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A New Synthesis of *o*-Quinonemethides and Their Inter- and Intramolecular Cyclization Reactions

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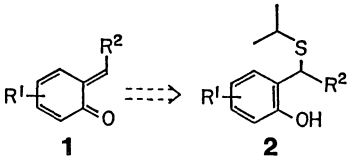
The reaction of *o*-[1-(alkylthio)alkyl]phenols with silver(I) oxide at room temperature generated *o*-quinonemethides in good yields along with silver alkanethiolate. This mechanism, based upon one-electron oxidation, is excluded in view of several experimental facts. The resulting *o*-quinonemethides reacted efficiently with ethyl vinyl ether to afford *cis*-chromans as the result of endo cycloaddition between (E)-*o*-quinonemethides and the ether. Similarly, *o*-[1-(alkylthio)allyl]phenols were converted to *cis*-chromans via the corresponding (*E*)-*o*-quinonemethides (6-allylidenecyclohexadienone). In the absence of dienophiles, some chromenes were obtained from the allylphenols.

The chemistry of quinonemethides has received much attention concerning their formation and behavior in organic chemistry[1] and their relation to their antitumor activity in biochemistry.[2] Since quinonemethides, especialy *o*-quinonemethide, act as heterodienes, precursors of chromenes or alkenylphenols, or electrophiles,[3] they are important intermediates in the synthetic field.

Although *p*-quinonemethides are prepared more easily by oxidation processes,[4] a variety of methods for *o*-quinonemethide generation have been reported; for example, pyrolysis of *o*-hydroxybenzyl compounds,[5] one-electron oxidation of *o*-substituted phenols,[6] desilylation of an *o*-hydroxybenzyl alcohol disilyl ether,[7] dehydrogenation of allylphenols with DDQ,[8] etc.[9] However, as most of these reactions have been carried out under forced conditions to generate a high-energy quinoid structure, the starting phenols are limited. Hence a general and efficient method for generation of *o*-quinonemethides under milder conditions has long been desired.

We recently reported that the treatment of a mixture of a phenol and an alkyl isopropyl sulfide with sulfuryl chloride followed by triethylamine at low temperature afforded *o*-[1-(isopropylthio)alkyl]-phenols (**2**) in good yields.[10a,b] We then expected that *o*-quinonemethides **1** could be generated from the



1 **2**

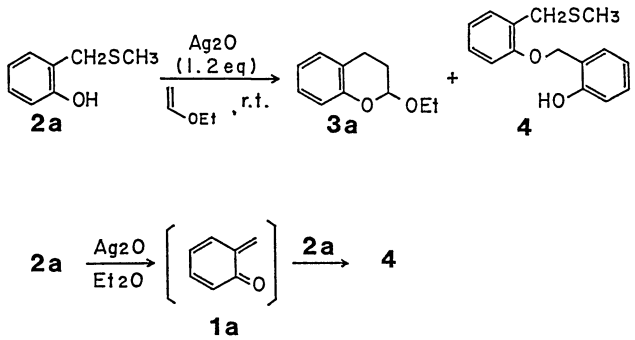
phenols by elimination of the alkylthio group on the benzyl position because of its small bond dissociation energy.[11] In this way we achieved an easy formation of *o*-quinonemethides by treatment of **2** with silver(I) oxide at room temperature. We describe herein, in full detail, the generation of *o*-quinonemethides and the application to the synthesis of oxygen heterocycles. We also discuss the reaction from a mechanistic viewpoint.[12]

Results and Discussion

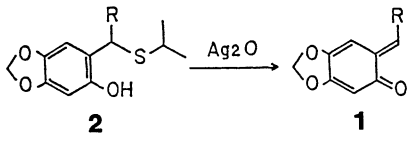
o-(Methylthiomethyl)phenol (**2a**) was selected as a prototype system to develop the basic methodology. Most of the *o*-alkylphenol species employed in this study were prepared from phenols and alkyl isopropyl sulfides or symmetrical dialkyl sulfides by using the improved procedure of the [2,3]sigmatropic rearrangement.[10] When allylic sulfides were used in the [2,3]sigmatropic rearrangement, *ortho*-allylated phenols were obtained in good yields, with the stereochemistry of the double bonds intact.

When **2a** was stirred with silver(I) oxide (1.2 mole equiv) in ethyl vinyl ether, (which was known to trap *o*-quinonemethides to give chromans in high efficiency[6a]) at room temperature for 18 h, 2-ethoxychroman (**3a**) and 2-[2-(methylthiomethyl)phenoxymethyl]phenol (**4**) were obtained in 32 and 30% yield, respectively, after column chromatography (Scheme 1). In the absence of ethyl vinyl ether, only the latter was obtained in 74% yield. Treatment of **2a** with mercury(II) oxide in ethyl vinyl ether also gave **3a** and **4** in similar yields. Other metal oxides such as manganese dioxide, lead dioxide, copper(II) oxide, and nickel dioxide failed to afford the chroman.

When 2-[α-(isopropylthio)-4-methoxybenzyl]-4,5-(methylenedioxy)phenol (**2b**) was treated with silver(I)



Scheme 1.



2 and **1**; b: R = p-C6H4OMe
c: R = Styryl

Scheme 2.

Table 1. Synthesis of **3a** by Use of Metal Salts

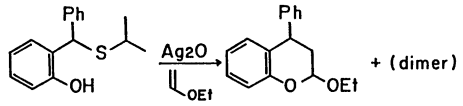
Reagent	(mole ratio)	Yield/%
Ag_2O	(1.2)	32
HgO	(1.2)	30
AgOAc	(1.2)	36
$Hg(OAc)_2$	(1.2)	17
$AgNO_3$	(1.2)	8
AgCl	(1.2)	—

oxide in diethyl ether at room temperature for 18 h in the absence of ethyl vinyl ether, an orange-colored crystalline material was isolated (36% yield). Its spectral and physical data agreed well with the reported data for (*E*)-6-(4-methoxybenzylidene)-3,4-methylenedioxy-2,4-cyclohexadien-1-one (**1b**).[13] In a similar way, another stable (*E*)-*o*-quinonemethide **1c**[13] was also isolated from 2-(1-isopropylthio-3-phenyl-2-propenyl)-4,5-(methylenedioxy)phenol (**2c**) in 50% yield (Scheme 2).

It is noteworthy that the treatment of **2a** with silver or mercury salts (silver acetate, mercury(II) acetate, and silver nitrate) in the presence of ethyl vinyl ether again afforded the same chroman **3a** (Table 1). Although certain kinds of phenols have been converted to the corresponding chromans by one-electron oxidation process with silver oxide,[6c,13,14] the present reaction seems different from the reported ones in the following features: (a) phenol **2a** was converted to chroman **3a** with silver(I) or mercury(II) oxide or their salts but not with other metallic oxidants including basic $K_3[Fe(CN)_6]$, whereas the one-electron oxidation of *o*-substituted phenols proceeds with various metallic oxidants but not with silver salts; (b) a half mole of silver oxide is enough to convert all the phenol **2a** to **3a** and **4** (vide infra), whereas one-electron oxidation process requires at least an equimolar amount of silver(I) oxide to the substrates.

The stoichiometry of the present reaction was investigated by using 2-[α-(isopropylthio)benzyl]phenol (**2d**) which gave mainly chroman **3d** and only a minor amount of the dimer upon treatment with silver oxide in ethyl vinyl ether. As Table 2 shows, the phenol **2d** was completely converted to the products with 0.6 mol of silver(I) oxide. If a phenoxyl radical intermediate resulted from one-electron transfer were involved in this reaction, the stoichiometric relationship should necessitate the β-elimination of a thiyl radical from the intermediate in order to generate *o*-quinonemethide. However diisopropyl disulfide, which would result from combination of the two thiyl radicals, was not detected by GC.

Table 2. Synthesis of **3d** under Various Conditions



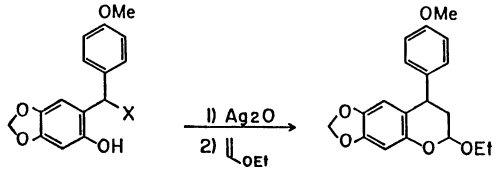
2d **3d**

Ag_2O (mole ratio)	Conversion %	Yield/% 3d	Dimer	Total
0.3	62	47	3	50
0.6	100	62	11	73
1.2	100	79	trace	79

The present reaction was next examined in the presence of galvinoxyl,[15] a radical scavenger which was reported to form a 1 : 1 adduct[16] with a phenolic compound in radical reactions. When **2b** was treated with silver(I) oxide and galvinoxyl in diethyl ether for 3 h and the filtered reaction mixture treated with ethyl vinyl ether, chroman **3b** was obtained in 50% yield. This is close to the yield of **3b** obtained in the absence of galvinoxyl (Table 3). On the contrary, the known reaction of *o*-benzylphenol **5** with silver(I) oxide to produce **1d**[13] was suppressed to a considerable extent by the galvinoxyl added in the reaction (Entries 3, 4). These results suggest that the present reaction does not proceed by a one-electron oxidation.

The alkylthio moiety, which is eliminated from *o*-[1-(alkylthio)alkyl]phenol upon the conversion of the phenol to the *o*-quinonemethide, was traced by using 2-[1-(citronellylthio)-3,7-dimethyl-6-octenyl]-4-methylphenol (**2e**) as a starting phenol (Scheme 3). When **2e** (1.0 mmol) was treated with silver(I) oxide (0.5 equiv) in ethyl vinyl ether, the resulting mixture was filtered and concentrated and then diluted with

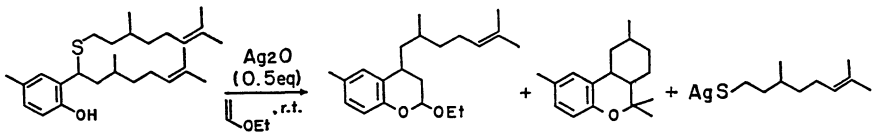
Table 3. Synthesis of **3b** in the Presence of a Free-Radical Scavenger



2b; X = ^{i}PrS
5; X = H
3b

Entry	Substrate	Ag_2O (mole ratio)	Scavenger[a] (mole ratio)	Yield/%[b]
1	**2b**	0.5	1.1	50
2	**2b**	0.5	—	49
3	**5**	3.0	1.1	38
4	**5**	3.0	—	55

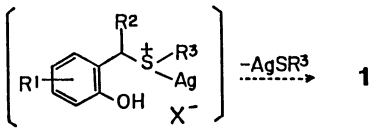
a) Galvinoxyl was used. b) Determined by GC.



2e 3e 6e 7

Scheme 3.

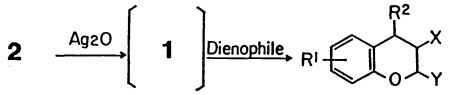
acetone to precipitate olive-drab-colored crystalline material, which was collected and treated with hydrochloric acid in ethyl acetate to give silver chloride (70%) and 3,7-dimethyl-6-octene-1-thiol (70%). 2-Ethoxychroman derivative (**3e**) and cycloadduct (**6e**) were isolated from the methanol solution by column chromatography in 57 and 10% yields, respectively. These results indicate that silver oxide is not reduced to metallic silver but converted to silver 3,7-dimethyl-6-octene-1-thiolate (**7**) during the reaction. It therefore seems most likely that the possible intermediate in this reaction is not a phenoxyl radical species, but a trivalent sulfur species such as **A**, by which the effectiveness of various silver and mercury compounds for the present reaction can be accounted for.



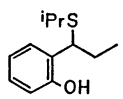
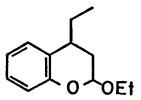
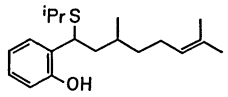
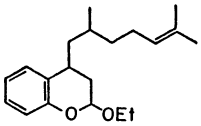
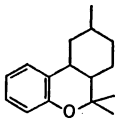
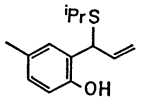
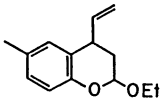
A

Next, we applied the present method to other *o*-substituted phenols (Table 4). All the phenols provided higher yields of chromans compared to that of **3a**. The steric hindrance of the substituents on the benzyl positions would interfere with the 1,4-addition between *o*-quinonemethides and the starting phenols. Moreover, in spite of the mild and neutral reaction conditions, cycloadduct (**6g**) was obtained by the intramolecular Diels-Alder reaction of *o*-quinonemethide with a simple olefin, with which the intermoleculer reaction of *o*-quinonemethide does not occur as readily.[17] Hence the present methodology is

Table 4. Chroman Synthesis from **2**



3,6

Entry	2	Dienophile[a]	Chroman (yield/%)
1	**2b**	CH_2=CHOEt	**3b**(60)
2	**2d**	CH_2=CHOEt	**3d**[b](79)
3	**2d**	CH_2=CHOEt	**3d**[b](50)[c]
4	**2d**	CH_2=CHOEt	**3d**[b](58)[d]
5	**2d**	CH_2=CHOEt	**3d**[b](54)[e]
6		CH_2=CHOEt	
	2f		**3f**[f](64)
7		CH_2=CHOEt	 
	2g		**3g**[f](61) **6g**(19)
8	**2g**	—[g]	**6g**(37)
9		CH_2=CHOEt	
	2h		**3h**[f](73)

a) Used as a solvent. b) trans : cis=3 : 97. c) A 3 : 7 (volume) mixture of CH_2=CHOEt and hexane was used as solvent. d) A 3 : 7 (volume) mixture of CH_2=CHOEt and benzene was used as solvent. e) A 3 : 7 (volume) mixture of CH_2=CHOEt and acetonitrile was used as solvent. f) trans : cis=1 : 99. g) Diethyl ether was used as solvent.

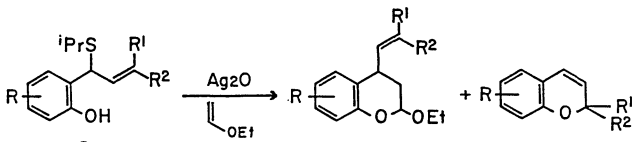
convenient and highly efficient for the chroman synthesis from various types of *o*-substituted phenols which can be prepared via [2,3]sigmatropic rearrangement.

The stereochemistry of the cycloadducts (**3b,d,f—h**) has been established by 270 MHz ^{1}H NMR analysis on the basis of the coupling constants of H-2 and H-4 protons.[5a] The thermal method gives a mixture of *cis*- and *trans*-4-substituted 2-alkoxychromans.[5a] However, our present method produced *cis*-chromans predominantly. These *cis*-chromans would be derived from endo attack of a vinyl ether on the (*E*)-*o*-quinonemethide through a concerted mechanism.[5a,3,18] A concerted cycloaddition process rather than an ionic process is also supported by the similar reaction rates in polar and nonpolar solvents (Entries 3—5).[19] The higher stereoselectivities compared with those observed for thermally-generated *o*-quinonemethides may be due to the mild reaction conditions.[3]

The easy conversion of allylphenol **2h** into (*E*)-6-allylidene-2,4-cyclohexadien-1-one (**1h**) is shown by trapping **1h** with ethyl vinyl ether in Entry 9. This is the first observation of intermolecular hetero-Diels-Alder reaction of 6-allylidenecyclohexadienones with dienophiles.

Finally, the behaviors of other allylphenols **2c,i—k** in this reaction were investigated. In the presence of dienophile, intermolecular cycloadducts **3c,i—k** were prepared with the intramolecular formation of chromenes **8c,i—k**, respectively (Table 5). These chromenes might have been obtained through the isomerization of (*E*)-6-allylidenecyclohexadienone or carbenium intermediates. However, the carbenium mechanism suffers from the disadvantage that the present reaction also proceeded on the basis of a concerted mechanism because of the predominant formation of *cis*-chromans **3c,i—k**. Without a dienophile, the treatment of **2j** and **k** with silver(I) oxide (1.2 mole equiv) in cyclohexane afforded the increased yields of chromene **8j** and **k** in 51 and 67%, respectively (cf. Entries 3 and 4). These results indicate that this methodology is also applicable to the synthesis of 2-substituted chromenes.

Table 5. Benzopyran Synthesis from Allylphenol



2 **3** **8**

2, **3**, and **8**; **c**: R=4,5-methylenedioxy, R^1=H, R^2=Ph
i: R=4-Me, R^1=H, R^2=Me
j: R=4-Me, R^1=R^2=Me
k: R=4-Me, R^1=H, R^2=Ph

Entry	Allylphenol	Dienophile[a]	Benzopyran (yield/%)	
1	**2c**	CH_2=CHOEt[b]	**3c**(42)	**8c**(44)
2	**2i**	CH_2=CHOEt	**3i**(47)	**8i**(10)
3	**2j**	CH_2=CHOEt	**3j**(57)	**8j**(14)
4	**2k**	CH_2=CHOEt	**3k**(49)	**8k**(20)

a) Used as a solvent. b) A 1:1 (volume) mixture of CH_2=CHOEt and acetone was used as a solvent.

In conclusion, we have found a new synthetic methodology for preparing *o*-quinonemethides from available *o*-[1-(alkylthio)alkyl]phenols, which is more effective and general than the methods previously described.[5a,6a,18] The resulting (*E*)-*o*-quinonemethides can be converted predominantly into *cis*-4-substituted 2-alkoxychromans in the manner of endo [4+2]-cycloaddition with vinyl ethers in high efficiency. Moreover, chromenes are obtained via the intermolecular reaction of *o*-[1-(alkylthio)allyl]phenols in the absence of a dienophile.

Experimental

Melting points were determined on a Shimadzu MM-2 hot-stage apparatus and are uncorrected. IR spectra were measured on a Hitachi 260-10 spectrometer. ^{1}H NMR spectra were obtained with a JEOL JNM-C-60M, a JEOL FT-90-Q or a JEOL JNM-FX270 with TMS as an internal standard. ^{13}C NMR spectra were measured on a JEOL FT-90-Q or a JEOL JNM-FX270. Mass spectra were recorded with a HITACHI M-80 (double-focusing GC mass spectrometer). Column chromatography was normally effected with Wakogel C-200 (Wako pure Chemical Industries).

General Procedure for the Preparation of *o*-[1-(Alkylthio)-alkyl]phenol 2. Sulfuryl chloride (1.62 g, 12 mmol) was added dropwise to a mixture of sulfide (10 mmol), phenol (30 mmol) and pyridine (0.95 g, 12 mmol) in dry dichloromethane (50 ml) at −40 °C for 5 min under nitrogen. After the reaction mixture had been stirred for 10 min at −40 °C, the mixture was poured into a solution of triethylamine (12 g, 0.12 mol) in cyclohexane (50 ml) under vigorous stirring. After 1 h of stirring, 100 ml of ether were added to the slurry, the suspension filtered, and the filter cake thoroughly washed with ether. The filtrate and washings were poured into 200 ml of water. The organic layer was washed successively with water and brine, dried ($MgSO_4$), and then evaporated. The residue was chromatographed on a column with 4% EtOAc-hexane containing 1% triethylamine to afford **2**, which was immediately used for the subsequent reaction because of its lability. The spectral data of the compounds are as follows.

2-[α-(Isopropylthio)benzyl]phenol (2d): ^{1}H NMR (90 MHz) (CCl_4) δ=1.22 (6H, d, $C(CH_3)_2$ *J*=6.4 Hz), 2.67 (1H, septet, $SCHMe_2$, *J*=6.4 Hz), 5.23 (1H, s, ArCH), and 6.47—7.43 (10H, m, ArH and OH); IR (neat) ν 3450, 2950, 750, and 700 cm^{-1}.

2-[1-(Citronellylthio)-3,7-dimethyl-6-octenyl]-4-methylphenol (2e): ^{1}H NMR (60 MHz) (CCl_4) δ=0.85 (6H, bd, Me-3′ and 3″ *J*=5 Hz), 1.58 (6H, s, Me-7′ and 7″), 1.67 (6H, s, H-8′ and 8″), 2.24 (3H, s, $ArCH_3$), 1.02—2.30 (16H, m, H-2′, 5′, and 1″—5″), 3.93 (1H, t, H-1′, *J*=7 Hz), 4.97 (2H, bt, H-6′ and 6″, *J*=8 Hz), 6.75 (1H, d, H-6, *J*=8 Hz), 6.80 (1H, s, H-3), 6.96 (1H, d, H-5′, *J*=8 Hz), and 7.01 (1H, s, OH); IR(neat) ν 3290, 2930, and 810 cm^{-1}.

2-[1-(Isopropylthio)propyl]phenol (2f): ^{1}H NMR (60 MHz) (CCl_4) δ=0.87 (3H, t, H-3′, *J*=7 Hz), 1.12, 1.20 (6H,

each d, $C(CH_3)2$, J=7 Hz), 1.83 (2H, quintet, H-2′, J=7 Hz), 2.55 (1H, septet, $SCHMe_2$, J=7 Hz), 3.77 (1H, t, H-1′, J=7 Hz), 6.43—7.10 (4H, m, ArH), and 7.19 (1H, s, OH); IR(neat) ν 3250, 2900, and 750 cm^{-1}.

2-(3,7-Dimethyl-1-isopropylthio-6-octenyl)phenol (2g): ^1H NMR (CCl_4) δ=0.91 (3H, bt, Me-3′, J=5 Hz), 1.15, 1.23 (6H, each d, $C(CH_3)_2$, J=7 Hz), 1.60 (3H, s, Me-7′), 1.66 (3H, s, H-8′), 1.07—2.11 (7H, m, H-2′—H-5′), 2.60 (1H, septet, $SCHMe_2$, J=7 Hz), 4.01 (1H, t, H-1′, J=7 Hz), 4.90 (1H, t, H-6′, J=8 Hz), 6.55—7.03 (4H, m, ArH), and 7.21 (1H, s, OH); IR(neat) ν 3250, 2900, and 750 cm^{-1}.

2-(1-Isopropylthio-2-propenyl)-4-methylphenol (2h): ^1H NMR (90 MHz) ($CDCl_3$) δ=1.25, 1.27 (6H, each d, $C(CH_3)_2$, J=7.0 Hz), 2.25 (3H, s, Me-4), 2.78 (1H, septet, $SCHMe_2$, J=7.0 Hz), 4.67 (1H, dd, H-1, J=1.2 and 7.6 Hz), 5.17 (1H, dd, H-3′, J=1.2 and 17.0 Hz), 5.18 (1H, dd, H-3′, J=1.2 and 10.0 Hz), 6.10 (1H, ddd, H-2′, J=7.6, 10.0, and 17.0 Hz), 6.32 (1H, s, OH), 6.77 (1H, d, H-6, J=8.0 Hz), 6.91 (1H, s, H-3), and 6.98 (1H, d, H-5, J=8.0 Hz); IR(neat) ν 3300, 2900, 910, and 810 cm^{-1}.

2-(1-Isopropylthio-2-butenyl)-4-methylphenol (2i): ^1H NMR (90 MHz) ($CDCl_3$) δ=1.22, 1.26 (6H, each d, $C(CH_3)_2$, J=7.0 Hz), 1.71 (3H, d, H-4′, J=5.0 Hz), 2.25 (3H, s, Me-4), 2.73 (1H, septet, $SCHMe_2$), 4.61 (1H, d, H-1′, J=6.0 Hz), 5.5—5.9 (2H, m, H-2′ and 3′), 6.78 (1H, d, H-6, J=8.1 Hz), 6.89 (1H, s, H-3), 6.98 (1H, d, H-5, J=8.1 Hz), and 7.0 (1H, s, OH); IR(neat) ν 3300, 2900, 960, and 810 cm^{-1}.

2-(1-Isopropylthio-3-methyl-2-butenyl)-4-methylphenol (2j): ^1H NMR (90 MHz) ($CDCl_3$) δ=1.21, 1.27 (6H, each d, $C(CH_3)_2$, J=7.0 Hz), 1.74 (3H, s, Me-3′), 1.78 (3H, s, H-4′), 2.25 (3H, s, Me-4), 2.69 (1H, septet, $SCHMe_2$, J=7.0 Hz), 4.87 (1H, d, H-1′, J=10.0 Hz), 5.50 (1H, d, H-2′, J=10.0 Hz), 6.79 (1H, d, H-6, J=8.1 Hz), 6.90 (1H, s, H-3), 6.98 (1H, d, H-5, J=8.1 Hz), and 7.31 (1H, s, OH); IR(neat) ν 3300, 2900, and 810 cm^{-1}.

2-(1-Isopropylthio-3-phenyl-2-propenyl)-4-methylphenol (2k): ^1H NMR (60 MHz) (CCl_4) δ=1.22 (6H, d, $C(CH_3)_2$, J=7 Hz), 2.19 (3H, s, Me-4), 2.58 (1H, septet, $SCHMe_2$, J=7 Hz), 4.80 (1H, dd, H-1′, J=2 and 5 Hz), 6.29 (2H, m, H-2′ and 3′), 6.70 (1H, d, H-6, J=8 Hz), 6.80 (1H, s, OH), 6.90 (1H, s, H-3), 6.98 (1H, d, H-5, J=8 Hz), and 7.1—7.4 (5H, m, ArH); IR(neat) ν 3250, 2950, 960, 810, 750, and 690 cm^{-1}.

2-[α-(Isopropylthio)-4-methoxybenzyl]-4,5-(methylenedioxy)phenol (2b). 2-Propanethiol (0.5 ml) was added dropwise to a solution of **1b**[13] (0.23 g, 0.90 mmol) in triethylamine (2 ml) at room temperature. After 10 h the reaction mixture was concentrated. The crude product was chromatographed on column with 30% EtOAc-hexane to afford **2b** (0.25 g, 83%): ^1H NMR (90 MHz) ($CDCl_3$) δ=1.26 (6H, d, $C(CH_3)_2$, J=6.9 Hz), 2.77 (1H, septet, $SCHMe_2$, J=6.9 Hz), 3.78 (3H, s, OCH_3), 5.28 (1H, s, ArCH), 5.87 (2H, s, OCH_2O), 6.49 (2H, s, H-3 and 6), 6.85 (2H, d, H-3′ and 5′, J=8.3 Hz), 7.27 (1H, s, OH), and 7.32 (2H, d, H-2′ and 6′, J=8.3 Hz); IR(neat) ν 3300, 2900, 1040, and 840 cm^{-1}. Found: C, 69.39; H, 5.46%. Calcd for $C_{22}H_{20}O_4S$: C, 69.47; H, 5.26%.

2-(1-Isopropylthio-3-phenyl-2-propenyl)-4,5-(methylenedioxy)phenol (2c). 6-Cinnamylidene-3,4-methylenedioxy-2,4-cyclohexadien-1-one **1c**[13] (0.32 g, 1.32 mmol) was converted to **2c** in a similar way in 82%: ^1H NMR (90 MHz) ($CDCl_3$) δ=1.29, 1.30 (6H, each d, $C(CH_3)_2$, J=7.0 Hz), 2.85 (1H, septet, $SCHMe_2$, J=7.0 Hz), 4.81 (1H, bd, H-1′, J=5.4 Hz), 5.89 (2H, s, OCH_2O), 6.4—6.5 (3H, m, H-6, 2′, and 3′), 6.66 (1H, s, H-6), and 7.2—7.5 (6H, m, ArH and OH); IR(neat) ν 3300, 2950, 960, and 840 cm^{-1}. Found: C, 69.34; H, 5.92%. Calcd for $C_{19}H_{20}O_3S$: C, 69.51; H, 6.10%.

Treatment of 2a with Ag_2O in Ethyl Vinyl Ether. Ag_2O (1.16 g, 5.0 mmol) was added to a solution of **2a** (0.62 g, 4.0 mmol) in ethyl vinyl ether (60 ml) at room temperature. After 18 h the reaction mixture was filtered, and evaporated. The residue was chromatographed on a column with 20% CH_2Cl_2-hexane to afford 2-ethoxychroman (**3a**) (0.23 g, 32%): ^1H NMR (270 MHz) ($CDCl_3$) δ=1.19 (3H, t, CH_3, J=7.3 Hz), 1.9—2.1 (2H, m, H-3[a] and 3[e]), 2.64 (1H, ddd, H-4[a], J=3.0, 6.2, and 11.6 Hz), 2.97 (1H, ddd, H-4[e], J=3.0, 3.3, and 6.2 Hz), 3.64 (1H, dq, $OCHMe_2$, J=9.9 and 7.3 Hz), 3.89 (1H, dq, $OCHMe_2$, J=9.9 and 7.3 Hz), 5.25 (1H, dd, H-2, J=3.0 and 3.0 Hz), 6.8—6.9 (2H, m, H-6 and 8), and 7.0—7.2 (2H, m, H-5 and 7); IR(neat) ν 2900, 1220, 1050, and 850 cm^{-1}.

Using 50% CH_2Cl_2-hexane as the eluting solvent 2-[2-(methylthiomethyl)phenoxymethyl]phenol (**4**) was obtained (0.39 g, 30%): ^1H NMR (90 MHz) ($CDCl_3$) δ=1.99 (3H, s, SCH_3), 3.68 (2H, s, SCH_2Ar), 5.13 (2H, s, OCH_2Ar), and 6.8—7.3 (9H, m, ArH and OH); IR(neat) ν 3400, 2920, 1240, 1110, 1010, and 760 cm^{-1}. Found: m/z 260.0862. Calcd for $C_{15}H_{16}O_2S$: M, 260.0869.

Treatment of 2e with Ag_2O in Ethyl Vinyl Ether. Ag_2O (0.116 g, 0.5 mmol) was added to a solution of **2e** (0.416 g, 0.5 mmol) in ethyl vinyl ether (20 ml) at room temperature. After 18 h the reaction mixture was filtered and the solvent removed in vacuo. The residual gum (0.55 g) was dissolved in acetone (50 ml) to precipitate olive-drab crystals. The crystals (0.21 g) were dissolved in 10 ml of EtOAc and concd HCl was added to separate the AgCl (0.1 g, 70% based on Ag_2O). The EtOAc filtrate from the separation of AgCl was evaporated and the residue was chromatographed on a column with 10% CH_2Cl_2-hexane to afford 3,7-dimethyl-6-octene-1-thiol (0.12 g, 70%): ^1H NMR (60 MHz) ($CDCl_3$) δ= 0.88 (3H, d, CH_3-3, J=6 Hz), 1.60 (3H, s, CH_3-7), 1.68 (3H, s, H-8), 1.2—1.7 (6H, m, H-2—4 and SH), 1.97 (2H, dt, H-5, J=7 and 7 Hz), 2.70 (2H, bt, H-1, J=7 Hz), and 5.08 (1H, bt, H-6, J=7 Hz); IR(neat) ν 2950, 1450, and 1380 cml^{-1}. Found: m/z 172.1278. Calcd for $C_{10}H_{20}S$: M, 172.1284.

The acetone filtrate was evaporated and the residual oil chromatographed on a column with 10% CH_2Cl_2-hexane to give 2,6,6,9-tetramethyl-6a,7,8,9,10,10a-hexahydro-6*H*-dibenzo[*b*,*d*]pyran (**6e**) (0.24 g, 10%): ^1H NMR (270 MHz) ($CDCl_3$) δ=0.89 (1H, q, H-10[a], J=13.2 Hz), 0.99 (3H, d, Me-9, J=6.6 Hz), 1.05 (1H, m, H-7 or 8), 1.12 (3H, s, Me-6), 0.95—1.14 (1H, m, H-7 or 8), 1.37 (3H, s, Me-6), 1.30—1.40 (1H, m, H-6a or 9), 1.57 (1H, m, H-6a or 9), 1.83 (2H, m, H-7′ and 8′), 2.26 (3H, s, Me-2), 2.39 (2H, m, H-10[e] and 10[a]), 6.66 (1H, d, H-4, J=8.2 Hz), 6.89 (1H, d, H-3, J=8.2 Hz), 7.03 (1H, s, H-1); ^{13}C NMR (270 MHz) ($CDCl_3$) δ=20.22, 20.92, 22.82, 27.80, 28.23, 32.69, 35.01, 35.77, 39.77, 47.08, 77.38, 116.98, 125.26, 126.54, 128.01, 128.68, 151.07; IR (neat) ν 2900, 1490, 1250, 1150, and 820 cm^{-1}. Found: m/z 244.1828. Calcd for $C_{17}H_{24}O$: M, 244.1825.

A later fraction for the chromatograph gave 2-ethoxy-4-(2,6-dimethyl-5-heptenyl)-6-methylchroman (**3e**) (0.18 g, 57%): ^1H NMR (90 MHz) ($CDCl_3$) δ=0.88 (3H, m, Me-2′), 1.22 (3H, t, $OCCH_3$, J=7.11 Hz), 1.59 (3H, s, Me-6′), 1.68 (3H, s, H-7′), 2.01 (1H, m, H-3[e]), 1.1—2.1 (8H, m, H-3[a], 1′, 2′, 3′, and 4′), 2.26 (3H, s, Me-6), 2.96 (1H, m, H-4), 3.58 (1H, dq, $OCHMe_2$, J=9.5 and 7.1 Hz), 3.98 (1H, dq, $OCHMe_2$, J=9.5 and 7.1 Hz), 5.11 (1H, m, H-5′), 5.12 (1H, dd, H-2,

J=3.0 and 5.9 Hz), 6.72 (1H, d, H-8, J=7.1 Hz), 6.90 (1H, d, H-7, J=7.1 Hz), and 6.94 (1H, s, H-5); IR(neat) ν 2900, 1500, 1220, 1120, 1020, and 820 cm^{-1}. Found: m/z 316.2401. Calcd for $C_{21}H_{32}O_2$: M, 316.2401.

General Procedure for the Preparation of 2-Alkoxychroman. Ag_2O (0.39 g, 18 mmol) was added to a solution of 2-[1-(isopropylthio)alkyl]phenol (15 mmol) in ethyl vinyl ether (15 ml) at room temperature. After 18 h the reaction mixture was filtered, and evaporated. The residual oil was chromatographed on a column to give 2-alkoxychroman.

***cis*-2-Ethoxy-4-phenylchroman (*cis*-3d):** mp 61.2—62.6 °C; ^{1}H NMR (270 MHz) ($CDCl_3$) δ=1.26 (3H, t, $OCCH_3$, J=7.3 Hz), 2.19 (1H, ddd, H-3^a, J=8.6, 11.2, and 13.2 Hz), 2.4 (1H, ddd, H-3^e, J=2.3, 5.9, and 13.2 Hz), 3.68 (1H, dq, $OCHMe_2$, J=9.6 and 7.3 Hz), 4.06 (1H, dq, $OCHMe_2$, J=9.6 and 7.3 Hz), 4.21 (1H, dd, H-4, J=5.9 and 11.2 Hz), 5.26 (1H, dd, H-2, J=2.3 and 8.6 Hz), 6.7—7.3 (9H, m, ArH); IR(KBr) ν 2900, 1230, 1050, 750, and 700 cm^{-1}. Found: m/z 254.1300. Calcd for $C_{17}H_{18}O_2$: M, 254.1306.

***trans*-2-Ethoxy-4-phenylchroman (*trans*-3d):** ^{1}H NMR (270 MHz) ($CDCl_3$) δ=1.21 (3H, t, $OCCH_3$, J=6.9 Hz), 2.14 (1H, ddd, H-3^a, J=2.6, 11.9, and 13.3 Hz), 2.26 (1H, ddd, H-3^e, J=2.6, 5.9, and 13.3 Hz), 3.68 (1H, dq, $OCHMe_2$, J=9.9 and 6.9 Hz), 3.91 (1H, dq, $OCHMe_2$, J=9.9 and 6.9 Hz), 4.30 (1H, dd, H-4, J=5.9 and 11.9 Hz), 5.29 (1H, dd, H-2, J=2.6 and 2.6 Hz), 6.7—7.3 (9H, m, ArH).

***cis*-2-Ethoxy-4-ethylchroman (3f):** ^{1}H NMR (270 MHz) ($CDCl_3$) δ=0.98 (3H, t, H-2′, J=7.6 Hz), 1.25 (3H, t, $OCCH_3$, J=6.9 Hz), 1.71 (1H, ddq, H-1′, J=9.3, 14.1, and 7.6 Hz), 1.83 (1H, ddd, H-3^a, J=6.6, 8.2, and 13.5 Hz), 1.95 (1H, ddq, H-1″, J=9.3, 14.1, and 7.6 Hz), 2.15 (1H, ddd, H-3^e, J=2.5, 6.5, and 13.5 Hz), 2.8 (1H, m, H-4), 3.62 (1H, dq, OCHMe, J=9.6 and 6.9 Hz), 3.96 (1H, dq, OCHMe, J=9.6 and 6.9 Hz), 5.15 (1H, dd, H-2, J=2.5 and 6.6 Hz), 6.84 (1H, dd, H-8, J=8.2 and 1.3 Hz), 6.89 (1H, ddd, H-6, J=1.3, 7.3, and 7.3 Hz), 7.11 (1H, ddd, H-7, J=1.0, 7.3, and 8.2 Hz), 7.14 (1H, dd, H-5, J=1.0 and 7.3 Hz); IR(neat) ν 2900, 1480, 1220, 1050, and 750 cm^{-1}. Found: m/z 206.1310. Calcd for $C_{13}H_{18}O_2$: M, 206.1305.

***cis*-2-Ethoxy-4-(2,6-dimethyl-5-heptenyl)chroman (3g):** ^{1}H NMR (270 MHz) ($CDCl_3$) δ=0.93, 0.95 (3H, each t, Me-2′, J=6.1 Hz), 1.22 (3H, t, $OCCH_3$, J=7.3 Hz), 1.59 (3H, bs, Me-6′), 1.66 (3H, bs, H-7′), 2.13 (1H, ddd, H-3^e, J=2.9, and 13.1 Hz), 1.1—2.1 (8H, m, H-3^a, 1′, 2′, 3′, and 4′), 2.92 (1H, m, H-4), 3.58 (1H, dq, OCHMe, J=9.6 and 7.3 Hz), 5.10 (1H, bt, H-5′, J=6.8 Hz), 5.16 (1H, dd, H-2, J=2.9 and 6.0 Hz), 6.8—6.9 (2H, m, H-6 and 8), 7.1—7.2 (2H, m, H-5 and 7); IR(neat) ν 2900, 1490, 1250, 1140, 950, and 740 cm^{-1}. Found: m/z 302.2248. Calcd for $C_{20}H_{30}O_2$; M, 302.2243.

***cis*-2-Ethoxy-6-methyl-4-vinylchroman (3h):** ^{1}H NMR (270 MHz) ($CDCl_3$) δ= 1.23 (3H, t, $OCCH_3$, J=6.92 Hz), 1.92 (1H, ddd, H-3^a, J=6.6, 7.7, and 13.5 Hz), 2.19 (1H, ddd, H-3^e, J=2.6, 6.6, and 13.5 Hz), 2.25 (3H, s, Me-6), 3.6 (1H, m, H-4), 3.62 (1H, dq, OCHMe, J=6.9 and 9.6 Hz), 3.96 (1H, dq, OCHMe, J=6.9 and 9.6Hz), 5.1—5.2 (3H, m, H-2 and 2′), 5.9—6.0 (1H, m, H-1′), 6.74 (1H, d, H-8, J=7.9 Hz), 6.90 (1H, s, H-5), and 6.92 (1H, d, H-7, J=7.9 Hz); IR(neat) ν 2900, 1490, 1210, 1010, 910, and 810 cm^{-1}. Found: m/z 218.1314. Calcd for $C_{14}H_{18}O_2$: M, 218.1306.

***cis*-2-Ethoxy-6-methyl-4-(1-propenyl)chroman (3i):** ^{1}H NMR (270 MHz) ($CDCl_3$) δ=1.25 (3H, t, $OCCH_3$, J=7.0 Hz), 1.74 (3H, d, H-3′, J=5.6 Hz), 1.92 (1H, ddd, H-3^a, J=7.3, 8.6, and 13.2 Hz), 2.16 (1H, ddd, H-3^e, J=2.6, 6.4, and 13.2 Hz), 2.24 (1H, s, H-6), 3.44 (1H, ddd, H-4, J=8.6, 8.6, and 6.3 Hz), 3.64 (1H, dq, OCHMe, J=9.6 and 7.0 Hz), 3.99 (1H, dq, OCHMe, J=9.6 and 7.0 Hz), 5.15 (1H, dd, H-2, J=2.6 and 7.3 Hz), 5.68 (1H, dq, H-2′m J=15.4 and 5.6 Hz), 5.57 (1H, dd, H-1′, J=8.6 and 15.2 Hz), 6.73 (1H, d, H-8, J=6.7 Hz), 6.89 (1H, s, H-5), and 6.92 (1H, d, H-7, J=6.7 Hz); IR(neat) ν 2900, 1490, 1210, 1020, 890, and 820 cm^{-1}. Found: m/z 232.1466. Calcd for $C_{15}H_{20}O_2$: M, 232.1462.

***cis*-2-Ethoxy-6-methyl-4-(2-methyl-1-propenyl)chroman (3j):** ^{1}H NMR (270 MHz) ($CDCl_3$) δ=1.24 (3H, t, $OCCH_3$, J=6.9 Hz), 1.75 (3H, d, Me-2′, J=1.3 Hz), 1.78 (3H, d, H-3′, J=1.0 Hz), 1.79 (1H, ddd, H-3^a, J=8.0, 9.2, and 13.3 Hz), 2.14 (1H, ddd, H-3^e, J=2.4, 6.4, and 13.3 Hz), 2.32 (3H, s, Me-6), 3.63 (1H, dq, OCHMe, J=9.6 and 6.9 Hz), 3.85 (1H, ddd, H-4, J=6.4, 9.2, and 9.2 Hz), 4.02 (1H, dq, OCHMe, J=9.6 and 6.9 Hz), 5.18 (1H, dd, H-2, J=2.4 and 8.0 Hz), 5.22 (1H, bd, H-1′, J=9.2 Hz), 6.72 (1H, d, H-8, J=7.0 Hz), 6.82 (1H, s, H-5), and 6.94 (1H, d, H-7, J=7.0 Hz); IR(neat) ν 2900, 1490, 1210, 1150, 890, and 840 cm^{-1}. Found: m/z 246.1611. Calcd for $C_{16}H_{22}O_2$: M, 246.1617.

***cis*-2-Ethoxy-6-methyl-4-[(*E*)-styryl]chroman (3k):** mp 119.0—120.5 °C; ^{1}H NMR (270 MHz) ($CDCl_3$) δ=1.24 (3H, t, $OCCH_3$, J=7.3 Hz), 2.01 (1H, ddd, H-3^a, J=6.3, 7.3, and 13.5 Hz), 2.24 (3H, s, Me-6), 2.26 (3H, ddd, H-3^e, J=2.6, 6.6 and 13.5 Hz), 3.6—3.7 (1H, m, H-4), 3.63 (1H, dq, OCHMe, J=9.6 and 7.3 Hz), 4.00 (1H, dq, OCHMe, J=9.6 and 7.3 Hz), 5.22 (1H, dd, H-2, J=2.6 and 6.3 Hz), 6.36 (1H, dd, H-1′, J=8.9 and 15.5 Hz), 6.54 (1H, d, H-2′, J=15.5 Hz), 6.77 (1H, d, H-8, J=8.6 Hz), 6.93 (1H, s, H-6), 7.07 (1H, d, H-5, J=8.6 Hz), and 7.2—7.4 (5H, m, ArH); IR(KBr) ν 2900, 1490, 1210, 1140, 1020, 900, 820, 750, and 690 cm^{-1}. Found: m/z 294.1614. Calcd for $C_{20}H_{22}O_2$; M, 294.1618.

6,6,9-Trimethyl-6a,7,8,9,10,10a-hexahydro-6*H*-dibenzo-[*b*,*d*]pyran (6g). Ag_2O (190 mg, 0.80 mmol) was added to a solution of **2g** (200 mg, 0.66 mmol) of diethyl ether (15 ml). The reaction mixture was stirred for 36 h and then filtered through Cerite. The filtrate was concentrated and the oil chromatographed on a column using 10% CH_2Cl_2–hexane as eluent to give **6g** (55 mg, 36%): ^{1}H NMR (270 MHz) ($CDCl_3$) δ=0.90 (1H, q, H-10^a, J=12.2 Hz), 0.99 (3H, d, Me-9, J=6.6 Hz), 1.08 (1H, m, H-7 or 8), 1.14 (3H, s, Me-6), 1.1—1.2 (1H, m, H-7 or 8), 1.39 (3H, s, Me-6), 1.30—1.40 (1H, m, H-6a or 9), 1.63 (1H, m, H-6a or 9), 1.82 (2H, m, H-7′ and 8′), 2.45 (2H, m, H-10^e and 10a), 6.76 (1H, dd, H-4, J=1.3 and 8.2 Hz), 6.82 (1H, ddd, H-2, J=1.3, 8.1, and 9.4 Hz), 7.08 (1H, s, H-3, J=0.8, 8.1, and 8.2 Hz), and 7.23 (1H, dd, H-1, J=0.8 and 9.4 Hz); ^{13}C NMR (270 MHz) ($CDCl_3$) δ=20.35 (q), 21.15 (q), 27.80 (t), 28.23 (q), 32.69 (d), 35.00 (t), 35.74 (d), 39.74 (t), 46.98 (d), 77.47 (s), 117.25 (d), 119.70 (d), 125.62 (s), 126.14 (d), 127.40 (d), 153.40 (s).[17]

***cis*-2-Ethoxy-6,7-methylenedioxy-4-[(*E*)-styryl]chroman (3c).** Acetone (3 ml), ethyl vinyl ether (3 ml), **2c** (70 mg, 0.21 mmol) and Ag_2O (60 mg, 0.25 mmol) were combined. The reaction mixture was stirred for 72 h and filtered through Cerite. The filtrate was concentrated in vacuo and the oil chromatographed on a column using 20% CH_2Cl_2–hexane as eluent. 6,7-Methylenedioxy-2-phenyl-2*H*-chromene (**8c**)[13] (24 mg, 44%) was first eluted followed by the chroman **3c** in the ratio ca. 1 : 1. **3c** had the following characteristics: mp 92.0—93.9 °C; ^{1}H NMR (270 MHz) ($CDCl_3$) δ=1.25 (3H, t, $OCCH_3$, J=7.3 Hz), 1.97 (1H, ddd, H-3^a, J=6.1, 7.3, and 13.7 Hz), 2.23 (1H, ddd, H-3^e, J=2.4, 6.8, and 13.7 Hz), 3.57 (1H, ddd, H-4, J=6.8, 7.3, and 9.2 Hz), 3.62 (1H, dq, OCHMe, J=9.7 and 7.3 Hz), 3.97 (1H, dq,

OCHMe, J=9.7 and 7.3 Hz), 5.18 (1H, dd, H-2, J=2.4 and 6.1 Hz), 5.85 (2H, s, OCH_2O), 6.36 (1H, dd, H-1′, J=9.2 and 15.4 Hz), 6.42 (1H, s, H-8), 6.51 (1H, d, H-2′, J=15.4 Hz), 6.60 (1H, s, H-5) and 7.2—7.4 (5H, m, ArH); IR(KBr) ν 2950, 1480, 1250, 1160, 1040, 940, 750, and 700 cm^{-1}. Found: m/z 324.1361. Calcd for $C_{20}H_{20}O_4$; M, 324.1362.

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