A SILVER SALT - IODINE REAGENT SYSTEM FOR THE DEPROTECTION OF MONOTHIOACETALS AND DITHIOACETALS[1]

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Abstract - A new reagent (silver salt - iodine) system was developed for the deprotection of monothioacetals and dithioacetals. The reactions using this reagent system afforded the parent carbonyl compounds in moderate to quantitative yields under mild conditions. These deprotections were also effective in the catalytic amount of this reagent. As an application of this deprotective reagent system, synthesizing optically active α-hydroxyaldehyde using chiral 1,3-oxathiane was demonstrated.

INTRODUCTION

We have studied on the reactivity of anion on the 2-position of 1,3-oxathiane to disclose that this species has an ability as a versatile conjunctive reagent to form a carbon-carbon bond.[2] Recently, a significant advance of asymmetric synthesis from the Eliel's work[3] using chiral 1,3-oxathianes as chiral auxiliaries was achieved by Utimoto group.[4] After the conjunctive reaction using this reagent, the deprotection of 1,3-oxathianes to carbonyl compounds is required. 1,3-Oxathianes have not been well used as the conjunctive reagent, compared with well-known 1,3-dithianes. One of the reasons is the lack of the suitable deprotective method for 1,3-oxathianes. Indeed, a few methods (*i.e.* isoamyl nitrite,[5] chloramine-T,[6] $AgNO_3$-NCS[7] and TMSOTf[8]) under mild conditions are known as the reagents for the deprotection of 1,3-oxathianes or 1,3-oxathiolanes, whereas many deprotective methods[9] for 1,3-dithianes or 1,3-dithiolanes are known. The conventional methods using mineral acids[10] or Raney nickel[11] for deprotection of 1,3-oxathiolanes or 1,3-oxathianes require the drastic conditions to give the ketones in moderate yields. The Corey's method (NCS-$AgNO_3$)[7] was applied to deprotection of 2-hydroxyalkyl-1,3-oxathianes in moderate yields of desired α-hydroxyaldehydes.[3a,3c,3f] Also, the use of conventional mercuric chloride for the deprotection of the same type of 1,3-oxathiane gave the corresponding aldehyde in moderate yield.[3g] These facts prompted us to develop a more effective reagent for the deprotection of monothioacetals. Here we describe the full account of a new reagent (silver salt - iodine) system for deprotection of monothioacetals as well as dithioacetals, and its application for the synthesis of optically active α-hydroxyaldehyde.

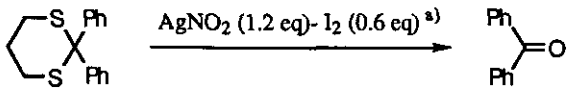
RESULTS AND DISCUSSION

In the preliminary communication, we have reported that silver nitrite - iodine system[12] was efficient for the desired transformation.[1] This reagent system was originally used for the iodonitration of olefins,[12] and

scope and limitations of this reagent system for demonothioacetalization are totally unknown, though an isolated example was reported.[13]

At first, the solvent was searched using 2,2-diphenyl-1,3-dithiane (**1**) as a substrate (Table 1). Tetrahydrofuran (THF) was the solvent of choice to give benzophenone quantitatively in a short reaction time.

Table 1



1

Solvent	Yield (%) [b]	Recov. (%) [c]
THF	99	0
Dioxane	82	18
CH_2Cl_2	79	20
MeCN	76	24
Et_2O	67	24
DMF	59	41

a) All reactions were carried out in 1.0 mmol scale in the solvent (5.0 ml) for 0. 5 h at room temperature.
b) Isolated yield c) Recovery of the starting material

Table 2. Comparison of Deprotective Reagents on 2-(Diphenylhydroxymethyl)-1,3-oxathiane (2)

2 **3**

Run [a]	**2** [b] (mmol)	Reagent (mmol)	Solvent (ml)	Time (h)	Yield (%)[c] of **3** [d]
1	0.10	$AgClO_4$ (0.12) - I_2 (0.12)	aq.- THF (1.0)	10 min	94
2	0.16	$AgNO_2$ (0.18) - I_2 (0.09)	aq.- THF (1.0)	5	92
3	0.14	AgOAc (0.17) - I_2 (0.34)	aq.- THF (2.0)	3	84
4	0.14	$AgNO_3$ (0.34) - I_2 (0.17)	aq.- THF (2.0)	5	80
5	0.14	Ag_2CO_3 (0.17) - I_2 (0.17)	aq.- THF (2.0)	1	52
6	0.16	Isoamyl Nitrite (0.16)	CH_2Cl_2 (1.0) H_2O (8 µl)	20	49
7	0.16	$AgNO_3$ (0.31) - NCS (0.31)	MeCN (2.6) H_2O (0.4)	2	75

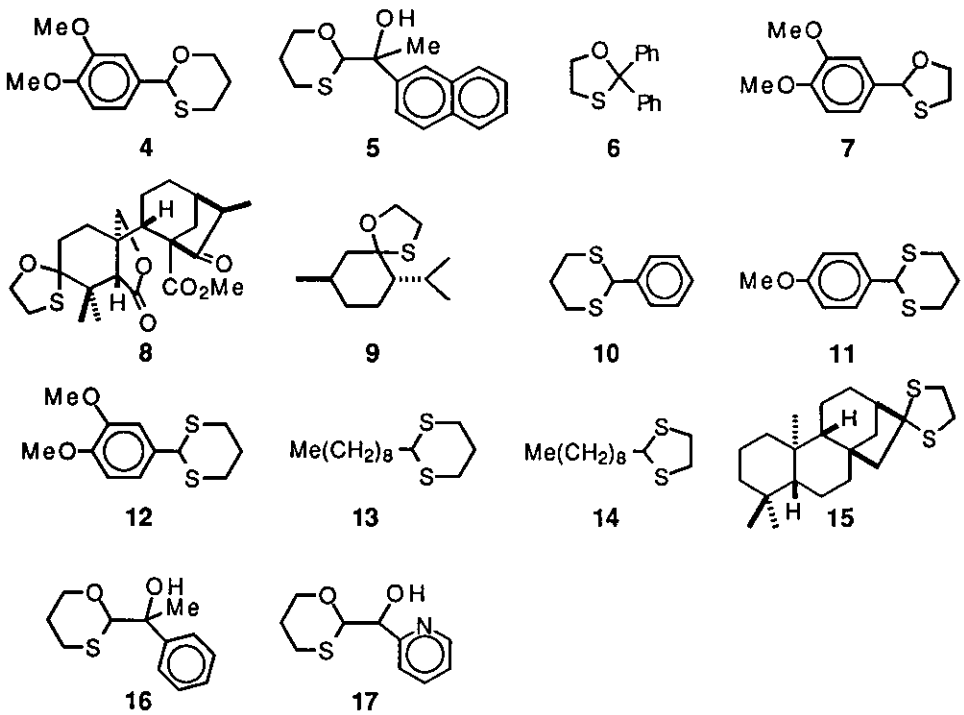
a) All reactions were carried out at room temperature. b) ref. 2b c) Isolated yields d) ref. 14

Only silver nitrite or silver perchlorate-iodine system was initially disclosed to be effective for the demonothioacetalization and dedithioacetalization.[1] Other silver salts were tested extensively. The results are listed on Table 2, compared with the known representative reagents (isoamyl nitrite and AgNO3-NCS). Silver perchlorate, silver nitrite, silver nitrate, silver acetate, or silver carbonate - iodine system was effective for the demonothioacetalization. Silver cyanide and silver iodide did not work due to their insolubility in

THF. Among these reagents a silver nitrite - iodine system was commendable from the points of efficiency and safety, *i.e.* silver perchlorate is known to be explosive.[15]

This reagent system was applied to the deprotection of some monothioacetals and dithioacetals shown in Figure 1. As the results are compiled in Table 3, yields of this deprotective reaction were moderate to high. Monothioacetals and dithioacetals of aromatic aldehydes and ketones were deprotected in higher yields than those of aliphatic aldehydes and ketones. The 1,3-oxathiolane (**4**) and 1,3-oxathiane (**7**) took almost same reaction time to complete the deprotection, though the hydrolysis rates between 1,3-dioxolanes and 1,3-dioxanes with hydrochloric acid were different.[16] Ether, Ester, and lactone remained intact with this reagent system (compounds **4**, **7**, **8**, **11**, and **12**). A chiral 1,3-oxathiolane (**9**) was converted into (-)-menthone without epimerization of α-substituent. The low yield in **15** is presumably due to the rearrangement of 17-norkaurane skeleton. With the limitations of this reagent system, the compounds (**16**)[2b] and (**17**) gave a complexed mixture, in spite of several trials. These results are probably due to susceptibility of the resultant α-hydroxyaldehydes to dehydration and air-oxidation, respectively.[3a]

Figure 1



We have found that the deprotection proceeded with the catalytic amount of reagents in monothioacetal (**2**) and dithioacetal (**11**). The results are summarized in Table 4. Silver nitrite, silver perchlorate, and silver acetate were effective for the catalytic deprotection of **2** and **11**. Although the catalytic reaction took the longer reaction time than the stoichiometric reaction, the amounts of silver salt and iodine could be reduced to 10-20 mol% to give the desired carbonyl compound in satisfactory yields.

Table 3. Deprotection of Monothioacetals and Dithioacetals

Entry [a]	Substrate (mmol)	Silver Salt (mol eq.)	Iodine (mol eq.)	Time (h)	THF (ml)	Yield [b] (%)
1	**4** (0.17)	$AgNO_2$ (2.4)	1.2	5	3.5	94
2	**5** (0.15)	$AgNO_2$ (2.4)	1.2	1	2.0	61
3	**6** (0.50)	$AgNO_2$ (2.0)	1.0	0.5	5.0	96
4	**7** (0.17)	$AgNO_2$ (2.4)	1.2	5	3.5	83
5	**8** (0.08)	$AgNO_2$ (6.0)	3.0	3	3.5	84
6	**9** (0.97)	$AgNO_2$ (2.4)	1.2	2	6.0	57 (67) [c]
7	**10** (0.18)	$AgNO_2$ (2.4)	1.2	20 min	2.0	89
8	**11** (0.18)	$AgClO_4$ (2.4)	1.2	5 min	2.0	95
9	**11** (0.18)	AgOAc (1.2)	2.4	0.5	2.0	100
10	**11** (0.18)	Ag_2CO_3 (1.2)	1.2	0.5	2.0	83
11	**12** (0.17)	$AgNO_2$ (2.4)	1.2	1.5	2.0	100
12	**12** (0.17)	AgOAc (1.2)	2.4	1.0	2.0	100
13	**12** (0.17)	$AgNO_3$ (2.4)	1.2	1.0	2.0	100
14	**12** (0.16)	Ag_2CO_3 (1.2)	1.2	1.0	2.0	100
15	**13** (1.0)	$AgNO_2$ (1.7)	0.9	5.5	5.0	88
16	**14** (0.46)	$AgNO_2$ (2.4)	2.4	2.5	5.0	73
17	**15** (0.2)	$AgNO_2$ (1.2)	0.6	43	2.0	47
18	**15** (0.09)	$AgClO_4$ (2.4)	1.2	5 min	1.0	53

a) All reaction were carried out at room temperature. b) Isolated yields

c) In parenthesis, calculated yield by ^1H nmr using 4-dimethylaminopyridine as an internal standard.

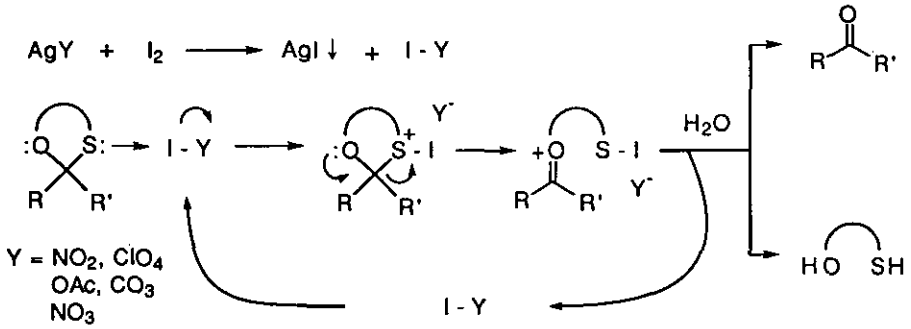
Table 4. Deprotection of Monothioacetal 2 and Dithioacetals 11 by Catalytic Amount of Reagents

Entry	Substrate (mmol)	Silver Salt (mol eq.)	Iodine (mol eq.)	Time (h)	Yield (%)
1	**2** (0.14)	$AgNO_2$ (0.5)	0.5	18	74
2	**2** (0.14)	$AgNO_2$ (0.2)	0.4	18	91
3	**2** (0.14)	$AgNO_2$ (0.2)	0.2	2 d	69
4	**2** (0.14)	$AgClO_4$ (0.2)	0.2	3 d	67
5	**2** (0.14)	AgOAc (0.2)	0.2	7 d	57
6	**11** (0.18)	$AgNO_2$ (0.1)	0.1	24	74
7	**11** (0.18)	$AgClO_4$ (0.2)	0.2	4 d	88

All reaction were carried out in THF (2.0 ml) at room temperature.

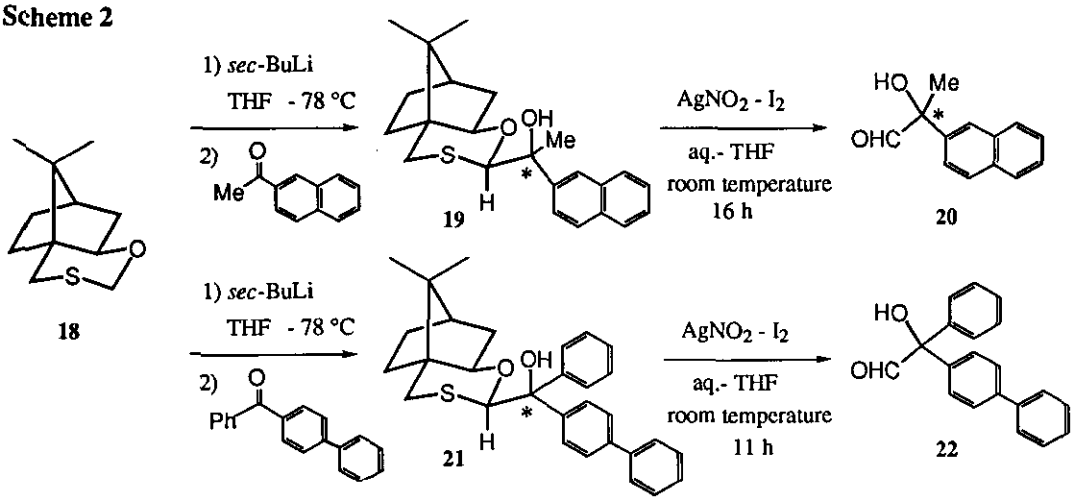
In the deprotective reaction of **2**, use of iodine, silver iodide, silver nitrite, or silver perchlorate alone gave no desired product but a complex mixture. The combination of silver salt and iodine was essential. The reaction was independent on the counter anion of silver. These facts indicate that an active species of this reagent system would be iodo cation. A possible mechanism of this reaction is illustrated in the Scheme 1. The precipitate of silver iodide was observed on all reactions by this system to give the I-Y species. The catalytic cycle must be formed by the regeneration of the I-Y species which could be afforded by the sulfur-iodine bond fission by Y anion, because sulfur has more negative inductive effect than iodine.

Scheme 1. A Possible Mechanism for Deprotection



An application of this reagent system to the Eliel's asymmetric synthesis[3f] was outlined in Scheme 2. A chiral 1,3-oxathiane (**18**)[3f] was used as a conjunctive reagent to give **19** in 66 % as a diastereomeric mixture (2.5 : 1), which were isolated in a pure form by hplc using a silica gel column. Deprotection of both diastereomers with $AgNO_2$ - I_2 system gave optically pure (+)- and (-)-α-hydroxyaldehydes (**20**), although the yields were low due to instability of α-hydroxyaldehyde.[3a] Unfortunately, two diastereomers (1 : 1) of chiral 1,3-oxathiane (**21**), prepared from **18** in 90 % yield in the same reaction as **19**, were not isolated by hplc. The deprotective reaction of **19** proceeded in 70 % yield.

Scheme 2



CONCLUSION

We have provided a new reagent (silver salt-iodine) system for the deprotection of monothioacetals and dithioacetals. The yields using this system ranged from moderate to excellent. Particularly, the yield in the deprotection of **2** with new reagent system was best among the other known methods so far. The active species of this reagent system would be iodo cation. Work-up of the reaction mixture and purification of the product are very easy, because both of the reagents are inorganic materials so that no contamination of organic materials from the reagents occurs.

ACKNOWLEDGMENT

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EXPERIMENTAL SECTION

General: Melting points are taken with a micro hot-stage apparatus (Yanagimoto) and are uncorrected. The infrared (ir) spectra are recorded with a Shimadzu IR-410 or JASCO IR-810 diffraction grating infrared spectrophotometer and ^{1}H-nmr spectra are obtained with a Varian XL-300 spectrometer with tetramethylsilane as an internal standard. Mass spectra (ms) are determined on a Hitachi M-80 or JEOL JMS-SX 102A QQ mass spectrometer. A hplc separation was performed by LC-908 series [Japan Analytical Industry, Co. LTD., silica gel column (JAIGEL SIL-043-15) or GPC column (JAIGEL 1H and 2H)]. Wakogel C-200 (silica gel) (100-200 mesh, Wako), Wakogel C-300 (200-300 mesh, Wako), or Kieselgel 60 (230-400 mesh Merck) was used for column chromatography. Kieselgel 60 F_{254} plate (Merck) was used for thin layer chromatography (tlc) and preparative thin layer chromatography (ptlc).

Materials: All parent carbonyl compounds are commercially available, except for the corresponding carbonyl compounds of **2**,[2b] **5**, *ent*-20-hydroxy-3,15-dioxo-6,7-secokaurane 6,7-dioic acid 6,20-lactone 7-methyl ester (**8**),[17] *ent*-17-norkauran-16-one (**15**),[18] **16**,[2b] and **17**. *sec*-Butyllithium (cyclohexane solution), boron trifluoride etherate, and zinc chloride (ether solution) were purchased from Aldrich Chemical Company, Inc. Anhydrous THF was distilled from benzophenone ketyl. Anhydrous dichloromethane was distilled from calcium hydride. Silver salts purchased were used without purification.

Preparation of monothioacetals and dithioacetals

2,2-Diphenyl-1,3-dithiane (1)

To a solution of benzophenone (10.0 g, 54.9 mmol) and 1,3-propanedithiol (6.00 g, 55.4 mmol) in anhydrous dichloromethane (14 ml) was added boron trifluoride etherate (3.92 g, 27.4 mmol) at 0 °C. After being stirred for 2 d at room temperature, the reaction mixture was poured into saturated solution of sodium hydrogen carbonate and extracted with dichloromethane (50 ml x 3). The combined organic layer was washed with brine, dried with magnesium sulfate and concentrated *in vacuo*. The residue was purified by recrystallization from methanol to give **1** (13.3 g, 89%) as colorless crystals: mp 109-110 °C (MeOH); ^{1}H nmr (300 MHz, $CDCl_3$) δ 7.70 (d, J = 7.4 Hz, 4H), 7.37-7.24 (m, 6H), 2.81-2.77 (m, 4H), 2.05-1.97 (m, 2H); ir ($CHCl_3$) 3070, 3000, 2910, 1590, 1490, 1480, 1440, 1275, 1030 cm^{-1}; ms (20 eV) *m/z* 272 (M^+, 31), 199 (16), 198 (100), 166 (15), 165 (69), 121 (21). Anal. Calcd for $C_{16}H_{16}S_2$: C, 70.54; H, 5.92. Found: C, 70.22; H, 5.92.

2-(3,4-Dimethoxyphenyl)-1,3-oxathiane (4)

A benzene (100 ml) solution of veratraldehyde (1.29 g, 7.8 mmol), 2-mercaptoethanol (725 mg, 7.9 mmol) and *p*-toluenesulfonic acid (148 mg, 0.78 mol) was refluxed for 17 h. The reaction mixture was poured into saturated solution of sodium hydrogen carbonate, extracted with ether (50 ml x 3). The combined organic layer was washed with brine, dried ($MgSO_4$), filtered, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel using hexane / ethyl acetate (7 / 2) and preparative hplc and recrystallization from hexane to give **4** (42.6 mg, 2.3 %) as colorless crystals: mp 68-69 °C (hexane); ^{1}H nmr (300 MHz, $CDCl_3$) δ 7.04 (d, J = 2.0 Hz, 1H, C2'), 7.00 (dd, J = 8.1, 2.0 Hz, 1H, C6'), 6.83 (d, J = 8.1 Hz, 1H, C5'), 5.74 (s, 1H, C2), 4.34 (dt of A part of AB, J_{AB} = 12.1, J = 4.1, 1.8 Hz, 1H, C6 eq), 3.91 (s, 3H, OMe), 3.87 (s, 3H, OMe), 3.79 (dd of B part of AB, J_{AB} = 12.1, J = 12.1, 2.1, 1H, C6 ax), 3.22 (dd of A part of AB, J_{AB} = 13.2, J = 13.2, 2.7, 1H, C4 ax), 2.84 (dt of B part of AB, J_{AB} = 13.2, J = 3.5, 1.8 Hz, 1H, C4 eq), 2.20-2.02 (m, 1H, C5 ax), 1.82-1.73 (m, 1H, C5 ax); ir ($CHCl_3$) 3000, 2960, 2910, 2840, 1590, 1510, 1460, 1415, 1260, 1150, 1135, 1070, 1020, 905 cm^{-1}; ms (20 eV) *m/z* 241 (M^++1, 13), 240 (M^+, 97), 209 (13), 182 (26), 166 (100), 165 (63), 151 (25), 139 (10), 95 (23), 77 (14), 46 (11), 41 (18). Anal. Calcd for $C_{12}H_{16}O_3S$: C, 59.97; H, 6.71. Found: C, 59.62; H, 6.65.

2-[1-Hydroxy-1-(2-naphthyl)ethyl]-1,3-oxathiane (5)

To a solution of 1,3-oxathiane[2a,b] (416 mg, 4.00 mmol) in anhydrous THF (8 ml) was added *sec*-butyllithium (4.36 ml, 4.80 mmol, 1.1 M in cyclohexane) over 10 min at -78 °C. After being stirred for 30 min, a solution of 2-acetonaphthone (880 mg, 5.17 mmol) in anhydrous THF (4 ml) was added dropwise. The mixture was stirred for 1 h at -78 °C until tlc indicated the completion of the reaction. The reaction mixture was poured into saturated solution of ammonium chloride and extracted with dichloromethane (50 ml x 3). The combined organic layer was dried ($MgSO_4$), filtered, and evaporated *in vacuo*. The residue was purified by chromatography on silica gel using hexane/ethyl acetate (4:1 [v/v]) to give **5** (738 mg, 68 %) as a 1 : 1 mixture of two diastereomers. colorless powder: mp 111-112 °C; ^{1}H nmr (300 MHz, $CDCl_3$) δ 8.02 (d, J = 1.4 Hz, 0.5 H, C1'), 7.87-7.81 (m, 3H), 7.62 (dd, J = 8.6, 1.9 Hz, 0.5 H, C8'), 7.53 (dd, J = 8.6, 1.9 Hz, 0.5 H, C8'), 7.50-7.42 (m, 2H), 5.08 (s, 0.5H, C2), 5.02 (s, 0.5H, C2), 4.30 (dt of A part of AB, J_{AB} = 12.1, J = 4.2, 2.0 Hz, 0.5H, C6 eq), 4.20 (dt of A part of AB, J_{AB} = 11.9, J = 4.2, 2.0 Hz, 0.5H, C6eq), 3.70 (dd of B part of AB, J_{AB} = 12.1, J = 12.1, 2.1 Hz, 0.5H, C6 ax), 3.65 (dd of B part of AB, J_{AB} = 11.9, J = 11.8, 2.1 Hz, 0.5H, C6 ax), 3.15 (s, 0.5H, OH), 3.00 (s, 0.5H, OH), 3.00-2.88 (m, 1H, C4 ax), 2.80-2.65 (m, 1H, C4 eq), 2.05-1.85 (m, 1H, C5 ax), 1.73 (s, 1.5H, CH_3), 1.71 (s, 1.5H, CH_3), 1.70-1.60 (m, 1H, C5 ax); ir ($CHCl_3$) 3500, 3040, 2880, 1605, 1375, 1075, 1028, 870, 828 cm^{-1}; ms (20 eV) *m/z* 274 (M^+, 2.6), 171 (31), 170 (25), 103 (100), 43 (29). Anal. Calcd for $C_{16}H_{18}O_2S$: C, 70.04; H, 6.61. Found: C, 69.79; H, 6.70.

2,2-Diphenyl-1,3-oxathiolane (6)

According to the Djerassi's method,[19] 2,2-diphenyl-1,3-oxathiolane (**6**) was prepared using benzophenone (1.82 g, 10 mmol) and sodium sulfate (3.84 g, 27 mmol), zinc chloride (0.73 M in ether, 38.2 ml, 2.8 eq.), 2-mercaptoethanol (2.74 ml, 39.0 mmol), and anhydrous 1,4-dioxane (5.0 ml). The residue was purified by chromatography on silica gel using hexane/ethyl acetate (5:1 [v/v]) to give **6** (1.27 g, 53 %) as colorless powder. mp 52-53 °C; ^{1}H nmr (300 MHz, $CDCl_3$) δ 7.53-7.49 (m, 4H), 7.33-7.21 (m, 6H), 4.21 (t, J = 6.3 Hz, 2H, C5), 3.24 (t, J = 6.3 Hz, 2H, C4); ir ($CHCl_3$) 3070, 3010, 2950, 2890, 1600, 1490, 1450, 1175, 1060, 1030, 1020, 980, 640 cm^{-1}; ms (20 eV) *m/z* 242 (M^+, 14), 182 (23), 181 (23), 165 (10), 105 (100), 77 (39). Anal. Calcd for $C_{15}H_{14}OS$: C, 74.34; H, 5.82. Found: C, 74.10; H, 5.87.

2-(3,4-Dimethoxyphenyl)-1,3-oxathiolane (7)

According to the same procedure described on the synthesis of 1, 2-(3,4-dimethoxyphenyl)-1,3-oxathiolane (**7**) was prepared using veratraldehyde (332 mg, 2.00 mmol), 2-mercaptoethanol (158 mg, 2.02 mmol), boron trifluoride etherate (142 mg, 1.00 mmol) in anhydrous dichloromethane (5 ml) (reaction time 2 d). The residue was purified by preparative tlc using hexane / ethyl acetate (2:1 [v/v]) and preparative hplc (GPC column, JAIGEL 1H and 2H) to give **7** (38.8 mg, 8.6 %) as colorless

crystals: mp 80-81 °C (hexane); ^{1}H nmr (300 MHz, $CDCl_3$) δ 7.05 (d, J = 2.0 Hz, 1H, C2'), 7.01 (dd, J = 8.2, 2.0 Hz, 1H, C6'), 6.83 (d, J = 2.0 Hz, 1H, C5'), 6.01 (s, 1H, C2), 4.54 (dd of A part of AB, J_{AB} = 9.2, J = 6.5, 3.0 Hz, 1H, C5), 3.93 (dd of B part of AB, J_{AB} = 9.2, J = 9.2, 6.3 Hz, 1H, C5), 3.91 (s, 3H, OMe), 3.88 (s, 3H, OMe), 3.29 (dd of A part of AB, J_{AB} = 9.5, J = 9.2, 6.5 Hz, 1H, C4), 3.21 (dd of B part of AB, J_{AB} = 9.5, J = J = 6.3, 3.0 Hz, 1H, C4); ir ($CHCl_3$) 3050, 2990, 2920, 2880, 1620, 1535, 1480, 1440, 1280, 1175, 1155, 1080, 1045, 880 cm^{-1}; ms (20 eV) *m/z* 226 (M^+, 50), 167 (12), 166 (100), 165 (37), 151 (12), 95 (12). Anal. Calcd for $C_{11}H_{14}O_3S$: C, 58.38; H, 6.24. Found: C, 58.52; H, 6.42.

ent-3,3-Ethyleneoxythio-20-hydroxy-15-oxo-6,7-secokaurane-6,7-dioic acid 6,20-lactone 7-methyl ester (8)

According to the Djerassi's method,[19] the parent diterpene ketone[17] (1.129 g, 3 mmol), zinc chloride (0.73 M in ether, 11.5 ml, 2.8 mol eq.) sodium sulfate (1.152 g, 8.1 mmol), 2-mercaptoethanol (0.822 ml, 11.7 mmol), and anhydrous 1,4-dioxane (5.0 ml). After usual work-up, recrystallization of the residue from methanol gave **8** (772 mg, 59 %) as a 1 : 2 mixture of two diastereomers. colorless crystals; mp 172-173 °C (MeOH); ^{1}H nmr (300 MHz, $CDCl_3$) δ 4.45-4.33 (m, 1H), 4.06-3.85 (m, 3H), 3.78 (s, 3H), 3.06-2.87 (m, 2H), 2.58-2.50 (br m, 1H), 2.40-2.00 (m, 8H), 1.95-1.67 (m, 4H), 1.55-1.40 (m, 1H), 1.29 (s, 3H), 1.12 (s, 3H), 1.12 and 1.10 (ca 1 : 2, each d, J = 6.8 Hz, 3H); ir ($CHCl_3$) 2980, 2950, 2870, 1765, 1750 (shoulder), 1715, 1435, 1275, 1150, 1085, 970, 870 cm^{-1}; ms m/z 436 (M^+, 25), 335 (14), 241 (14), 167 (48), 135 (31), 115 (100), 107 (40), 102 (50), 79 (29), 55 (29). HRms calcd for $C_{23}H_{32}O_6S$: 436.1920, found: 436.1929.

(2*S*,5*R*)-2-Isopropyl-5-methyl-1,1-ethyleneoxythiocyclohexane (9)

According to the same procedure described on the synthesis of **1**, (2*S*,5*R*)-2-isopropyl-5-methyl-1,1-ethyleneoxythiocyclohexane (**9**)[8] was prepared using L-menthone (2.314 g, 15.0 mmol), mercaptoethanol (1.18g, 15.2 mmol), boron trifluoride etherate (1.06 g, 7.5 mmol) in anhydrous dichloromethane (5 ml) (reaction time 4 d at room temperature). The residue was purified by column chromatography on silica gel using hexane /ethyl acetate (50:1 [v/v]) and preparative hplc (GPC column, JAIGEL 1H and 2H) to give **9** (1.128 g, 35.1 %) as a 1 : 1 mixture of two diastereomers. a colorless oil: ^{1}H Nmr (300 MHz, $CDCl_3$) δ 4.38-4.28 (m, 1H), 4.07-3.98 (m, 0.5H), 3.91 (ddd, J = 10.7, 9.2, 5.1 Hz, 0.5H), 3.20-2.88 (m, 2H), 2.45 (d of septet, J = 7.0, 1.0 Hz, 0.5H), 2.21 (ddd, J = 13.9, 3.4, 2.3 Hz, 0.5H), 2.04 (d of septet, J = 6.9, 3.0 Hz, 0.5H), 2.01 (ddd, J = 13.9, 3.4, 2.3 Hz, 0.5H), 1.82-1.00 (m, 7H), 0.94 (d, J = 7.0 Hz, 6H), 0.92 (d, J = 7.0 Hz, 3H), 0.90 (d, J = 7.0 Hz, 3H), 0.86 (d, J = 6.9 Hz, 6H); ir ($CHCl_3$) 2960, 2930, 2870, 1465 (shoulder), 1450, 1380, 1360, 1260, 1140, 1070, 1050, 1005, 905, 885 825 cm^{-1}; ms *m/z* 214 (M^+, 33), 139 (22), 129 (100), 112 (29), 69 (11), 55 (16), 41 (18). HRms calcd for $C_{12}H_{22}OS$: 214.1392, found: 214.1401.

2-Phenyl-1,3-dithiane (10)

According to the same procedure described on the synthesis of **1**, 2-phenyl-1,3-dithiane (**10**) was prepared using benzaldehyde (2.0 ml, 19.7 mmol), 1,3-propanedithiol (2.0 ml, 19.9 mmol), boron trifluoride etherate (1.21 ml, 9.8 mmol) in anhydrous dichloromethane (2 ml) (reaction time 7 h at room temperature). After usual work-up, recrystallization of the residue from methanol gave **10** (3.63 g, 94 %) as colorless crystals. mp 69-70 °C (MeOH); ^{1}H nmr (300 MHz, $CDCl_3$) δ 7.49-7.44 (m, 2H), 7.38-7.29 (m, 3H), 5.17 (s, 1H, C2), 3.07 (dd of A part of AB, J_{AB} = 14.5, J = 12.2, 2.5 Hz, 2H, C4 ax, C6 ax), 2.92 (dd of B part of AB, J_{AB} = 14.5, J = 4.2, 3.4 Hz, 2H, C4 eq, C6 eq), 2.22-2.13 (m, 1H, C5 eq), 2.02-1.86 (m, 1H, C5 ax); ir ($CHCl_3$) 3080, 2980, 1510, 1465, 1435, 1285, 1180, 700 cm^{-1}; ms (20 eV) *m/z* 196 (M^+, 100), 131 (36), 122 (98), 121 (92), 105 (25), 91 (22), 45 (21). Anal. Calcd for $C_{10}H_{12}S_2$: C, 61.18; H, 6.16. Found: C, 61.01; H, 6.22.

2-(4-Methoxyphenyl)-1,3-dithiane (11)

According to the same procedure described on the synthesis of **1**, 2-(4-methoxyphenyl)-1,3-dithiane (**11**) was prepared using 4-methoxybenzaldehyde (7.40 g, 54.4 mmol), 1,3-propanedithiol (6.00 g, 55.4 mmol), and boron trifluoride etherate (1.56 g, 11.0

mmol) in anhydrous dichloromethane (10 ml) (reaction time 24 h at room temperature). The residue was purified by recrystallization from dichloromethane-methanol to give **11** (10.9 g, 90%) as colorless crystals: mp 113-115 °C (CH_2Cl_2-MeOH); ^{1}H nmr (300 MHz, $CDCl_3$) 7.40 (AA' part of AA'XX', J = 8.8 Hz, 2H), 6.86 (XX' part of AA'XX', J = 8.8 Hz, 2H), 5.14 (s, 1H, C2), 3.79 (s, 3H, OMe), 3.05 (dd of A part of AB, J_{AB} = 14.1, J = 12.3, 2.5 Hz, 2H, C4 ax, C6 ax), 2.90 (dd of B part of AB, J_{AB} = 14.1, J = 4.2, 3.2 Hz, 2H, C4 eq, C6 eq), 2.16 (tt of A part of AB, J_{AB} = 14.1, J = 4.2, 2.5 Hz, 1H, C5 eq), 1.92 (tt of B part of AB, J_{AB} = 14.1, J = 12.3, 3.2 Hz, 1H, C5 ax); ir ($CHCl_3$) 3000, 2900, 1605, 1505, 1300, 1175, 1030, 840 cm^{-1}; ms (20 eV) *m/z* 226 (M^+, 55), 161 (10), 154 (17), 152 (100), 151 (66), 147 (18), 121 (21). Anal. Calcd for $C_{11}H_{14}OS_2$: C, 58.37; H, 6.23. Found: C, 58.16; H, 6.28.

2-(3,4-Dimethoxyphenyl)-1,3-dithiane (12)

According to the same procedure described on the synthesis of **1**, 2-(3,4-dimethoxyphenyl)-1,3-dithiane (**12**) was prepared using veratraldehyde (3.00 g, 18.05 mmol), 1,3-propanedithiol (1.97 g, 18.2 mmol), and boron trifluoride etherate (1.28 g, 9.03 mmol) in anhydrous dichloromethane (5 ml) (reaction time 2 d at room temperature). The residue was purified by recrystallization from methanol to give **12** (4.03 g, 87%) as colorless crystals: mp 93-94 °C (MeOH); ^{1}H nmr ($CDCl_3$) δ 7.05-7.00 (m, 2H), 6.84-6.80 (m, 1H), 5.13 (s, 1H, C2), 3.90 (s, 3H, OMe), 3.87 (s, 3H, OMe), 3.06 (dd of A part of AB, J_{AB} = 14.4, J = 12.4, 2.6 Hz, 2H, C4 ax, C6 ax), 2.91 (dd of B part of AB, J_{AB} = 14.4, J = 4.3, 3.2 Hz, 2H, C4 eq, C6 eq), 2.17 (tt of A part of AB, J_{AB} = 14.1, J = 4.3, 2.6 Hz, 1H, C5 eq), 1.93 (tt of B part of AB, J_{AB} = 14.1, J = 12.4, 3.2 Hz, 1H, C5 ax); ir ($CHCl_3$) 3090, 3010, 2990, 2900, 1605, 1520, 1475, 1280, 1145, 1028 cm^{-1}; ms (20 eV) *m/z* 256 (M^+, 50), 182 (100), 181 (25), 151 (15). Anal. Calcd for $C_{12}H_{16}O_2S_2$: C, 56.22; H, 6.29. Found: C, 56.05; H, 6.31.

2-Nonyl-1,3-dithiane (13)

According to the same procedure described on the synthesis of **1**, 2-nonyl-1,3-dithiane (**13**) was prepared using decanal (1.56 g, 10.0 mmol), 1,3-propanedithiol (1.09 g, 10.1 mmol), and boron trifluoride etherate (568 mg, 4.00 ml) in anhydrous dichloromethane (1.50 ml) (reaction time 15 h at room temperature). The residue was purified by chromatography on silica gel using hexane / ethyl acetate (5:1 [v/v]) to give **13** (2.20 g, 89%) as colorless oil: ^{1}H Nmr (300 MHz, $CDCl_3$) δ 4.05 (t, J = 6.8 Hz, 1H, C2), 2.93-2.78 (m, 4H, C4, C6), 2.17-2.07 (m, 1H, C5), 1.93-1.81 (m, 1H, C5), 1.80-1.70 (m, 2H), 1.56-1.43 (m, 2H), 1.26 (br m, 12H), 0.88 (br t, J = 6.7 Hz, 3H); ir ($CHCl_3$) 2950, 2860, 1465, 1420, 1380, 1180, 910 cm^{-1}; ms (20 eV) *m/z* 246 (M^+, 16), 171 (12), 119 (100) 106 (8). HRms calcd for $C_{13}H_{26}S_2$: 246.1475, found: 246.1488.

2-Nonyl-1,3-dithiolane (14)

According to the same procedure described on the synthesis of **1**, 2-nonyl-1,3-dithiolane (**14**) was prepared using decanal (1.56 g, 10.0 mmol), 1,3-ethanedithiol (951 mg, 10.1 mmol), and boron trifluoride etherate (568 mg, 4.00 ml) in anhydrous dichloromethane (1.50 ml) (reaction time 15 h at room temperature). The residue was purified by chromatography on silica gel using hexane/ethyl acetate (5:1 [v/v]) to give **14** (1.55 g, 67%) as colorless oil: ^{1}H Nmr (300 MHz, $CDCl_3$) δ 4.47 (t, J = 7.1 Hz, 1H), 3.30-3.15 (m, 4H), 1.86-1.78 (m, 2H), 1.50-1.37 (m, 2H), 1.26 (br m, 12H), 0.88 (br t, J = 6.7 Hz, 3H); ir ($CHCl_3$) 2950, 2860, 1465, 1435, 1430, 1380, 1280, 850 cm^{-1}; ms (20 eV) *m/z* 232 (M^+, 27), 105 (100). HRms calcd for $C_{12}H_{24}S_2$: 232.1319, found: 232.1358.

***ent*-16,16-Ethylenedithio-17-norkaurane (15)**

According to the same procedure described on the synthesis of **1**, *ent*-16,16-ethylenedithio-17-norkaurane (**15**) was prepared using *ent*-17-norkauran-16-one[18] (274 mg, 1.0 mmol), ethanedithiol (88 µl, 1.05 mmol), and boron trifluoride etherate (49 µl, 0.4 mmol) in anhydrous dichloromethane (3 ml) (reaction time 1 d at room temperature). The residue was purified by recrystallization from dichloromethane-methanol to give **15** (251 mg, 72%) as colorless crystals: mp 129-130 °C (CH_2Cl_2-MeOH); ^{1}H nmr (300 MHz, $CDCl_3$) δ 3.42-3.10 (m, 4H), 2.28-2.12 (m, 4H), 1.98-1.90 (m, 1H), 1.82-1.75 (m, 1H), 1.70-

1.22 (m, 12H), 1.18-1.05 (m, 1H), 1.02 (s, 3H), 0.84 (s, 3H), 0.80 (s, 3H), 0.80-0.68 (m, 2H); ir ($CHCl_3$) 3000, 2940, 2870, 1460, 1450, 1385, 1365 cm^{-1}; ms (20 eV) *m/z* 350 (M^+, 46), 322 (100), 289 (44), 232 (40), 231 (36), 230 (41), 215 (20), 172 (20), 137 (26), 119 (23), 118 (22), 95 (20), 81 (24), 69 (24). Anal. Calcd for $C_{21}H_{34}S_2$: C, 71.94; H, 9.77. Found: C, 71.81; H, 9.66.

2-(2-Pyridylhydroxymethyl)-1,3-oxathiane (17)

According to the same procedure described on the synthesis of **5**, 2-(2-pyridylhydroxymethyl)-1,3-oxathiane (**17**) was prepared using 1,3-oxathiane (490 mg, 4.70 mmol), *sec*-butyllithium (5.1 ml, 5.64 mmol, 1.1 M in cyclohexane), and 2-pyridinecarboxaldehyde (604 mg, 5.64 mmol) in the reaction time (1.5 h). The residue was purified by chromatography on silica gel using hexane/ethyl acetate (1:2 [v/v]) to give **17** (666 mg, 67 %) as a 56 : 44 mixture of two diastereomers. mp 106-108 °C (hexane); ^1H nmr ($CDCl_3$) δ 8.59-8.56 (m, 1H), 7.70 (dt, J = 7.7 and 1.7 Hz, 1H), 7.49-7.43 (m, triplet like, 1H), 7.28-7.22 (m, 1H), 5.16 (d, J = 4.7 Hz, 0.56H, C2), 5.10 (d, J = 4.7 Hz, 0.44H, C2), 4.94-4.88 (br m, 0.44H), 4.84-4.79 (br m, 0.56H), 4.30-4.14 (m, 2H, C6 eq and OH), 3.63 (dd of A part of AB, J_{AB} = 12.3, J = 12.3, 2.2 Hz, 1H, C6 ax), 3.01 (dd of A part of AB, J_{AB} = 13.4, J = 13.4, 2.9 Hz, 0.56H, C4 ax), 2.97 (dd of B part of AB, J_{AB} = 13.4, J = 13.4, 2.9 Hz, 0.44H, C4 ax), 2.82-2.72 (m, 1H, C4 eq), 2.06-1.89 (m, 1H, C5 ax), 1.72-1.63 (m, 1H, C5 eq); ir ($CHCl_3$) 3600-3400 (br), 3050, 2940, 2900, 1595, 1580, 1440, 1085, 1070 cm^{-1}; ms (20 eV) *m/z* 211 (M^+, 0.5), 193 (14), 118 (30), 103 (100), 75 (14), 41 (13). Anal. Calcd for $C_{10}H_{13}NO_2S$: C, 56.85; H, 6.20; N, 6.63. Found: C, 56.99; H, 6.32; N, 6.91.

(1*R*,3*R*,6*S*,9*R*)-3-[1-(2-Naphthyl)ethyl]-11,11-dimethyl-2-oxa-4-thiatricyclo[4,4,0,$1^{6,9}$]undecane (19)

According to the same procedure described on the synthesis of **5**, 1,3-oxathiane carbinol (**19**) was prepared using a chiral 1,3-oxathiane (**18**)[3f] (123 mg, 0.6 mmol), *sec*-butyllithium (0.75 ml, 0.74 mmol, 0.99 M in cyclohexane), and 2-acetonaphthone (116 mg, 0.68 mmol) in the reaction time (4 h). The residue was purified by chromatography on silica gel using hexane/ethyl acetate (10:1 [v/v]) to give **19** as a 5 : 2 mixture of two diastereomers. The hplc purification of the mixture (eluted with hexane / AcOEt = 20 :1) afforded a major diastereomer (104 mg) and minor diastereomer (46 mg) (total 66 %). major diastereomer: amorphous; $[\alpha]_D^{17}$ -168.6° (0.78, $CHCl_3$); ^1H nmr ($CDCl_3$) δ 7.99 (d, J = 1.5 Hz, 1H), 7.86-7.79 (m, 3H), 7.64 (dd, J = 8.7, 1.9 Hz, 1H), 7.48-7.41 (m, 2H), 4.87 (s, 1H), 3.62 (dd, J = 7.8, 3.1 Hz, 1H), 3.21 (s, 1H, OH), 2.92 (A part of AB, J_{AB} = 14.2 Hz, 1H), 2.67 (B part of AB, J_{AB} = 14.2 Hz, 1H), 1.96-1.88 (m, 1H), 1.73 (s, 3H), 1.72-1.63 (m, 3H), 1.47-1.36 (m, 1H), 1.32 (s, 3H), 1.06-0.96 (m, 1H), 0.91-0.81 (m, 1H), 0.88 (s, 3H); ir ($CHCl_3$) 3570 (br), 3070, 2970, 2965, 2880, 1600, 1505, 1453, 1385, 1368, 1120, 1100, 1065, 1040, 875 cm^{-1}; ms (70 eV) *m/z* 368 (M^+, 2.2), 197 (78), 171 (53), 155 (26), 135 (63), 128 (23), 127 (24), 93 (30), 91 (21), 79 (24), 43 (100). HRms calcd for $C_{23}H_{28}O_2S$: 368.1820, found: 368.1801. minor diastereomer: amorphous; $[\alpha]_D^{17}$ -124.1° (0.41, $CHCl_3$); ^1H nmr ($CDCl_3$) δ 8.02 (d, J = 1.7 Hz, 1H), 7.86-7.78 (m, 3H), 7.54 (dd, J = 8.6, 1.9 Hz, 1H), 7.48-7.41 (m, 2H), 4.98 (s, 1H), 3.66 (dd, J = 8.0, 3.1 Hz, 1H), 2.95 (s, 1H, OH), 2.94 (A part of AB, J_{AB} = 14.2 Hz, 1H), 2.68 (B part of AB, J_{AB} = 14.2 Hz, 1H), 2.01-1.93 (m, 1H), 1.77-1.57 (m, 3H), 1.73 (s, 3H), 1.49-1.39 (m, 1H), 1.28 (s, 3H), 1.08-0.99 (m, 1H), 0.96-0.86 (m, 1H), 0.87 (s, 3H); ir ($CHCl_3$) 3570 (br), 3060, 2990, 2960, 2860, 1598, 1503, 1450, 1385, 1365, 1260, 1180, 1125, 1065, 1040, 855 cm^{-1}; ms (70 eV) *m/z* 368 (M^+, 1.1), 197 (83), 171 (65), 155 (35), 135 (75), 128 (30), 127 (29), 107 (22), 93 (36), 91 (25), 79 (28), 67 (21), 43 (100). HRms calcd for $C_{23}H_{28}O_2S$: 368.1820, found: 368.1822.

(1*R*,3*R*,6*S*,9*R*)-3-[Hydroxy(4-biphenyl)phenylmethyl]-11,11-dimethyl-2-oxa-4-thiatricyclo[4,4,0,$1^{6,9}$]-undecane (21)

According to the same procedure described on the synthesis of **5**, (1*R*,3*R*,6*S*,9*R*)-3-[hydroxy(4-biphenyl)phenylmethyl]-11,11-dimethyl-2-oxa-4-thiatricyclo[4,4,0,$1^{6,9}$]undecane (**21**) was prepared using a chiral 1,3-oxathiane (**18**) [3f] (600 mg, 3.03 mmol), *sec*-butyllithium (3.67 ml, 3.63 mmol, 0.99 M in cyclohexane), and 4-benzoylbiphenyl (742 mg, 2.87 mmol) in the reaction

time (4 h). The residue was purified by chromatography on silica gel using hexane/ethyl acetate (15:1 [v/v]) to give **21** (1.24 g, 90 %) as a 1 : 1 mixture of two diastereomers. ^{1}H Nmr ($CDCl_3$) δ 7.26-7.48 (m, 8H), 7.45-7.23 (m, 6H), 5.61 (s, 1H), 3.82 (dd, J = 8.0, 3.1 Hz, 0.5H), 3.81 (dd, J = 8.1, 2.9 Hz, 0.5H), 3.38 (s, 1H, OH), 3.08 (A part of AB, J_{AB} = 14.3 Hz, 0.5H), 3.07 (A part of AB, J_{AB} = 14.2 Hz, 0.5H), 2.76 (B part of AB, J_{AB} = 14.3 Hz, 0.5H), 2.75 (B part of AB, J_{AB} = 14.2 Hz, 0.5H), 1.95-1.84 (m, 1H), 1.78-1.65 (m, 2H), 1.56-1.45 (m, 2H), 1.33 (s, 3H), 1.12-0.83 (m, 2H), 0.91 (s, 3H); ir ($CHCl_3$) 3630-3480 (br), 3070, 3010, 2960, 2880, 1605, 1485, 1450, 1390, 1062 cm^{-1}; ms (70 eV) *m/z* 438 [M^+-18 (H_2O), 1.4], 259 (60), 243 (21), 241 (21), 197 (100), 181 (42), 152 (25), 135 (70), 105 (69), 93 (28), 79 (21), 77 (32). HRms calcd for $C_{30}H_{30}OS$ (M-H_2O): 438.2017, found: 438.1992.

A General Procedure for Demonothioacetalization and Dedithioacetalization with a Silver Salt - Iodine System

A suspension of silver nitrite and iodine (indicated amounts in Table) in THF was stirred for 0.5 h at room temperature. Oxathiolane, oxathiane, dithiolane, or dithiane shown in Figure 1 was added and the resulting mixture was stirred for additional times indicated in Table. A dilute sodium thiosulfate solution was added to the mixture at 0 °C, and the resultant mixture was extracted with dichloromethane. The extract was washed with brine, drying ($MgSO_4$), concentration *in vacuo*. Preparative tlc on silica gel or silica gel column chromatography of the residue afforded the parent carbonyl compound except for **3**,[14] **20**, and **22** in the yield shown in Table. All the products were identical with the parent carbonyl compounds.

2-Hydroxy-2-naphthylpropanal (20)

colorless powder; ^{1}H nmr (300 MHz) 9.62 (s, 1H, CHO), 7.94 (d, J = 1.5 Hz, 1H), 7.90-7.75 (m, 3H), 7.60-7.40 (m, 3H), 3.98 (br s, 1H, OH), 1.80 (s, 3H); ir ($CHCl_3$) 3600-3400 (br), 3060, 3000, 2940, 1730, 1630, 1600, 1510, 1450, 1370, 1320, 1090 cm^{-1}; ms *m/z* 200 (M^+, 6.5), 172 (13), 171 (92), 155 (14), 129 (13), 128 (23), 127 (28), 43 (100). HRms calcd for $C_{13}H_{12}O_2$: 200.0837, found: 200.0831.

(-)-2-Hydroxy-2-naphthylpropanal (20)

According to the general procedure, **20** (3.8 mg, 25 %) {mp 73-77 °C, $[\alpha]_D^{17}$ -176.2° (0.19, $CHCl_3$)} was obtained using a major diastereomer (**19**) (28.2 mg, 0.077 mmol), $AgNO_2$ (28.3 mg, 0.18 mmol), iodine (23.3 mg, 0.092 mmol), and aq.-THF (2.5 ml) (reaction time 10 h).

(+)-2-Hydroxy-2-naphthylpropanal (20)

According to the general procedure, **20** (8.2 mg, 40 %) {$[\alpha]_D^{16}$ +160.8° (0.05, $CHCl_3$)} was obtained using a minor diastereomer (**19**) (37.5 mg, 0.10 mmol), $AgNO_2$ (18.8 mg, 0.12 mmol), iodine (31.0 mg, 0.12 mmol), and aq.-THF (2.0 ml) (reaction time 20 h).

Hydroxy(4-biphenyl)phenylacetaldehyde (22)

According to the general procedure, **22** (23.8 mg, 70 %) was obtained using **21** (53.9 mg, 0.12 mmol), $AgNO_2$ (43.5 mg, 0.28 mmol), iodine (36.0 mg, 0.14 mmol), and aq.-THF (2.0 ml) (reaction time 4 h). mp 91-93 °C (hexane); ^{1}H nmr (300 MHz) 10.02 (d, J = 1.4 Hz, 1H, CHO), 7.65-7.57 (m, 4H), 7.48-7.32 (m, 10H), 4.43 (d, J = 1.4 Hz, 1H, OH); ir ($CHCl_3$) 3620-3250 (br), 3075, 3005, 2960, 2940, 2890, 2860, 1720, 1605, 1485, 1450, 1175, 1070, 1005, 965, 910, 840 cm^{-1}; ms *m/z* 288 (M^+, 0.27), 260 (21), 259 (100), 181 (39), 153 (15), 152 (13), 105 (63), 91 (24), 77 (17). HRMS calcd for $C_{19}H_{15}O$ [M^+-29 (CHO)]: 259.1123, found: 259.1140.

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