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TETRAHEDRON

Mn(III)-Based Reactions of Alkenes and Alkynes with Thiols. An Approach toward Substituted 2,3-Dihydro-1,4-oxathiins and Simple Route to (*E*)-Vinyl Sulfides[†]

Van-Ha Nguyen,[a] Hiroshi Nishino,[b]* Shougo Kajikawa,[a] and Kazu Kurosawa[c]

[a]Department of Environmental Science, Graduate School of Science and Technology, Kumamoto University, Kurokami 2-39-1, Kumamoto 860-8555, Japan

[b]Department of Chemistry, Faculty of Science, Kumamoto University, Kurokami 2-39-1, Kumamoto 860-8555, Japan

[c]Department of Environmental Science, Faculty of Science, Kumamoto University, Kurokami 2-39-1, Kumamoto 860-8555, Japan

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Abstract: The first example using manganese(III) acetate in the reaction of 1,1-diarylethenes with α-mercaptoketones was examined. A mixture of the ethenes and α-mercaptoketones was treated with manganese(III) acetate in acetic acid, affording cycloaddition products in moderate yields, together with substituted products. The reaction may involve the formation of a carbocation and subsequent cyclization to give the substituted 2,3-dihydro-1,4-oxathiin **3**. A similar reaction with thioglycolic acid gave 1,4-oxathiolan-2-one **7**. While thiyl radicals easily formed by manganese(III) oxidation with ethanethiol or benzenethiol reacted with alkynes to give preferentially (*E*)-vinyl sulfides **10** in quantitative yields.

INTRODUCTION

The reversible addition of thiyl radicals to carbon-carbon unsaturated bonds is a well-known reaction and has found widespread use in organic synthesis.[1] In this reaction, thiyl radicals were produced from thiols or disulfides by thermolysis,[2,5] AIBN,[2-4] BEt_3/O_2,[4] di-*tert*-butyl peroxide,[5] photolysis,[6] electroinitiation,[7] or transition-metal-catalysis.[8] It was also reported that the addition of organic dichalcogenide to acetylenes could be catalyzed by palladium complexes *via* a ligand-transfer process.[8b,c] In spite of many reports available in the literature concerning the Mn(III)-induced addition of α-keto radicals to carbon-carbon unsaturated bonds,[9] the use of manganese(III) acetate in a thiol/unsaturated hydrocarbon system still remains unexplored. In searching for other sources of the radical for the Mn(III)-oxidant system, we found that thiols could be effective in playing a similar role to 1,3-dicarbonyl compounds. Thus, the Mn(III)-based reaction of alkenes with α-mercaptoketones provided a simple route to substituted 2,3-dihydro-1,4-oxathiins. On the other hand, thiyl radicals which were easily formed by manganese(III) oxidation with thiols added alkynes to give preferentially (*E*)-vinyl sulfides in excellent yields. In this paper, we describe the results of our study and discuss the reaction pathway.

[†] Dedicated to the Memory of Professor Sir Derek H. R. Barton.

*Corresponding author. Hiroshi Nishino, Fax: +81(96)342-3320; E-mail: nishino@aster.sci.kumamoto-u.ac.jp

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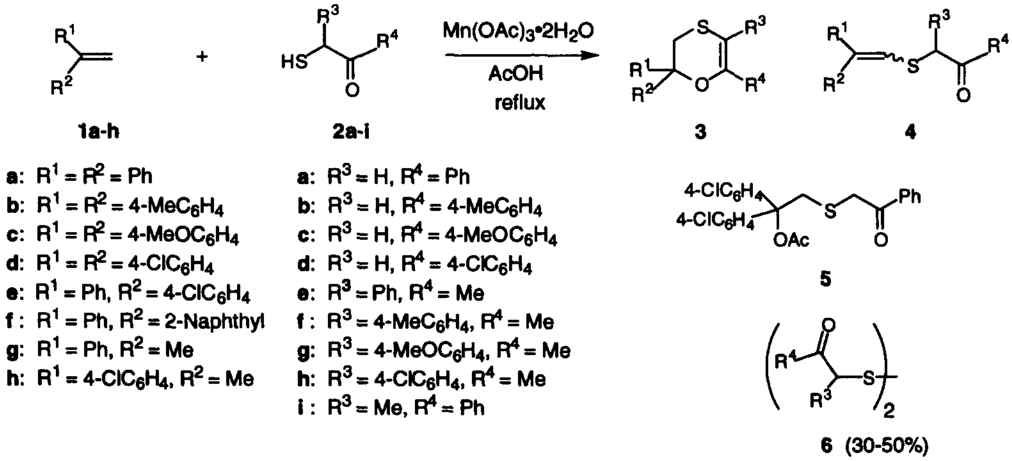
RESULTS AND DISCUSSION

Mn(III)-Based Reaction of 1,1-Disubstituted Ethenes 1a-h with α-Mercaptoketones 2a-i

Treatment of a mixture of 1,1-diphenylethene (**1a**, 1 mmol) and 2-mercaptoacetophenone (**2a**, 2 mmol) with manganese(III) acetate dihydrate (3 mmol) gave 2,3-dihydro-2,2,6-triphenyl-1,4-oxathiin (**3aa**) and 2-(2,2-diphenylethenylthio)acetophenone (**4aa**) in 46 and 26% yields, respectively (Scheme 1 and Table 1, Entry 1). Although both products have the same molecular formula ($C_{22}H_{18}OS$), their structures were easily established by spectroscopic methods. The vinylic proton of **3aa** appeared at $\delta = 5.75$ more shielded than that of **4aa** ($\delta = 6.67$). Furthermore, while the ^{13}C NMR and IR spectrum of **3aa** exhibited no sign of the presence of any carbonyl groups, those of **4aa** showed a carbonyl signal at $\delta = 193.9$ in ^{13}C NMR spectrum and at $\nu = 1680$ in IR spectrum. The same reaction in the absence of manganese(III) acetate did not give any products. Heating a solution of **1a** (1 mmol), **2a** (2 mmol), and AIBN (0.2 mmol) in benzene (16 mL) in a sealed tube at 120 °C for five hours resulted in the recovery of the starting materials.[2-4] A similar reaction of **1a** with other α-mercaptoketones **2b-i** also produced the corresponding 2,3-dihydro-1,4-oxathiins **3ab-ai** and vinyl sulfides **4ab-ai** in moderate yields as shown in Table 1. α-Mercaptoketones having an aryl group on the carbonyl group preferred the formation of the cyclized products **3** over the open-chain products **4** (Entries 1-4). Whereas, α-mercaptoketones bearing a methyl group preferentially afforded **4** (Entries 5-8). However, a similar reaction of **1a** with **2i** gave **3ai** only in 8% yield, together with **4ai** (61%) (Entry 9).

Reaction of other alkene **1b-h** with **2a** was also examined (Table 1, Entries 10-17). Using 1,1-bis(4-methylphenyl)ethene (**1b**) decreased the yield of **3** and increased the yield of **4** to 67% (Entry 10). Surprisingly, **5** (36%) was also isolated in a similar reaction of 1,1-bis(4-chlorophenyl)ethene (**1d**) along with **3da** (18%) and **4da** (14%) (Entry 12). Treatment of the reaction mixture with 10% sulfuric acid increased the yields of **3da** and **4da** to 22% and 34%, respectively (Entry 13). The reactions of unsymmetrical ethenes **1e** and **1f** afforded **4ea** and **4fa** as a 1:1 mixture of *E*/*Z* isomers, respectively (Entries 14, 15).



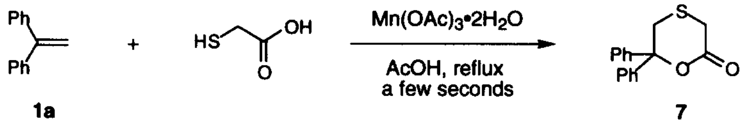
Scheme 1

Table 1. Mn(III)-Based Reaction of 1,1-Disubstituted Ethenes 1a-h and α-Mercaptoketones 2a-i in Boiling Acetic Acid[a]

Entry	Alkene	Thiol	Molar ratio[b]	Product (yield/%)[c]		
1	**1a**	**2a**	1:2:3	**3aa** (46)	**4aa** (26)	
2	**1a**	**2b**	1:3:4	**3ab** (39)	**4ab** (24)	
3	**1a**	**2c**	1:3:4	**3ac** (27)	**4ac** (24)	
4	**1a**	**2d**	1:2:3	**3ad** (29)	**4ad** (24)	
5	**1a**	**2e**	1:2:3	**3ae** (16)	**4ae** (42)	
6	**1a**	**2f**	1:3:4	**3af** (21)	**4af** (43)	
7	**1a**	**2g**	1:2:3	**3ag** (12)	**4ag** (36)	
8	**1a**	**2h**	1:3:4	**3ah** (12)	**4ah** (53)	
9	**1a**	**2i**	1:2:3	**3ai** (8)	**4ai** (61)	
10	**1b**	**2a**	1:2:3	**3ba** (9)	**4ba** (67)	
11	**1c**	**2a**	1:3:4		**4ca** (44)	
12	**1d**	**2a**	1:3:4	**3da** (18)	**4da** (14)	**5** (36)
13[d]	**1d**	**2a**	1:3:4	**3da** (22)	**4da** (34)	
14[d]	**1e**	**2a**	1:3:4	**3ea** (24)	**4ea** (18)[e]	
15	**1f**	**2a**	1:3:4	**3fa** (27)	**4fa** (36)[e]	
16	**1g**	**2a**	1:2:3	**3ga** (19)		
17	**1h**	**2a**	1:2:3	**3ha** (11)		

[a] All reactions finished within a few seconds. The reactions at lower temperature decreased product yields. [b] The best molar ratios of **1**:**2**:$Mn(OAc)_3 \cdot 2H_2O$ are shown. [c] Isolated yield based on the amount of **1** used. [d] After the reaction finished, several drops of 10% sulfuric acid were added and the mixture was stirred for another 30 min at 70 °C. [e] Products **4ea** and **4fa** were isolated as a 1:1 mixture of *E*/*Z* isomers which were determined by integration of the ^{1}H-NMR spectra.

The formation of cyclized product **3** prompted us to test this reaction with thioglycolic acid. Thus, manganese(III) acetate (5 mmol) was added to a boiling acetic acid solution of 1,1-diphenylethene **1a** (1 mmol) and thioglycolic acid (4 mmol) while vigorously stirring with a magnetic stirrer. After a normal work-up and the separation by silica gel TLC developing with chloroform, 1,4-oxathiolan-2-one **7** was obtained in 47% yield (Scheme 2).



1a

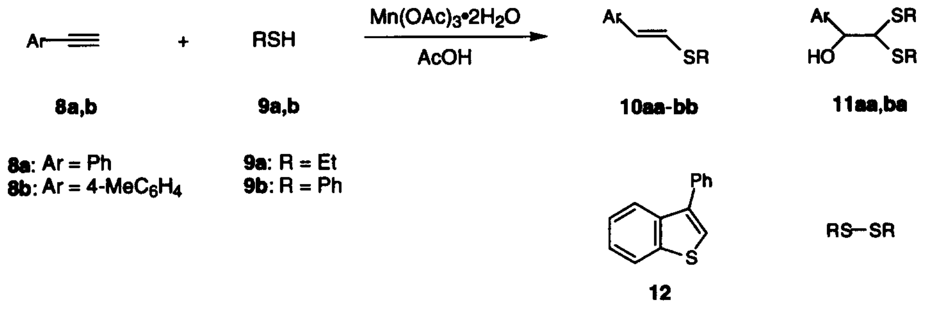
7

(47 %)

Scheme 2

Mn(III)-Based Reaction of Alkynes 8a,b with Thiols 9a,b

When ethanethiol (**9a**, 2 mmol) was put in a refluxing mixture of phenylacetylene (**8a**, 2 mmol) and manganese(III) acetate dihydrate (0.2 mmol) in acetic acid (16 mL), the dark-brown color of Mn(III) disappeared within 2 min. After the normal work-up, a separation of the resulting reaction mixture by TLC led to the isolation of vinyl sulfide **10aa** and thioacetal **11aa** in 90 and 4% yields, respectively (Scheme 3 and Table 2, Entry 18). It was interesting that **10aa** was obtained as a 6:4 mixture of *E*/*Z* isomers. The ratio of *E*/*Z* isomers was improved to 9:1 when the molar ratio of **9a** and manganese(III) acetate dihydrate increased (Entries



Scheme 3

Table 2. Mn(III)-Based Reaction of Alkynes 8a,b with Thiols 9a,b in Acetic Acid[a]

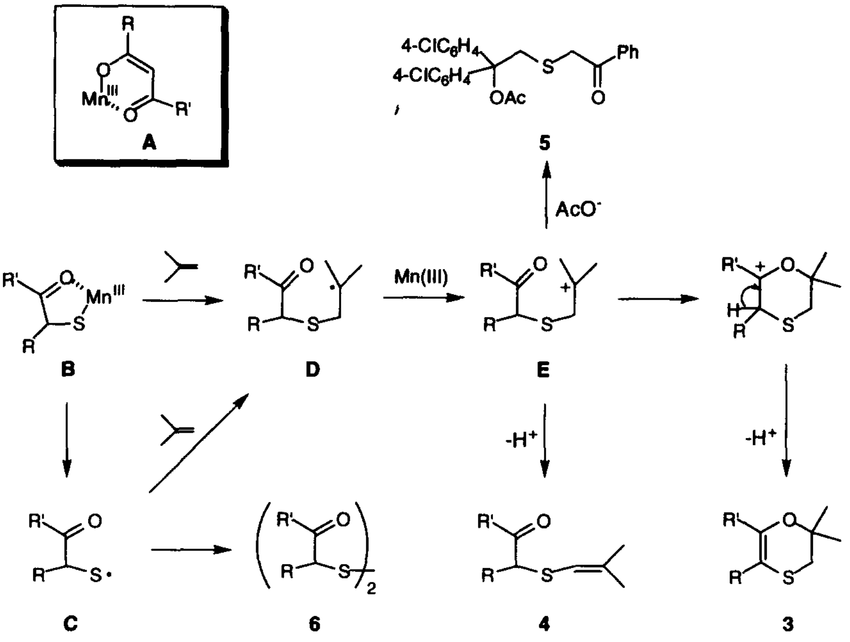
Entry	Alkyne	Thiol	Molar ratio[b]	Time min	Product (yield/%)[c] 10 (*E/Z*)[d]	11	12
18	**8a**	**9a**	1:1:0.1	2	**10aa** (90) (6/4)	**11aa** (4)	
19	**8a**	**9a**	1:1:0.25	2	**10aa** (90) (7/3)	**11aa** (5)	
20	**8a**	**9a**	1:1.25:0.25	2	**10aa** (90) (9/1)	**11aa** (5)	
21	**8a**	**9a**	1:1.5:0.5	2	**10aa** (78) (9/1)	**11aa** (7)	
22[e]	**8a**	**9a**	1:1:0.25	180	**10aa** (55) (7/3)	**11aa** (8)	
23	**8b**	**9a**	1:1:0.25	2	**10ba** (82) (7/3)	**11ba** (4)	
24	**8b**	**9a**	1:1.25:0.5	2	**10ba** (93) (9/1)	**11ba** (6)	
25	**8a**	**9b**	1:1.25:0.5	2	**10ab** (97) (9/1)		**12** (1)
26	**8b**	**9b**	1:1.25:0.5	2	**10bb** (98) (9.5/0.5)		

[a] The reaction was carried out at reflux temperature unless otherwise stated. [b] **8**:**9**:Mn(OAc)$_3$•2H$_2$O. [c] Isolated yield based on the amount of alkyne **8** used. [d] The *E/Z* ratio was determined by ^{1}H NMR. [e] The reaction was carried out under an argon atmosphere at 23 °C.

20, 21). However, the use of large amounts of **9a** and manganese(III) acetate dihydrate caused a decrease of the yield of **10aa** (Entry 21). A similar reaction of 4-methylphenylacetylene (**1b**) with **9a** also gave the corresponding vinyl sulfide **10ba** (93%) as a 9:1 mixture of *E/Z* isomers and thioacetal **11ba** (6%) (Entry 24). On the other hand, using benzenethiol (**9b**) instead of **9a** led to the formation of **10** in excellent yields (Entries 25, 26).

Reaction Pathway

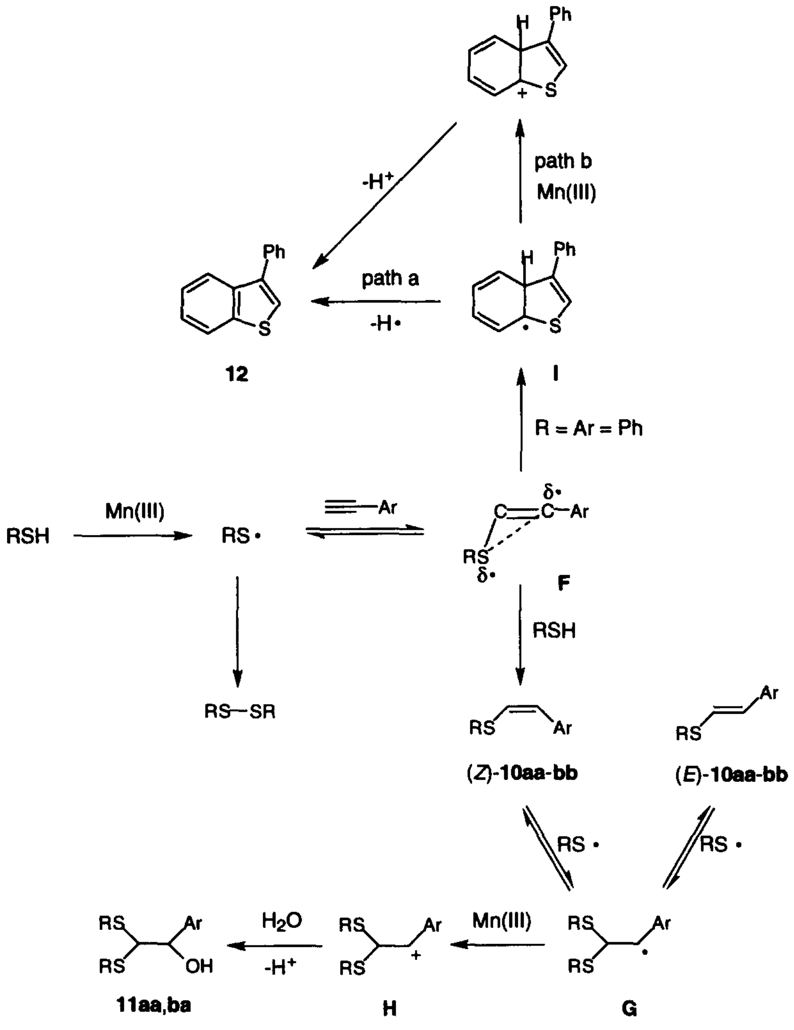
The formation of the products **3**, **4**, and **5** could be explained according to the pathway outlined in Scheme 4. It was reported that during the first step of the formation of α-keto radicals a new complex **A** was formed by a ligand-exchange process between Mn(III) acetate and enolizable carbonyl compounds.[10] It seemed reasonable to anticipate that a similar step would produce a complex **B** upon treatment of manganese(III) acetate with α-mercaptoketones. Subsequently, the interaction of an alkene and **B** itself[10c] or free thiyl radical **C** derived from the decomposition of **B** would produce a tertiary carbon radical **D**. Further oxidation of the radical **D** by manganese(III) acetate would give the corresponding carbocation **E**.[11] Cyclization of the electrophilic carbon onto the adjacent carbonyl group of **E** and subsequent β-proton elimination would give 2,3-dihydro-1,4-oxathiins **3**. On the other hand, β-proton elimination of **E** resulted in the formation of vinyl sulfides **4**, whereas the attack of an acetate ion in **E** produced **5**. Although we failed to confirm the formation



Scheme 4

of the new complex **B**, we were able to isolate disulfides **6** from the reaction mixture (30-50% yields based on the amount of α-mercaptoketone).

The formation of the anti-Markovnikov adducts **10aa-bb** supported a free radical mechanism in these thiol-alkyne additions.[12] Thus, an oxidation of thiols by manganese(III) acetate to produce thiyl radicals could be expected to be the first step of the process as shown in Scheme 5. When an excess amount of thiol RSH was used, disulfide RS-SR was isolated in 6-10% yields (based on the amount of the thiols). A reversible addition of these thiyl radicals to arylacetylenes could result in the formation of linear *sp*-hybridized π-radical **F**,[2,5,6b] which favors the approach of the radical scavenger from the side opposite to RS group (*trans*-addition) to form (*Z*)-vinyl sulfide **10**. The observed ratio of the *E*/*Z* isomers could be explained according to thermodynamic vinyl sulfide products (*E*)-**10aa-bb** which might have resulted from isomerization of the kinetic products (*Z*)-**10aa-bb** under the reaction conditions. Isomerization of alkenes, including vinyl sulfides, is known to be effectively promoted by reversible addition of thiyl radicals to carbon-carbon double bonds.[12] The reversible addition of thiyl radicals to vinyl sulfides **10** would produce carbon-centered radicals **G**, which could be further oxidized by manganese(III) acetate to give the corresponding carbocations **H**.[11] Subsequently, attack of water to **H** would afford α-hydroxythioacetals **11**. On the other hand, the *sp*-hybridized 2-(phenylthio)vinyl radical (**F**, R = Ar = Ph) could undergo homolytic intramolecular cyclization leading to the formation of radical **I**.[2,5] Benati and co-workers reported that the reaction of diphenyl disulfide with alkynes in the presence of a radical initiator afforded benzo[*b*]thiophene **12** *via* a radical pathway (path a) as shown in Scheme 5.[2,5] In the present reaction, it is reasonable that in the presence of manganese(III) acetate, the tertiary radical **I** would be



Scheme 5

easily oxidized to form the corresponding carbocation (path b in Scheme 5) which further eliminates one proton to give 3-phenylbenzo[*b*]thiophene **12**.

In conclusion, the Mn(III)-based reaction of 1,1-disubstituted ethenes with α-mercaptoketones provides a very simple route to 2,3-dihydro-1,4-oxathiin skeleton. It is worth to note that this skeleton is the core of carboxin (5,6-dihydro-*N*-phenyl-1,4-oxathiin-3-carboxamide) which is a well-known systemic plant fungicide.[13] On the other hand, the above results show that manganese(III) acetate was a quite effective radical initiator for the reaction of alkynes with thiols to produce vinyl sulfides in excellent yields and high regioselectivity.

EXPERIMENTAL

Measurements

The NMR spectra were recorded on a JNM EX400 FT NMR spectrometer (400 MHz for ^{1}H and 100 MHz for ^{13}C) or on a JNM EX90 (90 MHz for ^{1}H and 22.5 MHz for ^{13}C) with tetramethylsilane being used as the internal standard. Chemical shifts are reported in δ and coupling constants in Hz. The IR spectra were measured on a JASCO A-102 IR spectrometer. The IR spectral data are expressed in cm^{-1}. The Mass spectra were measured on either a Shimadzu GCMS QP2000GF or a JMS-LX1000 mass spectrometer. All the melting points were determined with a Yanaco micromelting-point apparatus MP-J3 and were uncorrected. Elemental analyses were performed at the Center of Instrumental Analysis, Kumamoto University, Kumamoto, and at the Elemental Analysis Center, Faculty of Science, Kyushu University, Fukuoka, Japan.

Materials

Manganese(II) acetate tetrahydrate was purchased from Wako Pure Chemical Ind., Ltd. Manganese(III) acetate dihydrate, $Mn(OAc)_3\bullet 2H_2O$, was prepared according to the method described in the literature.[14] 1,1-Diarylethenes were prepared by dehydration of the corresponding alcohols which were synthesized from substituted acetophenones and arylmagnesium bromides. α-Mercaptoketones were prepared according to the literature procedure.[15] Other alkenes, alkynes, ethanethiol, and benzenethiol were purchased from Wako Pure Chemical Ind., Ltd. and were used as received.

Manganese(III)-Based Reaction of 1,1-Disubstituted Ethenes 1a-h with α-Mercaptoketones 2a-i

A general procedure was as follows. An ethene **1** (1 mmol) was placed in a 50mL flask equipped with a magnetic stirrer. Glacial acetic acid (16 mL) and an α-mercaptoketone **2** (2-3 mmol) were added. The mixture was stirred and heated in an oil bath until reflux, and then manganese(III) acetate dihydrate (3-4 mmol) was added. The exact molar ratios of **1**:**2**:manganese(III) acetate dihydrate were shown in Table 1. The dark-brown color of Mn(III) disappeared within a few seconds. The solvent was removed *in vacuo* and the residue was triturated with water followed by an extraction with chloroform. The extract was dried over anhydrous sodium sulfate, filtered, and concentrated to dryness. The products were separated by silica gel TLC (Wakogel B-10 or Merck Kieselgel $60F_{254}$) using chloroform as the developing solvent. Analytical samples were further purified by recrystallization from the appropriate solvent mentioned below except for the liquid products.

2,3-Dihydro-2,2,6-triphenyl-1,4-oxathiin (3aa): colorless cubes (from $CHCl_3$), mp 180 °C; ^{1}H NMR ($CDCl_3$) 7.79-7.23 (15H, m, arom H), 5.75 (1H, s, H-5), 3.51 (2H, s, H-3); ^{13}C NMR ($CDCl_3$) 146.5, 143.4 (2C), 135.8 (arom C, C-6), 128.4 (6C), 127.7 (2C), 127.6, 126.2 (4C), 123.5 (2C) (arom CH), 91.1 (C-5), 79.7 (C-2), 33.4 (C-3). Anal. Calcd for $C_{22}H_{18}OS$: C, 79.96; H, 5.49. Found: C, 80.26; H, 5.47.

2,3-Dihydro-6-(4-methylphenyl)-2,2-diphenyl-1,4-oxathiin (3ab): colorless cubes (from diethyl ether-hexane), mp 169 °C; ^{1}H NMR ($CDCl_3$) 7.57-7.14 (14H, m, arom H), 5.66 (1H, s, H-5), 3.46 (2H, s, H-3), 2.34 (3H, s, Me); ^{13}C NMR ($CDCl_3$) 146.6, 143.4 (2C), 137.4, 133.1 (arom C, C-6), 129.1 (2C), 128.3 (4C), 127.6 (2C), 126.1 (4C), 123.4 (2C) (arom CH), 90.0 (C-5), 79.6 (C-2), 33.3 (C-3), 21.2 (Me). Anal. Calcd for $C_{23}H_{20}OS$: C, 80.19; H, 5.85. Found: C, 79.89; H, 5.93.

2,3-Dihydro-6-(4-methoxyphenyl)-2,2-diphenyl-1,4-oxathiin (3ac): colorless needles (from diethyl ether-hexane), mp 148 °C; ^1H NMR ($CDCl_3$) 7.62-6.88 (14H, m, arom H), 5.57 (1H, s, H-5), 3.80 (3H, s, OMe), 3.48 (2H, s, H-3); ^{13}C NMR ($CDCl_3$) 159.2, 146.4, 143.4 (2C), 128.8 (arom C, C-6), 128.3 (4C), 127.6 (2C), 126.2 (4C), 124.8 (2C), 113.7 (2C) (arom CH), 88.8 (C-5), 79.7 (C-2), 55.3 (OMe), 33.3 (C-3). Anal. Calcd for $C_{23}H_{20}O_2S$: C, 76.63; H, 5.59. Found: C, 76.57; H, 5.60.

6-(4-Chlorophenyl)-2,3-dihydro-2,2-diphenyl-1,4-oxathiin (3ad): colorless needles (from diethyl ether-hexane), mp 180 °C; ^1H NMR ($CDCl_3$) 7.58-7.26 (14H, m, arom H), 5.72 (1H, s, H-5), 3.47 (2H, s, H-3); ^{13}C NMR ($CDCl_3$) 145.5, 143.2 (2C), 134.2, 133.2 (arom C, C-6), 128.5 (2C), 128.4 (4C), 127.8 (2C), 126.1 (4C), 124.6 (2C) (arom CH), 92.0 (C-5), 79.7 (C-2), 33.3 (C-3). Anal. Calcd for $C_{22}H_{17}ClOS$: C, 72.42; H, 4.69. Found: C, 72.43; H, 4.86.

2,3-Dihydro-6-methyl-2,2,5-triphenyl-1,4-oxathiin (3ae): yellow liquid; ^1H NMR ($CDCl_3$) 7.45-7.10 (15H, m, arom H), 3.58 (2H, s, H-3), 2.00 (3H, s, Me); ^{13}C NMR ($CDCl_3$) 143.6 (2C), 142.8, 138.3 (arom C, C-6), 129.8 (2C), 128.2 (4C), 128.0 (2C), 127.5 (2C), 127.1, 126.2 (4C) (arom CH), 103.5 (C-5), 79.1 (C-2), 35.6 (C-3), 19.7 (Me); MS *m/z* (rel intensity) 344 (M^+, 30), 180 (100), 165 (27), 121 (37), 105 (14), 77 (16). HRMS Found: *m/z* 344.1194. Calcd for $C_{23}H_{20}OS$: M, 344.1235.

2,3-Dihydro-5-(4-methylphenyl)-6-methyl-2,2-diphenyl-1,4-oxathiin (3af): yellow liquid; ^1H NMR ($CDCl_3$) 7.44-7.00 (14H, m, arom H), 3.56 (2H, s, H-3), 2.27 (3H, s, Me), 2.00 (3H, s, Me); ^{13}C NMR ($CDCl_3$) 143.7 (2C), 142.6, 136.8, 135.3 (arom C, C-6), 129.6 (2C), 128.7 (2C), 128.2 (4C), 127.4 (2C), 126.2 (4C) (arom CH), 103.3 (C-5), 79.1 (C-2), 35.7 (C-3), 21.1, 19.7 (Me); MS *m/z* (rel intensity) 358 (M^+, 21), 342 (14), 267 (12), 180 (100), 165 (34), 135 (89), 105 (15), 91 (17). HRMS Found: *m/z* 358.1377. Calcd for $C_{24}H_{22}OS$: M, 358.1391.

2,3-Dihydro-5-(4-methoxyphenyl)-6-methyl-2,2-diphenyl-1,4-oxathiin (3ag): yellow liquid; ^1H NMR ($CDCl_3$) 7.44-6.75 (14H, m, arom H), 3.74 (3H, s, OMe), 3.56 (2H, s, H-3), 2.00 (3H, s, Me); ^{13}C NMR ($CDCl_3$) 158.7, 143.7 (2C), 142.6, 130.6 (arom C, C-6), 130.9 (2C), 128.2 (4C), 127.5 (2C), 126.2 (4C), 113.5 (2C) (arom CH), 103.0 (C-3), 79.1 (C-2), 55.2 (OMe), 35.7 (C-3), 19.7 (Me); MS *m/z* (rel intensity) 374 (M^+, 20), 194 (20), 180 (82), 165 (36), 151 (100), 136 (12), 108 (10). HRMS Found: *m/z* 374.1366. Calcd for $C_{24}H_{22}O_2S$: M, 374.1340.

5-(4-Chlorophenyl)-2,3-dihydro-6-methyl-2,2-diphenyl-1,4-oxathiin (3ah): yellow liquid; ^1H NMR ($CDCl_3$) 7.44-7.03 (14H, m, arom H), 3.56 (2H, s, H-3), 2.00 (3H, s, Me); ^{13}C NMR ($CDCl_3$) 143.5 (2C), 143.3, 136.8, 132.9 (arom C, C-6), 131.2 (2C), 128.3 (6C), 127.6 (2C), 126.2 (4C) (arom CH), 102.4 (C-5), 79.3 (C-2), 35.5 (C-3), 19.7 (Me); MS *m/z* (rel intensity) 378 (M^+, 50), 180 (100), 165 (78), 151 (71), 77 (14). HRMS Found: *m/z* 378.0867. Calcd for $C_{23}H_{19}ClOS$: M, 378.0845.

2,3-Dihydro-5-methyl-2,2,6-triphenyl-1,4-oxathiin (3ai): colorless prisms (from diethyl ether-hexane), mp 126 °C; ^{1}H NMR (CDCl$_3$) 7.52-7.24 (15H, m, arom H), 3.55 (2H, s, H-3), 1.78 (3H, s, Me); ^{13}C NMR (CDCl$_3$) 144.0 (2C), 143.0, 136.9 (arom C, C-6), 128.8 (2C), 128.2 (4C), 128.0 (2C), 127.6, 127.4 (2C), 126.2 (4C) (arom CH), 100.6 (C-5), 79.1 (C-2), 34.9 (C-3), 19.3 (Me). Anal. Calcd for $C_{23}H_{20}OS$: C, 80.19; H, 5.85. Found: C, 80.19; H, 5.96.

2,3-Dihydro-2,2-bis(4-methylphenyl)-6-phenyl-1,4-oxathiin (3ba): colorless cubes (from diethyl ether-hexane), mp 145-146 °C; ^{1}H NMR (CDCl$_3$) 7.67-7.11 (13H, m, arom H), 5.74 (1H, s, H-5), 3.47 (2H, s, H-3), 2.31 (6H, s, Me x 2); ^{13}C NMR (CDCl$_3$) 146.6, 140.7 (2C), 137.4 (2C), 135.9 (arom C, C-6), 129.1 (4C), 128.4 (2C), 127.5, 126.1 (4C), 123.5 (2C) (arom CH), 90.9 (C-5), 79.6 (C-2), 33.5 (C-3), 21.1 (2C) (Me). Anal. Calcd for $C_{24}H_{22}OS$: C, 80.41; H, 6.18. Found: C, 80.39; H, 6.40.

2,2-Bis(4-chlorophenyl)-2,3-dihydro-6-phenyl-1,4-oxathiin (3da): colorless needles (from diethyl ether-hexane), mp 118 °C; ^{1}H NMR (CDCl$_3$) 7.63-7.22 (13H, m, arom H), 5.74 (1H, s, H-5), 3.42 (2H, s, H-3); ^{13}C NMR (CDCl$_3$) 146.3, 141.5 (2C), 135.3, 133.8 (2C) (arom C, C-6), 128.7 (4C), 128.5 (2C), 127.8, 127.6 (4C), 123.3 (2C) (arom CH), 91.3 (C-5), 78.8 (C-2), 33.2 (C-3). Anal. Calcd for $C_{22}H_{16}Cl_2OS$: C, 66.17; H, 4.04. Found: C, 66.34; H, 4.22.

2-(4-Chlorophenyl)-2,3-dihydro-2,6-diphenyl-1,4-oxathiin (3ea): colorless neddles (from diethyl ether-hexane), mp 161 °C; ^{1}H NMR (CDCl$_3$) 7.66-7.27 (14H, m, arom H), 5.75 (1H, s, H-5), 3.46 (2H, s, H-3); ^{13}C NMR (CDCl$_3$) 146.4, 143.1, 141,8, 135.6, 133.6 (arom C, C-6), 128.6 (2C), 128.5 (2C), 128.4 (2C), 127.9, 127.8 (2C), 127.7, 126.0 (2C), 123.4 (2C) (arom CH), 91.2 (C-5), 79.3 (C-2), 33.3 (C-3). Anal. Calcd for $C_{22}H_{17}ClOS$: C, 72.42; H, 4.69. Found: C, 72.55; H, 4.75.

2,3-Dihydro-2-(2-naphthyl)-2,6-diphenyl-1,4-oxathiin (3fa): yellow liquid; ^{1}H NMR (CDCl$_3$) 7.92-7.25 (17H, m, arom H), 5.74 (1H, s, H-5), 3.60 (1H, d, J = 3.67, H$_a$-3), 3.55 (1H, d, J = 3.67, H$_b$-3); ^{13}C NMR (CDCl$_3$) 146.6, 143.4, 140.5, 135.8, 132.9, 132.7 (arom C, C-6), 128.4 (4C), 128.2, 127.7, 127.6, 127.5, 126.3 (4C), 126.1, 125.1, 124.4, 123.5 (2C) (arom CH), 91.3 (C-5), 79.8 (C-2), 33.3 (C-3); MS *m/z* (rel intensity) 380 (M$^+$, 17), 275 (20), 230 (100), 215 (32), 105 (40), 77 (24). HRMS Found: *m/z* 380.1260. Calcd for $C_{26}H_{20}OS$: M, 380.1235.

2,3-Dihydro-2-methyl-2,6-diphenyl-1,4-oxathiin (3ga): yellow liquid; ^{1}H NMR (CDCl$_3$) 7.63-7.27 (10H, m, arom H), 5.72 (1H, s, H-5), 3.14 (1H, d, J = 3.19, H$_a$-3), 3.00 (1H, d, J= 3.19, H$_b$-3), 1.74 (3H, s, Me); ^{13}C NMR (CDCl$_3$) 146.2, 144.7, 136.1 (arom C, C-6), 128.4 (2C), 128.3 (2C), 127.6, 127.4, 124.5 (2C), 123.7 (2C) (arom CH), 90.1 (C-5), 77.3 (C-2), 34.5 (C-3), 27.7 (Me); MS *m/z* (rel intensity) 268 (M$^+$, 20), 163 (34), 129 (20), 118 (100), 105 (76), 91 (20), 77 (85), 51 (31). HRMS Found: *m/z* 268.0929. Calcd for $C_{17}H_{16}OS$: M, 268.0922.

2-(4-Chlorophenyl)-2,3-dihydro-2-methyl-6-phenyl-1,4-oxathiin (3ha): yellow liquid; ^{1}H NMR (CDCl$_3$) 7.61-7.29 (9H, m, arom H), 5.72 (1H, s, H-5), 3.12 (1H, d, J = 3.19, H$_a$-3), 3.00 (1H, d, J

= 3.19, H_b-3), 1.73 (3H, s, Me); ^{13}C NMR ($CDCl_3$) 146.1, 143.2, 135.9, 133.2 (arom C, C-6), 128.6 (2C), 128.4 (2C), 127.8, 126.1 (2C), 123.6 (2C) (arom CH), 90.2 (C-5), 77.3 (C-2), 34.3 (C-3), 28.0 (Me); MS *m/z* (rel intensity) 302 (M^+, 23), 252 (12), 230 (20), 180 (30), 152 (63), 105 (100), 77 (62). HRMS Found: *m/z* 302.0551. Calcd for $C_{17}H_{15}ClOS$: M, 302.0532.

2-(2,2-Diphenylethenylthio)acetophenone (4aa): colorless needles (from diethyl ether-hexane), mp 97 °C; IR 1680 (C=O); ^{1}H NMR ($CDCl_3$) 7.94-7.17 (15H, m, arom H), 6.67 (1H, s, =CH), 3.99 (2H, s, CH_2); ^{13}C NMR ($CDCl_3$) 193.9 (C=O), 141.3, 140.6, 139.1, 135.1 (arom C, $Ph_2\underline{C}$=), 133.5, 129.6 (2C), 128.8 (2C), 128.7 (2C), 128.3 (2C), 128.2 (2C), 127.7, 127.2, 127.1 (2C) (arom CH), 122.9 (=CH), 39.3 (CH_2). Anal. Calcd for $C_{22}H_{18}OS$: C, 79.96; H, 5.49. Found: C, 80.05; H, 5.30.

4'-Methyl-2-(2,2-diphenylethenylthio)acetophenone (4ab): colorless prisms (from diethyl ether-hexane), mp 79-80 °C; IR 1680 (C=O); ^{1}H NMR ($CDCl_3$) 7.85-7.19 (14H, m, arom H), 6.68 (1H, s, =CH), 3.97 (2H, s, CH_2), 2.39 (3H, s, Me); ^{13}C NMR ($CDCl_3$) 193.7 (C=O), 144.4, 141.3, 140.3, 139.1, 132.5 (arom C, $Ph_2\underline{C}$=), 129.7 (2C), 129.4 (2C), 128.9 (2C), 128.3 (2C), 128.2 (2C), 127.6, 127.1 (3C) (arom CH), 123.0 (=CH), 39.2 (CH_2), 21.7 (Me). Anal. Calcd for $C_{23}H_{20}OS$: C, 80.19 H, 5.85. Found: C, 80.32; H, 5.97.

4'-Methoxy-2-(2,2-diphenylethenylthio)acetophenone (4ac): yellow liquid; IR 1680 (C=O); ^{1}H NMR ($CDCl_3$) 7.94-6.90 (14H, m, arom H), 6.69 (1H, s, =CH), 3.96 (2H, s, CH_2), 3.84 (3H, s, OMe); ^{13}C NMR ($CDCl_3$) 192.7 (C=O), 163.8, 141.3, 140.3, 139.2, 128.0 (arom C, $Ph_2\underline{C}$=), 131.1 (2C), 129.7 (2C), 128.3 (2C), 128.2 (2C), 127.6, 127.1 (3C), 113.9 (2C) (arom CH), 123.1 (=CH), 55.5 (OMe), 39.1 (CH_2); MS *m/z* (rel intensity) 360 (M^+, 77), 210 (34), 196 (28), 178 (45), 135 (100), 91 (29), 77 (71), 51 (15). HRMS Found: *m/z* 360.1181. Calcd for $C_{23}H_{20}O_2S$: M, 360.1184.

4'-Chloro-2-(2,2-diphenylethenylthio)acetophenone (4ad): yellow liquid; IR 1680 (C=O); ^{1}H NMR ($CDCl_3$) 7.86-7.18 (14H, m, arom H), 6.63 (1H, s, =CH), 3.94 (2H, s, CH_2); ^{13}C NMR ($CDCl_3$) 192.8 (C=O), 141.2, 141.0, 139.9, 139.0, 133.2 (arom C, $Ph_2\underline{C}$=), 130.2 (2C), 129.6 (2C), 129.0 (2C), 128.3 (2C), 128.2 (2C), 127.7, 127.3, 127.1 (2C) (arom CH), 122.4 (=CH), 39.2 (CH_2); MS *m/z* (rel intensity) 364 (M^+, 100), 225 (41), 191 (55), 139 (58), 91 (40). HRMS Found: *m/z* 364.0642. Calcd for $C_{22}H_{17}ClOS$: M, 364.0689.

1-(2,2-Diphenylethenylthio)-1-phenyl-2-propanone (4ae): colorless microcrystals (from diethyl ether-hexane), mp 67-68 °C; IR 1680 (C=O); ^{1}H NMR ($CDCl_3$) 7.35-7.10 (15H, m, arom H), 6.47 (1H, s, =CH), 4.85 (1H, s, CH), 2.14 (3H, s, Me); ^{13}C NMR ($CDCl_3$) 202.9 (C=O), 144.4, 141.3, 139.0, 135.1 (arom C, $Ph_2\underline{C}$=), 129.6 (2C), 129.0 (2C), 128.5 (2C), 128.4, 128.3 (2C), 128.2 (2C), 127.7, 127.2, 127.1 (2C) (arom CH), 121.5 (=CH), 62.5 (CH), 26.8 (Me). Anal. Calcd for $C_{23}H_{20}OS$: C, 80.19; H, 5.85. Found: C, 80.37; H, 6.12.

1-(4-Methylphenyl)-1-(2,2-diphenylethenylthio)-2-propanone (4af): colorless needles (from diethyl ether-hexane), mp 78 °C; IR 1680 (C=O); ^{1}H NMR ($CDCl_3$) 7.35-7.12 (14H, m, arom H), 6.48 (1H, s,

=CH), 4.82 (1H, s, CH), 2.30 (3H, s, Me), 2.13 (3H, s, Me); ^{13}C NMR ($CDCl_3$) 203.1 (C=O), 141.4, 141.0, 139.1, 138.2, 132.1 (arom C, $Ph_2\underline{C}=$), 129.7 (2C), 129.6 (2C), 128.4 (2C), 128.3 (2C), 128.2 (2C), 127.7, 127.2, 127.1 (2C) (arom CH), 121.7 (=CH), 62.3 (CH), 26.8, 21.1 (Me). Anal. Calcd for $C_{24}H_{22}OS$: C, 80.41; H, 6.18. Found: C, 80.62; H, 5.93.

1-(4-Methoxyphenyl)-1-(2,2-diphenylethenylthio)-2-propanone (4ag): colorless plates (from diethyl ether-hexane), mp 103 °C; IR 1680 (C=O); ^{1}H NMR ($CDCl_3$) 7.36-6.86 (14H, m, arom H), 6.47 (1H, s, =CH), 4.82 (1H, s, CH), 3.75 (3H, s, OMe), 2.13 (3H, s, Me); ^{13}C NMR ($CDCl_3$) 203.1 (C=O), 159.6, 141.5, 141.0, 139.1, 127.0 (arom C, $Ph_2\underline{C}=$), 129.7 (2C), 129.6 (2C), 128.3 (2C), 128.2 (2C), 127.7, 127.2, 127.1 (2C), 114.4 (2C) (arom CH), 121.7 (=CH), 61.9 (CH), 55.2, 26.8 (Me). Anal. Calcd for $C_{24}H_{22}O_2S$: C, 76.97; H, 5.92. Found: C, 77.17; H, 5.72.

1-(4-Chlorophenyl)-1-(2,2-diphenylethenylthio)-2-propanone (4ah): colorless needles (from diethyl ether-hexane), mp 107-108 °C; IR 1680 (C=O); ^{1}H NMR ($CDCl_3$) 7.36-7.12 (14H, m, arom H), 6.43 (1H, s, =CH), 4.80 (1H, s, CH), 2.16 (3H, s, Me); ^{13}C NMR ($CDCl_3$) 202.2 (C=O), 141.9, 141.2, 138.9, 134.3, 133.8 (arom C, $Ph_2\underline{C}=$), 129.9 (2C), 129.6 (2C), 129.1 (2C), 128.3 (2C), 128.2 (2C), 127.8, 127.4, 127.1 (2C) (arom CH), 120.8 (=CH), 61.4 (CH), 27.0 (Me). Anal. Calcd for $C_{23}H_{19}ClOS$: C, 72.91; H, 5.05. Found: C, 72.92; H, 5.04.

2-(2,2-Diphenylethenylthio)propiophenone (4ai): colorless needles (from diethyl ether-hexane), mp 78 °C; IR 1680 (C=O); ^{1}H NMR ($CDCl_3$) 7.95-7.12 (15H, m, arom H), 6.64 (1H, s, =CH), 4.40 (1H, q, J = 6.83, CH), 1.62 (3H, d, J = 6.83, Me); ^{13}C NMR ($CDCl_3$) 195.4 (C=O), 141.4 (2C), 139.2, 135.3 (arom C, $Ph_2\underline{C}=$) 133.1, 129.6 (2C), 128.6 (2C), 128.5 (2C), 128.2 (2C), 128.1 (2C), 127.5, 127.2, 127.0 (2C) (arom CH), 119.3 (=CH), 42.8 (CH), 17.1 (Me). Anal. Calcd for $C_{23}H_{20}OS$: C, 80.19; H, 5.85. Found: C, 80.19; H, 5.86.

2-[2,2-Bis(4-methylphenyl)ethenylthio]acetophenone (4ba): colorless needles (from diethyl ether-hexane), mp 88 °C; IR 1680 (C=O); ^{1}H NMR ($CDCl_3$) 7.90-7.01 (13H, m, arom H), 6.58 (1H, s, =CH), 3.92 (2H, s, CH_2), 2.30 (3H, s, Me), 2.27 (3H, s, Me); ^{13}C NMR ($CDCl_3$) 193.9 (C=O), 140.5, 138.7, 137.3, 136.8, 136.3, 135.0 (arom C, $Ar_2\underline{C}=$), 133.3, 129.5 (2C), 128.9 (2C), 128.8 (2C), 128.7 (2C), 128.6 (2C), 127.0 (2C) (arom CH), 121.5 (=CH), 39.3 (CH_2), 21.3, 21.0 (Me). Anal. Calcd for $C_{24}H_{22}OS$: C, 80.41; H, 6.18. Found: C, 80.44; H, 6.09.

2-[2,2-Bis(4-methoxyphenyl)ethenylthio]acetophenone (4ca): yellow liquid; IR 1680 (C=O); ^{1}H NMR ($CDCl_3$) 7.94-6.77 (13H, m, arom H), 6.47 (1H, s, =CH), 3.97 (2H, s, CH_2), 3.77 (3H, s, OMe), 3.75 (3H, s, OMe); ^{13}C NMR ($CDCl_3$) 194.1 (C=O), 158.9 (2C), 140.2, 135.1, 134.4, 131.6 (arom C, $Ar_2\underline{C}=$), 133.4, 130.9 (2C), 128.7 (2C), 128.6 (2C), 128.4 (2C), 113.5 (4C) (arom CH), 120.0 (=CH), 55.2, 55.1 (OMe), 39.4 (CH_2); MS *m/z* (rel intensity) 390 (M^+, 100), 271 (73), 256 (63), 252 (38), 227 (60), 152 (14), 121 (26), 105 (62), 77 (39). HRMS Found: *m/z* 390.1282. Calcd for $C_{24}H_{22}O_3S$: M, 390.1290.

2-[2,2-Bis(4-chlorophenyl)ethenylthio]acetophenone (4da): colorless needles (from diethyl ether-hexane), mp 85 °C; IR 1680 (C=O); ^{1}H NMR (CDCl$_3$) 7.96-7.07 (13H, m, arom H), 6.67 (1H, s, =CH), 4.03 (2H, s, CH$_2$); ^{13}C NMR (CDCl$_3$) 193.8 (C=O), 139.4 (2C), 138.2, 137.0, 134.9, 133.3 (arom C, Ar$_2\underline{C}$=), 133.7, 131.0 (2C), 128.8 (2C), 128.7 (2C), 128.6 (2C), 128.5 (2C), 128.3 (2C) (arom CH), 124.2 (=CH), 39.1 (CH$_2$). Anal. Calcd for $C_{22}H_{16}Cl_2OS$: C, 66.17; H, 4.04. Found: C, 66.35; H, 4.12.

A 1:1 (*E,Z*) Mixture of 2-[2-(4-Chlorophenyl)-2-phenylethenylthio]acetophenone (4ea): colorless microcrystals (from diethyl ether-hexane), mp 79 °C; IR 1680 (C=O); ^{1}H NMR (CDCl$_3$) 7.95-7.09 (28H, m, arom H), 6.67 (2H, s, =CH x 2), 4.02 (2H, s, CH$_2$), 4.00 (2H, s, CH$_2$); ^{13}C NMR (CDCl$_3$) 193.9, 193.8 (C=O), 140.9, 139.7, 139.4, 139.2 (2C), 138.6, 137.5, 134.9, 133.4, 132.9 (arom C, Ar$_2\underline{C}$=), 133.6 (2C), 131.0 (2C), 129.5 (2C), 128.7 (8C), 128.6 (2C), 128.5 (2C), 128.4 (2C), 128.3 (4C), 127.9, 127.4, 127.1 (2C) (arom CH), 123.6, 123.4 (=CH), 39.3, 39.1 (CH$_2$). Anal. Calcd for $C_{22}H_{17}ClOS$: C, 72.42; H, 4.69. Found: C, 72.38; H, 4.72.

A 1:1 (*E,Z*) Mixture of 2-[2-(2-Naphthyl)-2-phenylethenylthio]acetophenone (4fa): colorless microcrystals (from diethyl ether-hexane), mp 108 °C; IR 1680 (C=O); ^{1}H NMR (CDCl$_3$) 7.92-7.21 (34H, m, arom H), 6.81 (1H, s, =CH), 6.75 (1H, s, =CH), 3.99 (2H, s, CH$_2$), 3.96 (2H, s, CH$_2$); ^{13}C NMR (CDCl$_3$) 193.9 (2C) (C=O), 141.2, 140.4, 140.3, 139.0, 138.5, 136.5, 135.0, 134.9, 133.2, 133.1, 132.7, 132.5 (arom C, Ar$_2\underline{C}$=), 133.5 (2C), 129.7 (2C), 128.9, 128.7 (4C), 128.6 (4C), 128.4 (2C), 128.2 (2C), 128.1, 128.0, 127.9, 127.8 (2C), 127.6, 127.5 (2C), 127.3, 127.2 (2C), 126.1 (2C), 126.0 (2C), 125.8, 125.1 (arom CH), 123.6, 123.4 (=CH), 39.3, 39.2 (CH$_2$). Anal. Calcd for $C_{26}H_{20}OS$: C, 82.07; H, 5.29. Found: C, 82.16; H, 5.40.

2-[2-Acetoxy-2,2-bis(4-chlorophenyl)ethylthio]acetophenone (5): yellow liquid; IR 1742, 1680 (COO, C=O); ^{1}H NMR (CDCl$_3$) 7.80-7.23 (13H, m, arom H), 3.98 (2H, s, CH$_2$), 3.45 (2H, s, CH$_2$), 2.08 (3H, s, Ac); ^{13}C NMR (CDCl$_3$) 194.0 (C=O), 168.8 (COO), 141.4 (2C), 134.9, 133.6 (2C) (arom C), 133.4, 128.6 (2C), 128.5 (2C), 128.3 (4C), 127.6 (4C) (arom CH), 84.0 (C-O), 40.0, 37.7 (CH$_2$), 21.8 (Me). FABHRMS (MeOH-NBA-NaI) Found: *m/z* 481.0393. Calcd for $C_{24}H_{20}Cl_2O_3SNa$: 481.0408.

Bis(2-oxo-2-phenylethyl) disulfide (6a): colorless needles (from diethyl ether-hexane), mp 36-37 °C; IR 1680 (C=O); ^{1}H NMR (CDCl$_3$) 7.93-7.43 (10H, m, arom H), 4.19 (4H, s, CH$_2$ x 2); ^{13}C NMR (CDCl$_3$) 193.9 (2C) (C=O), 134.9 (2C) (arom C), 133.3 (2C), 128.3 (4C), 128.2 (4C) (arom CH), 45.0 (2C) (CH$_2$); MS *m/z* (rel intensity) 302 (M$^+$, 14), 152 (16), 105 (100), 77 (47). HRMS Found: *m/z* 302.0415. Calcd for $C_{16}H_{14}O_2S_2$: M, 302.0435. Anal. Calcd for $C_{16}H_{14}O_2S_2$: C, 63.55; H, 4.66. Found: C, 63.30; H, 4.74.

Bis[2-(4-methylphenyl)-2-oxoethyl] disulfide (6b): colorless plates (from diethyl ether-hexane), mp 73 °C; IR 1680 (C=O); ^{1}H NMR (CDCl$_3$) 7.81 (4H, m, arom H), 7.23 (4H, m, arom H), 4.14 (4H, s, CH$_2$ x 2), 2.39 (6H, s, Me x 2); ^{13}C NMR (CDCl$_3$) 194.0 (2C) (C=O), 144.6 (2C), 132.9 (2C) (arom C), 129.4

(4C), 128.8 (4C) (arom CH), 45.4 (2C) (CH_2), 21.7 (2C) (Me). Anal. Calcd for $C_{18}H_{18}O_2S_2$: C, 65.42; H, 5.49. Found: C, 65.42; H, 5.44.

Bis[2-(4-methoxyphenyl)-2-oxoethyl] disulfide (6c): colorless liquid; IR 1680 (C=O); ^{1}H NMR ($CDCl_3$) 7.89 (4H, m, arom H), 6.89 (4H, m, arom H), 4.12 (4H, s, CH_2 x 2), 3.83 (6H, s, MeO x 2); ^{13}C NMR ($CDCl_3$) 192.5 (2C) (C=O), 163.4 (2C), 127.8 (2C) (arom C), 130.5 (4C), 113.4 (4C) (arom CH), 55.0 (2C) (Me), 44.6 (2C) (CH_2); MS *m/z* (rel intensity) 362 (M^+, 4), 182 (11), 135 (100), 107 (13), 77 (24). HRMS Found: *m/z* 362.0662. Calcd for $C_{18}H_{18}O_4S_2$: M, 362.0646.

Bis[2-(4-chlorophenyl)-2-oxoethyl] disulfide (6d): colorless plates (from diethyl ether-hexane), mp 119 °C; IR 1680 (C=O); ^{1}H NMR ($CDCl_3$) 7.87 (4H, m, arom H), 7.44 (4H, m, arom H), 4.15 (4H, s, CH_2 x 2); ^{13}C NMR ($CDCl_3$) 193.0 (2C) (C=O), 140.3 (2C), 133.6 (2C) (arom C), 130.1 (4C), 129.1 (4C) (arom CH), 45.0 (2C) (CH_2). Anal. Calcd for $C_{16}H_{12}Cl_2O_2S_2$: C, 51.76; H, 3.26. Found: C, 51.79; H, 3.05.

Bis[2-oxo-1-phenylpropyl] disulfide (6e): yellow liquid; IR 1680 (C=O); ^{1}H NMR ($CDCl_3$) 7.36-7.24 (10H, m, arom H), 4.55 (1H, s, CH), 4.54 (1H, s, CH), 2.11 (3H, s, Me), 2.09 (3H, s, Me); ^{13}C NMR ($CDCl_3$) 203.2, 203.0 (C=O), 135.1, 134.9 (arom C), 129.1 (2C), 129.0 (2C), 128.9 (2C), 128.8 (2C), 128.7, 128.6 (arom CH), 66.4 (2C) (CH), 28.8, 28.7 (Me); MS *m/z* (rel intensity) 330 (M^+, 26), 222 (37), 176 (16), 133 (94), 123 (34), 105 (100), 77 (32). HRMS Found: *m/z* 330.0785. Calcd for $C_{18}H_{18}O_2S_2$: M, 330.0748.

Bis[1-(4-methylphenyl-2-oxopropyl] disulfide (6f): colorless liquid; IR 1680 (C=O); ^{1}H NMR ($CDCl_3$) 7.1-7.3 (8H, m, arom H), 4.56 (2H, s, CH x 2), 2.34 (3H, s, Me), 2.33 (3H, s, Me), 2.10 (3H, s, Me), 2.09 (3H, s, Me); ^{13}C NMR ($CDCl_3$) 203.4, 203.2 (C=O), 138.6, 138.5, 131.9, 131.8 (arom C), 129.7 (2C), 129.6 (2C), 128.8 (2C), 128.7 (2C) (arom CH), 66.1, 66.0 (CH), 28.7, 28.6, 21.1 (2C) (Me); MS *m/z* (rel intensity) 358 (M^+, 13), 315 (6), 294 (7), 250 (6), 147 (100), 135 (55), 119 (56), 91 (26). HRMS Found: *m/z* 358.1035. Calcd for $C_{20}H_{22}O_2S_2$: M, 358.1061.

Bis[1-(4-methoxyphenyl-2-oxopropyl] disulfide (6g): colorless liquid; IR 1680 (C=O); ^{1}H NMR ($CDCl_3$) 7.2-6.8 (8H, m, arom H), 4.60 (1H, s, CH), 4.58 (1H, s, CH), 3.79 (3H, s, OMe), 3.78 (3H, s, OMe), 2.12 (3H, s, Me), 2.11 (3H, s, Me); ^{13}C NMR ($CDCl_3$) 203.5, 203.4 (C=O), 159.9 (2C), 128.2, 128.0 (arom C), 130.2 (2C), 130.1 (2C), 114.5 (2C), 114.4 (2C) (arom CH), 65.7, 65.6 (CH), 55.3 (2C), 28.7, 28.6 (Me); MS *m/z* (rel intensity) 390 (M^+, 3), 374 (4), 331 (4), 194 (17), 163 (95), 151 (100), 135 (26). HRMS Found: *m/z* 390.0989. Calcd for $C_{20}H_{22}O_4S_2$: M, 390.0959.

Bis[1-(4-chlorophenyl-2-oxopropyl] disulfide (6h): colorless liquid; IR 1680 (C=O); ^{1}H NMR ($CDCl_3$) 7.4-7.2 (8H, m, arom H), 4.63 (1H, s, CH), 4.57 (1H, s, CH), 2.15 (3H, s, Me), 2.13 (3H, s, Me); ^{13}C NMR ($CDCl_3$) 202.6 (2C) (C=O), 134.8 (2C), 133.4, 133.3 (arom C), 130.3 (2C), 130.2 (2C), 129.2

(4C) (arom CH), 65.6, 65.4 (CH), 28.9, 29.8 (Me); MS *m/z* (rel intensity) 398 (M^+, 6), 200 (17), 167 (39), 155 (100), 139 (28). HRMS Found: *m/z* 398.0005. Calcd for $C_{18}H_{16}Cl_2O_2S_2$: M, 397.9969.

Bis[1-benzoylethyl] disulfide (6i): colorless liquid; IR 1680 (C=O); ^{1}H NMR ($CDCl_3$) 8.0-7.1 (10H, m, arom H), 4.47 (1H, q, *J* = 6.84, CH), 4.37 (1H, q, *J* = 6.84, CH), 1.55 (3H, d, *J* = 6.84, Me), 1.47 (3H, d, *J* = 6.84, Me); MS *m/z* (rel intensity) 330 (M^+, 66), 238 (13), 134 (29), 105 (100), 77 (98). HRMS Found: *m/z* 330.0764. Calcd for $C_{18}H_{18}O_2S_2$: M, 330.0748.

Manganese(III)-Based Reaction of 1,1-Diphenylethene 1a with Thioglycolic Acid

1,1-Diphenylethene **1a** (1 mmol) was placed in a 50mL flask equipped with a magnetic stirrer. Glacial acetic acid (16 mL) and thioglycolic acid (4 mmol) were added. The mixture was stirred and heated in an oil bath until reflux, and then manganese(III) acetate dihydrate (5 mmol) was added. The reaction has done for 1 min. After a similar work-up described above, 1,4-oxathiolan-2-one **7** was obtained in 47% yield.

6,6-Diphenyl-1,4-oxathiolan-2-one (7): colorless cubes (diethyl ether-hexane), mp 118 °C; IR 1740 (C=O); ^{1}H NMR ($CDCl_3$) 7.43-7.30 (10H, m, arom H), 3.51 (2H, s, CH_2), 2.97 (2H, s, CH_2); ^{13}C NMR ($CDCl_3$) 167.2 (C=O), 142.2 (2C) (arom C), 128.7 (4C), 128.3 (2C), 125.9 (4C) (arom CH), 87.7 (C-6), 33.3, 26.5 (CH_3). Anal. Calcd for $C_{16}H_{14}O_2S$: C, 71.08; H, 5.22. Found: C, 70.81; H, 5.44.

Mn(III)-Based Reaction of Alkynes 8a,b with Thiols 9a,b

A general procedure was as follows. An alkyne **8** (2 mmol) was placed in a 50mL flask equipped with a magnetic stirrer. Glacial acetic acid (16 mL) and manganese(III) acetate dihydrate (0.2-1 mmol) were added. The mixture was stirred and heated in an oil bath, and then a thiol **9** (2-3 mmol) was added just before refluxing. The exact molar ratios of **8**:**9**:manganese(III) acetate dihydrate were shown in Table 2. The dark-brown color of Mn(III) disappeared within 2 min. The solvent was removed *in vacuo* and the residue was triturated with water followed by an extraction with chloroform. The extract was dried over anhydrous sodium sulfate, filtered, and concentrated to dryness. The products were separated by silica gel TLC (Wakogel B-10 or Merck Kieselgel $60F_{254}$) using chloroform as the developing solvent. Diphenyl disulfide and diethyl disulfide were identified by comparison of their NMR and mass spectra with those of authetic samples. β-(Phenylthio)styrene (**10ab**)[2,10a] and 3-phenylbenzo[*b*]thiophene (**12**)[2,16] were also identified by comparison of their ^{1}H NMR spectra with those reported in the literature as well as mass spectral analysis. The new products were given below.

A 9:1 (*E,Z*) Mixture of β-(Ethylthio)styrene (10aa): pale yellow liquid; ^{1}H NMR ($CDCl_3$) 7.42-7.17 (5H, m, arom H), 6.56 (1.8H, *J* = 15.53, (*E*)-vinylic H), 6.21 (0.2H, *J* = 10.98, (*Z*)-vinylic H), 2.79 (2H, q, *J* = 7.20, $-\underline{CH_2}Me$), 1.33 (3H, t, *J* = 7.20, $-CH_2\underline{Me}$); MS *m/z* (rel intensity) 164 (M^+, 97), 135 (100), 91 (50), 77 (12). HRMS Found: *m/z* 164.0626. Calcd for $C_{10}H_{12}S$: M, 164.0660.

A 9:1 (*E,Z*) Mixture of β-Ethylthio-4-methylstyrene (10ba): pale yellow liquid; ^{1}H NMR ($CDCl_3$) 7.42-7.11 (4H, m, arom H), 6.5 (1.8H, *J* = 15.53, (*E*)-vinylic H), 6.16 (0.2H, *J* = 10.85, (*Z*)-vinylic H), 2.26 (3H, s, $-C_6H_4\underline{Me}$), 2.79, (2H, q, *J* = 7.20, $-\underline{CH_2}Me$), 1.33 (3H, t, *J* = 7.20, $-CH_2\underline{Me}$); MS *m/z* (rel intensity)

178 (M^+, 32), 149 (33), 134 (28), 119 (100), 105 (24), 91 (76). HRMS Found: *m/z* 178.0838. Calcd for $C_{11}H_{14}S$: M, 178.0816.

A 9.5:0.5 (*E*,*Z*) Mixture of β-Phenylthio-4-methylstyrene (10bb): pale yellow liquid; ^{1}H NMR ($CDCl_3$) 7.53-7.10 (9H, m, arom H), 6.74 (1.9H, *J* = 15.53, (*E*)-vinylic H), 6.46 (0.1H, *J* = 10.85, (*Z*)-vinylic H), 2.27 (3H, s, $-C_6H_4\underline{Me}$); MS *m/z* (rel intensity) 226 (M^+, 100), 211 (73), 181 (39), 178 (37), 135 (26), 121 (36), 115 (40), 91 (27), 77 (16). HRMS Found: *m/z* 226.0792. Calcd for $C_{15}H_{14}S$: M, 226.0816.

2,2-Bis(ethylthio)-1-phenylethanol (11aa): colorless liquid; IR ($CHCl_3$) 3500-3200 (OH); ^{1}H NMR ($CDCl_3$) 7.38-7.25 (5H, m, arom H), 4.69 (1H, dd, *J* = 2.78, 7.33, H-1), 3.96 (1H, d, *J* = 7.33, H-2), 3.39 (1H, d, *J* = 2.78, OH), 2.65 (2H, q, *J* = 7.33, $-C\underline{H}_2Me$), 2.45 (2H, q, *J* = 7.33, $-C\underline{H}_2Me$), 1.24 (3H, t, *J* = 7.33, $-CH_2\underline{Me}$), 1.15 (3H, t, *J* = 7.33, $-CH_2\underline{Me}$); ^{13}C NMR ($CDCl_3$) 140.6 (arom C), 128.2 (3C), 126.9 (2C) (arom CH), 75.2, 60.0 (CH), 26.0, 24.4 (CH_2), 14.6, 14.3 (Me).

2,2-Bis(ethylthio)-1-(4-methylphenyl)ethanol (11ba): colorless liquid; IR ($CHCl_3$) 3500-3200 (OH); ^{1}H NMR ($CDCl_3$) 7.29 (2H, m, arom H), 7.15 (2H, m, arom H), 4.64 (1H, br d, *J* = 7.32, H-1), 3.96 (1H, d, *J* = 7.32, H-2), 3.38 (1H, br s, OH), 2.61 (2H, q, *J* = 7.33, $-C\underline{H}_2Me$), 2.49 (2H, q, *J* = 7.33, $-C\underline{H}_2Me$), 2.39 (3H, s, Me), 1.24 (3H, t, *J* = 7.33, $-CH_2\underline{Me}$), 1.17 (3H, t, *J* = 7.33, $-CH_2\underline{Me}$); ^{13}C NMR ($CDCl_3$) 137.9, 137.5 (arom C), 128.9 (2C), 126.8 (2C) (arom CH), 74.9, 59.9 (CH), 25.9, 24.2 (CH_2), 21.3, 14.6, 14.3 (Me). FABHRMS (MeOH-NBA-NaI) Found: *m/z* 279.0835. Calcd for $C_{13}H_{20}OS_2Na$: 279.0853.

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