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Regio- and Stereoselective Terminal Allylic Carboxymethylation of *gem*-Dimethyl Olefins. Synthesis of Biologically Important Linear Degraded Terpenoids

YUKIO MASAKI,* KAZUHIKO SAKUMA, and KENJI KAJI

Gifu College of Pharmacy, 5–6–1 Mitahora Higashi, Gifu 502, Japan

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gem-Dimethyl olefins (III) were transformed regiospecifically to the terminal β-methallyl sulfides (IV) bearing the methoxycarbonylmethyl substituent on the sulfur atom *via* (A) methoxycarbonylmethanesulfenyl chloride addition followed by dehydrochlorination or (B) allylic chlorination with SO_2Cl_2 followed by sulfenylation with methyl thioglycolate. Treatment of the sulfides (IV) with *tert*-BuOK or NaH in *N*,*N*-dimethylformamide or dimethyl sulfoxide at room temperature gave stereoselectively the sulfur-free esters (V) through a novel one-pot desulfurizative [2,3]-sigmatropic rearrangement. By utilizing this method, biologically and pharmacologically important linear degraded terpenoids, a diol component (**1**) of the pheromonal secretion of the queen butterfly and several ω-quinoid acids (**4**, $n=1, 2$) and (**5**, $n=1, 2$), which are metabolites of polyisoprenoid-quinones, were synthesized.

Keywords——methoxycarbonylmethyl allyl sulfide; desulfurizative [2,3]-sigmatropic rearrangement; linear degraded terpenoid; queen butterfly pheromone; ω-quinoid acid

In nature, from microorganisms and insects to higher animals, several groups of degraded terpenoids (I), which are postulated to be the oxidative metabolites of linear terpenoids (II), are known to exist.[1)] Biologically and pharmacologically active representatives of those families, for example, include the constituents (**1**—**3**) of the pheromone isolated from the "hairpencils" of some species of male danaid butterflies,[1a,b)] as well as the ω-quinoid carboxylic acids (**4**—**6**, $n=1$) which have been suggested to be the metabolites of physiologically important polyisoprenoid quinones such as ubiquinones, phylloquinone, and menaquinones; these metabolites may be the physiologically active species of such quinones *in vivo*,[1c)] and have been recently reported to have inhibitory activities against the slow reacting substance of anaphylaxis (SRS-A) generation in addition to their effects on organella membranes.[1d)] The other examples are mycophenolic acid (**7**) and its prenylogues, isolated as mycotoxins with antibiotic and anti-tumor activities from *Penicillium brevicompactum*.[1e)] During the past two decades there have been many attempts to synthesize such degraded terpenoids in view of their biological and pharmacological interest.[1a,2)] In terms of synthetic strategies those reports may be classified into three categories: (1) biomimetic methods involving degradation of polyisoprenyl carbon chains;[1a,2a)] (2) tandem sequences consisting of synthesis of an ω-functionalized 4-methyl-4-hexenoic acid derivative or its prenylogues and C–C coupling of the synthons with the other part of the carbon skeleton, such as a latent quinone moiety;[2b)] (3) regioselective introduction of the acetic acid moiety at the terminal allylic position of the functionalized polyisoprenoids.[2c,d)] Although the last method seems to be attractive because several methods for terminal functionalization of the *gem*-dimethyl olefin terminus of isoprenoids have been established,[3)] only a few reports along this line have appeared. Thus, Trost and Weber reported a regio- and stereoselective synthesis of the dimethyl ester of a pheromone (**3**) of the Monarch butterfly *via* terminal palladation of methyl

geranate and introduction of malonate at the terminal allylic position.[2c] Katzenellenbogen[2e] and Miles[2f] utilized the [3,3]-Claisen-type rearrangement of the acetate or the orthoacetate of terminal β-methallylic alcohols to afford the pheromonal components (**1**, **2**) of the danaid butterflies with high stereoselectivity. Recently, successful applications of the Claisen rearrangement and the Carrol reaction of the terminal β-methallylic alcohols derived from isoprenoidquinones to the synthesis of quinone derivatives (**4**—**6**, $n=1$—9) with modified polyprenyl side chains have been reported by Terao and co-workers.[2d]

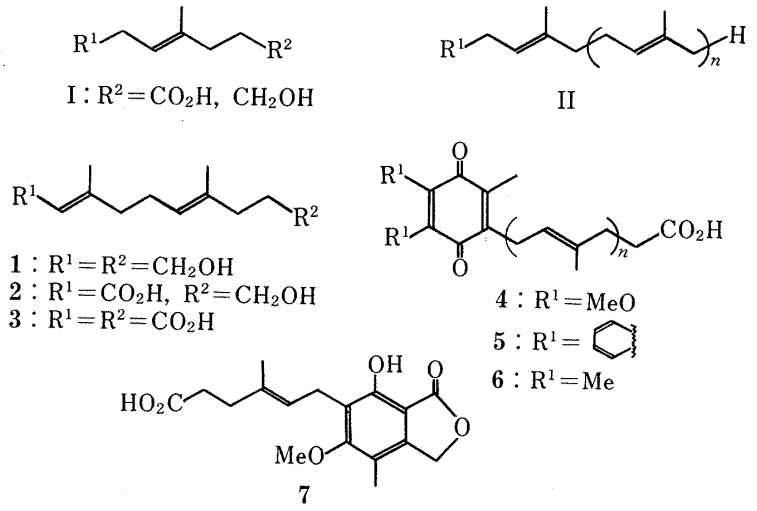

Chart 1

The anionic [2,3]-sigmatropic rearrangement of allylic sulfides is generally claimed to be a useful alternative method for regio- and stereoselective C–C bond formation at the γ-position with migration of the double bond.[4] In the course of synthetic studies on isoprenoid natural products, we have developed a facile method for terminal functionalization of isoprenoids *via* benzenesulfenyl chloride addition to provide the terminal β-methallyl phenyl sulfides.[3] This terminal functionalization led us to consider the direct conversion of isoprenoids (III) to the terminal β-methallyl sulfides of type IV, which possess the acetic acid moiety as the other substituent on the sulfur atom and appear to be key intermediates for the synthesis of such degraded terpenoids (I).[5] Here we describe the regio- and stereoselective terminal allylic carboxymethylation of *gem*-dimethyl olefins of type III by way of the allylic sulfides IV, leading to the γ,δ-unsaturated esters (V), and report syntheses of biologically and pharmacologically important degraded terpenoids, a diol component (**1**) of the pheromonal secretion of the queen butterfly[1b] and ω-quinoid carboxylic acids (**4**, $n=1$, 2) and (**5**, $n=1$, 2).[1c,2d] The synthetic sequence involves two stages. At first the acetic acid moiety was introduced as a substituent on sulfur into the isoprenoid skeleton (III) to give regiospecifically the terminal β-methallyl sulfides (IV) by the following methods: one involves addition of the sulfenyl chloride [$ClSCH_2CO_2Me$][6] derived from methyl thioglycolate [$HSCH_2CO_2Me$] to the isopropylidene terminus of isoprenoids (III) followed by mild dehydrochlorination of the resulting regioisomeric mixture of adducts (VI) and the other involves allylic chlorination of isoprenoids (III) with SO_2Cl_2 followed by sulfenylation of the chlorides (VII) with methyl thioglycolate in the presence of base. Secondly, stereoselective anionic [2,3]-sigmatropic rearrangement with concomitant sulfur extrusion of the allylic sulfides (IV) was carried out by treatment with a strong base such as potassium *tert*-butoxide (*tert*-BuOK) or NaH in *N*,*N*-dimethylformamide (DMF) or dimethyl sulfoxide (DMSO) to furnish the sulfur-free esters (V).

Synthesis of Terminal β-Methallyl Sulfides (IV) from Isoprenoids (III) (Chart 2)

(A) *Via* Addition of Methoxycarbonylmethanesulfenyl Chloride and Subsequent Dehydrochlorination——Application of the method for the terminal functionalization of iso-

prenoids involving the sulfenyl chloride addition[3] to the synthesis of the allylic sulfides of type IV gave successful results. Thus, treatment of an isoprenoid (IIIa) in CCl_4 at $-20\,°C$ with an equimolar amount of the sulfenyl chloride [$ClSCH_2CO_2Me$],[6] prepared from methyl thioglycolate with SO_2Cl_2 at $0\,°C$ in the presence of pyridine in CCl_4, provided instantaneously a regioisomeric mixture of adducts (VIa). The mixture of adducts was, without further purification, warmed in DMF at $60\,°C$ for 20 h to lead regiospecifically by way of the intermediary episulfonium ion[3] to the terminal β-methallyl sulfide (IVa) in 79% overall yield from IIIa. The structure of the sulfide (IVa) was characterized by spectral analysis (see the experimental section). This transformation to the allylic sulfide of type IV was generally effective with high site-selectivity for a variety of *gem*-dimethyl olefins, as summarized in Table I.

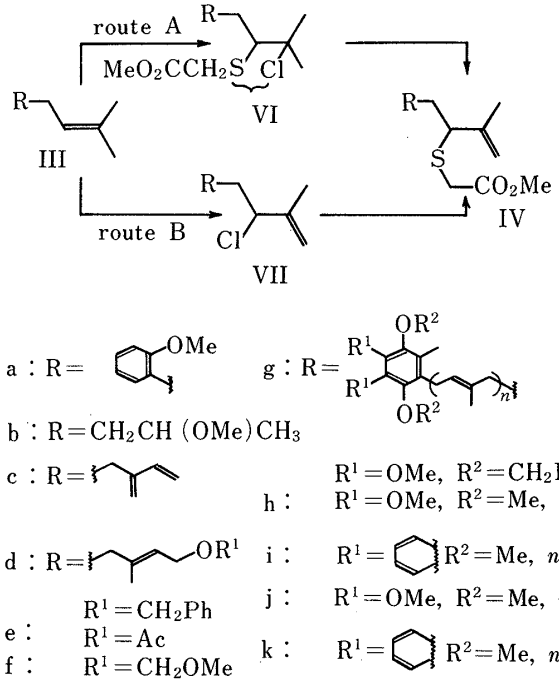

Chart 2

TABLE I. Preparation of Terminal β-Methallylic Sulfides (IV) Starting with *gem*-Dimethyl Olefins (III)

	% yield of sulfide (IV)										
	a	b	c	d	e	f	g	h	i	j	k
Method A[a]	79	75	24	73	70	33	70	66	70	54	55
Method B[b]	72	70	49	49	63	66	0[c]	0[c]	0[c]	62	55

a) *Via* the sulfenyl chloride addition (III→VI→IV). *b*) *Via* the allylic chlorination (III→VII→IV). *c*) Although the chloride (VII) was produced, the sulfenylation step did not proceed under the conditions described.

(B) *Via* Allylic Chlorination with SO_2Cl_2 and Subsequent Sulfenylation with Methyl Thioglycolate——Recently, much attention has been focused on the direct allylic chlorination with migration of the double bond of *gem*-dimethyl olefins from the viewpoint of terminal functionalization of isoprenoids.[7] We have recently observed that SO_2Cl_2, which is commercially available and easier to handle in a laboratory than chlorine and *tert*-

butylhypochlorite, can convert the isopropylidene terminus of a certain isoprenoid to a terminal β-methallyl chloride of type VII in the presence of pyridine and that the chloride could be transformed to an α-substituted terminal β-methallyl phenyl sulfide without allylic 1,3-transposition by the use of sodium thiophenoxide in DMF.[8] We adopted this method in order to have an alternative route to the allylic sulfides (IV). Treatment of the olefin (IIIa) with 1 eq each of SO_2Cl_2 and pyridine in CCl_4 at 0 °C for 1 h gave the allylic chloride (VIIa) as the major component, which was supported by proton nuclear magnetic resonance (^{1}H-NMR) measurement of the crude product. On treatment of the crude chloride with methyl thioglycolate and NaH (0 °C, 1 h) or K_2CO_3 (15 °C, 15 h) in DMF, the same allylic sulfide (IVa) as obtained according to method (A) was produced in 68% or 72% overall yield, respectively. This transformation (III→VII→IV) proceeded generally with the isoprenoids examined except for the protected hydroquinone derivatives (IIIg—i) with the prenyl side chain ($n=0$) in which, although the allylic chlorination smoothly took place, the subsequent sulfenylation was unsuccessful probably because of steric hindrance of the adjacent arylic methyl group. The results are summarized in Table I.

Sulfur-Contractive Anionic [2,3]-Sigmatropic Rearrangement of the Allylic Sulfides (IV) Leading to Direct Access to the Esters (V) (Chart 3)

It is well known that allylic sulfides with a carbanion-stabilizing group at the α′-position to sulfur undergo the [2,3]-sigmatropic rearrangement with base to furnish a new C–C bond at the γ-allylic position.[4] The allylic sulfide (IVd) was stirred with 1.2 eq of *tert*-BuOK in a solvent mixture of tetrahydrofuran (THF)–DMSO (1 : 1) at 0 °C for 2 h and the product, obtained in 73% yield, was characterized as the α-mercaptoester (VIIId), which was desulfurized with Raney-nickel in acetone to give the sulfur-free ester (Vd) in 82% yield. The stereoselectivity of the [2,3]-sigmatropic rearrangement was determined as 89 : 11 for *E*-Vd : *Z*-Vd by gas-liquid chromatography (GLC) and gas chromatography-mass spectrometry (GC-MS) of the ester (Vd). During optimization of the reaction conditions for the rearrangement of the allylic sulfides (IV), we found a novel one-pot desulfurizative rearrangement directly providing the sulfur-free ester (V). Thus, treatment of the sulfide (IVd) with 1.5 eq of *tert*-BuOK in DMF or DMSO at room termperature gave the ester (Vd) in 53—67% yield. The stereoisomeric ratio of the product (Vd) was almost identical ($E:Z=87:13$) with that observed in the two-step conversion. This unique desulfurizative rearrangement proved to be the result of a set of one-pot stepwise reactions, *i.e.* rearrangement and desulfurization, since the isolated α-mercaptoester (VIIId) afforded the sulfur-free ester (Vd) on treatment with *tert*-BuOK in DMSO at room temperature. This finding was reminiscent of two precedents: Eschenmoser's sulfide contraction *via* the [1,2]-sigmatropic rearrangement of thioester and thio-iminoester with an acylmethyl or carboxymethyl substituent on the sulfur[9] and Oki's observation of the desulfurizative reduction of α-alkyl (or aryl) thio-carbonyl compounds with nucleophiles.[10] This stereoselective one-pot transformation of the allylic sulfide (IV) to the

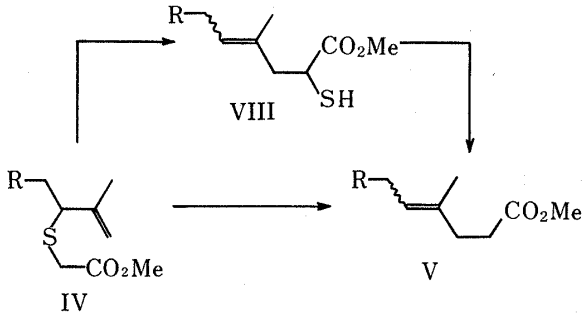

Chart 3

TABLE II. The Anionic [2,3]-Sigmatropic Rearrangement of the Allylic Sulfides (IV) Providing the α-Mercaptoesters (VIII) or the Sulfur-Free Esters (V)

Allylic sulfide (IV)	Conditions,[a] % yield, and E/Z-ratio for product α-Mercaptoester (VIII)	Sulfur-free ester (V)
a	—[b]	C 58% 88/12
b	—	B 54% 87/13
c	A 47% 89/11	C 27% 88/12
d	A 73% 87/13	B 53% 89/11 C 67% 88/12
e	A 35% 85/15	B 47% 86/14
f	A 73% 88/12	C 66% 87/13
g	D[c] 57% 84/16	D 48% 82/18
h	—	D 37% 85/15
i	—	D 48% 84/16
j	—	D 38% 87/13
k	—	D 48% 87/13

a) Conditions A: 1.2 eq *tert*-BuOK, THF–DMSO (1 : 1), 0 °C, 2 h. B: 1.5 eq *tert*-BuOK, DMF, 15 °C, 5 h. C: 1.5 eq *tert*-BuOK, DMSO, 15 °C, 15 h. D: 1.5 eq NaH, DMSO, 15 °C, 5 h. *b*) Dashes indicate that attempts to obtain the α-mercaptoesters (VIII) were not made. *c*) Reaction was carried out for 1.5 h under condition D.

sulfur-free ester (V) appeared to be general under the conditions described in Table II, although the yields were still only moderate. Determination of the E : Z-ratio of the esters (V) obtained was carried out for Vc—f by GLC and GC-MS analysis and for the esters (Va, b) and (Vg—k) by ^{1}H-NMR analysis, since the signal of the carbomethoxyl group of each stereoisomer appeared at a different chemical shift. The preponderance of the (*E*)-stereoisomer (V) was confirmed finally by conversion of the esters (V) into the known (*E*)-olefins, *vide infra*. It is worth noting that particularly for the allylic sulfides (IVg—i), the basic treatment with *tert*-BuOK was neither effective for the direct conversion into the esters (V), nor gave rise to the α-mercapto esters (VIII), probably because of the steric effect of the neighboring arylic methyl group and the bulkiness of the base, but replacement of the base with NaH led to the occurrence of the desirable desulfurizative rearrangement to provide the esters (Vg—i). Thus, treatment of the allylic sulfide (IVg) with NaH in DMSO at room temperature for a short time (1.5 h) gave the α-mercapto ester (VIIIg) in 57% yield, and prolonged exposure of the sulfide (IVg) to the same conditions for 5 h led to formation of the sulfur-free ester (Vg) in 48% yield.

Synthesis of Linear Degraded Terpenoids

(a) Terpenoid Diol Component (1) of the Pheromonal Secretion of the Queen Butterfly[5] ——The pheromonal component (**1**) was derived easily from the ester (Vd) by the routine procedures. Thus, reduction of Vd with $LiAlH_4$ in Et_2O afforded the mono-alcohol in 89% yield, and this was debenzylated by the Birch reduction with lithium in liq. NH_3 to give the diol (**1**) in 76% yield. The spectroscopic properties of the synthetic diol (**1**) and its diacetate were consistent with the assigned structure of the pheromonal compound[1b,2e] except for the observation of minor contamination with the (6*Z*)-isomer (*ca.* 11%) in GLC analysis.

(b) ω-Quinoid Carboxylic Acids (4, $n=1, 2$) and (5, $n=1, 2$)——Alkaline hydrolysis of the esters (Vh—k) followed by deprotective oxidation of the resulting acids according to the known methods[2d] using argentic oxide (AgO) or ceric ammonium nitrate (CAN) provided the physiologically and pharmacologically interesting degraded isoprenoids, ω-quinoid acids (**4**, $n=1, 2$) and (**5**, $n=1, 2$), in 47—55% overall yields after recrystallization. The quinone acids obtained were identified by spectral comparisons with the authentic compounds.[2b,d]

In conclusion, a tandem sequence consisting of the terminal sulfur-containing functionalization of isoprenoids (III) and the anionic [2,3]-sigmatropic rearrangement of the resulting allylic sulfides (IV) offers a new regio- and stereoselective route to a variety of degraded terpenoids of type I. In the present study, we also found a novel one-pot sulfur-contractive [2,3]-sigmatropic rearrangement of allylic sulfides (IV) allowing the direct transposition of the acetate block from the sulfur to the γ-allylic position.

Experimental

General——All reactions were run under a nitrogen atmosphere unless otherwise noted. Solvents were distilled before use: dichloromethane (CH_2Cl_2) over P_2O_5; DMF, DMSO, 1,2-dimethoxyethane (DME), carbon tetrachloride (CCl_4), and pyridine from calcium hydride (CaH_2); diethyl ether (Et_2O) over $LiAlH_4$; THF from sodium benzophenone ketyl; acetone over K_2CO_3. Reaction mixtures were worked up as follows unless otherwise noted. A mixture was extracted with Et_2O, and the extract was washed with water, brine, or saturated $NaHCO_3$, dried over anhyd. $MgSO_4$, and concentrated to give a crude product, which was purified by column chromatography. Silica gel Wakogel B-5F and Wakogel C-200 were used for thin layer chromatography (TLC) and column chromatography, respectively, and the hexane–Et_2O solvent system was employed as the eluent. Infrared (IR) spectra were recorded in $CHCl_3$ solution on a JASCO IRA-1 spectrometer and characteristic bands (ν_{max}) 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* (%). ^{1}H-NMR spectra were recorded in CCl_4 solution on a Hitachi R-20B spectrometer (60 MHz), unless otherwise noted, with tetramethylsilane (TMS) as an internal standard; chemical shifts are reported in δ (ppm) relative to TMS and coupling constants (*J*) in hertz (Hz). GLC was performed analytically on a JGC-1100 gas chromatograph (FID) using a stainless steel column (3 mm × 2 m) packed with 2% silicone OV-105 on Chromosorb W-AW-DMCS (80—100 mesh). GC-MS was performed on a JMS-D300 instrument with a gas chromatograph having a glass column (2 mm × 2 m) with the same packing as described above.

Materials——*o*-Methoxyprenylbenzene (IIIa) was prepared by prenylation of phenol with prenyl bromide and sodium (Et_2O, reflux, 1.5 h) according to the reported method[11] followed by methylation of the resulting *o*-prenylphenol (NaH, CH_3I, DMF–DME, 0—15 °C, 1.5 h). ^{1}H-NMR data for IIIa: 1.71 (6H, s, 2 × $=CCH_3$), 3.25 (2H, d, J=7.0, Ar-C$\underline{H}_2$CH=), 3.76 (3H, s, OCH_3), 5.25 (1H, bt, J=7.0, Ar-$CH_2C\underline{H}$=), 6.58—7.20 (4H, m, arom-H).

6-Methoxy-2-methyl-2-heptene (IIIb) was obtained by reduction of 2-methyl-2-hepten-6-one with $NaBH_4$ (EtOH, 15 °C, 1 h) followed by methylation of the resulting alcohol (NaH, CH_3I, DME, 15 °C, 15 h). ^{1}H-NMR data for IIIb: 1.05 (3H, d, J=6.0, C$\underline{H}_3$CH(OMe)), 1.59, 1.67 (each 3H, s, 2 × $=CCH_3$), 3.22 (3H, s, OCH_3), 2.92—3.45 (1H, m, $CH_3C\underline{H}$(OMe)), 5.06 (1H, bt, J=7.0, =CH).

Myrcene (IIIc) was purchased from Tokyo Kasei Co.

Protected geraniol derivatives (IIId—f)[3] were prepared from geraniol by benzylation (NaH, $PhCH_2Br$, DME, 15 °C, 15 h), acetylation (Ac_2O, pyridine, 15 °C, 15 h), and methoxymethylation (NaH, $ClCH_2OCH_3$, 15 °C, 15 h), respectively.

Protected 2-prenyl- and 2-geranyl-1,4-hydroquinones (IIIg, h, j) and 1,4-naphthohydroquinones (IIIi, k) were synthesized according to the reported methods,[2d,12] from 2,3-dimethoxy-5-methyl-1,4-benzoquinone and 2-methyl-1,4-naphthoquinone, respectively.

Preparation of 3-Carbomethoxymethylthio-4-(2-methoxyphenyl)-2-methyl-1-butene (IVa) from *o*-Methoxyprenylbenzene (IIIa) *via* Addition of Carbomethoxymethanesulfenyl Chloride ($ClSCH_2CO_2Me$), General Method for Preparation of Terminal β-Methallyl Sulfides (IV) via the Addition Reaction of *gem*-Dimethyl Olefins (III) with $ClSCH_2CO_2Me$ (Method A)——A solution of $ClSCH_2CO_2Me$ in CCl_4 was freshly prepared and used *in situ*. Thus, SO_2Cl_2 (400 mg, 3.0 mmol) was added dropwise over 5 min to a cold solution (0 °C) of methyl thioglycolate ($HSCH_2CO_2Me$) (320 mg, 3.0 mmol) and pyridine (240 μl) in CCl_4 (4.0 ml) and the mixture was stirred for 1 h at the same temperature. The solution of $ClSCH_2CO_2Me$ in CCl_4 obtained was added dropwise over 10 min to a solution of *o*-methoxyprenylbenzene (IIIa) (530 mg, 3.0 mmol) in CCl_4 (9.0 ml) at −20 °C. Stirring was continued for 20 min and the mixture was concentrated *in vacuo* to leave a crude mixture of adducts (VIa) (830 mg). ^{1}H-NMR: 1.43, 1.55 (minor pair of singlets, C(SPh)$(CH_3)_2$) and 1.72, 1.79 (major pair of singlets, C(Cl)$(CH_3)_2$) (overall 6H), 3.38 (major) and 3.70 (minor) (overall 3H, s, CO_2CH_3), 3.87 (3H, s, Ar-OCH_3). The mixture of adducts was, without purification, warmed in DMF (12 ml) at 60 °C for 20 h. Usual work-up and product isolation gave the pure oily sulfide (IVa) (662 mg, 79%). IR: 1735, 1640, 1605, 1590, 1495, 1470, 1440. MS: 280 (M^+, 18%), 175 (23%), 174 (27%), 159 (100%), 121 (85%). ^{1}H-NMR: 1.76 (3H, s, $=CCH_3$), 2.85 (2H, d, J=8.0, Ar-C$\underline{H}_2$CH(S)), 2.96 (2H, s, SCH_2CO_2Me), 3.58 (3H, s, CO_2CH_3), 3.78 (3H, s, Ar-OCH_3), 3.78 (1H, t, J=8.0, Ar-$CH_2C\underline{H}$(S)), 4.73 (2H, br s, $=CH_2$), 6.60—7.35 (4H, m, arom-H). *Anal.* Calcd for $C_{15}H_{20}O_3S$: C, 64.27; H, 7.19. Found: C, 64.15; H, 7.23.

Preparation of IVa *via* the Terminal Allyl Chloride (VIIa), General Procedure for Preparation of IV by Way of the

Terminal Allylic Chlorination of III (Method B)——To a solution of the olefin (IIIa) (350 mg, 2.0 mmol) and pyridine (160 mg, 2.0 mmol) in CCl_4 (5.0 ml) was added dropwise a solution of SO_2Cl_2 (270 mg, 2.0 mmol) in CCl_4 (2.0 ml) at −5 °C. The mixture was stirred for 1 h at −5—0 °C and the reaction was quenched by addition of water. The reaction mixture was extracted with Et_2O, and the extract was washed with saturated $NaHCO_3$, dried, and concentrated to give the crude allylic chloride (VIIa) (500 mg). ^{1}H-NMR: 1.85 (3H, s, $=CCH_3$), 3.04 (2H, d, J=8.0, Ar-C$\underline{H}_2$CH(Cl)), 3.25 (3H, s, OCH_3), 4.59 (1H, t, J=8.0, Ar-CH$_2$C$\underline{H}$(Cl)), 4.72, 4.78 (each 1H, br s, $=CH_2$), 6.58—7.20 (4H, m, arom-H). To a suspension of NaH (hexane-washed powder obtained from 100 mg of 50% mineral oil dispersion) in DMF (4.0 ml) was added dropwise a solution of methyl thioglycolate (233 mg, 2.2 mmol) in DME (1.5 ml) at 0 °C. After 10 min stirring of the mixture, a solution of the crude chloride (VIIa) in DME (2.0 ml) was added dropwise to the cold (0 °C) solution of $NaSCH_2CO_2Me$ in DMF–DME and the whole was stirred at 0 °C for 1 h, then at room temperature for another 1 h. The reaction was quenched by addition of AcOH and the reaction mixture was worked up in the usual manner. Purification of the crude product gave pure IVa (380 mg, 68%). The sulfide (IVa) was also obtained in 72% yield from the chloride (VIIa), methyl thioglycolate, and K_2CO_3 in DMF at room temperature for 15 h.

Yields and physicochemical properties for the other terminal β-metallylic sulfides (IV) obtained are listed in Table I and below.

IVb: Oil. IR: 1730, 1630, 1440, 1370. MS: 246 (M^+, 4%), 214 (4%), 174 (48%), 173 (30%), 159 (13%), 141 (61%), 109 (100%). ^{1}H-NMR: 1.08 (3H, d, J=6.0, C$\underline{H}_3$CH(OMe)), 1.70 (3H, s, $=CCH_3$), 2.98 (2H, s, SCH_2CO_2Me), 3.23 (3H, s, OCH_3), 3.65 (3H, s, CO_2CH_3), 4.82 (2H, br s, $=CH_2$). *Anal.* Calcd for $C_{12}H_{22}O_3S$: C, 58.51; H, 9.00. Found: C, 58.32; H, 9.11.

IVc: Oil. ^{1}H-NMR: 1.71 (3H, s, $=CCH_3$), 2.99 (2H, s, SCH_2CO_2Me), 3.45 (1H, t, J=7.5, $=CC\underline{H}$(S)), 3.64 (3H, s, CO_2CH_3), 4.80—5.33 (6H, m, 3 × $=CH_2$), 6.06—6.55 (1H, dd, J=17.0, 10.5, C$\underline{H}=CH_2$). *Anal.* Calcd for $C_{13}H_{20}O_2S$: C, 64.98; H, 8.39. Found: C, 64.87; H, 8.55.

IVd: Oil. IR: 1730, 1660, 1630, 1490, 1455, 1440, 1400, 1370. MS: 348 (M^+, 2%), 275 (25%), 257 (15%), 240 (13%), 174 (21%), 167 (30%), 159 (100%), 151 (47%), 135 (62%). ^{1}H-NMR: 1.61, 1.71 (each 3H, s, 2 × $=CCH_3$), 2.97 (2H, s, SCH_2CO_2Me), 3.42 (1H, t, J=6.5, $=CCH$(S)), 3.60 (3H, s, CO_2CH_3), 3.93 (2H, d, J=6.0, $=CHC\underline{H}_2OBn$), 4.40 (2H, s, OCH_2Ph), 4.83 (2H, br s, $=CH_2$), 5.35 (1H, br t, J=6.0, $=C\underline{H}CH_2O$), 7.20 (5H, s, arom-H). *Anal.* Calcd for $C_{20}H_{28}O_3S$: C, 68.94; H, 8.10. Found: C, 68.79; H, 8.35.

IVe: Oil. IR: 1730, 1630, 1435, 1380. 1360. ^{1}H-NMR: 1.71 (6H, s, 2 × $=CCH_3$), 1.96 (3H, s, CH_3CO_2), 2.97 (2H, s, SCH_2CO_2Me), 3.40 (1H, t, J=7.0, $=CCH$(S)), 3.63 (3H, s, CO_2CH_3), 4.47 (2H, d, J=7.0, $=CHC\underline{H}_2OAc$), 4.80, 4.86 (each 1H, br s, $=CH_2$), 5.30 (1H, br t, J=7.0, $=C\underline{H}CH_2OAc$). *Anal.* Calcd for $C_{15}H_{24}O_4S$: C, 59.98; H, 8.05. Found: C, 59.69; H, 8.21.

IVf: Oil. IR: 1730, 1630, 1430, 1370. MS: 302 (M^+, 6%), 257 (8%), 241 (12%), 229 (14%), 167 (16%), 159 (100%), 151 (17%), 135 (39%). ^{1}H-NMR: 1.67, 1.71 (each 3H, s, 2 × $=CCH_3$), 2.97 (2H, s, SCH_2CO_2Me), 3.26 (s, 3H, OCH_3), 3.40 (1H, t, J=7.5, $=CCH$(S)), 3.64 (3H, s, CO_2CH_3), 3.95 (2H, J=7.0, $=CHC\underline{H}_2O$), 4.45 (2H, s, OCH_2OMe), 4.81, 4.87 (each 1H, br s, $=CH_2$), 5.27 (1H, br t, J=7.0, $=C\underline{H}CH_2O$). *Anal.* Calcd for $C_{15}H_{26}O_4S$: C, 59.98; H, 8.67. C. 59.72; H, 8.64.

IVg: Oil. IR: 1740, 1470, 1430, 1370, 1350. MS: 536 (M^+, 4%), 445 (4%), 431 (3%), 413 (5%), 377 (7%), 249 (100%), 217 (18%). ^{1}H-NMR: 1.70 (3H, s, $=CCH_3$), 2.10 (3H, s, Ar-CH_3), 2.70—2.86 (2H, m, Ar-C$\underline{H}_2$CH(S)), 3.52 (3H, s, CO_2CH_3), 3.84, 3.87 (each 3H, s, 2 × OCH_3), 4.65, 4.73 (each 1H, br s, $=CH_2$), 4.90, 4.98 (each 2H, s, 2 × OCH_2Ph), 7.10—7.50 (10H, br s, arom-H). *Anal.* Calcd for $C_{31}H_{36}O_6S$: C, 69.38; H, 6.76. Found: C, 69.31; H, 6.77.

IVh: Oil. IR: 1730, 1630, 1460, 1400, 1365, 1345. MS: 384 (M^+, 7%), 279 (6%), 225 (100%), 210 (15%), 195 (10%). ^{1}H-NMR: 1.82 (3H, s, $=CCH_3$), 2.13 (3H, s, Ar-CH_3), 2.70—2.95 (2H, m, Ar-C$\underline{H}_2$CH(S)), 3.57 (3H, s, CO_2CH_3), 3.71, 3.82 (each 3H, s, 2 × OCH_3), 3.78 (6H, s, 2 × OCH_3), 4.77 (2H, br s, $=CH_2$). *Anal.* Calcd for $C_{19}H_{28}O_6S$: C, 59.36; H, 7.34. Found: C, 59.41; H, 7.28.

IVi: Oil. IR: 1730, 1630, 1590, 1445, 1430, 1370, 1345. MS: 374 (M^+, 20%), 269 (7%), 215 (100%), 200 (22%), 184 (20%). ^{1}H-NMR: 1.85 (3H, s, $=CCH_3$), 2.40 (3H, s, Ar-CH_3), 2.93 (3H, s, SCH_2CO_2Me), 2.90—3.20 (2H, m, Ar-C$\underline{H}_2$CH(S)), 3.50 (3H, s, CO_2CH_3), 3.78, 3.81 (each 3H, s, 2 × OCH_3), 4.73 (2H, br s, $=CH_2$), 7.22—7.50, 7.75—8.05 (each 2H, m, arom-H). *Anal.* Calcd for $C_{21}H_{26}O_4S$: C, 67.36; H, 7.00. Found: C, 67.08; H, 6.84.

IVj: Oil. IR: 1730, 1630, 1460, 1435, 1400, 1345. MS: 452 (M^+, 19%), 347 (10%), 247 (33%), 225 (100%). ^{1}H-NMR: 1.68, 1.76 (each 3H, s, 2 × $=CCH_3$), 2.06 (3H, s, Ar-CH_3), 2.92 (2H, s, SCH_2CO_2Me), 3.22 (2H, d, J=6.5, Ar-C$\underline{H}_2$CH=), 3.35 (1H, t, J=7.5, $=CCH$(S)), 3.59 (3H, s, CO_2CH_3), 3.70, 3.79 (each 6H, s, 4 × OCH_3), 4.74, 4.81 (each 1H, br s, $=CH_2$), 5.00 (1H, br t, J=6.5, Ar-CH$_2$C$\underline{H}$=). *Anal.* Calcd for $C_{24}H_{36}O_6S$: C, 63.70; H, 8.02. Found: C, 63.49; H, 8.22.

IVk: Oil. IR: 1730, 1630, 1590, 1450, 1430, 1370, 1345. MS: 442 (M^+, 47%), 429 (20%), 241 (67%), 215 (100%), 200 (29%). ^{1}H-NMR: 1.68, 1.82 (each 3H, s, 2 × $=CCH_3$), 2.32 (3H, s, Ar-CH_3), 2.92 (2H, s, SCH_2CO_2Me), 3.36 (1H, t, J=7.0, $=CCH$(S)), 3.54 (3H, s, CO_2CH_3), 3.60 (2H, d, J=6.5, Ar-C$\underline{H}_2$CH=), 3.30 (6H, s, 2 × OCH_3), 4.74, 4.83 (each 1H, br s, $=CH_2$), 5.13 (1H, br t, J=6.5, Ar-CH$_2$C$\underline{H}$=), 7.20—7.50, 7.80—8.07 (each 2H, m, arom-H). *Anal.* Calcd for $C_{26}H_{34}O_4S$: C, 70.56; H, 7.74. Found: C, 69.97; H, 7.69.

Preparation of Methyl 10-Benzyloxy-4,8-dimethyl-2-mercaptodeca-(4*E*),(8*E*)-dienoate (VIIId), General Procedure for the Stereoselective [2,3]-Sigmatropic Rearrangement of the Allylic Sulfides (IV) Providing the α-Mercapto Esters (VIII) (Conditions A)——To a mixture of *tert*-BuOK (135 mg, 1.2 mmol), DMSO (8.0 ml), and THF (4.0 ml) was added dropwise over 10 min a solution of the sulfide (IVd) (350 mg, 1.0 mmol) in THF (4.0 ml) at 0 °C, and the mixture was stirred for 2 h at the same temperature. The reaction was quenched by addition of 3% HCl in a ice-water bath. The whole was extracted with Et_2O and the organic layer was worked up in the usual manner to give a crude product (288 mg), which was purified by column chromatography on silica gel to afford the TLC-pure oily α-mercapto ester (VIIId) (254 mg, 73%). The stereoisomeric ratio of the ester was determined as $E:Z=87:13$ by GLC and GC-MS analysis of the corresponding sulfur-free ester (Vd) derived from VIIId, *vide infra*. Physicochemical properties for VIIId and its acetate (VIIId-acetate) follow: VIIId: IR: 1730, 1660, 1500, 1455, 1440, 1380, 1360, 1340. MS: 348 (M^+, 2%), 316 (3%), 257 (19%), 240 (100%), 225 (20%), 207 (22%). ^{1}H-NMR: 1.60 (6H, s, $2\times=CCH_3$), 1.89 (1H, d, $J=9.0$, SH), 2.00—2.20 (4H, br s, $=CHC\underline{H}_2C\underline{H}_2C=$), 2.15—2.60 (2H, m, $CH(SH)C\underline{H}_2C=$), 3.05—3.60 (1H, m, $=CCH_2C\underline{H}(SH)$), 3.62 (3H, s, CO_2CH_3), 3.92 (2H, d, $J=6.5$, $=CHC\underline{H}_2OBn$), 4.40 (2H, s, OCH_2Ph), 5.20 (1H, br s, =CH), 5.31 (1H, br t, $J=6.5$, $=C\underline{H}CH_2OBn$), 7.20 (5H, s, arom-H). *Anal.* Calcd for $C_{20}H_{28}O_3S$: C, 68.94; H, 8.10. Found: C, 68.65; H, 8.32.

VIIId-Acetate: IR: 1730, 1690, 1495, 1455, 1435, 1380, 1350, 1335. ^{1}H-NMR: 1.62 (6H, s, $2\times=CCH_3$), 2.00—2.15 (4H, br, $=CHC\underline{H}_2C\underline{H}_2C=$), 2.28 (3H, s, CH_3CO_2), 2.20—2.60 (2H, m, $=CC\underline{H}_2CH(SAc)$), 3.61 (3H, s, CO_2CH_3), 3.92 (2H, d, $J=6.5$, $=CHC\underline{H}_2OBn$), 4.20 (1H, t, $J=8.0$, $=CCH_2C\underline{H}(SAc)$), 4.40 (2H, s, OCH_2Ph), 5.20 (1H, br, =CH), 5.30 (1H, br t, $J=6.5$, $=C\underline{H}CH_2O$), 7.20 (5H, s, arom-H). Other α-mercapto esters (VIII) were obtained analogously by this method except for some methyl 2-mercapto-4-hexenoates bearing protected hydroquinone nuclei at the 6 position, such as VIIIg, which was obtained by the use of NaH in DMSO as described later. Yields for other α-mercapto esters (VIII) are listed in Table II and the spectral properties are given below.

VIIIc: ^{1}H-NMR: 1.60 (3H, s, $=CCH_3$), 1.88 (1H, d, $J=9.5$, $CH(S\underline{H})$), 2.10—2.25 (4H, br, $=CHC\underline{H}_2C\underline{H}_2C=$), 2.25—2.65 (2H, m, $=CC\underline{H}_2CH(SH)$), 3.10—3.60 (1H, m, $=CCH_2C\underline{H}(SH)$), 3.65 (3H, s, CO_2CH_3), 4.85—5.35 (5H, m, $2\times=CH_2$ and =CH), 6.04—6.56 (1H, dd, $J=17.0$, 10.0, $C\underline{H}=CH_2$).

VIIIe: IR: 1730, 1430, 1380, 1360. ^{1}H-NMR: 1.61, 1.70 (each 3H, s, $2\times=CCH_3$), 1.88 (1H, d, $J=9.5$, $CH(S\underline{H})$), 1.96 (3H, s, CH_3CO_2), 2.00—2.20 (4H, br, $=CHC\underline{H}_2C\underline{H}_2C=$), 2.20—2.65 (2H, m, $=CC\underline{H}_2CH(SH)$), 3.10—3.60 (1H, m, $=CCH_2C\underline{H}(SH)$), 3.65 (3H, s, CO_2CH_3), 4.46 (2H, $J=7.0$, $=CHC\underline{H}_2OAc$), 5.15 (1H, br, =CH), 5.27 (1H, br t, $J=7.0$, $=C\underline{H}CH_2OAc$).

VIIIf: IR: 1730, 1435, 1380, 1335. ^{1}H-NMR: 1.62, 1.65 (each 3H, s, $2\times=CCH_3$), 1.92 (1H, d, $J=9.5$, $CH(S\underline{H})$), 2.00—2.15 (4H, br, $=CHC\underline{H}_2C\underline{H}_2C=$), 2.20—2.65 (2H, m, $=CC\underline{H}_2CH(SH)$), 3.27 (3H, s, OCH_3), 3.66 (3H, s, CO_2CH_3), 3.95 (2H, d, $J=7.0$, $\times CHC\underline{H}_2O$), 4.46 (2H, s, OCH_2OMe), 5.16 (1H, br, =CH), 5.26 (1H, br t, $J=7.0$, $=C\underline{H}CH_2O$).

VIIIg: IR: 1730, 1460, 1450, 1420, 1370, 1340. ^{1}H-NMR: 1.65 (3H, s, $=CCH_3$), 1.83 (1H, d, $J=9.5$, $CH(S\underline{H})$), 2.20 (3H, s, Ar-CH_3), 2.20—2.55 (2H, m, $=CC\underline{H}_2CH(SH)$), 3.21 (2H, d, $J=7.0$, Ar-$C\underline{H}_2CH=$), 3.50 (3H, s, CO_2CH_3), 3.86 (6H, s, $2\times OCH_3$), 4.91 (4H, s, $2\times OCH_2Ph$), 4.85—5.10 (1H, br, =CH), 7.10—7.50 (10H, br, arom-H).

Preparation of Methyl 10-Benzyloxy-4,8-dimethyldeca-(4*E*),(8*E*)-dienoate (Vd) and 1,4-Dibenzyloxy-2,3-dimethoxy-6-(5-methoxycarbonyl-3-methyl-(2*E*)-penten-1-yl)-5-methylbenzene (Vg), General Procedure for the Desulfurizative [2,3]-Sigmatropic Rearrangement of the Allylic Sulfides (IV) Providing the Esters (V) (Conditions B, C, and D)——*tert*-BuOK (168 mg, 1.5 mmol) was added in portions to the solution of the sulfide (IVd) (350 mg, 1.0 mmol) in DMF (10 ml) at room temperature and stirring was continued for 5 h at the temperature (condition B). The reaction was quenched by addition of 3% HCl in an ice-water bath. The whole was worked up in the usual manner to give a crude product (252 mg), which was purified by column chromatography on silica gel to afford the TLC-pure oily ester (Vd) (167 mg, 53%). The stereoisomeric ratio was determined as $E:Z=89:11$ by GLC and GC-MS analysis, although the two components could not be isolated. Physicochemical data for Vd follow: IR: 1730, 1660, 1500, 1455, 1440. MS: 316 (M^+, 5%), 225 (16%), 208 (40%), 195 (29%), 141 (78%), 121 (58%), 109 (100%). ^{1}H-NMR: 1.60 (6H, s, $2\times=CCH_3$), 2.00—2.20 (4H, br, $=CHC\underline{H}_2C\underline{H}_2C=$), 2.28 (4H, s, $=CC\underline{H}_2C\underline{H}_2CO_2$), 3.55 (3H, s, CO_2CH_3), 3.90 (2H, d, $J=6.5$, $=CHC\underline{H}_2OBn$), 4.38 (2H, s, OCH_2Ph), 5.10 (1H, br, =CH), 5.30 (1H, br t, $J=6.5$, $=C\underline{H}CH_2O$), 7.20 (5H, s, arom-H). *Anal.* Calcd for $C_{20}H_{28}O_3$: C, 75.91; H, 8.92. Found: C, 75.86; H, 8.99. Nearly identical results were obtained with DMSO as a solvent at room temperature for 15 h (condition C) as indicated in Table II. Unfortunately the above conditions B and C were not effective for the conversion of the protected hydroquinones (IVg—i) with the C_5-side chain into the sulfur-free esters (V). For this purpose NaH proved to be effective as a base (condition D). To a suspension of NaH (18 mg, 0.75 mmol) in DMSO (7.0 ml) was added dropwise a solution of the sulfide (IVg) (270 mg, 0.5 mmol) in DMSO (3.0 ml) at room temperature, and the mixture was stirred for 5 h at the same temperature. After the usual work-up of the mixture and product isolation, the TLC-pure ester (Vg) was obtained (121 mg, 48%). The stereoisomeric ratio was determined as $E:Z=82:18$ by ^{1}H-NMR analysis; the signals of the carbomethoxy group at δ 3.49 and 3.57 were diagnostic. Physicochemical properties for Vg follow: IR: 1735, 1475, 1460, 1430, 1375, 1350. MS: 504 (M^+, 29%), 413 (48%), 381 (100%), 349 (12%), 321 (13%), 289 (13%), 235 (29%), 197 (38%). ^{1}H-NMR: 1.64 (3H, s, $=CCH_3$), 2.02 (3H, s, Ar-CH_3), 2.25 (4H, s, $=CCH_2CH_2CO_2$), 3.23

(2H, d, J=6.5, Ar-C$\underline{H}_2$CH=), 3.49 (major) and 3.57 (minor) (overall 3H, s, CO_2CH_3), 3.85 (6H, s, 2×OCH_3), 4.88 (4H, s, 2×OCH_2Ph), 7.10—7.50 (10H, br, arom-H). *Anal.* Calcd for $C_{31}H_{36}O_6$: C, 73.78; H, 7.19. Found: C, 73.85; H, 7.43. Exposure of IVg to the above conditions for a shorter time (1.5 h) provided the α-mercapto ester (VIIIg) in 57% yield. Results for the esters (V) are listed in Table II and the spectral properties are given below.

Va: Oil. IR: 1735, 1600, 1595, 1495, 1470, 1445. MS: 248 (M^+, 44%), 216 (9%), 174 (35%), 161 (59%), 159 (32%), 121 (100%). ^{1}H-NMR: 1.70 (3H, s, =C$\underline{H}_3$), 2.33 (4H, s, =CC$\underline{H}_2$C$\underline{H}_2$CO$_2$), 3.25 (2H, d, J=7.5, Ar-C$\underline{H}_2$CH=), 3.54 (major) and 3.60 (minor) (overall 3H, s, CO_2CH_3), 3.80 (3H, s, OCH_3), 5.30 (1H, br t, J=7.5, Ar-CH$_2$C$\underline{H}$=), 6.10—7.13 (4H, m, arom-H). *Anal.* Calcd for $C_{15}H_{20}O_3$: C, 72.55; H, 8.12. Found: C, 72.42; H, 8.34.

Vb: Oil. IR: 1730, 1435, 1370, 1340. MS: 214 (M^+, 9%), 182 (52%), 151 (39%), 141 (21%), 122 (30%), 108 (100%). ^{1}H-NMR: 1.05 (3H, d, J=6.0, C$\underline{H}_3$CH(OMe)), 1.62 (3H, s, =C$\underline{H}_3$), 2.28 (4H, s, =CC$\underline{H}_2$C$\underline{H}_2$CO$_2$), 3.20 (3H, s, OCH_3), 3.58 (major) and 3.66 (minor) (overall 3H, s, CO_2CH_3), 5.11 (1H, br t, J=6.0, =CH). *Anal.* Calcd for $C_{12}H_{22}O_3$: D, 67.25; H, 10.35. Found: C, 67.11; H, 10.32.

Vc: Oil. MS: 208 (M^+, 28%), 169 (26%), 141 (28%), 134 (68%), 121 (45%), 119 (52%), 115 (39%), 109 (81%), 105 (49%), 99 (100%). ^{1}H-NMR: 1.60 (3H, s, =C$\underline{H}_3$), 2.10—2.25 (4H, br, =CHC$\underline{H}_2$C$\underline{H}_2$C=), 2.28 (4H, s, =CC$\underline{H}_2$C$\underline{H}_2$CO$_2$), 3.58 (3H, s, CO_2CH_3), 4.85—5.35 (5H, m, 2×=C$\underline{H}_2$ and =CH), 6.05—6.55 (1H, dd, J=17.0, 10.0, C$\underline{H}$=CH$_2$). *Anal.* Calcd for $C_{13}H_{20}O_2$: C, 74.96; H, 9.68. Found: C, 74.75; H, 9.79.

Ve: Oil. ^{1}H-NMR: 1.62, 1.70 (each 3H, s, 2×=C$\underline{H}_3$), 1.96 (3H, s, CH_3CO_2), 2.00—2.20 (4H, br, =CHC$\underline{H}_2$C$\underline{H}_2$C=), 2.28 (4H, s, =CC$\underline{H}_2$C$\underline{H}_2$CO$_2$), 3.58 (3H, s, CO_2CH_3), 4.48 (2H, d, J=8.0, =CHC$\underline{H}_2$OAc), 5.17 (1H, br, =CH), 5.28 (1H, br t, J=8.0, =C$\underline{H}$CH$_2$OAc). *Anal.* Calcd for $C_{15}H_{24}O_4$: C, 67.13; H, 9.02. Found: C, 66.87; H, 9.31.

Vf: Oil. IR: 1730, 1435, 1380, 1340. MS: 270 (M^+, 3%), 208 (25%), 195 (13%), 141 (74%), 121 (51%), 109 (100%). ^{1}H-NMR: 1.62, 1.65 (each 3H, s, 2×=C$\underline{H}_3$), 2.00—2.20 (4H, br, =CHC$\underline{H}_2$C$\underline{H}_2$C=), 2.28 (4H, s, =CC$\underline{H}_2$C$\underline{H}_2$CO$_2$), 3.26 (3H, s, OCH_3), 3.58 (3H, s, CO_2CH_3), 3.95 (2H, d, J=6.5, =CHC$\underline{H}$OMM), 4.44 (2H, s, OCH_2OMe), 5.10 (1H, br, =CH), 5.24 (1H, br t, J=6.5, =C$\underline{H}$CH$_2$OMM). *Anal.* Calcd for $C_{15}H_{26}O_4$: C, 66.63; H, 9.69. Found: C, 66.76; H, 9.84.

Vh: Oil. IR: 1725, 1460, 1400, 1340. MS: 352 (M^+, 100%), 305 (15%), 265 (25%), 225 (74%). ^{1}H-NMR: 1.76 (3H, s, =C$\underline{H}_3$), 2.03 (3H, s, Ar-CH$_3$), 2.27 (4H, s, =CC$\underline{H}_2$C$\underline{H}_2$CO$_2$), 3.20 (2H, d, J=7.5, Ar-C$\underline{H}_2$CH=), 3.50 (major) and 3.62 (minor) (overall 3H, s, CO_2CH_3), 3.70, 3.79 (each 6H, s, 4×OCH_3), 5.05 (1H, br t, J=7.5, Ar-CH$_2$C$\underline{H}$=). *Anal.* Calcd for $C_{19}H_{28}O_6$: C, 64.75; H, 8.01. Found: C, 64.62; H, 7.95.

Vi: Oil. IR: 1725, 1590, 1440, 1370, 1345. MS: 342 (M^+, 100%), 295 (26%), 215 (30%), 205 (39%), 169 (30%). ^{1}H-NMR: 1.82 (3H, s, =C$\underline{H}_3$), 2.29 (7H, s, Ar-CH$_3$ and =CC$\underline{H}_2$C$\underline{H}_2$CO$_2$), 3.47 (2H, d, J=6.5, Ar-C$\underline{H}_2$CH=), 3.48 (major) and 3.63 (minor) (overall 3H, s, CO_2CH_3), 3.78 (6H, s, 2×OCH_3), 5.13 (1H, br t, J=6.5, Ar-CH$_2$C$\underline{H}$=), 7.20—7.50, 7.75—8.07 (each 2H, m, arom-H). *Anal.* Calcd for $C_{21}H_{26}O_4$: C, 73.66; H, 7.66. Found: C, 73.58; H, 7.89.

Vj: Oil. IR: 1725, 1460, 1400, 1340. MS: 420 (M^+, 75%), 362 (6%), 351 (8%), 279 (25%), 265 (17%), 225 (100%). ^{1}H-NMR: 1.59, 1.75 (each 3H, s, 2×=C$\underline{H}_3$), 1.97—2.15 (4H, br, =CHC$\underline{H}_2$C$\underline{H}_2$C=), 2.07 (3H, s, Ar-CH$_3$), 2.24 (4H, s, =CC$\underline{H}_2$C$\underline{H}_2$CO$_2$), 3.22 (2H, d, J=6.5, Ar-C$\underline{H}_2$CH=), 3.46 (minor) and 3.56 (major) (overall 3H, s, CO_2CH_3), 3.70, 3.79 (each 6H, s, 4×OCH_3), 4.85—5.20 (2H, br, 2×=CH). *Anal.* Calcd for $C_{24}H_{36}O_6$: C, 68.54; H, 8.63. Found: C, 68.31: H, 8.84.

Vk: Oil. IR: 1725, 1590, 1440, 1370, 1345. MS: 410 (M^+, 100%), 396 (20%), 241 (65%), 215 (67%). ^{1}H-NMR: 1.58, 1.80 (each 3H, s, 2×=C$\underline{H}_3$), 1.94—2.15 (4H, br, =CHC$\underline{H}_2$C$\underline{H}_2$C=), 2.22 (4H, s, =CC$\underline{H}_2$C$\underline{H}_2$CO$_2$), 2.31 (3H, s, Ar-CH$_3$), 3.48 (2H, d, J=6.5, Ar-C$\underline{H}_2$CH=), 3.44 (minor) and 3.53 (major) (overall 3H, s, CO_2CH_3), 3.78, 3.80 (each 3H, s, 2×OCH_3), 4.95—5.30 (2H, br, 2×=CH), 7.20—7.50, 7.80—8.17 (each 2H, m, arom-H). *Anal.* Calcd for $C_{26}H_{34}O_4$: C, 76.06; H, 8.34. Found: C, 75.83; H, 8.46.

Preparation of the Ester (Vd) from the α-Mercapto Ester (VIIId), General Procedure for Desulfurization of the α-Mercapto Esters (VIII) with Raney-Nickel——A suspension of Raney-nickel (1.0 g) in acetone (10 ml) was refluxed for 15 min, then a solution of the α-mercapto ester (VIIId) (175 mg, 0.5 mmol) in acetone (2.0 ml) was added at room temperature. The mixture was stirred for 20 min at room temperature. The whole was filtered and the filtrate was concentrated to give a crude product (154 mg), which was purified by column chromatography on silica gel to afford the sulfur-free ester (Vd) (130 mg, 82%). The spectra properties of this compound were identical with those obtained by the desulfurizative [2,3]-sigmatropic rearrangement of IVd and the *E*/*Z*-ratio was determined as 87:13 by GLC and GC-MS analysis. Other α-mercapto esters (VIIIc, e—g) were desulfurized analogously to provide the esters (Vc, e—g) in 73—85% yield.

Synthesis of a Terpenoid Diol Component (1)——To a suspension of $LiAlH_4$ (130 mg, 3.4 mmol) in Et_2O (8.0 ml) was added dropwise a solution of the ester (Vd) (210 mg, 0.66 mmol) in Et_2O (2.0 ml) at 0 °C, and the mixture was stirred for 30 min at 0 °C, then for 3 h at room temperature. The reaction was quenched by careful addition of water (0.5 ml) to the mixture under cooling in an ice-water bath. The whole was diluted with Et_2O and the organic layer was washed with brine, dried, and concentrated to give a crude product (225 mg). Purification of the product by column chromatography on silica gel afforded the oily mono-alcohol (170 mg, 89%). ^{1}H-NMR: 1.60 (6H, s, 2×=C$\underline{H}_3$), 1.50—1.90 (2H, m, HOCH$_2$C$\underline{H}_2$CH$_2$C=), 1.94 (1H, s, OH), 1.87—2.23 (6H, br, CH$_2$C$\underline{H}_2$C=CHC$\underline{H}_2$C$\underline{H}_2$C=), 3.43 (2H, t, J=6.5, HOC$\underline{H}_2$CH$_2$), 3.90 (2H, d, J=7.0, =CHC$\underline{H}_2$OBn), 4.39 (2H, s, OCH_2Ph), 5.09 (1H, br, =CH), 5.30

(1H, br t, $J=7.0$, $=CHCH_2O$), 7.20 (5H, s, arom-H). To a chilled (-70 °C) blue solution of Li (100 mg, 14 mg atom) in liquid NH_3 (*ca.* 5 ml) was added dropwise a solution of the mono-alcohol (160 mg, 0.55 mmol) in THF (1.0 ml), and the mixture was stirred for 30 min at the same temperature. The reaction was quenched by the introduction of gaseous butadiene to discharge the blue color of the mixture followed by addition of MeOH (0.5 ml). The NH_3 was evaporated off, and the residue was extracted with CH_2Cl_2. The organic layer was washed with brine, dried, and concentrated to give a crude product (105 mg). Purification of the product by column chromatography on silica gel afforded the diol (**1**) (83 mg, 76%) as an oil. The diacetate of **1** was easily prepared by treatment of **1** with Ac_2O in pyridine at room temperature for 20 h. GLC and GC-MS analysis of the acetate revealed that the acetate contained a little of its (6*Z*)-stereoisomer (approximately 11%) as an impurity. The spectral properties of **1** and its acetate obtained follow: **1**: IR: 3570, 3400, 1660, 1440, 1380. MS: 198 (M^+, 1%), 180 (2%), 177 (3%), 159 (4%), 121 (9%), 111 (8%), 95 (100%). ^{1}H-NMR ($CDCl_3$) : 1.63, 1.66 (each 3H, s, $2\times=CCH_3$), 1.45—1.90 (2H, m, $HOCH_2CH_2CH_2C=$), 1.90—2.25 (6H, br, $CH_2CH_2C=CHCH_2CH_2C=$), 2.07 (2H, s, $2\times OH$), 3.60 (2H, t, $J=6.5$, $HOCH_2CH_2$), 4.12 (2H, d, $J=7.0$, $=CHCH_2OH$), 5.14 (1H, br, $=CH$), 5.39 (1H, br t, $J=7.0$, $=CHCH_2OH$).

1-Diacetate: IR: 1730, 1510, 1440, 1380, 1365. MS: 222 ($(M-60)^+$, 12%), 162 (28%), 147 (23%), 134 (11%), 121 (39%), 107 (18%), 95 (100%). ^{1}H-NMR: 1.60, 1.70 (each 3H, s, $2\times=CCH_3$), 1.55—1.85 (2H, m, $AcOCH_2CH_2CH_2C=$), 1.94 (6H, s, $2\times CH_3CO_2$), 1.90—2.23 (6H, br, $CH_2CH_2C=CHCH_2CH_2C=$), 3.93 (2H, t, $J=6.5$, $AcOCH_2CH_2$), 4.46 (2H, d, $J=7.0$, $=CHCH_2OAc$), 5.10 (1H, br, $=CH$), 5.28 (1H, br t, $J=7.0$, $=CHCH_2OAc$). *Anal.* Calcd for $C_{16}H_{26}O_4$: C, 68.05; H, 9.28. Found: C, 67.89; H, 9.25.

Synthesis of ω-Quinoid Acids (4, *n* = 1, 2) and (5, *n* = 1, 2)——The ω-quinoid acids (**4**, $n=1, 2$) and (**5**, $n=1, 2$) were obtained according to the reported method[2d] *via* alkaline hydrolysis of the esters (Vg—k) and deprotective oxidation of the hydroquinone nuclei by using AgO or CAN. A mixture of 3-(5-carbomethoxy-3-methyl-(2*E*)-penten-1-yl)-1,4-dimethoxy-2-methylnaphthalene (Vi) (225 mg, 0.6 mmol) and 5% aqueous NaOH (2.0 ml) in EtOH (6.0 ml) was stirred for 5 h at room temperature. After 5% HCl (3 ml) had been added to the reaction mixture, the whole was extracted with EtOAc. The organic layer was washed with brine, dried, and concentrated to give a crude acid (164 mg). Then 6 M nitric acid (0.1 ml) was added to a mixture of the above acid and AgO (200 mg, 1.6 mmol) in dioxane (4.0 ml) and water (0.2 ml) at 0 °C and the whole was stirred for 1 h at 0 °C. The reaction mixture was extracted with EtOAc and the organic layer was washed with brine, dried, and concentrated to give a crude crystalline product (132 mg). Recrystallization of the product from Et_2O–hexane afforded 3-(5-carboxy-3-methyl-(2*E*)-penten-1-yl)-2-methyl-1,4-naphthoquinone (**5**, $n=1$) (93 mg, 52%) as yellow needles, mp 130—132 °C. IR: 1705, 1660, 1630, 1600. ^{1}H-NMR ($CDCl_3$): 1.76 (3H, s, $=CCH_3$), 2.10 (3H, s, quinone-CH_3), 2.32 (4H, s, $HO_2CCH_2CH_2C=$), 3.28 (2H, d, $J=8.0$, quinone-$CH_2CH=$), 5.04 (1H, br t, $J=8.0$, quinone-$CH_2CH=$), 7.60—7.75, 7.95—8.15 (each 2H, m, arom-H), 10.20 (1H, br, CO_2H). *Anal.* Calcd for $C_{18}H_{18}O_4$: C, 72.46; H, 6.08. Found, C, 72.36; H, 6.12. The physicochemical properties of the quinone acid (**5**, $n=1$) thus obtained were consistent with those of the authentic compound.[2b] This quinone acid was also obtained in 49% yield by oxidation of the protected naphthohydroquinone acid with CAN in CH_2Cl_2–CH_3CN–H_2O (2 : 2 : 1) at 0 °C for 1 h.

Other quinone acids (**4**, $n=1, 2$) and (**5**, $n=2$) were synthesized analogously and identified by spectral comparison with authentic compounds.[2b,d]

4 ($n=1$): 48% yield *via* AgO oxidation from Vh; mp 60—64 °C (Et_2O–hexane). IR: 1700, 1660, 1650, 1610, 1460. ^{1}H-NMR ($CDCl_3$): 1.76 (3H, s, $=CCH_3$), 2.00 (3H, s, quinone-CH_3), 2.36 (4H, s, $HO_2CCH_2CH_2C=$), 3.16 (2H, d, $J=8.0$, quinone-$CH_2CH=$), 3.96 (6H, s, $2\times OCH_3$), 5.00 (1H, br t, $J=8.0$, quinone-$CH_2CH=$), 10.24 (1H, br s, CO_2H). *Anal.* Calcd for $C_{16}H_{20}O_6$: C, 62.32; H, 6.54. Found: C, 62.30; H, 6.43.

4 ($n=2$): 47% yield *via* CAN oxidation from Vj; mp 54—56 °C (Et_2O–hexane). IR: 1700, 1660, 1610, 1450. ^{1}H-NMR ($CDCl_3$): 1.60, 1.75 (each 3H, s, $2\times=CCH_3$), 1.82—2.20 (4H, br, $=CHCH_2CH_2C=$), 2.01 (3H, s, quinone-CH_3), 2.35 (4H, s, $HO_2CCH_2CH_2C=$), 3.20 (2H, d, $J=8.0$, quinone-$CH_2CH=$), 3.97, 3.99 (each 3H, s, $2\times OCH_3$), 5.00 (1H, br s, $=CH$), 5.27 (1H, br t, $J=8.0$, quinone-$CH_2CH=$), 10.81 (1H, br s, CO_2H). *Anal.* Calcd for $C_{21}H_{28}O_6$: C, 67.00; H, 7.50. Found: C, 66.93; H, 7.59.

5 ($n=2$): 55% yield *via* AgO oxidation from Vk; mp 94—96 °C (Et_2O–hexane). IR: 1700, 1660, 1630, 1600, 1440. ^{1}H-NMR ($CDCl_3$): 1.59, 1.89 (each 3H, s, $2\times=CCH_3$), 1.85—2.20 (4H, br, $=CHCH_2CH_2C=$), 2.21 (3H, s, quinone-CH_3), 2.35 (4H, s, $HO_2CCH_2CH_2C=$), 3.37 (2H, d, $J=8.0$, quinone-$CH_2CH=$), 4.51 (1H, br, $=CH$), 5.27 (1H, br t, $J=8.0$, quinone-$CH_2CH=$), 7.60—7.75, 7.95—8.15 (each 2H, m, arom-H), 10.75 (1H, br s, CO_2H). *Anal.* Calcd for $C_{23}H_{26}O_4$: C, 75.38; H, 7.15. Found: C, 75.23; H, 7.11.

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