Convenient Synthesis of 2,4-Cyclohexadien-1-ones by Regioselective Methylthiomethylation of Phenols

Sadamu KATAYAMA, Toshio WATANABE, and Masashige YAMAUCHI*

Faculty of Pharmaceutical Sciences, Josai University, Keyakidai, Sakado, Saitama 350-02, Japan.
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A convenient synthesis of a variety of 2,4-cyclohexadien-1-ones 3—7 is described. Reaction of various phenols 2 having appropriate substituents with an excess of *S,S*-dimethylsuccinimidosulfonium chloride (Corey–Kim reagent, 1) in the presence of triethylamine proceeded with regioselective methylthiomethylation to give methylthiomethyl, bis(methylthiomethyl), or tris(methylthiomethyl)-2,4-cyclohexadien-1-ones 3—7 in satisfactory yields.

Keywords 2,4-cyclohexadien-1-one; *S,S*-dimethylsuccinimidosulfonium chloride; Corey–Kim reagent; regioselective methylthiomethylation; regioselectivity; regioisomer

It would be useful in organic synthesis to prepare 2,4-cyclohexadien-1-ones, convertible into complex acyclic molecules by means of cycloaddition, from easily available phenols.[1-4] These dienes have been chiefly prepared from phenols by the following methods; (a) treatment with dimethylsulfoxide (DMSO)–dicyclohexylcarbodiimide (DCC)–anhydrous phosphoric acid[5] or DMSO–*tert*-butyl bromide,[6] (b) treatment with *n*-butyllithium (*n*-BuLi)–alkoxymethyl chloride or *n*-BuLi–alkylthiomethyl chloride,[7] (c) treatment with an oxidizing agent such as periodic acid or thallium(III) nitrate trihydrate,[3] (d) a sequential procedure of oxidation with sodium periodate, acetylation, and retro-Diels Alder reaction,[4] (e) formation of the sodium salt followed by 6-alkylation with alkyl halide.[8] However, in methods (a, b) the starting materials are restricted to 2,6-disubstituted phenols, and in methods (c—e) the desired products are apt to dimerize, and are obtained only in low yields (5 to 34%).

Our attention was drawn to the report[9] that 2,4-cyclohexadien-1-ones might be reaction intermediates in the *ortho*-methylthiomethylation of phenols involving [2,3]-sigmatropic rearrangement of the oxasulfonium salts, using *S,S*-dimethylsuccinimidosulfonium chloride (Corey–Kim reagent, **1**).[10] We thought that if *ortho*-methylthiomethylation was carried out repeatedly with phenols having two or more reactive sites to reagent **1**, such as 2-substituted or 2,6-unsubstituted phenols, by use of an excess of **1**, 2,4-cyclohexadien-1-ones might be isolated as final methylthiomethylation products. In this paper, we would like to report a general synthesis of 2,4-cyclohexadien-1-ones **3**—**7** from various phenols **2** by use of an excess of the Corey–Kim reagent **1** in the presence of triethylamine (Chart 1).

Results and Discussion

The reaction of the phenols **2** with an excess of reagent **1** (method A, 1.5 eq to 2,6-disubstituted phenols **2a**—**g**; method B, 4 eq to 2-substituted phenols **2h**—**q**; and method C, 5—8 eq to 2,6-unsubstituted phenols **2r**—**v**) was carried out in dry methylene chloride at −78 °C in the presence of triethylamine to give the 2,4-cyclohexadien-1-ones **3**—**7**. The results are summarized in Tables I, II, and III.

6-Methylthiomethyl-2,4-cyclohexadien-1-ones **3a**—**g** were obtained from 2,6-disubstituted phenols **2a**—**g** by method A in satisfactory yields (Table I). Methylthiomethylation of the unsymmetrical phenols **2e**—**g** proceeded regioselectively at the less hindered site to afford **3e**—**g** as sole products (entries 5—7). The structures of these compounds were confirmed from examination of the ^{1}H- and ^{13}C-nuclear magnetic resonance (^{1}H- and ^{13}C-NMR)

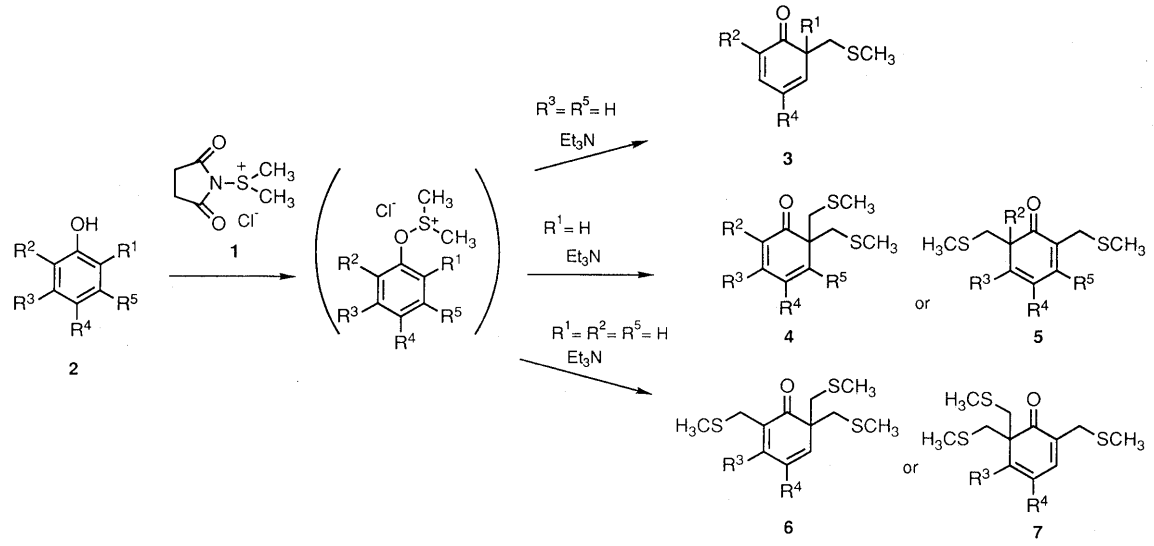


Chart 1

TABLE I. Reactions of 2,6-Disubstituted Phenols **2** ($R^3=R^5=H$) with the Corey–Kim Reagent **1**

Entry	Mol ratio **1**/**2**	R^1	R^2	R^4	2,4-Cyclohexadien-1-ones[a]	yield (%)	bp (°C)/mmHg[b]
1	1.5	CH_3	CH_3	H	**3a**[c]	90	125—130/0.15
2	1.5	CH_3	CH_3	CH_3	**3b**[c]	94	128—132/0.15
3	1.5	$CH(CH_3)_2$	$CH(CH_3)_2$	H	**3c**	96	180—183/0.01
4	1.5	OCH_3	OCH_3	H	**3d**[d]	90	175—180/0.055
5	1.5	CH_3	*tert*-Bu	H	**3e**	61	138—141/0.05
6	1.5	Allyl	*sec*-Bu	H	**3f**	88	155—160/0.07[e]
7	1.5	Allyl	*tert*-Bu	H	**3g**	80	135—140/0.07[e]

a) All products were obtained as yellow oils. *b*) Bath temperature of Kugelrohr distillation. *c*) Reference 5*a*. *d*) Reference 5*c*. *e*) Distillation was accompanied by partial decomposition.

TABLE II. Reactions of 2-Substituted Phenols ($R^1=H$) **2** with the Corey–Kim Reagent **1**

Entry	Mol ratio **1**/**2**	R^2	R^3	R^4	R^5	2,4-Cyclohexadien-1-ones[a]	yield (%)	bp (°C)/mmHg[b]
8	4	*tert*-Bu	H	H	H	**4h**	60	160—165/0.05
9	4	*sec*-Bu	H	H	H	**4i**	60	205—210/0.1
10	4	*tert*-Bu	H	*tert*-Bu	CH_3	**4j**	51	200—205/0.03
11	4	$CH(CH_3)_2$	H	H	H	**4k**:**5k** (1:2)[c]	77	184—188/0.01
12	4	$PhCH_2$	H	H	H	**41**:**51** (1:2)[c]	83	230—234/0.01
13	4	Et	H	H	H	**4m**:**5m** (1:3)[c]	81	163—167/0.05
14	4	CH_3	H	H	H	**5n**	77	155—160/0.05
15	4	CH_3	H	CH_3	H	**5o**	61	170—175/0.1
16	4	CH_3	CH_3	H	H	**5p**	73	169—173/0.1
17	4	Allyl	H	H	H	**5q**	76	150—155/0.1[d]

a) All products were obtained as yellow oils. *b*) Bath temperature of Kugelrohr distillation. *c*) The products were obtained as inseparable mixtures of two regioisomers and their ratio were determined from the ^{1}H-NMR spectra. *d*) Distillation was accompanied by partial decomposition.

spectra. The signals at *ca.* δ1.2 (s) or *ca.* δ2.2—2.6 (m) and at *ca.* δ25 or *ca.* δ45 were shifted to higher field than those of the starting phenols, and were assigned to C6-methyl or C6-allylic methylene protons and carbons attached to quaternary carbon, respectively.

In the reaction of 2-substituted phenols **2h—q** by method B (Table II), the phenols **2h—j** having a bulkier substituent at the C2-position than the methylthiomethyl group gave 6,6-bis(methylthiomethyl)-2,4-cyclohexadien-1-ones **4h—j** as sole products (entries 8—10). On the other hand, from the phenols **2n—q** having a less bulky substituent, 2,6-bis(methylthiomethyl)-2,4-cyclohexadien-1-ones **5n—q** were obtained as sole products (entries 14—17). This suggests that methylthiomethylation of the phenols takes place firstly at an unsubstituted *ortho* position, and then subsequent methylthiomethylation at the less hindered site of the two *ortho* positions occurs regioselectively. The product **5q** isomerized *via* Claisen rearrangement to the phenol **8** upon heating at 160 °C for 5 h in 75% yield (Chart 2). Moderate regioselectivity was also observed in the reaction of the phenols **2k—m**, having an *ortho* substituent not so different from the methylthiomethyl group in bulkiness, and major products **5k—m** were obtained along with inseparable minor regioisomers **4k—m** (entries 11—13). The structures of these compounds were determined from the ^{1}H- and ^{13}C-NMR spectra. In the spectra of the compounds **4h—j**, the signals at *ca.* δ2.9 (ABq) and at *ca.* δ44, were assigned to "non-allylic" C6-thiomethylene protons and carbons. In compounds **5n—q**, the signals assignable to "allylic" C2-thiomethylene protons and carbons appeared at *ca.* δ3.4 (ABq) and *ca.* δ32 along with signals assignable to

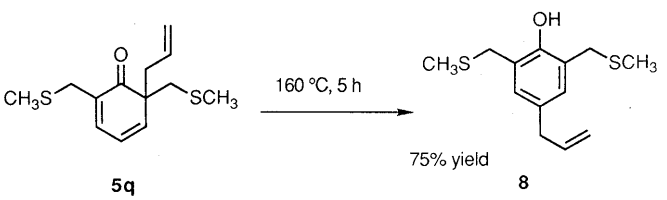


Chart 2

"non-allylic" C6-thiomethylene groups at *ca.* δ2.8—3.0 (ABq) and *ca.* δ42—45. The ratios of **4k—m** and **5k—m** in the inseparable regioisomeric mixtures were determined from the signal intensities of the C6- and C2-thiomethylene groups in their ^{1}H-NMR spectra. Application of method A to the 2-substituted phenols gave a mixture of the starting materials and the methylthiomethylated phenols together with the cyclohexadienones. This means that there is no significant difference in the reactivities of the starting materials and the methylthiomethylated phenols, and from the reaction of the 2-substituted phenols with reagent **1**, the mono-methylthiomethylated products can not be obtained effectively under method A conditions.

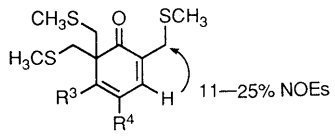
2,6,6-Tris(methylthiomethyl)-2,4-cyclohexadien-1-ones **6**, **7** were produced from the phenols **2r—v**, having no substituent at the *ortho* positions, by method C (Table III). Geminal methylthiomethylation took place predominantly at the *ortho*-position adjacent to the unsubstituted *meta* position in the case of the *meta*-monosubstituted phenols **2s—u**, owing to the steric hindrance of the substituent (entries 19—21). On the other hand, with 3,4-cyclohexanophenol **2v**, geminal methylthiomethylation occurred at the *ortho* position adjacent to the substituted *meta* position

TABLE III. Reactions of 2,6-Unsubstituted Phenols **2** ($R^1=R^2=R^5=H$) with the Corey–Kim Reagent **1**

Entry	Mol ratio **1/2**	R^3	R^4	2,4-Cyclohexadien-1-ones[a] yield (%)	bp (°C)/mmHg[b]
18	8	H	H	**6r**[c,d] 65	190—195/0.07
19	5	CH_3	H	**6s**:**7s** (3:2)[e] 84	198—203/0.01
20	5	CH_3	CH_3	**6t**:**7t** (3.6:1)[e] 71	225—230/0.01
21	5	C_2H_5	H	**6u**:**7u** (8:3)[e] 76	200—205/0.01
22	5	$CH_2(CH_2)_2CH_2$		**7v** 80	230—235/0.07

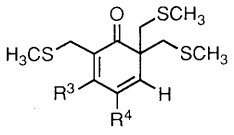
a) All products were obtained as yellow oils. *b*) Bath temperature of Kugelrohr distillation. *c*) Reference 5*c*. *d*) In this case there is no difference between **6** and **7**, which are identical substance. *e*) The products were obtained as inseparable mixtures of two regioisomers, and their ratio were determined from the ^{1}H-NMR spectra.

NOEs observed in NOE difference spectra



7s—v

NOEs not detected



6s—u

Chart 3

to give 1,1,3-tris(methylthiomethyl)-1,2,5,6,7,8-hexahydro-2-oxonaphthalene (**7v**) as a sole product (entry 22). These results could be explained in terms of the thermodynamic stability of the product **7v** having an *endo* double bond in the cyclohexane ring, compared with regioisomer **6v** having two *exo* double bonds.[11] The structure of **7v** was confirmed by observations of nuclear Overhauser effects (NOEs) in the NOE difference spectra between the allylic C3-thiomethylene group and olefinic C4-proton; that is, on irradiation of the C3-thiomethylene protons or C4-proton, the signal intensity of the C4-proton or C3-thiomethylene protons was enhanced by 11% or 16%, respectively. Similarly, the structures of **6s—u** and **7s—u**, as the regioisomeric mixtures, were established by NOE experiments involving irradiation of the C2-thiomethylene protons. The signal intensities of the olefinic C3-protons were enhanced in **7s** (22%), **7t** (25%), and **7u** (18%), while no NOEs were detected in **6s—u**, in which the C2-thiomethylene protons and olefinic C5-protons are far apart. The ratios of **6s—u** and **7s—u** were determined from the signal intensities of the olefinic C5- or C3-protons (Chart 3).

Until now, the 2,4-cyclohexadien-1-ones could be obtained only when the starting materials were 2,6-substituted phenols in the reaction *via* the oxasulfonium salt of the phenols,[5] while the reaction of 2-substituted or 2,6-unsubstituted phenols with DMSO–DCC–H^+ gave not 2,4-cyclohexadien-1-ones but monomethylthiomethylated or bismethylthiomethylated phenols at the C2- and/or C6-position.[5a,9,12] Here we have demonstrated that the 2,4-cyclohexadien-1-ones can be easily prepared by using excess reagent **1** even in the absence of *ortho*-substituents in the phenols, and considerable regioselectivity may be expected in the case of phenols having an *ortho*- or *meta*-substituent clearly distinguishable from the newly introduced methylthiomethyl group in bulkiness.

Experimental

Apparatus and Methods Spectral data were obtained using the following apparatus: NMR spectra in chloroform-*d* ($CDCl_3$) at 270 MHz on a JEOL JMN-GX270 instrument with chemical shifts being reported in δ units from tetramethylsilane as an internal standard and coupling constants in hertz; infrared spectra (IR) on a JASCO IR-810 spectrophotometer; mass spectra (MS) on a JEOL JMS-DX300 mass spectrometer by direct insertion at 70 eV; UV spectra on a Hitachi spectrophotometer U-3200 in ethanol. Column chromatography was carried out on silica gel (100—200 mesh, Micro Bead 4B, Fuji-Davison Chemical Ltd.). The 2,4-cyclohexadiene-1-ones were so unstable that micro analysis could not be done. Therefore, their structures were confirmed by high-resolution MS measurements except for the mixture of **6t** and **7t**, in which the molecular ion peak was too small to be measurable.

2-Allyl-6-(1-methylpropyl)phenol (2f) Allyl bromide (21.2 g, 175.2 mmol) was added to a mixture containing 2-(1-methylpropyl)phenol (23.9 g, 159.2 mmol), potassium carbonate (22.0 g, 159.2 mmol), and dry acetone (100 ml) at room temperature, and the whole was stirred under reflux for 24 h. The reaction mixture was filtered through Celite, washed with dry acetone (50 ml), and evaporated. The residue was dissolved in ether (100 ml), and the solution was washed with cooled aqueous sodium hydroxide (10%, 1 × 30 ml), aqueous ammonium chloride (1 × 30 ml), and brine (1 × 30 ml), and then dried ($MgSO_4$). Removal of the solvent gave 1-allyloxy-2-(1-methylpropyl)benzene (28.1 g) as a crude oil. This product was stirred at 220 °C for 2.5 h followed by purification by chromatography on silica gel (hexane–ether, 19:1) to afford the title compound (**2f**) (20.0 g, 60% total yield) as a colorless oil. IR (neat): 3540, 1635 cm^{-1}. ^{1}H-NMR δ: 0.85 (3H, t, J=6.8 Hz, $C\underline{H}_3$–CH_2), 1.20 (3H, d, J=6.5 Hz, $C\underline{H}_3$–CH), 1.38—1.90 (2H, m, $C\underline{H}_2$–CH_3), 2.70—3.17 (1H, m, C6-CH), 3.28—3.41 (2H, m, C2-CH_2), 4.90—5.30 (2H, m, $C\underline{H}_2$=CH), 5.68—6.33 (1H, m, $C\underline{H}$=CH_2), 6.65—7.12 (3H, m, arom-H). MS *m/z* (%): 191 (M^++1, 5), 190 (M^+, 31), 161 (base), 133 (33). HRMS *m/z*: M^+ Calcd for $C_{13}H_{18}O$: 190.1358. Found: 190.1362.

2-Allyl-6-*tert*-butylphenol (2g) Allyl bromide (6.32 g, 52.2 mmol) was added to a mixture containing 2-*tert*-butylphenol (7.14 g, 47.5 mmol), potassium carbonate (6.57 g, 47.5 mmol), and dry acetone (50 ml) at room temperature, and the whole was then stirred under reflux for 24 h. Subsequent procedure was similar to that in the case of **2f** to give 1-allyloxy-2-*tert*-butylbenzene (7.10 g) as a crude oil. This oil was treated as described for **2f** to afford the title compound (**2g**) (5.62 g, 62% total yield) as a colorless oil. IR (neat): 3540, 1635 cm^{-1} ^{1}H-NMR δ: 1.38 (9H, s, CH_3), 3.28—3.48 (2H, m, C2-CH_2), 5.00—5.33 (2H, m, $C\underline{H}_2$=CH), 5.68—6.33 (1H, m, $C\underline{H}$=CH_2), 6.60—7.23 (3H, m, arom-H). MS *m/z* (%): 192 (M^++2, 1), 191 (M^++1, 11), 190 (M^+, 71), 175 (base), 161 (52). HRMS *m/z*: M^+ Calcd for $C_{13}H_{18}O$: 190.1358. Found: 190.1362.

General Method for Preparation of 2,4-Cyclohexadien-1-ones (3) from Phenols (2) Method A: Synthesis of 6-Methylthiomethyl-2,4-cyclohexadien-1-ones (3a—g) Dimethyl sulfide (1.1 ml, 15.0 mmol) was added dropwise to a suspension of *N*-chlorosuccinimide (NCS, 1875 mg, 14.0 mmol) in anhydrous CH_2Cl_2 (100 ml) at −78 °C under Ar, and stirring was continued for 1 h at the same temperature. Then, a solution of a 2,6-disubstituted phenol (**2**) (9.3 mmol) in anhydrous CH_2Cl_2 (15 ml) was added at the same temperature. After 1 h, triethylamine (2.0 ml, 14.3 mmol) was added to the mixture, and stirring was continued for 1 h at the same temperature. Cooled 10% aqueous NaOH (6 ml) was added to the mixture, and the whole was extracted with hexane (115 ml). The organic layer was washed with saturated aqueous NH_4Cl (1 × 30 ml) and brine (2 × 30 ml), and dried over anhydrous magnesium sulfate. The solvent was evaporated off, and the resulting residue was purified by column chromatography on silica gel (eluent, 5% ether in hexane) to afford the corresponding 6-methylthiomethyl-2,4-cyclohexadien-1-one (**3**).

2,6-Dimethyl-6-methylthiomethyl-2,4-cyclohexadien-1-one (3a)[5a] IR (neat): 1654, 1636 cm^{-1}. UV nm (log ε): 305 (3.55). ^{1}H-NMR δ: 1.22 (3H, s, C6-CH_3), 1.90 (3H, d, J=1.1 Hz, C2-CH_3), 2.05 (3H, s, CH_3–S), 2.86 (2H, ABq, J=12.5 Hz, CH_2–S), 6.20—6.29 (2H, m, C4-H and C3-H or C5-H), 6.86—6.90 (1H, m, C5-H or C3-H). ^{13}C-NMR δ: 15.4 (C2-$\underline{C}H_3$), 17.6 (CH_3–S), 25.2 (C6-$\underline{C}H_3$), 44.2 (CH_2–S), 51.8 (C6), 121.2 (C4), 133.2 (C2), 138.3 (C3 or C5), 144.0 (C5 or C3), 204.4 (C1). MS *m/z* (%): 184 (M^++2, 1), 183 (M^++1, 2), 182 (M^+, 20), 135 (34), 61 (base). HRMS *m/z*: M^+ Calcd for $C_{10}H_{14}OS$: 182.0765. Found: 182.0746.

6-Methylthiomethyl-2,4,6-trimethyl-cyclohexadien-1-one (3b)[5a] IR (neat): 1665, 1650, 1645 cm^{-1}. UV nm (log ε): 318 (3.55). ^{1}H-NMR δ:

1.18 (3H, s, C6-CH_3), 1.89 (3H, s, C4-CH_3), 1.94 (3H, d, J=1.8 Hz, C2-CH_3), 2.04 (3H, s, CH_3–S), 2.82 (2H, ABq, J=12.5 Hz, CH_2–S), 5.92 (1H, br s, C5-H), 6.74—6.75 (1H, m, C3-H). ^{13}C-NMR δ: 15.4 (C2-CH_3), 17.6 (CH_3–S), 21.2 (C4-CH_3), 25.4 (C6-CH_3), 44.7 (CH_2–S), 50.8 (C6), 128.4 (C4), 132.6 (C2), 138.3 (C5 or C3), 142.7 (C3 or C5), 204.4 (C1). MS m/z (%): 196 (M^+, 9), 149 (8), 60 (base). HRMS m/z: M^+ Calcd for $C_{11}H_{16}OS$: 196.0922. Found: 196.0929.

2,6-Diisopropyl-6-methylthiomethyl-2,4-cyclohexadien-1-one (3c) IR (neat): 1655, 1637 cm^{-1}. UV nm (log ε): 307 (3.54). ^{1}H-NMR δ: 0.74 (3H, d, J=6.9 Hz, C6-CH–CH_3), 0.94 (3H, d, J=6.9 Hz, C6-CH–CH_3), 1.06 (3H, d, J=6.9 Hz, C2-CH–CH_3), 1.08 (3H, d, J=6.9 Hz, C2-CH–CH_3), 2.02 (3H, s, CH_3–S), 2.04—2.12 (1H, m, C6-CH), 2.95 (2H, ABq, J=11.9 Hz, CH_2–S), 2.93—3.04 (1H, m, C2-CH), 6.19—6.23 (1H, m, C5-H or C3-H), 6.42—6.48 (1H, m, C4-H), 6.74—6.77 (1H, m, C3-H or C5-H). ^{13}C-NMR δ: 17.2 (C2-C–CH_3), 17.5 (CH_3–S), 21.5 (C6-C–CH_3), 21.7 (C6-C–CH_3), 26.1 (C2-CH), 39.1 (C6-CH), 42.4 (C6-CH_2), 58.9 (C6), 124.3 (C4), 134.3 (C3 or C5), 140.4 (C5 or C3), 144.1 (C2), 204.1 (C1). MS m/z (%): 239 (M^++1, 1), 238 (M^+, 8), 191 (45), 176 (68), 61 (base). HRMS m/z: M^+ Calcd for $C_{14}H_{22}OS$: 238.1391. Found: 238.1366.

2,6-Dimethoxy-6-methylthiomethyl-2,4-cyclohexadien-1-one (3d)[5c] IR (neat): 1680, 1640 cm^{-1}. ^{1}H-NMR δ: 2.13 (3H, s, CH_3–S), 2.83 (2H, br s, CH_2–S), 3.17 (3H, s, CH_3–O), 3.41 (3H, s, CH_3–O), 6.06—6.12 (2H, m, C4-H and C3-H or C5-H), 6.40—6.44 (1H, m, C5-H or C3-H). ^{13}C-NMR δ: 18.2 (CH_3–S), 44.0 (CH_2–S), 53.8 (CH_3–O), 55.6 (CH_3–O), 84.2 (C6), 111.0, 125.0, and 133.4 (C3, C4, and C5), 152.7 (C2), 198.0 (C1). MS m/z (%): 216 (M^++2, 1), 215 (M^++1, 2), 214 (M^+, 15), 167 (2), 153 (5), 61 (base). HRMS m/z: M^+ Calcd for $C_{10}H_{14}O_3S$: 214.0664. Found: 214.0639.

2-*tert*-Butyl-6-methyl-6-methylthiomethyl-2,4-cyclohexadien-1-one (3e) IR (neat): 1660, 1640 cm^{-1}. UV nm (log ε): 303 (3.53). ^{1}H-NMR δ: 1.19 (3H, s, C6-CH_3), 1.23 [9H, s, $(CH_3)_3$], 2.06 (3H, s, CH_3–S), 2.85 (2H, ABq, J=12.8 Hz, CH_2–S), 6.21—6.31 (2H, m, C4-H and C3-H or C5-H), 6.85—6.88 (1H, m, C5-H or C3-H). ^{13}C-NMR δ: 17.6 (CH_3–S), 25.1 (C6-CH_3), 29.1 [$(CH_3)_3$], 34.3 (C2-C), 43.9 (CH_2–S), 53.0 (C6), 121.3 (C4), 135.4 (C3 or C5), 144.1 (C2), 144.2 (C5 or C3), 203.6 (C1). MS m/z (%): 224 (M^+, 9), 177 (37), 61 (base). HRMS m/z: M^+ Calcd for $C_{13}H_{20}OS$: 224.1235. Found: 224.1245.

6-Allyl-2-(1-methylpropyl)-6-methylthiomethyl-2,4-cyclohexadien-1-one (3f) IR (neat): 1654, 1636 cm^{-1}. UV nm (log ε): 309 (3.52). ^{1}H-NMR δ: 0.74—0.95 (3H, m, CH_3–CH_2), 1.01—1.06 (3H, m, CH_3–CH), 1.30—1.58 (2H, m, CH_2–CH_3), 2.04 (3H, s, CH_3–S), 2.27—2.56 (2H, s, C6-CH_2–C=), 2.87 (2H, ABq, J=12.4 Hz, CH_2–S), 2.74—3.06 (1H, m, C2-CH), 4.91—5.01 (2H, m, CH_2=CH), 5.42—5.58 (1H, m, CH=CH_2), 6.21—6.80 (3H, m, C3-H, C4-H, and C5-H). ^{13}C-NMR δ: 11.8 (CH_3–CH_2), 17.7 (CH_3–S), 19.2 (CH_3–CH), 28.7 (CH_2–CH_3), 33.0 (C2-CH), 43.5 (CH_2–S), 44.7 (C6-CH_2–C=), 55.9 (C6), 118.3 (CH_2=CH), 122.9 (C4), 132.1 (CH=CH_2), 135.8 (C5 or C3), 137.6 (C2), 142.0 (C3 or C5), 203.0 (C1). MS m/z (%): 252 (M^++2, 1), 251 (M^++1, 4), 250 (M^+, 22), 189 (7), 61 (base). HRMS m/z: M^+ Calcd for $C_{15}H_{22}OS$: 250.1391. Found: 250.1403.

6-Allyl-2-*tert*-butyl-6-methylthiomethyl-2,4-cyclohexadien-1-one (3g) IR (neat): 1655, 1638 cm^{-1}. UV nm (log ε): 306 (3.52). ^{1}H-NMR δ: 1.22 [9H, s, $(CH_3)_3$], 2.04 (3H, s, CH_3–S), 2.24—2.56 (2H, m, C6-CH_2–C=), 2.86 (2H, ABq, J=12.9 Hz, CH_2–S), 4.91—5.17 (2H, m, CH_2=CH), 5.42—5.78 (1H, m, CH=CH_2), 6.42—6.87 (3H, m, C3-H, C4-H, and C5-H). ^{13}C-NMR δ: 17.7 (CH_3–S), 29.1 [$(CH_3)_3$C], 34.4 (C2-C), 43.3 (CH_2–S), 44.9 (C6-CH_2–C=), 56.6 (C6), 118.3 (CH_2=CH), 122.9 (C4), 131.9 (CH=CH_2), 135.7 (C5 or C3), 142.6 (C3 or C5), 144.9 (C2), 203.0 (C1). MS m/z (%): 252 (M^++2, 1), 251 (M^++1, 3), 250 (M^+, 16), 147 (11), 61 (base). HRMS m/z: M^+ Calcd for $C_{15}H_{22}OS$: 250.1391. Found: 250.1376.

General Method for Preparation of 2,4-Cyclohexadien-1-ones (4, 5) from Phenols (2) Method B: Synthesis of 6,6-Bis(methylthiomethyl)- or 2,6-Bis(methylthiomethyl)-2,4-cyclohexadien-1-ones (4h—m or 5k—q) Dimethyl sulfide (2.1 ml, 28.6 mmol) was added dropwise to a suspension of NCS (3578 mg, 26.8 mmol) in anhydrous methylene chloride (190 ml) at −78 °C under argon, and stirring was continued for 1 h at the same temperature. Then a solution of a 2-substituted phenol (**2**) (6.7 mmol) in anhydrous methylene chloride (15 ml) was added at the same temperature. After 1 h, triethylamine (3.9 ml, 28.0 mmol) was added to the mixture, and stirring was continued for 1 h at the same temperature. Cooled 10% aqueous NaOH (11 ml) was added to the mixture. The subsequent procedure was similar to method A, giving 2,6-, or 6,6-bis(methylthiomethyl)-2,4-cyclohexadien-1-one (**4** or **5**).

6,6-Bis(methylthiomethyl)-2-*tert*-butyl-2,4-cyclohexadien-1-one (4h) IR (neat): 1655, 1638 cm^{-1}. UV nm (log ε): 287 (3.51). ^{1}H-NMR δ: 1.24 [9H, s, $C(CH_3)_3$], 2.05 (6H, s, CH_3–S), 2.86 (4H, ABq, J=12.5 Hz, CH_2–S), 6.30—6.43 (2H, m, C4-H and C3-H or C5-H), 6.88—6.91 (1H, m, C5-H or C3-H). ^{13}C-NMR δ: 17.9 (CH_3–S), 29.1 [$(CH_3)_3$], 34.4 (C2-C), 43.9 (CH_2–S), 57.2 (C6), 123.7, 135.9, and 142.0 (C3, C4, and C5), 145.0 (C2), 202.2 (C1). MS m/z (%): 270 (M^+, 7), 223 (19), 119 (62), 61 (base). HRMS m/z: M^+ Calcd for $C_{14}H_{22}OS_2$: 270.1112. Found: 270.1126.

6,6-Bis(methylthiomethyl)-2-(1-methylpropyl)-2,4-cyclohexadien-1-one (4i) IR (neat): 1650, 1630 cm^{-1}. UV nm (log ε): 303 (3.39). ^{1}H-NMR δ: 0.85 (3H, t, J=7.3 Hz, CH_3–CH_2), 1.06 (3H, d, J=7.0 Hz, CH_3–CH), 1.34—1.58 (2H, m, CH_2–CH_3), 2.05 (6H, s, CH_3–S), 2.87 (2H, ABq, J=12.5 Hz, CH_2–S), 2.88 (2H, ABq, J=12.5 Hz, CH_2–S), 2.72—3.05 (1H, m, C2-CH), 6.26—6.34 (1H, m, C4-H), 6.40—6.47 (1H, m, C5-H), 6.78—6.92 (1H, m, C3-H). ^{13}C-NMR δ: 11.8 (CH_3–CH_2), 17.9 (CH_3–S), 19.3 (CH_3–CH), 28.7 (CH_2–CH_3), 32.9 (C2-CH), 43.9 (CH_2–S), 56.4 (C6), 123.7 (C4), 136.0 (C3 or C5), 138.2 (C2), 141.4 (C5 or C3), 202.4 (C1). MS m/z (%): 272 (M^++2, 1), 271 (M^++1, 2), 270 (M^+, 9), 61 (base). HRMS m/z: M^+ Calcd for $C_{14}H_{22}OS_2$: 270.1112. Found: 270.1093.

6,6-Bis(methylthiomethyl)-2,4-di-*tert*-butyl-5-methyl-2,4-cyclohexadien-1-one (4j) IR (neat): 1645, 1623 cm^{-1}. UV nm (log ε): 342 (3.58). ^{1}H-NMR δ: 1.25 [9H, s, $(CH_3)_3$], 1.35 [9H, s, $C(CH_3)_3$], 1.96 (6H, s, CH_3–S), 2.05 (3H, s, C5-CH_3), 2.90 (4H, ABq, J=11.9 Hz, CH_2–S), 7.19 (1H, s, C3-H). ^{13}C-NMR δ: 17.0 (CH_3–S), 17.4 (C5-CH_3), 29.1 and 31.1 [C2-C(CH_3)$_3$ and C4-C(CH_3)$_3$], 34.5 and 35.9 (C2-C and C4-C), 44.4 (CH_2–S), 59.8 (C6), 139.3 (C4), 139.9 (C3), 141.7 and 142.9 (C2 and C5), 202.1 (C1). MS m/z (%): 342 (M^++2, 1), 341 (M^++1, 3), 340 (M^+, 14), 279 (17), 217 (base), 61 (74). HRMS m/z: M^+ Calcd for $C_{19}H_{32}OS_2$: 340.1895. Found: 340.1908.

6,6-Bis(methylthiomethyl)-2-isopropyl-2,4-cyclohexadien-1-one (4k) and 2,6-Bis(methylthiomethyl)-6-isopropyl-2,4-cyclohexadien-1-one) (5k) From 2-isopropylphenol (**2k**), an inseparable mixture of **4k** and **5k** was obtained. IR (neat): 1650, 1635 cm^{-1}. UV nm (log ε): 307 (3.50). MS m/z (%): 258 (M^++2, 1), 257 (M^++1, 2), 256 (M^+, 11), 209 (20), 108 (82), 61 (base). HRMS m/z: M^+ Calcd for $C_{13}H_{20}OS_2$: 256.0956. Found: 256.0955. **4k**: ^{1}H-NMR δ: 1.08 (6H, d, J=6.4 Hz, CH_3–CH), 2.05 (6H, s, CH_3–S), 2.96 or 2.88 (4H, ABq, J=11.9 Hz, or 12.4 Hz, CH_2–S), 2.95—3.03 (1H, m, C2-CH), 6.29—6.33 (1H, m, C5-H or C3-H), 6.41—6.50 (1H, m, C4-H), 6.82—6.84 (1H, m, C3-H or C5-H). ^{13}C-NMR δ: 17.9 or 17.5 (C6-C–S–CH_3), 21.7 (CH_3–CH), 26.2 (C2-CH), 43.8 or 42.2 (CH_2–S), 56.4 (C6), 123.7 (C5 or C3), 135.0 (C3 or C5), 141.4 (C4), 143.8 (C2), 202.3 (C1). **5k**: ^{1}H-NMR δ: 0.78 (3H, d, J=7.0 Hz, CH_3–CH), 0.96 (3H, d, J=7.0 Hz, CH_3–CH), 2.03 (3H, s, C6-C–S–CH_3), 2.04 (3H, s, C2–C–S–CH_3), 2.88 or 2.96 (2H, ABq, J=12.4 Hz, or 11.9 Hz, C6-CH_2–S), 3.37 (2H, ABq, J=13.9 Hz, C2-CH_2), 6.29—6.33 (1H, m, C5-H or C3-H), 6.41—6.50 (1H, m, C4-H), 6.91—6.93 (1H, m, C3-H or C5-H). ^{13}C-NMR δ: 15.6 (C2-C–S–CH_3), 17.2 (CH_3–CH), 17.3 (CH_3–CH), 17.5 or 17.9 (C6-C–S–CH_3), 31.9 (C2-CH_2), 39.2 (C6-CH), 42.2 or 43.8 (C6-CH_2), 59.3 (C6), 124.0 (C5 or C3), 133.7 (C2), 138.1 (C3 or C5), 142.3 (C4), 203.8 (C1).

2-Benzyl-6,6-bis(methylthiomethyl)-2,4-cyclohexadien-1-one (4l) and 6-Benzyl-2,6-bis(methylthiomethyl)-2,4-cyclohexadien-1-one (5l) From 2-benzylphenol (**2l**), an inseparable mixture of **4l** and **5l** was obtained. IR (neat): 1660, 1645 cm^{-1}. UV nm (log ε): 311 (3.54). MS m/z (%): 305 (M^++1, 1), 304 (M^+, 7), 195 (53), 165 (11), 91 (24), 61 (base). HRMS m/z: M^+ Calcd for $C_{17}H_{20}OS_2$: 304.0956. Found: 304.0959. **4l**: ^{1}H-NMR δ: 2.04 (6H, s, CH_3–S), 2.86 or 2.82 (4H, ABq, J=12.6 Hz, or 12.5 Hz, CH_2–S), 3.64 (2H, s, CH_2–Ph), 6.22—6.74 (3H, m, C3-H, C4-H, and C5-H), 7.00—7.28 (5H, m, arom-H). **5l**: ^{1}H-NMR δ: 1.84 (3H, s, C6-C–S–CH_3), 1.95 (3H, s, C2-C–S–CH_3), 2.82 or 2.86 (2H, ABq, J=12.5 Hz or 12.6 Hz, C6-CH_2–S), 3.12 (2H, ABq, J=13.0 Hz, C6-CH_2–Ph), 3.26 (2H, ABq, J=14.3 Hz, C2-CH_2–S), 6.22—6.74 (3H, m, C3-H, C4-H, and C5-H), 7.00—7.28 (5H, m, arom-H).

6,6-Bis(methylthiomethyl)-2-ethyl-2,4-cyclohexadien-1-one (4m) and 2,6-Bis(methylthiomethyl)-6-ethyl-2,4-cyclohexadien-1-one (5m) From 2-ethylphenol (**2m**), an inseparable mixture of **4m** and **5m** was obtained. IR (neat): 1655, 1638 cm^{-1}. UV nm (log ε): 306 (3.57). MS m/z (%): 244 (M^++2, 3), 243 (M^++1, 4), 242 (M^+, 26), 195 (base), 147 (59). HRMS m/z: M^+ Calcd for $C_{12}H_{18}OS_2$: 242.0799. Found: 242.0799. **4m**: ^{1}H-NMR δ: 1.08 (3H, t, J=7.3 Hz, C2-C–CH_3), 2.05 (6H, s, CH_3–S), 2.25—2.38 (2H, m, C2-CH_2), 2.71—3.02 (4H, m, CH_2–S), 6.27—7.10 (3H, m, C3-H, C4-H, and C5-H). ^{13}C-NMR δ: 12.5 (C2-C–CH_3), 17.7 (CH_3–S), 22.0 (C2-CH_2), 43.8 (CH_2–S), 56.3 (C6), 123.7 (C4), 136.8 (C3

or C5), 139.6 (C2), 142.0 (C5 or C3), 202.9 (C1). **5m**: ^{1}H-NMR δ: 0.70 (3H, t, J=7.3 Hz, C6-C-CH$_3$), 1.54—1.98 (2H, m, C6-CH$_2$), 2.04 (3H, s, C6-C-S-CH$_3$), 2.05 (3H, s, C2-C-S-CH$_3$), 2.71—3.02 (2H, m, C6-CH$_2$-S), 3.38 (2H, ABq, J=13.9 Hz, C2-CH$_2$), 6.27—7.10 (3H, m, H-3, H-4, and H-5). ^{13}C-NMR δ: 8.5 (C6-C-CH$_3$), 15.6 (C2-C-S-CH$_3$), 17.9 (C6-C-S-CH$_3$), 31.8 (C2-CH$_2$-S), 34.1 (C6-CH$_2$-CH$_3$), 44.0 (C6-CH$_2$-S), 57.0 (C6), 123.0 (C4), 133.6 (C2), 138.9 (C3 or C5), 144.3 (C5 or C3), 203.3 (C1).

2,6-Bis(methylthiomethyl)-6-methyl-2,4-cyclohexadien-1-one (5n) IR (neat): 1660, 1640 cm^{-1}. UV nm (log ε): 306 (3.50). ^{1}H-NMR δ: 1.24 (3H, s, C6-CH$_3$), 2.05 (3H, s, C6-C-S-CH$_3$), 2.07 (3H, s, C2-C-S-CH$_3$), 2.88 (2H, ABq, J=12.8 Hz, C6-CH$_2$-S), 3.38 (2H, ABq, J=13.9 Hz, C2-CH$_2$-S), 6.28—6.38 (2H, m, C4-H and C5-H), 6.98—7.02 (1H, s, C3-H). ^{13}C-NMR δ: 15.6 (C2-C-S-CH$_3$), 17.7 (C6-C-S-CH$_3$), 25.2 (C6-CH$_3$), 31.6 (C2-CH$_2$), 43.9 (C6-CH$_2$), 52.3 (C6), 120.9 (C4), 132.8 (C2), 138.6 (C3 or C5), 145.4 (C5 or C3), 202.8 (C1). MS m/z (%): 228 (M$^+$, 2), 180 (9), 108 (50), 91 (41), 61 (base). HRMS m/z: M$^+$ Calcd for $C_{11}H_{16}OS_2$: 228.0643. Found: 228.0646.

2,6-Bis(methylthiomethyl)-4,6-dimethyl-2,4-cyclohexadien-1-one (5o) IR (neat): 1670, 1650 cm^{-1}. UV nm (log ε): 320 (3.59). ^{1}H-NMR δ: 1.21 (3H, s, C6-CH$_3$), 1.99 (3H, d, J=1.5 Hz, C4-CH$_3$), 2.04 (3H, s, C6-C-S-CH$_3$), 2.06 (3H, s, C2-C-S-CH$_3$), 2.84 (2H, ABq, J=12.7 Hz, C6-CH$_2$-S), 3.38 (2H, ABq, J=13.9 Hz, C2-CH$_2$-S), 5.99 (1H, s, C3-H), 6.86 (1H, d, J=1.5 Hz, C5-H). ^{13}C-NMR δ: 15.7 (C2-C-S-CH$_3$), 17.7 (C6-C-S-CH$_3$), 21.3 (C4-CH$_3$), 25.4 (C6-CH$_3$), 31.6 (C2-CH$_2$-S), 44.5 (C6-CH$_2$-S), 51.5 (C6), 128.4 (C4), 132.4 (C2), 139.7 (C3), 143.1 (C5), 203.1 (C1). MS m/z (%): 242 (M$^+$, 2), 182 (6), 134 (40), 91 (31), 61 (base). HRMS m/z: M$^+$ Calcd for $C_{12}H_{18}OS_2$: 242.0799. Found: 242.0771.

2,6-Bis(methylthiomethyl)-5,6-dimethyl-2,4-cyclohexadien-1-one (5p) IR (neat): 1658, 1638 cm^{-1}. UV nm (log ε): 326 (3.66). ^{1}H-NMR δ: 1.25 (3H, s, C6-CH$_3$), 1.99 (3H, d, J=1.5 Hz, C5-CH$_3$), 2.02 (3H, s, C6-C-S-CH$_3$), 2.05 (3H, s, C2-C-S-CH$_3$), 3.00 (2H, ABq, J=12.4 Hz, C6-CH$_2$-S), 3.37 (2H, ABq, J=13.9 Hz, C2-CH$_2$-S), 6.13 (1H, dd, J=6.4 Hz, 1.5H, C4-H), 6.95 (1H, d, J=6.4 Hz, C3-H). ^{13}C-NMR δ: 15.6 (C2-C-S-CH$_3$), 17.0 (C6-C-S-CH$_3$), 19.4 (C5-CH$_3$), 26.1 (C6-CH$_3$), 31.8 (C2-CH$_2$), 42.0 (C6-CH$_2$), 55.2 (C6), 119.8 (C4), 130.5 (C2), 139.5 (C3), 153.5 (C5), 203.5 (C1). MS m/z (%): 244 (M$^+$+2, 1), 243 (M$^+$+1, 2), 242 (M$^+$, 13), 181 (7), 61 (base). HRMS m/z: M$^+$ Calcd for $C_{12}H_{18}OS_2$: 242.0799. Found: 242.0799.

6-Allyl-2,6-bis(methylthiomethyl)-2,4-cyclohexadien-1-one (5q) IR (neat): 1655, 1635 cm^{-1}. UV nm (log ε): 308 (3.17). ^{1}H-NMR δ: 2.03 (3H, s, CH$_3$-S), 2.06 (3H, s, CH$_3$-S), 2.30—2.59 (2H, m, C6-CH$_2$-C=), 2.89 (2H, ABq, J=12.5 Hz, C6-CH$_2$-S), 3.42 (2H, ABq, J=14.1 Hz, C2-CH$_2$-S), 4.94—5.15 (2H, m, CH$_2$=CH), 5.45—5.51 (1H, m, CH=CH$_2$), 6.31—6.45 (2H, m, C4-H and C5-H), 6.85—7.06 (1H, m, C3-H). ^{13}C-NMR δ: 15.6 (C2-C-S-CH$_3$), 17.7 (C6-C-S-CH$_3$), 31.7 (C2-CH$_2$), 43.2 (C6-CH$_2$-S), 44.6 (C6-CH$_2$-C=), 56.5 (C6), 118.6 (CH$_2$=CH), 123.6 (C4), 131.7 (CH=CH$_2$), 133.6 (C2), 134.4 and 143.7 (C3 and C5), 202.4 (C1). MS m/z (%): 256 (M$^+$+2, 6), 255 (M$^+$+1, 9), 254 (M$^+$, 56), 191 (95), 159 (base), 91 (50). HRMS m/z: M$^+$ Calcd for $C_{13}H_{18}OS_2$: 254.0799. Found: 254.0806.

Reaction of 2-*tert*-Butylphenol (2h) with Reagent 1 under Method A Dimethyl sulfide (1.1 ml, 15.0 mmol) was added dropwise to a suspension of NCS (1875 mg, 14.0 mmol) in anhydrous CH_2Cl_2 (100 ml) at −78 °C under Ar, and stirring was continued for 1 h at the same temperature. Then, a solution of 2-*tert*-butylphenol (**2h**) (1.40 g, 9.3 mmol) in anhydrous CH_2Cl_2 (15 ml) was added at the same temperature. After 1 h, triethylamine (2.0 ml, 14.3 mmol) was added to the mixture, and stirring was continued for 1 h at the same temperature. Cooled brine (30 ml) was added to the mixture, and the whole was extracted with hexane (100 ml). The organic layer was washed with brine (2 × 30 ml) and dried over anhydrous magnesium sulfate. The solvent was evaporated off, and the resulting residue was purified by column chromatography on silica gel (eluent, 5% ether in hexane). The first eluates yielded 2-*tert*-butyl-6-methylthiomethylphenol (0.63 g, 32% yield) as a colorless oil. IR (neat): 3580 cm^{-1}. ^{1}H-NMR δ: 1.43 [9H, s, C(CH$_3$)$_3$], 1.95 (3H, s, CH$_3$-S), 3.78 (2H, s, CH$_2$-S), 6.60—7.27 (3H, m, arom-H). MS m/z (%): 210 (M$^+$, 17), 163 (72), 147 (base). HRMS m/z: M$^+$ Calcd for $C_{12}H_{18}OS$: 210.1078. Found: 210.1070. The second eluates yielded a mixture of the starting material and **4h** (5 : 1, 0.58 g) as an oil.

General Method for Preparation of 2,4-Cyclohexadien-1-ones (6, 7) from Phenols (2) Method C: Synthesis of 2,6,6-Tris(methylthiomethyl)-2,4-cyclohexadien-1-ones (6q—u and/or 7r—v) Dimethyl sulfide (2.6 ml, 35.4 mmol) was added dropwise to a suspension of NCS (4473 mg, 33.5 mmol) in anhydrous CH_2Cl_2 (238 ml) at −78 °C under argon, and stirring was continued for 1 h at the same temperature. Then, a solution of a 2,6-unsubstituted phenol (**2**) (6.7 mmol) in anhydrous CH_2Cl_2 (15 ml) was added at the same temperature. After 1 h, triethylamine (4.9 ml, 35.2 mmol) was added to the mixture, and stirring was continued for 1 h at the same temperature. Cooled 10% aqueous NaOH (14 ml) was added to the mixture. The subsequent procedure was similar to method A, giving 2,6,6-tris(methylthiomethyl)-2,4-cyclohexadien-1-one (**6** and/or **7**).

2,6,6-Tris(methylthiomethyl)-2,4-cyclohexadien-1-one (6r)[5c] IR (neat): 1655, 1636 cm^{-1}. UV nm (log ε): 305 (3.86). ^{1}H-NMR δ: 2.05 (3H, s, CH$_3$-S), 2.07 (6H, s, CH$_3$-S), 2.90 (4H, ABq, J=12.6 Hz, CH$_2$-S), 3.38 (2H, s, CH$_2$-S), 6.36—6.49 (2H, m, C4-H and C5-H), 7.00—7.03 (1H, m, C3-H). ^{13}C-NMR δ: 15.6 (CH$_3$-S), 17.9 (CH$_3$-S), 31.7 (C2-CH$_2$), 43.8 (C6-CH$_2$), 56.8 (C6), 123.4 (C4), 133.8 (C2), 139.0 (C5 or C3), 143.2 (C3 or C5), 201.8 (C1). MS m/z (%): 274 (M$^+$, 2), 227 (3), 214 (18), 151 (48), 119 (50), 108 (43), 91 (47), 61 (base). HRMS m/z: M$^+$ Calcd for $C_{12}H_{18}OS_3$: 274.0520. Found: 274.0540.

3-Methyl-2,6,6-tris(methylthiomethyl)-2,4-cyclohexadien-1-one (6s) and 5-Methyl-2,6,6-tris(methylthiomethyl)-2,4-cyclohexadien-1-one (7s) From 3-methylphenol (**2s**), an inseparable mixture of **6s** and **7s** was obtained. IR (neat): 1648, 1635 cm^{-1}. UV nm (log ε): 309 (3.85). MS m/z (%): 290 (M$^+$+2, 1), 289 (M$^+$+1, 2), 288 (M$^+$, 10), 227 (6), 180 (77), 165 (base), 61 (84). HRMS m/z: M$^+$ Calcd for $C_{13}H_{20}OS_3$: 288.0676. Found: 288.0692. **6s**: ^{1}H-NMR δ: 2.06 (6H, s, C6-C-S-CH$_3$), 2.10 (3H, s, C2-C-S-CH$_3$), 2.20 (3H, s, C3-CH$_3$), 2.88 (4H, ABq, J=12.4 Hz, C6-CH$_2$), 3.53 (2H, s, C2-CH$_2$), 6.34 (2H, s, C4-H and C5-H). ^{13}C-NMR δ: 15.8 (C2-C-S-CH$_3$), 17.9 (C6-C-S-CH$_3$), 20.8 (C3-CH$_3$), 27.2 (C2-CH$_2$), 43.8 (C6-CH$_2$), 55.0 (C6), 128.7 (C4), 131.1 (C2), 141.4 (C5), 150.4 (C3), 200.6 (C1). **7s**: ^{1}H-NMR δ: 1.98 (3H, s, C5-CH$_3$), 2.01 (6H, s, C6-C-S-CH$_3$), 2.04 (3H, s, C2-C-S-CH$_3$), 2.93 (4H, ABq, J=12.4 Hz, C6-CH$_2$), 3.37 (2H, s, C2-CH$_2$), 6.28 (1H, d, J=6.4 Hz, C4-H), 6.96 (1H, d, J=6.4 Hz, C3-H). ^{13}C-NMR δ: 15.4 (C2-C-S-CH$_3$), 17.1 (C6-C-S-CH$_3$), 19.3 (C5-CH$_3$), 31.7 (C2-CH$_2$), 43.4 (C6-CH$_2$), 58.9 (C6), 122.8 (C4), 131.6 (C2), 140.0 (C3), 150.4 (C5), 202.4 (C1).

3,4-Dimethyl-2,6,6-tris(methylthiomethyl)-2,4-cyclohexadien-1-one (6t) and 4,5-Dimethyl-2,6,6-tris(methylthiomethyl)-2,4-cyclohexadien-1-one (7t) From 3,4-dimethylphenol (**2t**), an inseparable mixture of **6t** and **7t** was obtained. IR (neat): 1658, 1635 cm^{-1}. UV nm (log ε): 338 (3.50). MS m/z (%): 302 (M$^+$, 0.5), 242 (1), 194 (24), 61 (base). **6t**: ^{1}H-NMR δ: 1.98 (3H, s, C4-CH$_3$), 2.05 (9H, s, C6-C-S-CH$_3$ and C3-CH$_3$), 2.10 (3H, s, C2-C-S-CH$_3$), 2.85 (4H, ABq, J=12.4 Hz, C6-CH$_2$), 3.57 (2H, s, C2-CH$_2$), 6.09 (1H, s, C5-H). ^{13}C-NMR δ: 15.8 (C2-C-S-CH$_3$), 17.1 C4-CH$_3$), 17.9 (C6-C-S-CH$_3$), 20.6 (C3-CH$_3$), 27.7 (C2-CH$_2$), 44.0 (C6-CH$_2$), 54.9 (C6), 131.3 and 132.9 (C4 and C2), 137.6 (C5), 152.3 (C3), 200.9 (C1). **7t**: ^{1}H-NMR δ: 1.88 (6H, br s, C2-C-S-CH$_3$ and C4-CH$_3$), 1.99 (3H, s, C5-CH$_3$), 2.19 (6H, s, C6-C-S-CH$_3$), 2.94 (4H, ABq, J=12.4 Hz, C6-CH$_2$), 3.38 (2H, s, C2-CH$_2$), 6.89 (1H, s, C3-H). ^{13}C-NMR δ: 15.2 and 15.5 (C2-C-S-CH$_3$ and C4-CH$_3$), 17.8 (C6-C-S-CH$_3$), 18.8 (C5-CH$_3$), 31.4 (C2-CH$_2$), 43.7 (C6-CH$_2$), 58.6 (C6), 127.9 (C4), 137.9 (C2), 143.1 (C5), 146.0 (C3), 202.4 (C1).

3-Ethyl-2,6,6-tris(methylthiomethyl)-2,4-cyclohexadien-1-one (6u) and 5-Ethyl-2,6,6-tris(methylthiomethyl)-2,4-cyclohexadien-1-one (7u) From 3-ethylphenol (**2u**), an inseparable mixture of **6u** and **7u** was obtained. IR (neat): 1645, 1635 cm^{-1}. UV nm (log ε): 305 (3.45). MS m/z (%): 302 (M$^+$, 3), 194 (base), 179 (90), 108 (66). HRMS m/z: M$^+$ Calcd for $C_{14}H_{22}OS_3$: 302.0833. Found: 302.0837. **6u**: ^{1}H-NMR δ: 1.20 (3H, t, J=7.4 Hz, CH$_3$-CH$_2$), 2.06 (6H, s, C6-C-S-CH$_3$), 2.12 (3H, s, C2-C-S-CH$_3$), 2.49 (2H, q, J=7.4 Hz, C3-CH$_2$), 2.88 (4H, ABq, J=12.6 Hz, C6-CH$_2$), 3.53 (2H, s, C2-CH$_2$), 6.38 (2H, s, C4-H and C5-H). ^{13}C-NMR δ: 12.8 (CH$_3$-CH$_2$), 16.0 (C2-C-S-CH$_3$), 17.9 (C6-C-S-CH$_3$), 26.8 (C2-CH$_2$), 27.1 (C3-CH$_2$), 43.8 (C6-CH$_2$), 54.9 (C6), 127.0 (C4), 130.1 (C2), 141.8 (C5), 155.6 (C3), 201.1 (C1). **7u**: ^{1}H-NMR δ: 1.20 (3H, t, J=7.4 Hz, CH$_3$-CH$_2$), 1.99 (6H, s, C6-C-S-CH$_3$), 2.05 (3H, s, C2-C-S-CH$_3$), 2.27 (2H, q, J=7.4 Hz, C5-CH$_2$), 2.95 (4H, ABq, J=12.1 Hz, C6-CH$_2$), 3.38 (2H, s, C2-CH$_2$), 6.30—6.32 (1H, m, C4-H), 7.03—7.05 (1H, m, C3-H). ^{13}C-NMR δ: 11.4 (CH$_3$-CH$_2$), 15.4 (C2-C-S-CH$_3$), 17.1 (C6-C-S-CH$_3$), 23.8 (C5-CH$_2$), 31.7 (C2-CH$_2$), 43.7 (C6-CH$_2$), 59.2 (C6), 119.8 (C4), 131.2 (C2), 140.0 (C3), 155.8 (C5), 202.5 (C1).

1,1,3-Tris(methylthiomethyl)-1,2,5,6,7,8-hexahydro-2-oxonaphthalene (7v) IR (neat): 1655, 1530 cm^{-1}. UV nm (log ε): 346 (3.56). ^{1}H-NMR δ: 1.73—1.74 (4H, m, C6-H and C7-H), 1.99 (6H, s, C1-C-S-CH$_3$), 2.06 (3H, s, C3-C-S-CH$_3$), 2.16—2.23 (2H, m, C8-H or C5-H), 2.31—2.36 (2H, m, C5-H or C8-H), 2.91 (4H, ABq, J=11.9 Hz, C1-CH$_2$-S), 3.38 (2H, s, C3-CH$_2$), 6.78 (1H, s, C4-H). ^{13}C-NMR δ: 15.5 (C3-C-S-CH$_3$),

17.1 (C1-C–S–$\underline{C}H_3$), 22.0 and 22.3 (C6 and C7), 25.2 and 29.3 (C5 and C8), 31.5 (C3-$\underline{C}H_2$), 43.8 (C1-$\underline{C}H_2$), 58.0 (C1), 129.3 (C4a), 131.2 (C3), 144.3 (C8a), 144.8 (C4), 202.8 (C2). MS *m/z* (%): 328 (M^+, 3), 280 (5), 267 (18), 220 (71), 205 (base), 173 (81), 108 (46), 61 (94). HRMS *m/z*: M^+ Calcd for $C_{16}H_{24}OS_3$: 328.0989. Found: 328.0977.

4-Allyl-2,6-bis(methylthiomethyl)phenol (8) 6-Allyl-2,6-bis(methylthiomethyl)-2,4-cyclohexadien-1-one (**5q**) was stirred at 160 °C under Ar for 5 h. Subsequently, purification by column chromatography on silica gel (hexane–ether, 8:2) afforded the title compound (**8**) in 75% yield as a colorless oil, bp 170—175 °C (0.15 Torr). IR (neat): 3300, 1635 cm^{-1}. ^{1}H-NMR δ: 1.97 (6H, s, CH_3–S), 3.26 (2H, d, J=6.6 Hz, C-4-CH_2), 3.71 (4H, s, CH_2–S), 5.00—5.05 (2H, m, $C\underline{H}_2$=CH), 5.84—5.96 (1H, m, $C\underline{H}$=CH_2), 6.88 (2H, s, C3-H and C5-H), 6.91 (1H, s, OH). ^{13}C-NMR δ: 14.6 (CH_3–S), 33.6 (CH_2–S), 39.1 (C4-$\underline{C}H_2$), 115.5 ($\underline{C}H_2$=CH), 124.0 (C2 and C6), 129.8 (C3 and C5), 131.2 (C4), 137.6 ($\underline{C}H$=CH_2), 151.7 (C1). MS *m/z* (%): 255 (M^++1, 2), 254 (M^+, 13), 159 (base), 61 (33). HRMS *m/z*: M^+ Calcd for $C_{13}H_{18}OS_2$: 254.0799. Found: 254.0807.

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