Construction of 1,3-Oxathiane Ring through Pummerer Reaction of γ,δ-Unsaturated Sulfinyl Compounds

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Several γ,δ-unsaturated sulfinyl compounds were prepared and their reactions with *p*-toluenesulfonic acid were examined. Conformationally rigid γ,δ-unsaturated sulfinyl compounds such as *endo*-(alkylsulfinyl)norbornene or 1-(alkylsulfinyl)-2-isopropenylbenzene derivatives afforded 1,3-oxathianes through intramolecular Pummerer rearrangement.

Key words oxathiane; Pummerer rearrangement; *p*-toluenesulfonic acid; sulfinyl compound

1,3-Oxathiane derivatives are used as important tools to obtain masked acyl anion equivalents,[1] as are methyl methylsulfinylmethyl sulfide (FAMSO),[2] methyltyrosine (MT)-sulfone[3] and 1,3-dithianes.[4] Recently, efficient asymmetric inductions using optically active 1,3-oxathiane derivatives as chiral auxiliaries have been reported.[5] In spite of such growing interest, few methods for the preparation of 1,3-oxathiane derivatives are known, other than the hemithioacetalization of carbonyl compounds.[6] Considering the mechanism of the Pummerer rearrangement, we supposed that the rearrangement might be applicable to the construction of the 1,3-oxathiane ring from a sulfinyl compound.[7]

It is well known that the Pummerer rearrangement takes place when a sulfinyl compound is treated with an electrophile such as acid anhydride, acyl halide, protonic acid, Lewis acid, and so on, to afford an α-substituted sulfide.[8] Although many types of Pummerer reaction have been thoroughly investigated, there has been no report regarding the reaction with γ,δ-unsaturated sulfinyl compounds. We envisioned that 1,3-oxathiane derivatives would be formed from γ,δ-unsaturated sulfinyl compounds through intramolecular Pummerer reaction if an appropriate electrophile were employed. Here we wish to report a new type of Pummerer reaction of γ,δ-unsaturated sulfinyl compounds, and also preparation of the sulfinyl compounds **1**—**8** (Chart 1).[9]

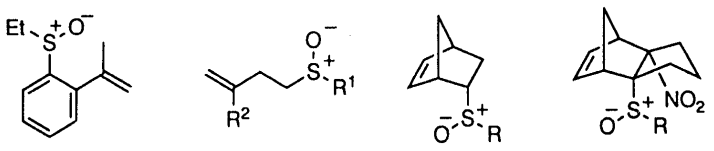
Results and Discussion

Preparation of γ,δ-Unsaturated Sulfinyl Compounds 1—8 The sulfinyl compounds **1**—**8** were prepared as shown in Chart 2. *S*-Ethylation of methyl thiosalicylate gave **9**, which was successively treated with methyl magnesium iodide to afford the tertiary alcohol. Dehydration of the alcohol with acetyl bromide to give **10**, followed by oxidation with *m*-chloroperbenzoic acid (*m*CPBA) afforded the sulfinyl compound **1**.

The γ,δ-unsaturated sulfinyl compounds **2** and **3** were prepared from β-chlorocarbonyl compounds. The sulfides **11** and **12** were obtained from β-chloropropiophenone and 1-chloro-3-pentanone, respectively, by treatment with sodium thiolate. The Wittig reaction of **11** and **12** afforded the sulfides **13** and **14**, which were oxidized with *m*CPBA to give the sulfinyl compounds **2** and **3**, respectively.

Generally, γ,δ-unsaturated sulfinyl compounds can be prepared through the Diels–Alder reaction between vinyl sulfoxide and conjugated diene.[10] The [4+2] cycloaddition reaction of a simple vinyl sulfoxide **15** with cyclopentadiene yielded bicyclo compounds **4** and **17**. The *endo*-adduct **4** included two epimers as an inseparable mixture, in which the ratio of the epimers **4a** and **4b** was determined as 3.0 : 1 from ^{1}H-NMR integration of their olefinic proton signals. Similarly, the *exo*-adduct **17** included two inseparable diastereoisomers **17a** and **17b** in a 2.4 : 1 ratio. On the other hand, benzyl vinyl sulfoxide **16** generated four diastereomers **5a**, **5b**, **18a** and **18b**, which could easily be isolated by chromatography.[11]

Recently, we demonstrated that 1-alkylsulinyl-2-nitroalkenes[12] are excellent dienophiles for the Diels–Alder reaction.[13] However, tetrasubstituted olefins such as **19** exhibited poor reactivities under conventional conditions.[13c] Here we examined Lewis acid-promoted Diels–Alder reaction of the 1-alkylsulfinyl-2-nitroalkenes **19**—**22** with cyclopentadiene (Table 1). When no Lewis acid was used, the cycloadducts were obtained in poor yields (entries 1 and 2). However, zinc chloride effectively accelerated this cycloaddition reaction to afford the *endo*-adduct **6** and *exo*-adduct **23** in moderate yields (entries 5 and 6).



1 **2**: R^1 = Et, R^2 = Ph; **3**: R^1 = CH_2Ph, R^2 = Et **4**: R = Et; **5**: R = CH_2Ph **6**: R = Et; **7**: R = ^{n}Pr; **8**: R = CH_2Ph

Chart 1

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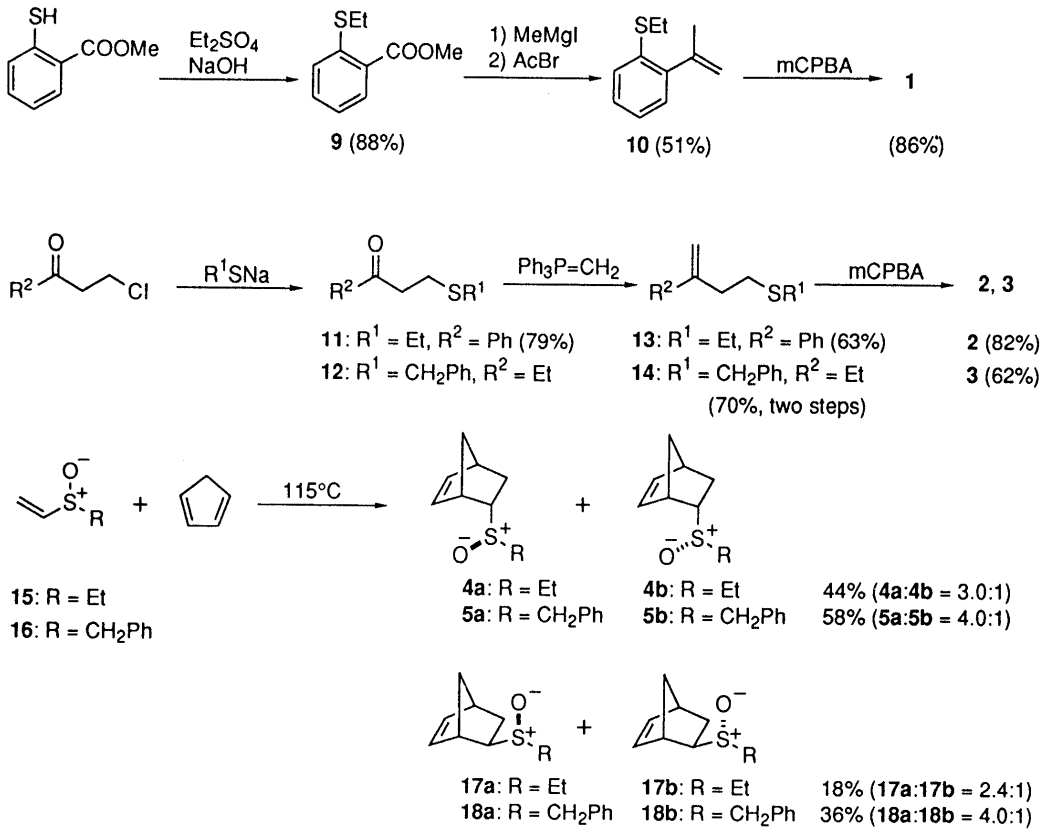
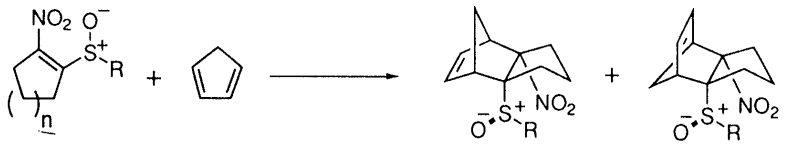


Chart 2

Table 1. Reaction of **19**—**22** with Cyclopentadiene



19: n=1, R=Et
20: n=1, R="Pr
21: n=1, R=CH_2Ph
22: n=2, R=Et

6: R=Et
7: R="Pr
8: R=CH_2Ph

23: R=Et
24: R="Pr
25: R=CH_2Ph

Entry	Dienophile	Additive	Time (h)	Temperature	Product (Yield (%)[a])	
1	**19**	None	44	Room temperature	**6** (7)	**23** (2)
2	**19**	None	17	60 °C	**6** (39)	**23** (9)
3	**19**	$AlCl_3$	17	Room temperature	**6** (13)	**23** (3)
4	**19**	$EtAlCl_2$	44	Room temperature	**6** (17)	**23** (—[b])
5	**19**	$ZnCl_2$	44	Room temperature	**6** (47)	**23** (6)
6	**19**	$ZnCl_2$	17	60 °C	**6** (57)	**23** (15)
7	**20**	$ZnCl_2$	17	60 °C	**7** (53)	**24** (26)
8	**21**	$ZnCl_2$	17	60 °C	**8** (55)	**25** (16)
9	**22**	$ZnCl_2$	17	60 °C	No reaction	

a) Isolated yield. *b*) Not isolated.

In contrast to the case of the simple vinyl sulfoxides, adducts **6** and **23** included no diastereoisomer. Similarly, cycloadducts **7** and **24** were obtained from **20**, and cycloadducts **8** and **25** from **21**, without generating their diastereoisomers (entries 7 and 8). However, the sulfinyl alkene **22** having a six-membered ring was inert toward cyclopentadiene, even if zinc chloride was employed as the Lewis acid (entry 9).

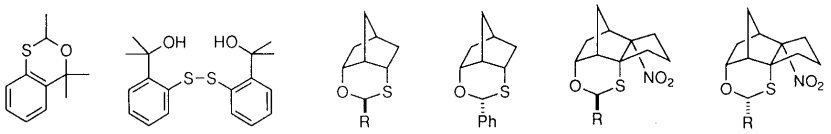
The poorer reactivity of compound **22** may be due to the lack of flatness in the ring conformation. We suppose that he non-bonded interaction between the methylene groups in the cyclohexene moiety and cyclopentadiene lowers the reactivity for the Diels–Alder cycloaddition reaction.[13a)]

Intramolecular Pummerer Reaction of γ,δ-Unsaturated Sulfinyl Compound We examined the reaction of γ,δ-unsaturated sulfinyl compound **1** with some protonic acids (Table 2). The reaction of **1** with *p*-toluenesulfonic acid

Table 2. Intramolecular Pummerer Reaction of γ,δ-Unsaturated Sulfinyl Compounds[a]

Entry	Sulfinyl comp.	Acid (eq)	Time (h)	Product	Yield (%)[b]
1	**1**	*p*-TSA·H_2O (1.0)	0.8	**26**	53
2	**1**	CH_3COOH (1.0)	5.2	**27**	27
3	**1**	CF_3COOH (1.0)	2.7	—[c]	—
4	**1**	TfOH (1.0)	1.0	—[c]	—
5	**4**[d]	*p*-TSA·H_2O (1.0)	2.5	**28**	40
6	**4**[d]	*p*-TSA·H_2O (1.2)	1.0	**28**	50
7	**4**[d]	*p*-TSA·H_2O (0.3)	1.0	**28**	2
8	**4**[d]	*p*-TSA·H_2O (5.0)	1.0	**28**	<18
9	**5a**	*p*-TSA·H_2O (1.2)	1.0	**29a**, **29b**	96 (**29a**:**29b**=38:1)[e]
10	**5a**	*p*-TSA (1.2)	1.0	**29a**, **29b**	91 (**29a**:**29b**=35:1)[e]
11	**5b**	*p*-TSA·H_2O (1.2)	1.0	**29a**, **29b**	8 (**29a**:**29b**=32:1)[e,f]
12	**6**	*p*-TSA·H_2O (1.0)	1.0	**30a**, **30b**	77 (**30a**:**30b**=18:1)
13	**7**	*p*-TSA·H_2O (1.0)	1.0	**31a**, **31b**	83 (**31a**:**31b**=12:1)[e]
14	**8**	*p*-TSA·H_2O (1.0)	1.0	**32a**, **32b**	83 (**32a**:**32b**=59:1)[e]

a) Reactions were carried out in xylene under reflux. *b*) Isolated yield. *c*) Many spots appeared on TLC. *d*) A mixture of two diastereomers in 3:1 ratio was used. *e*) The ratio was calculated from ^{1}H-NMR signal integration. *f*) A 55% yield of **5b** was recovered.



26 **27** **28**: R=Me, **29a**: R=Ph **29b** **30a**: R=Me, **31a**: R=Et, **32a**: R=Ph **30b**: R=Me, **31b**: R=Et, **32b**: R=Ph

(*p*-TSA) monohydrate in refluxing xylene for 0.8 h afforded the 1,3-oxathiane derivative **26** in 53% yield (entry 1). The reaction with other acids such as trifluoroacetic acid or trifluoromethanesulfonic acid showed many spots on TLC (entries 3 and 4). When acetic acid was used, the disulfide **27** was unexpectedly obtained as the only isolatable product (entry 2). In order to optimize the reaction conditions, we investigated the reaction of the sulfinyl compound **4** under various conditions. As can be seen in Table 2, about 1 eq. of *p*-TSA and refluxing temperature in xylene were essential for this reaction (entries 6—8). Long reaction time lowered the yield of the oxathiane **28** (entry 5 *vs.* 6), which might be due to instability of the generated oxathiane under the reaction conditions. The reaction of the *S*-benzyl derivative **5a** afforded 1,3-oxathiane **29a** with a trace amount of its diastereoisomer **29b** (entry 9). The crystal water of the reagent did not seem to affect the Pummerer rearrangement (entries 9 and 10). Surprisingly, the minor adduct **5b** showed very low reactivity (entry 11). These results mean that the relative configuration at the sulfur atom is important for this reaction.

Nitrosulfinyl compounds **6**—**8** were also subjected to the reaction with *p*-TSA in refluxing xylene. The reaction of **6** proceeded smoothly to afford oxathiane **30a** in good yield, and its epimer **30b** as a minor product (entry 12). Similarly, nitrosulfinyl compounds **7** and **8** gave **31a** and **32a** as major, and **31b** and **32b** as minor products, respectively. In order to clarify the structure of **30a**, an X-ray diffraction analysis was carried out (Fig. 1).[14] It was found that the 2-methyl group is in equatorial position with a chair conformation. On the other hand, the stereostructure of the minor oxathiane **30b** was confirmed by means of a nuclear Overhauser effect (NOE) experiment, as shown in Fig. 2; 7% NOE was observed at the

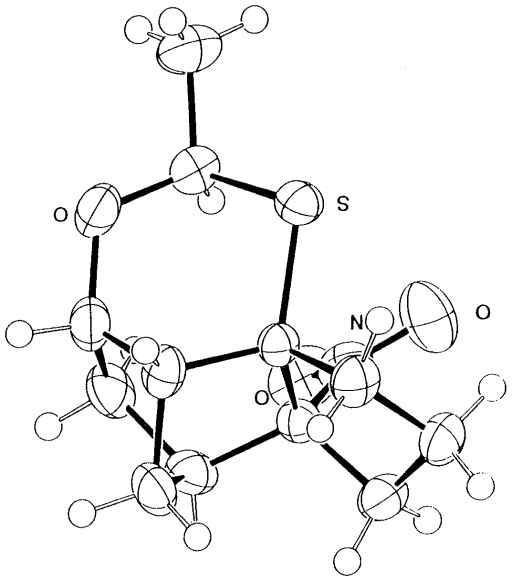


Fig. 1. ORTEP Drawing of the Major Oxathiane **30a**

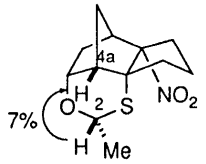


Fig. 2. NOE Interaction Observed in the Minor Oxathiane **30b**

4a-H (δ 2.76) on irradiation at 2-H (δ 5.28). Furthermore, chemical correlation between **30a** and **30b** was investigated. Although all attempts to transform the oxathiane into the corresponding mercaptoalcohol were unsuccessful, oxidative cleavage with *N*-chlorosuccinimide–silver nitrate[5f,15] gave the same sultine **33** from both **30a** and **30b** (Chart

3). The stereostructures of other products were elucidated by comparison of the ^{1}H-NMR chemical shifts of the monothioacetal protons with those of **30a** and **30b**. The data are compiled in Table 3. Lower-field chemical shifts would be indicative of α-configuration of the proton at the monothioacetal position.[16]

In contrast to the above results, the reaction of γ,δ-unsaturated sulfinyl compounds **2** and **3** gave only complicated mixtures. This is probably due to the thermal elimination of the sulfinyl group, rather than Pummerer type reaction.

Chart 4 shows two plausible processes of this intramolecular Pummerer reaction. The first process involves a five-membered sulfonium intermediate derived by intramolecular nucleophilic attack of sulfoxide oxygen toward the benzylic carbocation (path A). The second is conventional Pummerer rearrangement giving α-hydroxy sulfide followed by cyclization to construct the oxathiane ring (path B). Entries 9 and 11 in Table 2, in which a difference in reactivities between the two epimeric sulfinyl compounds **5a** and **5b** was observed, might offer crucial information to determine the reaction pathway. However, there are at least two possible explanations to rationalize this difference of the reactivities: i) the reaction rate of transformation of **5a** into the sulfonium intermediate is very much faster than that of **5b** (path A mode), and ii) the reaction rate of **5a** to afford the α-hydroxysulfide intermediate is very much faster than that of **5b** (path B mode). Consequently, we cannot determine the reaction pathway from these results alone. To establish the precise mechanism, it is necessary to carry out further experiments.

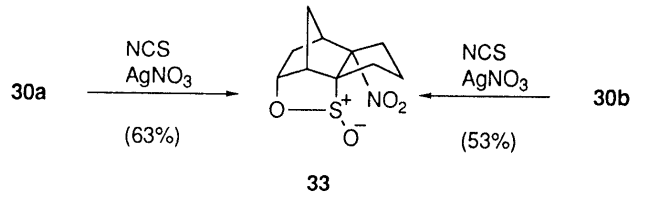


Chart 3

Table 3. Composition of Acetal-H Chemical Shifts of Major and Minor Products

Major product	Chemical shift for acetal-H (ppm)	Minor product	Chemical shift for acetal-H (ppm)
28	5.07		
29a	5.98	**29b**	6.12
30a	4.54	**30b**	5.28
31a	4.35	**31b**	5.04
32a	5.58	**32b**	6.17

In conclusion, the Pummerer-type rearrangement of γ,δ-unsaturated sulfinyl compounds has been developed. The reaction of conformationally rigid substrates such as **1**, **4**, **5a**, **6**, **7** and **8** with *p*-TSA in refluxing xylene proceeded to give the corresponding 1,3-oxathianes in good yields. We believe that this method provides a synthetic application of 1,3-oxathianes.

Experimental

Melting points were measured with a Yanagimoto micro melting point hot-stage apparatus and are uncorrected. Infrared (IR) spectra were recorded on a JASCO A-102 spectrometer. Nuclear magnetic resonance (NMR) spectra were taken with a Hitachi R-1500 (60 MHz), Varian VXR-200 (200 MHz) or Varian VXR-500 (500 MHz) instrument in $CDCl_3$ with the chemical shift being reported as δ ppm from tetramethylsilane as an internal standard; couplings are expressed in hertz. Fast atom bombardment-mass spectra (FAB-MS) were obtained with a VG-70SE mass spectrometer. All organic solutions obtained in extraction were dried over anhydrous magnesium sulfate. Silica gel column chromatography was carried out with Wako-gel C-200 or Merck No. 9385.

Methyl 2-(Ethylthio)benzoate (9) Et_2SO_4 (17 g, 107 mmol) was added to a solution of methyl 2-mercaptobenzoate (18 g, 107 mmol) and NaOH (4.4 g, 110 mmol) in a mixture of MeOH (90 ml) and H_2O (90 ml) at 0 °C. The mixture was stirred for 1 h at 0 °C and then for 17 h at room temperature. The resulting precipitate was collected on a filter, and taken up in Et_2O. The Et_2O solution was washed with water and brine, dried, and evaporated to leave crystalline **9** (18 g, 88%), which was recrystallized from Et_2O to yield colorless prisms, mp <30 °C. IR ($CHCl_3$) cm^{-1}: 1720, 1280, 1250. ^{1}H-NMR (60 MHz, $CDCl_3$) δ: 1.38 (t, 3H, J=7.6), 2.96 (q, 2H, J=7.6), 3.92 (s, 3H), 7.09—7.48 (m, 3H), 7.89—8.01 (m, 1H). *Anal.* Calcd for $C_{10}H_{12}O_2S$: C, 61.20; H, 6.16. Found: C, 60.80; H, 6.11.

2-(2-Ethylthiophenyl)-2-propanol A solution of MeMgI in Et_2O (25 ml), prepared from Mg (866 mg, 35.7 mmol) and MeI (5.1 g, 35.7 mmol), was added dropwise to a solution of **9** (1.4 g, 7.13 mmol) in Et_2O (15 ml) under gentle reflux. The mixture was refluxed for 1 h and the reaction was quenched with saturated aqueous NH_4Cl solution (14 ml). The mixture was poured into H_2O, and extracted with Et_2O, then the extract was washed with brine, and dried. The solvent was removed under reduced pressure. The residue was subjected to silica gel column chromatography with hexane–EtOAc (7 : 1) to yield a colorless oil (1.3 g, 91%). IR ($CHCl_3$) cm^{-1}: 3500, 3000, 1380, 1180. ^{1}H-NMR (60 MHz, $CDCl_3$) δ: 1.32 (t, 3H, J=7.3), 1.69 (s, 1H), 2.98 (q, 2H, J=7.3), 4.66 (s, 1H), 7.11—7.56 (m, 4H). *Anal.* Calcd for $C_{11}H_{16}OS$: C, 67.30; H, 8.21. Found: C, 66.90; H, 8.07.

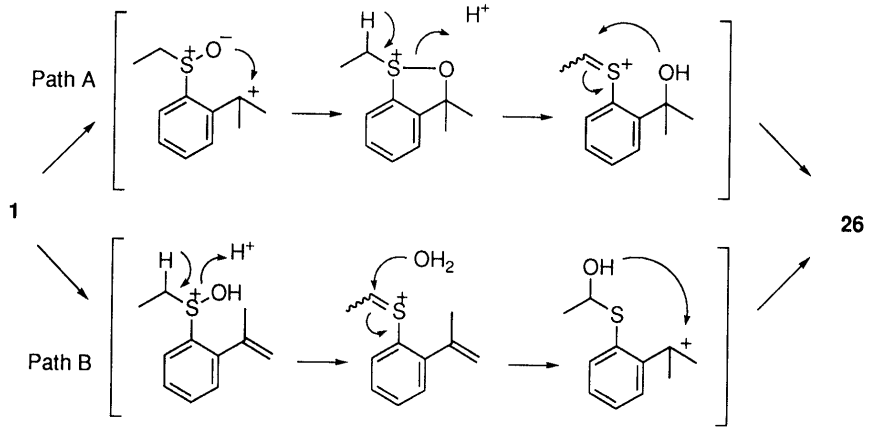


Chart 4

Ethyl 2-Isopropenylphenyl Sulfide (10) According to Ruff's procedure,[17] a mixture of 2-(2-ethylthiophenyl)-2-propanol (9.0 g, 45.8 mmol) and acetyl bromide (23 g, 183.4 mmol) was refluxed for 2.5 h under an argon atmosphere. The reaction mixture was poured into saturated aqueous $NaHCO_3$ solution and extracted with Et_2O. The extract was washed with brine, dried and evaporated to give an oily residue. Again, acetyl bromide (23 g, 183.4 mmol) was added to the residue and the mixture was refluxed for 1 h. After work-up as above, distillation under reduced pressure gave **10** (4.6 g, 56%) as a colorless oil, bp 102 °C/8 mmHg. IR ($CHCl_3$) cm^{-1}: 3000, 1480, 910. ^1H-NMR (60 MHz, $CDCl_3$) δ: 1.30 (t, 3H, $J=7.1$), 2.11 (s, 3H), 2.92 (q, 2H, $J=7.1$), 4.92 (m, 1H), 5.23 (m, 1H), 7.10—7.33 (m, 4H). FAB-MS (positive ion mode) *m/z*: 179 $(M+1)^+$. *Anal.* Calcd for $C_{11}H_{14}S$: C, 74.10; H, 7.92. Found: C, 73.77; H, 7.88.

Ethyl 2-Isopropenylphenyl Sulfoxide (1) A solution of **10** (3.0 g, 16.8 mmol) in CH_2Cl_2 (150 ml) was treated with 80% *m*CPBA (4.0 g, 18.5 mmol) at −20 °C. The mixture was stirred for 10 min at −20 °C and then poured into saturated aqueous $NaHCO_3$ solution. After extraction with $CHCl_3$, the extract was washed with brine, dried, and evaporated. The resulting residue was purified by silica gel column chromatography with hexane–AcOEt (2:1) to give **1** (2.8 g, 86%) as a colorless oil. IR ($CHCl_3$) cm^{-1}: 3000, 1020, 910. ^1H-NMR (200 MHz, $CDCl_3$) δ: 1.20 (t, 3H, $J=7.4$), 2.11 (t, 3H, $J=1.2$), 2.69 (dq, 1H, $J=13.4$, 7.4), 2.92 (dq, 1H, $J=13.4$, 7.4), 4.99 (m, 1H), 5.29 (m, 1H), 7.21 (m, 1H), 7.40—7.54 (m, 2H), 7.97 (m, 1H). FAB-MS (positive ion mode) *m/z*: 195 $(M+1)^+$.

3-(Ethylthio)propiophenone (11) EtSH (8.1 g, 130 mmol) was added to a solution of EtONa in EtOH, prepared from Na (2.7 g, 117 mmol) and EtOH (200 ml). The mixture was refluxed for a few minutes and cooled to room temperature. β-Chloropropiophenone (20 g, 119 mmol) was added at room temperature and the whole was stirred for 2 h. A white precipitate was removed and then the solvent was evaporated. The resulting residue was poured into H_2O and extracted with Et_2O. The extract was washed with brine, dried, and evaporated to leave crystalline material, which was recrystallized from Et_2O–hexane to yield colorless plates **11** (18.3 g, 79%), mp 43.5—44 °C. IR ($CHCl_3$) cm^{-1}: 1690. ^1H-NMR (500 MHz, $CDCl_3$) δ: 1.29 (t, 3H, $J=7.5$), 2.60 (q, 2H, $J=7.5$), 2.93 (t, 2H, $J=7.5$), 3.28 (t, 2H, $J=7.5$), 7.47 (m, 2H), 7.57 (m, 1H), 7.97 (m, 2H). *Anal.* Calcd for $C_{11}H_{14}OS$: C, 68.00; H, 7.26. Found: C, 68.30; H, 7.23.

4-Ethylthio-2-phenyl-1-butene (13) A solution of *n*-BuLi in hexane solution (14.0 mmol) was added to a solution of Ph_3PCH_3Br (5.0 g, 13.9 mmol) in THF (26 ml) at 0 °C. The mixture was stirred for 30 min at 0 °C and for 1.5 h at room temperature. A solution of **11** (220 mg, 1.13 mmol) in THF (10 ml) was added and the reaction mixture was stirred for 1 h at room temperature and then poured into H_2O. After extraction with Et_2O, the extract was washed with brine, dried, and evaporated. The resulting residue was purified by silica gel column chromatography with hexane–$CHCl_3$ (10:1) to afford a colorless oil **13** (136 mg, 63%). IR ($CHCl_3$) cm^{-1}: 3000, 1500, 1460, 900, 700. ^1H-NMR (200 MHz, $CDCl_3$) δ: 1.23 (t, 3H, $J=7.4$), 2.55 (q, 2H, $J=7.4$), 2.58—2.67 (m, 2H), 2.75—2.83 (m, 2H), 5.12 (d, 1H, $J=1.4$), 5.33 (br s, 1H), 7.30—7.40 (m, 5H). *Anal.* Calcd for $C_{12}H_{16}S$: C, 74.94; H, 8.39. Found: C, 75.26; H, 8.31.

4-Ethylsulfinyl-2-phenyl-1-butene (2) A solution of **13** (56 mg, 0.291 mmol) in CH_2Cl_2 (6 ml) was added treated with *m*CPBA (63 mg, 0.292 mmol) at −78 °C. The mixture was stirred for 20 min at −78 °C and then poured into saturated aqueous $NaHCO_3$ solution. After extraction with $CHCl_3$, the extract was washed with brine, dried, and evaporated. The resulting residue was purified by silica gel column chromatography with AcOEt to give **2** (50 mg, 82%) as a colorless oil, IR ($CHCl_3$) cm^{-1}: 3000, 1020. ^1H-NMR (500 MHz, $CDCl_3$) δ: 1.31 (t, 3H, $J=7.5$), 2.66—2.84 (m, 4H), 2.92—3.08 (m, 2H), 5.21 (d, 1H, $J=1.0$), 5.40 (s, 1H), 7.27—7.37 (m, 3H), 7.40—7.42 (m, 2H). FAB-MS (positive ion mode) *m/z*: 209 $(M+1)^+$.

4-Benzylthio-2-ethyl-1-butene (14) Benzyl mercaptan (2.1 g, 17.3 mmol) was added to a solution of EtONa in EtOH, prepared from Na (397 mg, 17.3 mmol) and EtOH (10 ml). The mixture was refluxed for a few minutes and cooled to room temperature. 1-Chloro-3-pentanone (2.1 g, 17.3 mmol) was added dropwise, and the whole was refluxed for 2 h. A white precipitate was removed and then the solvent was evaporated. The resulting residue was subjected to silica gel column chromatography with hexane–AcOEt (10:1) to afford crude **12** (3.89 g). This was used directly for the next reaction without further purification.

A solution of Ph_3PCH_3Br (7.6 g, 21.4 mmol) in tetrahydrofuran (THF) (50 ml) was treated with *n*-BuLi in hexane (21.4 mmol) at 0 °C. The mixture was stirred for 1 h at 0 °C and for 1.5 h at room temperature. A solution of **12** (3.89 g) in THF (10 ml) was then added, and the whole was stirred for 1 h and poured into H_2O. After extraction with Et_2O, the extract was washed with brine, dried, and evaporated. The resulting residue was purified by silica gel column chromatography with hexane–AcOEt (12:1) to afford a colorless oil **14** (2.58 g, 70% from 1-chloro-3-pentanone). IR (neat) cm^{-1}: 2950, 1460, 700. ^1H-NMR (500 MHz, $CDCl_3$) δ: 1.00 (t, 3H, $J=7.5$), 1.98 (q, 2H, $J=7.5$), 2.27 (t, 2H, $J=7.5$), 2.51 (m, 2H), 3.72 (s, 2H), 4.70 (br s, 1H), 4.75 (br s, 1H), 7.21—7.35 (m, 5H). HRMS (FAB) Calcd for $C_{13}H_{19}S$ $(M+H)^+$: 207.1201. Found: 207.1207.

4-Benzylsulfinylthio-2-ethyl-1-butene (3) A solution of **14** (2.46 g, 11.9 mmol) in CH_2Cl_2 (50 ml) was treated with 80% *m*CPBA (2.70 g, 12.5 mmol) at −78 °C. The mixture was stirred for 20 min at −78 °C and then poured into saturated aqueous $NaHCO_3$ solution. After extraction with $CHCl_3$, the extract was washed with brine, dried, and evaporated. The resulting residue was recrystallized from Et_2O–hexane to give **3** (1.65 g, 62%) as colorless prisms, mp 46 °C. IR (KBr) cm^{-1}: 1035. ^1H-NMR (60 MHz, $CDCl_3$) δ: 1.02 (t, 3H, $J=7.6$), 1.80—2.90 (m, 6H), 4.00 (s, 2H), 4.75 (br s, 1H), 4.81 (br s, 1H), 7.34 (m, 5H). FAB-MS (positive ion mode) *m/z*: 223 $(M+1)^+$. *Anal.* Calcd for $C_{13}H_{18}OS$: C, 70.23; H, 8.16. Found: C, 70.33; H, 8.18.

Ethyl Vinyl Sulfoxide (15) A solution of ethyl vinyl sulfide[18] (1.2 g, 13.6 mmol) in CH_2Cl_2 (100 ml) was treated with 80% *m*CPBA (3.2 g, 15.0 mmol) at 0 °C. The mixture was stirred for 30 min at 0 °C and then poured into saturated aqueous $NaHCO_3$ solution. After extraction with CH_2Cl_2, the extract was washed with brine, dried, and evaporated. The resulting residue was purified by silica gel column chromatography with AcOEt to give **15** (786 mg, 56%) as a colorless oil. IR ($CHCl_3$) cm^{-1}: 3030, 1060, 960. ^1H-NMR (200 MHz, $CDCl_3$) δ: 1.26 (t, 3H, $J=7.4$), 2.40 (dq, 1H, $J=13.3$, 7.4), 2.83 (dq, 1H, $J=13.3$, 7.4), 5.96 (d, 1H, $J=9.8$), 6.07 (d, 1H, $J=16.6$), 6.55 (dd, 1H, $J=16.6$, 9.8).

5-Ethylsulfinylbicyclo[2.2.1]hept-2-ene (4a, 4b, 17a and 17b) A mixture of **15** (750 mg, 7.20 mmol), cyclopentadiene (1.44 g, 21.8 mmol) and hydroquinone (7.9 mg, 0.072 mmol) was heated for 10 h at 115 °C in a sealed tube. Removal of volatile materials under reduced pressure gave a residue, which was subjected to silica gel column chromatography with AcOEt to give the cycloadducts. An inseparable mixture of *endo*-adducts **4a** (400 mg, 33%) and **4b** (135 mg, 11%) was obtained from the less polar fractions, and an inseparable mixture of *exo*-adducts **17a** (158 mg, 13%) and **17b** (65 mg, 5%) was obtained from the more polar fractions. The yields were determined by the integration of ^1H-NMR signals.

4a and **4b**: Inseparable mixture (3.0:1). IR ($CHCl_3$) cm^{-1}: 3030, 1020. ^1H-NMR (200 MHz, $CDCl_3$) δ: (selected signals of **4a**): 0.73 (ddd, 1H, $J=12.4$, 4.2, 2.8), 1.31 (t, 3H, $J=7.4$), 1.89 (ddd, 1H, $J=12.4$, 9.0, 3.6), 2.97 (br s, 1H), 3.39 (br s, 1H), 6.23 (m, 2H); (selected signals of **4b**: 5.89 (dd, 1H, $J=5.8$, 2.6). FAB-MS (positive ion mode) *m/z*: 171 $(M+1)^+$.

17a and **17b**: Inseparable mixture (2.4:1). IR ($CHCl_3$) cm^{-1}: 3030, 1020. ^1H-NMR (200 MHz, $CDCl_3$) δ: (selected signals of **17a**): 1.36 (t, 3H, $J=7.4$), 2.98 (br s, 1H), 3.42 (m, 1H), 6.12 (dd, 1H, $J=5.4$, 3.1), 6.20 (dd, 1H, $J=5.4$, 3.1); (selected signals of **17b**): 6.24 (dd, 1H, $J=5.8$, 3.0). FAB-MS (positive ion mode) *m/z*: 171 $(M+1)^+$.

Benzyl Vinyl Sulfoxide (16) Benzyl mercaptan (25.0 g, 0.2 mol) was added to a solution of EtONa in EtOH, prepared from Na (4.6 g, 0.2 mol) and EtOH (100 ml). The mixture was refluxed for a few minutes and cooled to room temperature. Ethylene chlorohydrin (16.2 g, 0.2 mol) was added dropwise at room temperature and the reaction mixture was refluxed for 2 h. A white precipitate was removed and the solvent was evaporated. The resulting residue was distilled under reduced pressure to give benzyl 2-hydroxyethyl sulfide (30.3 g, 89%) as a colorless oil, bp 140 °C/4 mmHg. IR (neat) cm^{-1}: 3420, 1505, 1460, 700. ^1H-NMR (200 MHz, $CDCl_3$) δ: 2.34 (br s, 1H, exchangeable with D_2O), 2.61 (t, 2H, $J=6.0$), 3.65 (t, 2H, $J=6.0$), 3.71 (s, 2H), 7.28—7.34 (m, 5H). *Anal.* Calcd for $C_9H_{12}OS$: C, 64.25; H, 7.19. Found: C, 64.53; H, 7.18.

$SOCl_2$ (29.7 g, 0.25 mol) was added dropwise to a solution of benzyl 2-hydroxyethyl sulfide (34.4 g, 0.20 mol) and pyridine (17.4 g, 0.22 mol) in CH_2Cl_2 (200 ml) at −15 °C. The mixture was stirred for 1 h at room temperature, refluxed for 4 h, and poured into 1 N HCl solution. After extraction with CH_2Cl_2, the extract was washed with brine, dried and evaporated to give a residue, which was purified by distillation under reduced pressure to afford benzyl 2-chloroethyl sulfide (34.4 g, 92%) as a colorless oil, bp 114 °C/6 mmHg. IR (neat) cm^{-1}: 1510, 1470, 710.

^{1}H-NMR (200 MHz, $CDCl_3$) δ: 2.75 (m, 2H), 3.52 (m, 2H), 3.75 (s, 2H), 7.21—7.39 (m, 5H).

A solution of benzyl 2-chloroethyl sulfide (14.7 g, 76.3 mmol) in CH_2Cl_2 (250 ml) was treated with 80% *m*CPBA (19.8 g, 91.5 mmol) at −78 °C. The mixture was stirred for 4 h at −78 °C and then poured into saturated aqueous $NaHCO_3$ solution. After extraction with $CHCl_3$, the extract was washed with brine, dried, and evaporated. The resulting residue was recrystallized from hexane–Et_2O to give benzyl 2-chloroethyl sulfoxide (12.1 g, 81%) as colorless prisms, mp 92 °C. IR (KBr) cm^{-1}: 1025. ^{1}H-NMR (200 MHz, $CDCl_3$) δ: 2.94 (dd, 2H, J=7.2, 6.0), 3.86 (dd, 1H, J=11.6, 6.0), 3.92 (dd, 1H, J=11.6, 7.2), 4.04 (d, 1H, J=12.8), 4.09 (d, 1H, J=12.8), 7.25—7.46 (m, 5H). *Anal.* Calcd for $C_9H_{11}ClOS$: C, 53.33; H, 5.47. Found: C, 53.09; H, 5.38.

A solution of benzyl 2-chloroethyl sulfoxide (1.27 g, 6.27 mmol) in THF (30 ml) was treated with *tert*-BuOK (774 mg, 6.9 mmol) at 0 °C. The mixture was stirred for 1 h at 0 °C and then poured into H_2O. After extraction with CH_2Cl_2, the extract was washed with brine, dried and evaporated to give a residue, which was purified by silica gel column chromatography with AcOEt to leave crystalline **16** (0.89 g, 85%). Recrystallization of **16** from CH_2Cl_2–Et_2O afforded colorless needles, mp 43—45 °C. IR (KBr) cm^{-1}: 1040. ^{1}H-NMR (200 MHz, $CDCl_3$) δ: 3.97 (d, 1H, J=12.7), 4.03 (d, 1H, J=12.7), 5.90 (d, 1H, J=9.8), 5.99 (d, 1H, J=16.5), 6.57 (dd, 1H, J=16.5, 9.8), 7.23—7.45 (m, 5H). *Anal.* Calcd for $C_9H_{10}OS$: C, 65.03; H, 6.06. Found: C, 64.94; H, 6.03.

5-Benzylsulfinylbicyclo[2.2.1]hept-2-ene (5a, 5b, 18a and 18b) A mixture of **16** (0.5 g, 3.0 mmol), cyclopentadiene (5.95 g, 90.0 mmol) and hydroquinone (3.3 mg, 0.03 mmol) was heated for 12 h at 115 °C in a sealed tube. Removal of volatile materials under reduced pressure gave a residue, which was subjected to silica gel column chromatography with AcOEt to give the cycloadducts **5a** (324 mg, 46%), **5b** (81 mg, 12%), **18a** (156 mg, 22%) and **18b** (98 mg, 14%). Recrystallization of **5a**, **5b**, **18a** and **18b** from CH_2Cl_2–Et_2O gave colorless prisms for **5a**, **5b** and **18b**, and colorless plates for **18a**, respectively.

5a (*endo*-Major): mp 98 °C. IR ($CHCl_3$) cm^{-1}: 3030, 1030, 695. ^{1}H-NMR (200 MHz, $CDCl_3$) δ: 0.70 (ddd, 1H, J=12.4, 4.0, 2.4), 1.26 (d, 1H, J=8.8), 1.57 (d, 1H, J=8.8), 1.82 (ddd, 1H, J=12.4, 9.0, 3.6), 2.95 (br s, 1H), 3.20 (dt, 1H, J=9.0, 4.0), 3.34 (br s, 1H), 3.74 (d, 1H, J=13.2), 3.97 (d, 1H, J=13.2), 6.23 (br s, 2H), 7.23—7.44 (m, 5H). *Anal.* Calcd for $C_{14}H_{16}OS$: C, 72.37; H, 6.94. Found: C, 72.50; H, 6.98.

5b (*endo*-Minor): mp 124 °C. IR (KBr) cm^{-1}: 3000, 1022, 700. ^{1}H-NMR (200 MHz, $CDCl_3$) δ: 1.34 (d, 1H, J=8.2), 1.53 (m, 1H), 1.68 (m, 1H), 2.05 (ddd, 1H, J=12.6, 9.0, 3.6), 2.89 (br s, 1H), 2.99 (br s, 1H), 3.25 (dt, 1H, J=9.0, 3.6), 3.91 (d, 1H, J=13.0), 4.09 (d, 1H, J=13.0), 5.87 (dd, 1H, J=5.8, 2.8), 6.26 (dd, 1H, J=5.8, 3.1), 7.29—7.46 (m, 5H). *Anal.* Calcd for $C_{14}H_{16}OS$: C, 72.37; H, 6.94. Found: C, 72.33; H, 6.92.

18a (*exo*-Major): mp 111 °C. IR (KBr) cm^{-1}: 3000, 1035, 695. ^{1}H-NMR (200 MHz, $CDCl_3$) δ: 1.26—1.35 (m, 2H), 1.46 (d, 1H, J=9.0), 1.61 (d, 1H, J=9.0), 2.45 (m, 1H), 2.98 (br s, 1H), 3.41 (m, 1H), 3.82 (d, 1H, J=13.2), 4.06 (d, 1H, J=13.2), 6.07 (dd, 1H, J=5.4, 3.0), 6.19 (dd, 1H, J=5.4, 3.0), 7.25—7.43 (m, 5H). *Anal.* Calcd for $C_{14}H_{16}OS$: C, 72.37; H, 6.94. Found: C, 72.51; H, 6.89.

18b (*exo*-Minor): mp 98 °C. IR (KBr) cm^{-1}: 3000, 1032, 705. ^{1}H-NMR (200 MHz, $CDCl_3$) δ: 1.20—1.45 (m, 2H), 1.74 (d, 1H, J=8.2), 2.18—2.40 (m, 2H), 2.89 (br s, 1H), 2.99 (br s, 1H), 3.91 (d, 1H, J=12.8), 4.02 (d, 1H, J=12.8), 6.06 (dd, 1H, J=5.6, 3.2), 6.23 (dd, 1H, J=5.6, 3.0), 7.24—7.45 (m, 5H). *Anal.* Calcd for $C_{14}H_{16}OS$: C, 72.37; H, 6.94. Found: C, 72.67; H, 6.95.

1-Ethylsulfinyl-2-nitrocyclopentene (19) and 1-Ethylsulfinyl-2-nitrocyclohexene (22) Compounds **19** and **22** were prepared by the reported method.[19]

1-Nitro-2-propylsulfinylcyclopentene (20) A solution of **19** (103 mg, 0.54 mmol) and ^{n}PrSH (41 mg, 0.54 mmol) in CH_2Cl_2, was treated with Et_3N (0.08 ml, 0.58 mmol) at −78 °C. The mixture was stirred for 55 min at −78 °C and poured into 1 N HCl solution. After extraction with $CHCl_3$, the extract was washed with brine, dried, and evaporated to dryness. The residue was purified by silica gel column chromatography with hexane–AcOEt (10 : 1) to afford 1-nitro-2-propylthiocyclopentene (102 mg, 100%). Recrystallization from hexane gave yellow needles, mp 69—70 °C. IR ($CHCl_3$) cm^{-1}: 1580, 1470, 1340, 1320. ^{1}H-NMR (200 MHz, $CDCl_3$) δ: 1.05 (t, 3H, J=7.4), 1.70 (sextet, 2H, J=7.4), 2.10—2.15 (m, 2H), 2.81—2.99 (m, 6H). *Anal.* Calcd for $C_8H_{13}NO_2S$: C, 51.31; H, 7.00; N, 7.48. Found: C, 51.07; H, 6.83; N, 7.57.

Oxone (217 mg, 0.35 mmol) was added to a solution of 1-nitro-2-propylthiocyclopentene (102 mg, 0.55 mmol) in a mixture of THF (1.8 ml), MeOH (0.9 ml), and H_2O (1.8 ml). The mixture was stirred for 70 min at room temperature, then extracted with $CHCl_3$ and the extract was washed with brine, dried, and evaporated to give a residue, which was subjected to silica gel column chromatography with hexane–AcOEt (1 : 1). The resulting **20** (95.8 mg, 87%) was recrystallized from Et_2O to give yellow prisms, mp 48—49 °C. IR (KBr) cm^{-1}: 1520, 1350, 1060. ^{1}H-NMR (200 MHz, $CDCl_3$) δ: 1.14 (t, 3H, J=7.2), 1.87—2.24 (m, 4H), 2.88—3.20 (m, 6H). *Anal.* Calcd for $C_8H_{13}NO_3S$: C, 47.27; H, 6.45; N, 6.89. Found: C, 47.09; H, 6.29; N, 6.82.

1-Benzylsulfinyl-2-nitrocyclopentene (21) A solution of **19** (100 mg, 0.53 mmol) and benzylthiol (66 mg, 0.53 mmol) in CH_2Cl_2, was treated with Et_3N (0.08 ml, 0.58 mmol) at −78 °C. The mixture was stirred for 50 min at −78 °C and poured into 1 N HCl solution. After extraction with $CHCl_3$, the extract was washed with brine, dried, and evaporated. The residue was purified by silica gel column chromatography with hexane–CH_2Cl_2 (1 : 1) to afford 1-benzylthio-2-nitrocyclopentene (112 mg, 86%). Recrystallization from CH_2Cl_2 gave yellow prisms, mp 158—159.5 °C. IR ($CHCl_3$) cm^{-1}: 1580, 1480, 1340, 1320. ^{1}H-NMR (200 MHz, $CDCl_3$) δ: 1.99—2.15 (m, 2H), 2.92—3.00 (m, 4H), 4.13 (s, 2H), 7.26—7.36 (m, 5H). *Anal.* Calcd for $C_{12}H_{13}NO_2S$: C, 61.25; H, 5.57; N, 5.95. Found: C, 60.86; H, 5.67; N, 5.97.

A solution of 1-benzylthio-2-nitrocyclopentene (1.5 g, 6.37 mmol) in CH_2Cl_2 was treated with 80% *m*CPBA (1.8 g, 8.28 mmol) at 0 °C. The mixture was stirred for 50 min at 0 °C and then poured into saturated aqueous $NaHCO_3$ solution. After extraction with $CHCl_3$, the extract was washed with brine, dried, and evaporated. The resulting residue was subjected to silica gel column chromatography with hexane–AcOEt (2 : 1). Elution with the same solvent gave **21** (1.0 g, 64%), which was recrystallized from CH_2Cl_2–Et_2O to afford yellow prisms, mp 106—107 °C. IR (KBr) cm^{-1}: 1520, 1360, 1060, 700. ^{1}H-NMR (200 MHz, $CDCl_3$) δ: 1.76—2.06 (m, 3H), 2.72—3.10 (m, 3H), 4.24, 4.32 (ABq, 2H, J=12.9), 7.28—7.39 (m, 5H). *Anal.* Calcd for $C_{12}H_{13}NO_3S$: C, 57.36; H, 5.21; N, 5.57. Found: C, 57.10; H, 5.19; N, 5.58.

2,3,3a,4,7,7a-Hexahydro-3a-ethylsulfinyl-7a-nitro-4,7-methano-1*H*-indene (6 and 23) (Table 1, Entry 6) A mixture of **19** (59.2 mg, 0.31 mmol), cyclopentadiene (620.3 mg, 9.38 mmol) and $ZnCl_2$ (10.7 mg, 0.079 mmol) in CH_2Cl_2 (2 ml) was heated at 60 °C for 17 h in a sealed tube. The mixture was poured into H_2O and extracted with $CHCl_3$, then the organic layer was washed with brine, dried, and evaporated to leave a residue. The residue was subjected to silica gel column chromatography with AcOEt to give **6** (45.8 mg, 57%), and a mixture of **19** (5.7 mg, 10%) and **23** (12.0 mg, 15%). The yields of **19** and **23** were calculated from integration of the ^{1}H-NMR signals. Compounds **6** and **23** were recrystallized from Et_2O–CH_2Cl_2 to leave colorless needles, in each case.

6 (*endo*-Adduct): mp 101—102 °C. IR (KBr) cm^{-1}: 3000, 1540, 1450, 1360, 1060, 1020. ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 1.44 (t, 3H, J=7.5), 1.74 (m, 1H), 1.80 (d, 1H, J=10.2), 1.85 (dt, 1H, J=10.2, 1.8), 2.09—2.19 (m, 3H), 2.48 (m, 1H), 2.52 (dq, 1H, J=12.1, 7.5), 2.69 (m, 1H), 3.17 (dq, 1H, J=12.1, 7.5), 3.18 (br s, 1H), 3.33 (br s, 1H), 6.35 (dd, 1H, J=5.8, 2.9), 6.66 (dd, 1H, J=5.8, 2.9). *Anal.* Calcd for $C_{12}H_{17}NO_3S$: C, 56.45; H, 6.71; N, 5.49. Found: C, 56.27; H, 6.60; N, 5.22.

23 (*exo*-Adduct): mp 152—152.5 °C. IR (KBr) cm^{-1}: 3000, 1540, 1460, 1350, 1060, 1020. ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 1.47 (t, 3H, J=7.5), 1.50 (m, 1H), 1.83—1.94 (m, 4H), 2.09 (m, 1H), 2.47 (m, 1H), 2.64 (d, 1H, J=9.7), 2.68 (dq, 1H, J=12.4, 7.5), 2.77 (dq, 1H, J=12.4, 7.5), 3.40 (br s, 1H), 3.61 (br s, 1H), 6.42 (dd, 1H, J=5.4, 3.4), 6.84 (dd, 1H, J=5.4, 3.3). *Anal.* Calcd for $C_{12}H_{17}NO_3S$: C, 56.45; H, 6.71; N, 5.49. Found: C, 56.24; H, 6.53; N, 5.56.

2,3,3a,4,7,7a-Hexahydro-3a-nitro-7a-propylsulfinyl-4,7-methano-1*H*-indene (7 and 24) (Table 1, Entry 7) In a way similar to that described above, the *endo*-adduct **7** (59 mg, 53%), the *exo*-adduct **24** (28 mg, 26%), and recovered **20** (10 mg, 12%) were obtained from **20** (84 mg, 0.41 mmol). Compounds **7** and **24** were recrystallized from Et_2O–CH_2Cl_2 to leave colorless needles, in each case.

7 (*endo*-Adduct): mp 109.5—110 °C. IR ($CHCl_3$) cm^{-1}: 3000, 1540, 1370, 1020. ^{1}H-NMR (200 MHz, $CDCl_3$) δ: 1.09 (t, 3H, J=7.4), 1.69—1.98 (m, 5H), 2.07—2.18 (m, 3H), 2.44—2.73 (m, 3H), 3.01—3.11 (m, 1H), 3.17 (br s, 1H), 3.33 (br s, 1H), 6.34 (dd, 1H, J=5.6, 2.8), 6.66 (dd, 1H, J=5.6, 2.8). *Anal.* Calcd for $C_{13}H_{19}NO_3S$: C, 57.97; H, 7.11; N, 5.20. Found: C, 57.65; H, 6.98; N, 5.27.

24 (*exo*-Adduct): mp 89.5—91 °C. IR ($CHCl_3$) cm^{-1}: 3000, 1550, 1360, 1030. ^{1}H-NMR (200 MHz, $CDCl_3$) δ: 1.21 (t, 3H, J=7.4), 1.50—1.56 (m, 1H), 1.83—2.11 (m, 7H), 2.44—2.48 (m, 1H), 2.62—2.72 (m, 3H),

3.41 (br s, 1H), 3.61 (br s, 1H), 6.43 (dd, 1H, J=5.1, 3.3), 6.49 (dd, 1H, J=5.1, 3.3). FAB-MS (positive ion mode) m/z: 270 $(M+1)^+$.

2,3,3a,4,7,7a-Hexahydro-3a-benzylsulfinyl-7a-nitro-4,7-methano-1*H*-indene (8 and 25) (Table 1, Entry 8) In a way similar to that described above, the *endo*-adduct **8** (556 mg, 55%), the *exo*-adduct **25** (164 mg, 16%), and recovered **21** (67 mg, 8%) were obtained from **21** (800 mg, 3.18 mmol). Compound **8** was recrystallized from CH_2Cl_2 to leave colorless needles, and compound **25** was recrystallized from Et_2O–CH_2Cl_2 to leave colorless prisms.

8 (*endo*-Adduct): mp 142—144 °C. IR ($CHCl_3$) cm^{-1}: 3000, 1540, 1020. ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 1.76—1.90 (m, 3H), 2.16—2.29 (m, 3H), 2.53—2.56 (m, 1H), 2.87—2.90 (m, 1H), 3.23 (br s 1H), 3.38 (br s, 1H), 3.62 (d, 1H, J=11.5), 4.58 (d, 1H, J=11.5), 6.36 (dd, 1H, J=5.5, 2.8), 6.61 (dd, 1H, J=5.5, 3.0). *Anal.* Calcd for $C_{17}H_{19}NO_3S$: C, 64.33; H, 6.03; N, 4.41. Found: C, 63.98; H, 6.00; N, 4.39.

25 (*exo*-Adduct): mp 134—136 °C. IR ($CHCl_3$) cm^{-1}: 2950, 1540, 1350, 1040. ^{1}H-NMR (200 MHz, $CDCl_3$) δ: 1.63 (m, 1H), 1.90—2.25 (m, 5H), 2.48 (m, 1H), 2.66 (d, 1H, J=9.8), 3.52 (br s, 1H), 3.64 (br s, 1H), 3.79 (d, 1H, J=12.4), 4.13 (d, 1H, J=12.4), 6.45 (dd, 1H, J=5.0, 3.5), 6.53 (dd, 1H, J=5.0, 3.5). FAB-MS (positive ion mode) m/z: 318 $(M+1)^+$.

2,4,4-Trimethyl-3,1-benzoxathian (26) (Table 2, Entry 1) A solution of **1** (107 mg, 0.55 mmol) and *p*-TSA·H_2O (105 mg, 0.55 mmol) in xylene (15 ml) was refluxed for 50 min, then poured into saturated aqueous $NaHCO_3$ solution, and extracted with $CHCl_3$. The extract was washed with brine, dried, and evaporated. The residue was subjected to silica gel column chromatography with hexane–AcOEt (30 : 1) to afford **26** (57 mg, 53%). Recrystallization of **26** from hexane gave colorless prisms, mp 58.5—59 °C. IR (KBr) cm^{-1}: 1265, 1120, 765. ^{1}H-NMR (200 MHz, $CDCl_3$) δ: 1.58 (s, 3H), 1.60 (s, 3H), 1.61 (d, 3H, J=6.1), 5.29 (q, 1H, J=6.1), 7.03—7.18 (m, 4H). *Anal.* Calcd for $C_{11}H_{14}OS$: C, 68.00; H, 7.26. Found: C, 67.90; H, 7.16.

2,2′-(2,2′-Dithiodiphenyl)-2,2′-dipropanol (27) (Table 2, Entry 2) A solution of **1** (200 mg, 1.03 mmol) and acetic acid (61 mg, 1.03 mmol) in xylene (22 ml) was refluxed for 5.2 h, then poured into saturated aqueous $NaHCO_3$ solution, and extracted with $CHCl_3$. The extract was washed with brine, dried, and evaporated. The residue was subjected to silica gel column chromatography with hexane–AcOEt (3 : 1) to afford **27** (47 mg, 27%). Recrystallization of **27** from hexane gave colorless needles, mp 141.5—143 °C. IR ($CHCl_3$) cm^{-1}: 3250, 1440, 1300, 1190. ^{1}H-NMR (200 MHz, $CDCl_3$) δ: 1.75 (s, 12H), 2.35 (br s, 2H), 7.15—7.19 (m, 4H), 7.35—7.40 (m, 2H), 7.70—7.18 (m, 2H). *Anal.* Calcd for $C_{18}H_{22}O_2S_2$: C, 64.64; H, 6.63. Found: C, 64.82; H, 6.58.

5-Methyl-4-oxa-6-thiatricyclo[5.2.1.0^{3,8}]decane (28) (Table 2, Entry 6) A solution of **4** (66 mg, 0.389 mmol) and *p*-TSA·H_2O (91 mg, 0.479 mmol) in xylene (20 ml) was refluxed for 1 h, then poured into saturated aqueous $NaHCO_3$ solution, and extracted with $CHCl_3$. The extract was washed with brine, dried, and evaporated. The residue was subjected to silica gel column chromatography with hexane–AcOEt (5 : 1) to afford **28** (33 mg, 50%). Recrystallization of **27** from hexane gave pale brown prisms, mp 32—33.5 °C. IR ($CHCl_3$) cm^{-1}: 3000, 1100. ^{1}H-NMR (200 MHz, $CDCl_3$) δ: 1.36 (m, 2H), 1.45 (d, 3H, J=6.1), 1.53—1.64 (m, 2H), 1.77—1.94 (m, 1H), 2.15—2.35 (m, 3H), 3.08—3.15 (m, 1H), 4.49—4.54 (m, 1H), 5.07 (q, 1H, J=6.1). *Anal.* Calcd for $C_9H_{14}OS$: C, 63.49; H, 8.28. Found: C, 63.21; H, 8.17.

Hexahydro-2-phenyl-4,6-methanocyclopent[*e*]-1,3-oxathiin (29a and 29b) (Table 2, Entry 9) A solution of **5a** (92.9 mg, 0.40 mmol) and *p*-TSA·H_2O (91.3 mg, 0.48 mmol) in xylene (20 ml) was refluxed for 1 h, then poured into saturated aqueous $NaHCO_3$ solution, and extracted with $CHCl_3$. The extract was washed with brine, dried, and evaporated. The residue was subjected to silica gel column chromatography with hexane–AcOEt (5 : 1) to afford **29a** and **29b** (89 mg, 96%, **29a** : **29b** = 38 : 1 from ^{1}H-NMR integration). Recrystallization of the mixture from hexane gave pure **29a** as colorless prisms, mp 88 °C. IR (KBr) cm^{-1}: 2980, 1040, 720. ^{1}H-NMR (200 MHz, $CDCl_3$) δ: 1.41 (m, 2H), 1.60—2.00 (m, 3H), 2.28—2.46 (m, 3H), 3.10—3.30 (m, 1H), 4.62—4.76 (m, 1H), 5.98 (s, 1H), 7.20—7.57 (m, 5H). *Anal.* Calcd for $C_{14}H_{16}OS$: C, 72.37; H, 6.94. Found: C, 72.41; H, 7.09.

8-Methyl-2-nitro-9-oxa-7-thiatetracyclo[8.2.1.0^{2,6}.0^{6,11}]tridecane (30a and 30b) (Table 2, Entry 12) A solution of **6** (639 mg, 2.50 mmol) and *p*-TSA·H_2O (482 mg, 2.53 mmol) in xylene (75 ml) was refluxed for 1 h. The reaction mixture was poured into saturated aqueous $NaHCO_3$ solution, and extracted with $CHCl_3$. The extract was washed with brine, dried, and evaporated. The residue was subjected to silica gel column chromatography with hexane–AcOEt (6 : 1) to afford **30a** (458 mg, 73%) and **30b** (21 mg, 4%). Compounds **30a** and **30b** were recrystallized from Et_2O to give colorless prisms, in each case.

30a (Major Product): mp 130.5—132.5 °C. IR ($CHCl_3$) cm^{-1}: 3000, 1535, 1470, 1360, 1120. ^{1}H-NMR (200 MHz, $CDCl_3$) δ: 1.30 (m, 1H), 1.33 (d, 3H, J=6.0), 1.75—2.45 (m, 10H), 2.71 (m, 1H), 4.54 (m, 2H). ^{13}C-NMR ($CDCl_3$, 50 Hz) δ: 20.81, 24.99, 25.59, 31.61, 43.71, 44.39, 44.59, 44.64, 57.20, 67.74, 75.15, 103.97. *Anal.* Calcd for $C_{12}H_{17}NO_3S$: C, 56.45; H, 6.71; N, 5.49. Found: C, 56.12; H, 6.63; N, 5.47.

Crystal Structure Determination for **30a**: A colorless prismatic crystal having dimensions of 0.25 × 0.10 × 0.45 mm was mounted on a glass fiber. Crystal data: $C_{12}H_{17}NO_3S$, M_r=255.33, triclinic, space group $P\bar{1}$, Z=2; a=7.081(3), b=13.380(8), c=6.764(3) Å, α=103.46(4), β=105.12(3), γ=89.08(5)°, V=601.0(6) Å^3, D_x=1.411 g/cm^3, μ(MoK_α)=0.25 mm^{-1}. The data were collected at 295 K using the ω–2θ scan technique to a maximum 2θ value of 52.0° with scan widths of (1.26+0.30 tan θ)° in ω and a scan speed of 6° min^{-1} in ω. Of the 2583 reflections 2370 were unique ($R_{int.}$=0.008). The fluctuation of three standard reflections measured after every 97 reflections was within 0.8%. The structure was solved by direct methods[20] and refined anisotropically for non-hydrogen atoms and isotropically for hydrogen atoms by a full-matrix least-squares technique. The quantity minimized was $\Sigma w(|F_o|-|F_c|)^2$, where $w=1/\sigma^2(F_o)$. The final R=0.032, $_wR$=0.028 for 1771 reflections with $I_o>3\sigma(I_o)$, S=1.53. Atomic scattering factors were taken from Cromer and Weber.[21] Calculations were performed using TEXSAN.[22]

30b (Minor Product): mp 126—128 °C. IR ($CHCl_3$) cm^{-1}: 3000, 1540, 1465, 1365, 1115. ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 1.33 (d, 3H, J=6.0), 1.50 (d, 1H, J=11.5), 1.78 (m, 1H), 1.86—1.99 (m, 3H), 2.07—2.28 (m, 3H), 2.45 (m, 2H), 2.71 (d, 1H, J=4.0), 2.76 (br s, 1H), 4.46 (dt, 1H, J=10.3, 4.2), 5.28 (q, 1H, J=6.0). *Anal.* Calcd for $C_{12}H_{17}NO_3S$: C, 56.45; H, 6.71; N, 5.49. Found: C, 56.31; H, 6.57; N, 5.43.

8-Ethyl-2-nitro-9-oxa-7-thiatetracyclo[8.2.1.0^{2,6}.0^{6,11}]tridecane (31a and 31b) (Table 2, Entry 13) A solution of **7** (1.9 g, 7.1 mmol) and *p*-TSA·H_2O (1.3 g, 7.1 mmol) in xylene (230 ml) was refluxed for 1 h, then poured into saturated aqueous $NaHCO_3$ solution, and extracted with $CHCl_3$. The extract was washed with brine, dried, and evaporated. The residue was subjected to silica gel column chromatography with hexane–AcOEt (8 : 1) to afford a mixture of **31a** (1.47 g, 77%) and **31b** (0.12 g, 6%). The yields were calculated from ^{1}H-NMR signal integration. Recrystallization of **31a** from CH_2Cl_2–Et_2O gave colorless prisms, mp 96—97.5 °C. IR ($CHCl_3$) cm^{-1}: 3000, 1540, 1470, 1360, 1120. ^{1}H-NMR (200 MHz, $CDCl_3$) δ: 0.92 (t, 3H, J=7.5), 1.31 (d, 1H, J=11.7), 1.58—2.43 (m, 12H), 2.72 (br s, 1H), 4.35 (t, 1H, J=6.0), 4.55 (dt, 1H, J=11.1, 4.2). *Anal.* Calcd for $C_{13}H_{19}NO_3S$: C, 57.97; H, 7.11; N, 5.20. Found: C, 58.33; H, 7.09; N, 5.20.

2-Nitro-8-phenyl-9-oxa-7-thiatetracyclo[8.2.1.0^{2,6}.0^{6,11}]tridecane (32a and 32b) (Table 2, Entry 14) A solution of **8** (108 mg, 0.339 mmol) and *p*-TSA·H_2O (64 mg, 0.339 mmol) in xylene (20 ml) was refluxed for 1 h, then poured into saturated aqueous $NaHCO_3$ solution, and extracted with $CHCl_3$. The extract was washed with brine, dried, and evaporated. The residue was subjected to silica gel column chromatography with hexane–AcOEt (6 : 1) to afford a mixture of **32a** (87 mg, 82%) and **32b** (2 mg, 1%). The yields were calculated from ^{1}H-NMR signal integration. Recrystallization of **32a** from CH_2Cl_2–Et_2O gave colorless prisms, mp 129—130 °C. IR (KBr) cm^{-1}: 1530, 1460, 1360, 1120, 1070. ^{1}H-NMR (200 MHz, $CDCl_3$) δ: 1.38 (d, 1H, J=11.7), 1.79—2.46 (m, 10H), 2.79 (m, 1H), 4.76 (dt, 1H, J=11.2, 4.1), 5.47 (s, 1H), 7.26—7.43 (m, 5H). *Anal.* Calcd for $C_{17}H_{19}NO_3S$: C, 64.33; H, 6.03; N, 4.41. Found: C, 64.28; H, 6.05; N, 4.38.

2-Nitrotetracyclo[7.2.1.0^{2,6}.0^{6,10}]dodecane 7-Oxide (33) A solution of NCS (211 mg, 1.6 mmol) in CH_3CN (1.3 ml) was added to a solution of **30a** (200 mg, 0.78 mmol) in CH_3CN–H_2O (4 : 1, 16 ml). The mixture was stirred at room temperature for 30 min, and poured into saturated aqueous Na_2CO_3 solution. After extraction with Et_2O, the extract was washed with brine, dried, and evaporated. The resulting residue was recrystallized from CH_2Cl_2–Et_2O to give **33** (120.8 mg, 63.4%) as colorless prisms, mp 201 °C (dec.). IR ($CHCl_3$) cm^{-1}: 3000, 1560, 1460, 1370, 1150, 1000. ^{1}H-NMR (200 MHz, $CDCl_3$) δ: 1.53 (d, 1H, J=11.9), 1.69—1.98 (m, 2H), 2.12—2.43 (m, 4H), 2.52—2.71 (m, 2H), 2.80—3.01 (m, 3H), 5.01 (ddd, 1H, J=9.4, 4.4, 2.2). *Anal.* Calcd for $C_{10}H_{13}NO_4S$: C, 49.37; H, 5.39; N, 5.76. Found: C, 49.16; H, 5.37; N, 5.86.

In a similar way, the sultine **33** (11.4 mg, 53%) was obtained from the minor oxathiane **30b** (23 mg, 0.09 mmol).

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References and Notes

1) *a*) Fuji K., Ueda M., Fujita E., *J. Chem. Soc., Chem. Commun.*, **1977**, 814; *b*) Fuji K., Ueda M., Sumi K., Fujita E., *Tetrahedron Lett.*, **22**, 2005—2008 (1981); *c*) Fuji K., Ueda M., Fujita E., *J. Chem. Soc., Chem. Commun.*, **1983**, 49—50; *d*) Fuji K., Ueda M., Sumi K., Kajiwara K., Fujita E., Iwashita T., Miura I., *J. Org. Chem.*, **50**, 657—661 (1985); *e*) Fuji K., Ueda M., Sumi K., Fujita E., *J. Org. Chem.*, **50**, 662—666 (1985).

2) *a*) Ogura K., Tsuchihashi G., *Tetrahedron Lett.*, **1971**, 3151—3154; *b*) *Idem*, *ibid.*, **1972**, 1383—1386; *c*) *Idem*, *J. Am. Chem. Soc.*, **96**, 1960—1962 (1974); *d*) Ogura K., Yamashita M., Suzuki M., Tsuchihashi G., *Tetrahedron Lett.*, **1974**, 3653—3656; *e*) Ogura K., Yoshimura I., Katoh N., Tsuchihashi G., *Chem. Lett.*, **1975**, 803—804; *f*) Ogura K., Yamashita M., Furukawa S., Suzuki M., Tsuchihashi G., *Tetrahedron Lett.*, **1975**, 2767—2770; *g*) Ogura K., Yamashita M., Tsuchihashi G., *ibid.*, **1976**, 759—762; *h*) Ogura K., Katoh N., Yoshimura I., Tsuchihashi G., *ibid.*, **1978**, 375—378; *i*) Ogura K., Itoh Y., Tsuchihashi G., *Bull. Chem. Soc. Jpn.*, **52**, 2013—2022 (1979); *j*) Ogura K., Yamashita M., Suzuki M., Furukawa S., Tsuchihashi G., *ibid.*, **57**, 1637—1642 (1984).

3) *a*) Ogura K., Yahata N., Watanabe J., Takahashi K., Iida H., *Bull. Chem. Soc. Jpn.*, **56**, 3543—3544 (1983); *b*) Ogura K., Yahata N., Hashizume K., Tsuyama K., Takahashi K., Iida H., *Chem. Lett.*, **1983**, 767—770; *c*) Ogura K., Ohtsuki K., Nakamura M., Yahata N., Takahashi K., Iida H., *Tetrahedron Lett.*, **26**, 2455—2458 (1985).

4) Seebach D., *Synthesis*, **1969**, 17—36.

5) *a*) Eliel E. L., Koskimies J. K., Lohri B., *J. Am. Chem. Soc.*, **100**, 1614—1616 (1978); *b*) Eliel E. L., Frazee W. J., *J. Org. Chem.*, **44**, 3598—3599 (1979); *c*) Eliel E. L., Lynch J. E., *Tetrahedron Lett.*, **22**, 2855—2858 (1981); *d*) Eliel E. L., Soai K., *ibid.*, **22**, 2859—2862 (1981); *e*) Eliel E. L., Morris-Natschke S., *J. Am. Chem. Soc.*, **106**, 2937—2942 (1984); *f*) Lynch J. E., Eliel E. L., *ibid.*, **106**, 2943—2948 (1984); *g*) Ko K.-Y., Frazee W. J., Eliel E. L., *Tetrahedron*, **40**, 1333—1343 (1984); *h*) Frye S. V., Eliel E. L., *Tetrahedron Lett.*, **26**, 3907—3910 (1985); *i*) Ko K.-Y., Eliel E. L., *J. Org. Chem.*, **51**, 5353—5362 (1986); *j*) Frye S. V., Eliel E. L., *J. Am. Chem. Soc.*, **110**, 484—489 (1988); *k*) Isobe M., Obeyama J., Funabashi Y., Goto T., *Tetrahedron Lett.*, **29**, 4773—4776 (1988); *l*) Utimoto K., Nakamura A., Matsubara S., *J. Am. Chem. Soc.*, **112**, 8189—8190 (1990).

6) *a*) Pihlaja K., Pasanen P., *Acta Chem. Scand.*, **24**, 2257—2258 (1970); *b*) Pasanen P., Pihlaja K., *ibid.*, **25**, 1908—1910 (1971); *c*) Danneels D., Anteunis M., van Acker L., Tavernier D., *Tetrahedron*, **31**, 327—331 (1975); *d*) Greene T. W., "Protective Groups in Organic Synthesis," John Wiley & Sons, New York, 1981, pp. 138—140.

7) *a*) Oae S., Numata T., *Tetrahedron*, **30**, 2641—2646 (1974); *b*) Numata T., Oae S., *ibid.*, **32**, 2699—2703 (1976); *c*) Findlay J. B. C., Fishwick C. W. G., Kersey I. D., Ward P., *Tetrahedron Lett.*, **36**, 2299—2302 (1995); *d*) Kersey I. D., Fishwick C. W. G., Findlay J. B. C., Ward P., *Tetrahedron*, **51**, 6819—6834 (1995).

8) De Lucchi O., Miotti U., Modena G., *Org. React.*, **40**, 157—405 (1991).

9) A part of this work has been published in a preliminary communication: Abe H., Itani J., Masunari C., Kashino S., Harayama T., *J. Chem. Soc., Chem. Commun.*, **1995**, 1197—1198.

10) *a*) Paquette L. A., Moerck R.E., Harirchian B., Magnus P. D., *J. Am. Chem. Soc.*, **100**, 1597—1599 (1978); *b*) Danishefsky S., Harayama T., Singh R. K., *ibid.*, **101**, 7008—7012 (1979); *c*) Maignan C., Raphael R., *Tetrahedron*, **39**, 3245—3249 (1983).

11) The relative configurations at the sulfur atom of the Diels–Alder cycloadducts **4**, **5**, **17**, and **18**[10c] could be deduced from theoretical studies on the stereochemical features of vinyl sulfoxide; *a*) Kahn S. D., Hehre W. J., *J. Am. Chem. Soc.*, **108**, 7399—7400 (1986); *b*) *Idem*, *Tetrahedron Lett.*, **27**, 6041—6044 (1986).

12) *a*) Jung M. E., Grove D. D., *J. Chem. Soc., Chem. Commun.*, **1987**, 753—755; *b*) Ono N., Kamimura A., Kaji A., *J. Org. Chem.*, **53**, 251—258 (1988).

13) *a*) Fuji K., Tanaka K., Abe H., Itoh A., Node M., Taga T., Miwa Y., Shiro M., *Tetrahedron: Asymmetry*, **2**, 179—182, 1319—1327 (1991); *b*) Fuji K., Tanaka K., Abe H., Matsumoto K., Taga T., Miwa Y., *ibid.*, **3**, 609—612 (1992); *c*) Fuji K., Tanaka K., Abe H., Matsumoto K., Harayama T., Ikeda A., Taga T., Miwa Y., Node M., *J. Org. Chem.*, **59**, 2211—2218 (1994).

14) Johnson C. K., ORTEP II, Report ORNL-5138, Oak Ridge National Laboratory, Tennessee, U.S.A., 1976.

15) Corey E. J., Erickson B. W., *J. Org. Chem.*, **36**, 3553—3560 (1971).

16) Although no minor oxathiane was detected in the reaction with **4**, the relative configuration of **28** was elucidated as depicted in Table 2, based upon studies on the conformational features of 1,3-oxathiane derivatives. Since it has been documented that 2-alkylated-1,3-oxathianes generally exist in a chair conformation, the 2-alkyl group should be in equatorial direction, in order to avoid steric interaction. *a*) Gelan J., Anteunis M., *Bull. Soc. Chim. Belges*, **77**, 423—432 (1968); *b*) *Idem*, *ibid.*, **77**, 447—454 (1968); *c*) Pasanen P., Pihlaja K., *Tetrahedron*, **28**, 2617—2626 (1972).

17) Ruff F., Kucsman A., *J. Chem. Soc., Perkin Trans. 2*, **1988**, 1123—1128.

18) *a*) Böhme H., Bentler H., *Chem. Ber.*, **89**, 1464—1468 (1956); *b*) Okuyama T., Nakada M., Fueno T., *Tetrahedron*, **32**, 2249—2252 (1976).

19) Node M., Itoh A., Nishide K., Abe H., Kawabata T., Masaki Y., Fuji K., *Synthesis*, **1992**, 1119—1124.

20) Gilmore C. J., *J. Appl. Cryst.*, **17**, 42—46 (1984).

21) Cromer D. T., Weber J. T., "International Tables for X-Ray Crystallography," Vol. 4, The Kynoch Press, Birmingham, 1974, Table 2.2 A.

22) TEXSAN-TEXRAY Structure Analysis Package, Molecular Structure Corporation, 3200 Research Forest Drive, The Woodlands, Texas 77381, U.S.A.