chem. Soc.* **94**, 2891 (1972). J. Ohishi, *Synthesis* 690 (1980). K. C. Nicolaou and Z. Lysenko, *J. Chem. Soc.* Chem. Commun. 293 (1977), *J. Am. Chem. Soc.* **101**, 3884 (1979). D. Heissler and J-J. Riehl, *Tetrahedron Letters* **21**, 4707 and 4711 (1980).

[14] [a] M. T. Mustafaeva, M. Z. Krumer, V. A. Smit, A. V. Semenovskii and V. F. Kucherov, *Izv. Akad. Nauk. SSSR, Ser. Khim.* 2632 (1972) (*Chem. Abstr.* **78**, 84551b (1973)). M. T. Mustafaeva, V. A. Smit and V. F. Kucherov, *Ibid.* 1349 (1973) (*Chem. Abstr.* **79**, 105431a (1973)). [b] M. Alderdice and L. Weiler, *Can. J. Chem.* **59**, 2239 (1981).

[15] [a] T. Kato and I. Ichinose, *J. Chem. Soc.* Perkin I 1051 (1980); [b] E. E. van Tamelen, *Acc. Chem. Res.* **1**, 111 (1968).

[16] [a] Y. Masaki, K. Hashimoto and K. Kaji, *Tetrahedron Letters* 4539 (1978); [b] Y. Masaki, K. Hashimoto and K. Kaji, *Ibid.* 5123 (1978). Y. Masaki, K. Hashimoto, K. Sakuma and K. Kaji, *J. Chem. Soc.* Chem. Commun. 855 (1979). Y. Masaki, K. Sakuma and K. Kaji, *Chem. Letters* 1235 (1979).

[17] B. M. Trost, K. Hiroi and S. Kurozumi, *J. Am. Chem. Soc.* **97**, 438 (1975).

[18] P. Brownbridge and S. Warren, *J. Chem. Soc.* Perkin I 2125 (1976) and *Ibid.* 1131 (1977).

[19] J. A. Katzenellenbogen and A. L. Crumrine, *J. Am. Chem. Soc.* **98**, 4925 (1976).

[20] D. A. Evans, G. C. Andrews, T. T. Fujimoto and D. Wells, *Tetrahedron Letters* 1385 and 1389 (1973) and Ref. 8*a*.

[21] For the direct hydroxyselenation of olefins see: A. Toshimitu, T. Aoai, H. Owada, S. Umemura and Okano, *J. Chem. Soc.* Chem. Commun. 412 (1980).

[22]M. Julia, C. Perez and L. Saussine, *J. Chem. Res. Miniprint* 3401 (1978).
[23]U. T. Bhalerao and H. Rapoport, *J. Am. Chem. Soc.* **93**, 4835 (1971).
[24]A. Hofer and C. H. Eugster, *Helv. Chim. Acta* **65**, 365 (1982).
[25]P. A. Grieco and Y. Masaki, *J. Org. Chem.* **39**, 2135 (1974). S. Terao, K. Kato, M. Shiraishi and H. Morimoto, *J. Chem. Soc.* Perkin I 1101 (1978).
[26]F. H. A. Rummens, *Rec. Trav. Chim.* **84**, 1009 (1965). J. W. de Haan and L. J. M. van de Ven, *Tetrahedron Letters* 2703 (1971).
[27]Y. Morizawa, I. Mori, T. Hiyama and H. Nozaki, *Synthesis* 899 (1981). M. Miyashita, A. Yoshikoshi and P. A. Grieco, *J. Org. Chem.* **42**, 3772 (1977).
[28]R. M. Coates and M. W. Johnson, *Ibid.* **45**, 2685 (1980).
[29]D. Valentine, Jr., K. K. Johnson, W. Priester, R. C. Sun, K. Toth and G. Saucy, *Ibid.* **45**, 3698 (1980).
[30]P. Brownbridge and S. Warren, *J. Chem. Soc.* Perkin I 1131 (1977).
[31]W. E. Parham and L. D. Edwards, *J. Org. Chem.* **33**, 4150 (1968). T. L. Jacobs and G. E. Illingworth, Jr., *Ibid.* **28**, 2692 (1963).
[32]T. Katagiri, T. Suzuki, K. Takabe and J. Tanaka, *Nippon Kagaku Kaishi* 2246 (1975).
[33]F. Camps, J. Coll and A. Parente, *Synthesis* 215 (1978).
[34]W. G. Taylor, *J. Org. Chem.* **44**, 1020 (1979).
[35]T. Hirata, T. Aoki, Y. Hirano, T. Ito and T. Suga, *Bull. Chem. Soc. Jpn.* **54**, 3527 (1981).
[36]L. J. Altman, L. Ash and S. Marson, *Synthesis* 129 (1974).
[37]K. Sato, S. Inoue, A. Onishi, N. Uchida and N. Minowa, *J. Chem. Soc.* Perkin I 761 (1981).
[38]G. Wüchi and H. Wüest, *Helv. Chim. Acta.* **50**, 2440 (1967).