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Reactions of Cyclic Sulfur Ylides with Some Carbonyl Compounds

Hitoshi Akiyama,[1] Katsuyoshi Ohshima,[1] Tetsuya Fujimoto,[1] Iwao Yamamoto,[1] and Ryozo Iriye[2]

[1]*Department of Functional Polymer Science, Faculty of Textile Science and Technology, Shinshu University, Ueda, Nagano 386-8567, Japan*

[2]*Department of Bioscience and Biotechnology, Faculty of Agriculture, Shinshu University, Minowa, Kami-ina, Nagano 399-4598, Japan*

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ABSTRACT: *The reaction of a six-membered sulfonium ylide* **5** *with aldehydes or ketones afforded the oxirane derivatives* **6a–d** *as a mixture of cis and trans isomers in excellent yields. In addition, the same reactions, using five- or six-membered cyclic oxosulfonium ylides* **7** *and* **11**, *gave the corresponding oxirane derivatives in good yields. Moreover, the reaction of* **11** *with two equimolar amounts of base and 4-hexen-3-one afforded the cyclooctene oxide derivative* **16** *with high stereoselectivity in 59% yield via a sequential Michael–Michael-type addition of the ylide and the resulting enolate ion followed by an intramolecular Corey–Chaykovsky reaction.* © 2002 Wiley Periodicals, Inc. Heteroatom Chem 13:216–222, 2002; Published online in Wiley Interscience (www.interscience.wiley.com). DOI 10.1002/hc.10022

INTRODUCTION

The Corey–Chaykovsky reaction of sulfonium or oxosulfonium ylides has provided a useful method for the synthesis of oxirane [1,2] or cyclopropane [1,3] derivatives by the reaction initiated by nucleophilic attack of the ylides on a carbonyl group or on an activated carbon–carbon double bond. In addition, the nucleophilic addition of the ylides to imine functionalities provided a method for the synthesis of aziridine derivatives [1c,1d,4]. However, only limited examples of the Corey–Chaykovsky reaction of cyclic sulfonium ylides along with a ring-opening reaction have been thus far reported [5] and no instances concerning the cyclic oxosulfonium ylide have been reported.

Recently, we developed the novel tandem reactions of a cyclic oxosulfonium ylide with β-acetoxy-α-methylene ketones derived from a Baylis–Hillman adduct [6]. In these tandem reactions, a Michael-type addition of the ylide, an elimination of acetate anion, and an intramolecular Corey–Chaykovsky reaction of the regenerated ylide proceed sequentially in one-pot to provide a cycloheptene or a cyclooctene oxide derivative with a high level of stereoselectivity [7]. However, it was found that the stereoselectivities and the yields of the products depended on the ring size of the cyclic sulfur ylides. To elucidate these differences in the reactivities corresponding to the cyclic sulfur ylides, we examined the reactivity of the cyclic sulfur ylides toward some carbonyl compounds. In this paper, we describe the reaction of the cyclic sulfur ylides with simple carbonyl compounds and novel tandem reactions using 4-hexen-3-one leading to a multifunctionalized cyclooctene oxide derivative.

RESULTS AND DISCUSSION

A five- or six-membered cyclic sulfonium salt, **1** or **2**, was easily prepared by arylation [8] of the tetra-

Correspondence to: Tetsuya Fujimoto; e-mail: tfujimo@shinshu-u.ac.jp.
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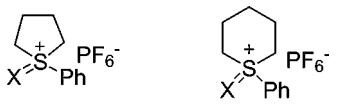
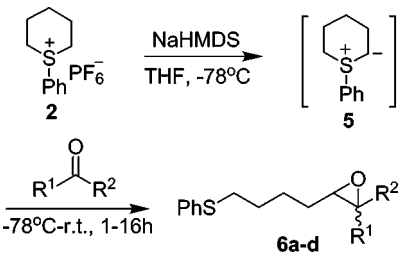


FIGURE 1 Structure of cyclic sulfonium and oxosulfonium salts.

or pentamethylene sulfide using a diphenyliodonium salt in the presence of a catalytic amount of copper(II) benzoate. In addition, the corresponding oxosulfonium salts, **3** and **4**, were derived from **1** and **2** by oxidation using *m*-CPBA in alkaline aqueous media [9], respectively (Fig. 1).

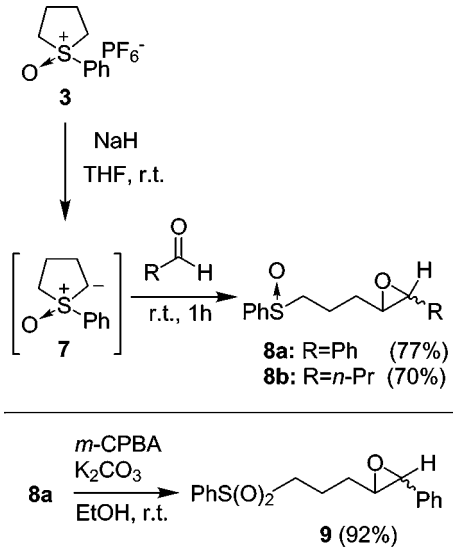
At first, the reaction of a six-membered sulfonium ylide **5**, generated from **2** at −78°C by using NaHMDS as a base, with benzaldehyde was attempted [10]. The oxirane derivative **6a** was obtained as a mixture of cis and trans stereoisomers in excellent yield (Table 1, Entry 1). In the ^{1}H NMR spectrum of **6a**, two kinds of peaks assigned to R^2(H) bonded to the oxirane ring were observed. A major product was ascribed to a trans isomer from their coupling constants and the ratio of the cis and trans isomers was 4:6. Moreover, the reaction of the ylide **5** with some carbonyl compounds was examined under the same reaction conditions. Consequently, oxirane derivatives **6b–d** were obtained from the reaction with acetophenone, *n*-butyraldehyde and acetone in 95–97% yields (Table 1). Although the products **6b,c** were obtained as a mixture of cis and trans isomers, the ratio could not be determined because the signals assigned to the methine proton(s) on the oxirane ring were not sufficiently resolved from the other signals in their ^{1}H NMR spectra.

TABLE 1 Reaction of **5** with Carbonyl Compounds



Entry	*R^1*	*R^2*	*Products*	*Yield (%)*
1	Ph	H	**6a**	96[a,b]
2	Ph	Me	**6b**	96[a,c]
3	*n*-Pr	H	**6c**	97[a,c]
4	Me	Me	**6d**	95

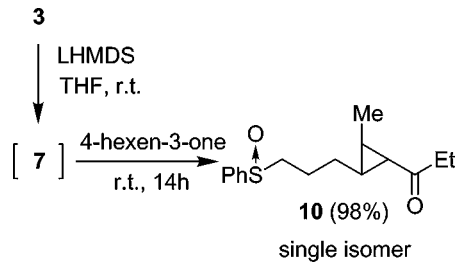
[a] Yields of a mixture of cis and trans isomers.
[b] The ratio of cis:trans = 4:6.
[c] The ratio of cis:trans was not determined.



SCHEME 1

We next examined the reaction of a five-membered cyclic oxosulfonium ylide **7**, generated from **3** in the presence of NaH as a base, with an aromatic and an aliphatic aldehyde (Scheme 1). Consequently, the desired oxirane derivatives **8a,b** [11] (77 and 70% yields) were obtained as a mixture of the isomers, which would be related to both the geometry of the oxirane ring and the configuration of the sulfur atom. To obtain information about the stereochemistry of the isomers of the resulting oxirane derivative, the sulfoxide **8a** was converted into the corresponding sulfone **9**. The treatment of a mixture of isomers of **8a** with *m*-CPBA in the presence of K_2CO_3 [12] provided the sulfone **9** in 92% yield as a ca. 1:9 mixture of cis and trans isomers (Scheme 1). Therefore, it was clarified that the stereoisomers relevant to different configurations on the sulfur atom were included in the oxirane derivative **8a**. The ratio of the isomers related to the configuration of the sulfur atom in the major trans isomer was ca. 4:6 from the ^{1}H NMR spectrum of **8a**. The same reaction using LHMDS or NaHMDS as a base supplied the oxirane as a similar stereoisomeric mixture.

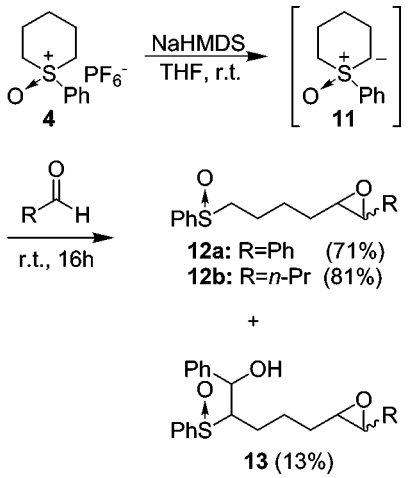
To reveal the reactivity of the oxosulfonium ylide **7** to the enone, the reaction of the ylide **7** with 4-hexen-3-one was attempted using LHMDS as a base [13]. The cyclopropane derivative **10** was formed in 98% yield (Scheme 2). Although many stereoisomers relevant to the configuration of the substituents on the cyclopropane ring and of the sulfur atom are possible, the cyclopropane derivative **10** was a single stereoisomer. No peaks ascribed to the other possible isomers were observed in the ^{13}C NMR spectrum. This result showed that the reaction of the five-membered cyclic oxosulfonium ylide



SCHEME 2

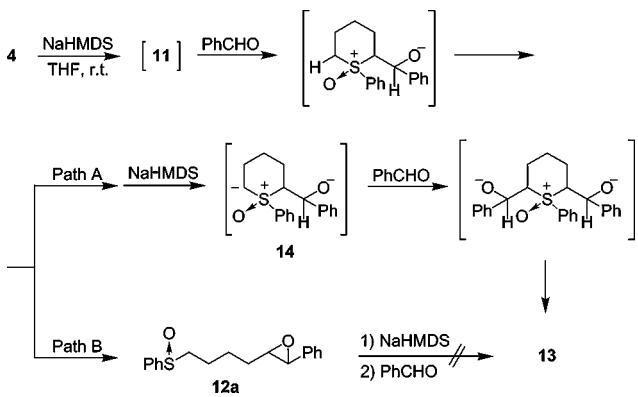
7 with enones proceeds with high stereoselectivity compared to the reaction with the aldehydes described above. Similar results were observed in the reaction with the Baylis–Hillman adduct derivative [7].

The reaction of a six-membered cyclic oxosulfonium ylide **11** with aldehydes or an enone were also performed using NaHMDS as a base. Although the reaction of the ylide **11** with *n*-butyraldehyde provided the corresponding oxirane derivative **12b** [11] in 81% yield as a mixture of cis and trans stereoisomers, the same reaction using benzaldehyde as a substrate produced the 1:2 adduct **13** in 13% yield along with the oxirane derivative **12a** in 71% yield (Scheme 3). The oxirane **12a** was indicated to be only a mixture of cis and trans isomers (ca. 1:9) from the ^{1}H NMR spectrum. The other possible stereoisomers relevant to the configuration of the sulfur atom in **12a** were not observed. To clarify the formation pathway of the 1:2 adduct **13**, the reaction of the ylide **11** with benzaldehyde was attempted under several reaction conditions. The reaction using two equimolar amounts of benzaldehyde in the presence of one equimolar amount of base afforded a oxirane derivative **12a** in 95% yield but the 1:2 adduct **13** was not observed. On the other hand, the same reaction in the presence of two equimolar amounts of NaHMDS provided the 1:2 adducts **13** in 51% yield as the major product along with **12a** (20%). Therefore, the formation of the 1:2 adducts **13** makes it necessary to employ an excess amount of base and benzaldehyde. We assumed two possible reaction pathways leading to the 1:2 adduct **13** as shown in Scheme 4. In order to determine whether **13** was obtained via path A or path B, the reaction of the oxirane derivative **12a** with benzaldehyde was conducted using NaHMDS at room temperature. The desired product **13** was not obtained and the starting material was recovered in 85% yield. Therefore, this reaction was considered to proceed via nucleophilic attack of the ylide **11** on the carbonyl group followed by sequential addition of the regenerated ylide **14** to the excess amount of aldehyde and an intramolecular Corey–Chaykovsky reaction (Scheme 4).

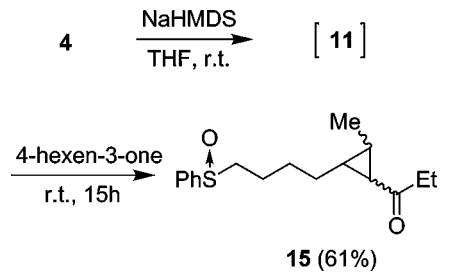


SCHEME 3

Finally, the reaction of the six-membered cyclic ylide **11** with 4-hexen-3-one was performed under various reaction conditions. Although the reaction using an equimolar amount of base and enone afforded the cyclopropane derivative **15** as a mixture of stereoisomers in 61% yield (Scheme 5), the reaction using two equimolar amounts of base and enone provided the novel cyclooctene oxide derivative **16** in 59% yield along with **15** (6%). The structure of the cyclooctene oxide derivative **16** was determined by ^{1}H NMR, ^{13}C NMR, ^{13}C DEPT, COSY, HMQC, and MS. All of the spectra supported the cyclic structure of **16**. In addition, although many stereoisomers can possibly be generated, the cyclooctene oxide derivative **16** was a single stereoisomer. Any peaks ascribed to the other possible isomers were not observed in the ^{1}H and ^{13}C NMR spectra. The reaction was considered to proceed via the Michael-type addition of the ylide **11** to the 4-hexen-3-one followed by the sequential Michael addition of the enolate ion to an additional enone and an intramolecular Corey–Chaykovsky reaction of the ylide **17** generated by an excess amount of NaHMDS (Scheme 6).



SCHEME 4



SCHEME 5

As described above, we have examined the reactivity of the cyclic sulfur ylide toward some carbonyl compounds. As a result, it was clarified that the conjugate addition reaction of a five-membered oxosulfonium ylide to enones proceeds with high stereoselectivity. Moreover, the reaction of the six-membered cyclic oxosulfonium ylide **11** with two equimolar amounts of base and 4-hexen-3-one was clarified to provide the novel eight-membered carbocyclic compound **16** as a single isomer. Further studies on the reaction mechanism and application of the resulting products for the synthesis of other complex molecules are currently underway.

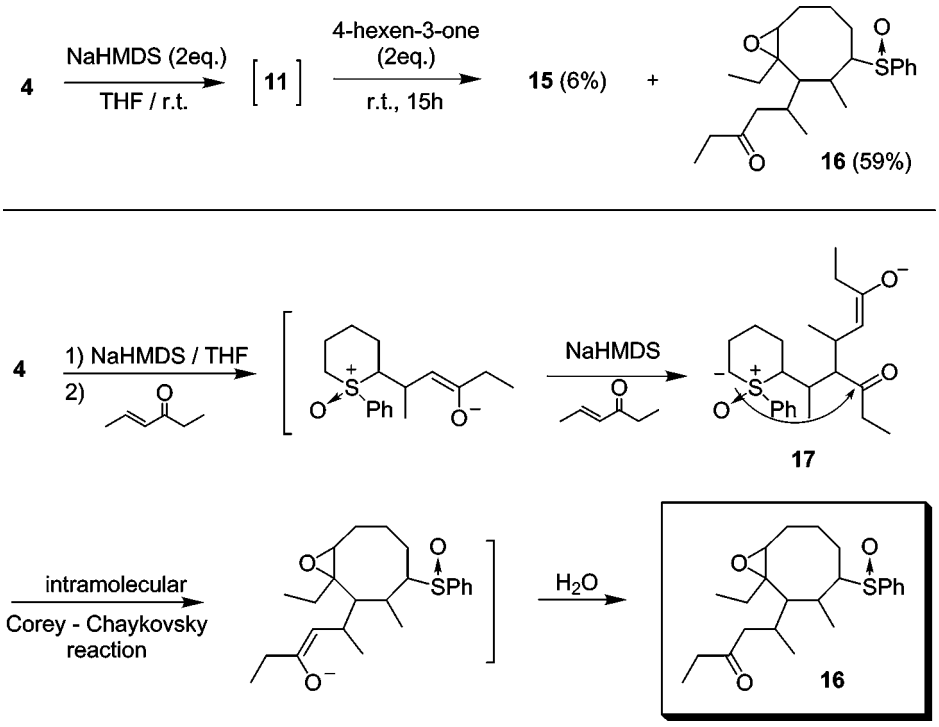
EXPERIMENTAL

Reactions were run in dried glassware under a nitrogen atmosphere. THF was distilled from sodium benzophenone ketyl prior to use. Flash column chromatography was carried out on silica gel 60. The ^1H and ^{13}C NMR spectra were acquired on a 500, 400, or 90 MHz spectrometer using $CDCl_3$ as the solvent. Chemical shifts are reported in δ from TMS as the internal standard. Mass spectra and HRMS were obtained by electron impact (EI) at 70 eV. Melting points are uncorrected. Preparation of the cyclic (oxo-)sulfonium hexafluorophosphates **1–4** and the spectral data of the products are reported in Ref. [7].

General Procedure for the Reaction of a Six-Membered Sulfonium Ylide **5** *with Carbonyl Compounds*

To a solution of a six-membered sulfonium salt **2** (0.29 g, 0.91 mmol) in dry THF (10 ml) was added dropwise a solution of sodium bis(trimethylsilyl) amide (1.00 ml, 1.00 mmol in THF 1 M sol.) at −78°C, and the mixture was then stirred at −78°C for 30 min. A solution of aldehyde or ketone (0.91 mmol) in dry THF (5 ml) was then added dropwise to the mixture and the resulting solution was stirred for 1 h. After having been warmed to room temperature, the mixture was stirred for 16 h. The mixture was treated with water and extracted with CH_2Cl_2. The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel using $CHCl_3$ as the eluent.

6a: 248.5 mg (96%) colorless syrup; ^1H NMR (90 MHz, $CDCl_3$) a mixture of isomers: δ = 7.12–7.46



SCHEME 6

(m, 10H, aromatic H), 4.05 (d, $J = 4.2$ Hz, 0.4H) (cis), 3.58 (d, $J = 2.0$ Hz, 0.6H) (trans), 2.77–2.91 (m, 3H), 1.30–1.80 (m, 6H); ^{13}C NMR (22.49 MHz, $CDCl_3$) trans isomer: $\delta = 25.07$, 28.93, 31.81, 33.57, 58.49, 62.71 and aromatic carbons, cis isomer: $\delta = 25.12$, 26.18, 28.63, 33.37, 57.34, 59.12 and aromatic carbons; IR (neat) 1095 cm^{-1}; MS (70 eV, EI) *m/z*: 284 (M^+); HRMS: Found, *m/z* 284.1238, Calcd. for $C_{18}H_{20}OS$: M^+, 284.1234.

6b: 260.7 mg (96%) colorless syrup; ^{1}H NMR (90 MHz, $CDCl_3$) a mixture of isomers: $\delta = 7.19$–7.29 (m, 10H, aromatic H), 2.62–3.09 (m, 3H), 1.05–1.79 (m, 9H); ^{13}C NMR (22.49 MHz, $CDCl_3$): $\delta = 17.74$, 24.49, 25.19, 25.60, 28.12, 28.52, 28.69, 28.93, 33.40, 33.62, 60.43, 62.44, 65.31, 66.47 and aromatic carbons; IR (neat) 1095 cm^{-1}; MS (70 eV, EI) *m/z*: 298 (M^+).

6c: 221.0 mg (97%) colorless syrup; ^{1}H NMR (90 MHz, $CDCl_3$) a mixture of isomers: $\delta = 7.19$–7.32 (m, 5H, aromatic H), 2.75–3.00 (m, 3H), 2.57–2.70 (m, 1H), 1.19–1.82 (m, 10H), 0.75–1.09 (m, 3H); ^{13}C NMR (22.49 MHz, $CDCl_3$) mixture of isomer: $\delta = 13.96$, 14.02, 19.35, 19.94, 25.25, 25.83, 27.50, 29.04, 29.90, 31.68, 33.65, 34.15, 56.77, 56.93, 58.40, 58.57 and aromatic carbons; IR (neat) 1100 cm^{-1}; MS (70 eV, EI) *m/z*: 250 (M^+); HRMS: Found, *m/z* 250.1391, Calcd. for $C_{15}H_{22}OS$: M^+, 250.1390.

6d: 204.3 mg (95%) colorless syrup; ^{1}H NMR (90 MHz, $CDCl_3$): $\delta = 7.17$–7.31 (m, 5H, aromatic H), 2.92 (brt, 2H), 2.68 (brt, 1H), 1.36–1.98 (m, 6H), 1.28 (s, 3H), 1.23 (s, 3H); ^{13}C NMR (22.49 MHz, $CDCl_3$): $\delta = 18.73$, 24.81, 25.68, 28.41, 28.95, 33.61, 58.01, 64.06, 125.81, 128.83, 129.20, 136.78; IR (neat) 1100 cm^{-1}; MS (70 eV, EI) *m/z*: 236 (M^+); HRMS: Found, *m/z* 236.1171, Calcd. for $C_{14}H_{20}OS$: M^+, 236.1233.

Reaction of a Five-Membered Oxosulfonium Ylide **7** *with Aldehydes*

A mixture of sodium hydride (60% dispersion in mineral oil, 6.1 mg, 0.15 mmol) and a five-membered oxosulfonium salt **3** (50.0 mg, 0.15 mmol) in dry THF (1 ml) was stirred for 30 min at room temperature. A solution of aldehyde (0.15 mmol) in dry THF (1 ml) was then added dropwise to the mixture, and the resulting solution was stirred for 1 h. The mixture was treated with water and extracted with diethyl ether. The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel using AcOEt-*n*-hexane (2/1) as the eluent.

8a: 33.0 mg (77%) colorless syrup; ^{1}H NMR (400 MHz, $CDCl_3$) a mixture of isomers: $\delta = 7.48$–7.65 (m, 5H, aromatic H), 7.20–7.35 (m, 5H, aromatic H), 4.06 (d, $J = 4.0$ Hz, 0.1H), 3.61 (d, $J = 2.0$ Hz, 0.54H), 3.58 (d, $J = 2.0$ Hz, 0.36H), 3.15–3.21 (m, 0.1H), 2.81–2.97 (m, 2.7H), 2.64–2.77 (m, 0.2H), 1.36–2.09 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) trans (including two kinds of isomers related to the configuration of the sulfur atom): $\delta = 18.93$, 18.95, 31.11, 31.18, 56.56, 56.59, 58.25, 58.25, 62.11, 62.19 and aromatic carbons; IR (neat) 1090, 1050 cm^{-1}; MS (70 eV, EI) *m/z*: 286 (M^+); HRMS: Found, *m/z* 286.1014, Calcd. for $C_{17}H_{18}O_2S$: M^+, 286.1028.

8b: 26.4 mg (70%) colorless syrup; ^{1}H NMR (400 MHz, $CDCl_3$) a mixture of isomers: $\delta = 7.46$–7.64 (m, 5H, aromatic H), 2.78–2.93 (m, 2H), 2.63–2.70 (m, 2H), 1.70–2.00 (m, 3H), 1.36–1.62 (m, 5H) 0.92–0.96 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) a mixture of isomers: $\delta = 14.28$, 19.44, 19.50, 19.65, 31.32, 31.42, 34.32, 57.03, 57.13, 58.22, 58.32, 58.67 and aromatic carbons; IR (neat) 1090, 1040 cm^{-1}; MS (70 eV, EI) *m/z*: 252 (M^+); HRMS, Found: *m/z* 252.1171, Calcd. for $C_{14}H_{20}O_2S$: M^+, 252.1184.

Oxidation of Sulfoxide **8a**

To a solution of sulfoxide **8a** (68.1 mg, 0.24 mmol) and K_2CO_3 (86.2 mg, 0.62 mmol) in 95% ethyl alcohol (2 ml)–water (1 ml), a solution of *m*-CPBA (80%, 103.5 mg, 0.48 mmol) in 95% ethyl alcohol (0.7 ml) was slowly added dropwise over 20 min and the mixture was stirred at room temperature. After the sulfoxide was completely consumed (3 h), the mixture was then diluted with a solution of sodium thiosulfate and extracted with diethyl ether. The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel using AcOEt-*n*-hexane (1/2) as the eluent to give the sulfone **9**.

9: 66.6 mg (92%) colorless syrup; ^{1}H NMR (400 MHz, $CDCl_3$) a mixture of isomers: $\delta = 7.19$–7.98 (m, 10H, aromatic H), 4.04 (d, $J = 4$ Hz, 0.1H) (cis), 3.58 (d, $J = 2$ Hz, 0.9H) (trans), 3.12–3.27 (m, 1.8H), 2.95–3.08 (m, 0.2H), 2.87–2.93 (m, 1H), 1.76–1.89 (m, 2.8H), 1.59–1.70 (m, 1H), 1.32–1.45 (m, 0.2H); ^{13}C NMR (100 MHz, $CDCl_3$) trans isomer: $\delta = 19.51$, 30.57, 55.64, 58.03, 61.77, 125.40, 127.95, 128.14, 128.40, 129.26, 133.68, 136.98, 138.93, cis isomer: $\delta = 19.61$, 25.46, 55.55, 56.96, 58.21 and aromatic carbons; IR (neat) 1310, 1150, 1090 cm^{-1}; MS (70 eV, EI) *m/z*: 302 (M^+); HRMS: Found, *m/z* 302.0957, Calcd. for $C_{17}H_{18}O_3S$: M^+, 302.0977.

Reaction of a Five-Membered Oxosulfonium Ylide **7** *with 4-Hexen-3-one*

To a solution of a five-membered oxosulfonium salt **3** (0.10 g, 0.31 mmol) in dry THF (2 ml) was

added dropwise a solution of lithium bis(trimethylsilyl)amide (0.32 ml, 0.32 mmol in THF 1 M sol.), and the mixture was stirred at room temperature for 10 min. A solution of 4-hexen-3-one (0.03 g, 0.31 mmol) in dry THF (2 ml) was then added dropwise to the mixture and the resulting solution was stirred for 14 h. The mixture was treated with water and extracted with CH_2Cl_2. The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel using AcOEt-$CHCl_3$ (1/1) as the eluent to give **10**.

10: 83.9 mg (98%) colorless syrup; ^{1}H NMR (90 MHz, $CDCl_3$): δ = 0.94–2.76 (m, 17H), 7.44–7.55 (m, 5H); ^{13}C NMR (22.49 MHz, $CDCl_3$): δ = 8.07, 18.01, 22.40, 23.51, 25.06, 33.53, 33.86, 37.95, 56.91, 123.98, 129.18, 130.89, 144.19, 209.36; IR (neat) 1695, 1050 cm^{-1}; MS (70 eV, EI) *m/z*: 278 (M^+); HRMS: Found, *m/z* 278.1368, Calcd. for $C_{16}H_{22}O_2S$: M^+, 278.1341.

Reaction of a Six-Membered Oxosulfonium Ylide **11** *with Aldehydes*

To a solution of six-membered oxosulfonium salt **4** (0.50 g, 1.46 mmol) in dry THF (15 ml) was added dropwise a solution of sodium bis(trimethylsilyl)amide (1.70 ml, 1.70 mmol in THF 1 M sol.) and the mixture was stirred at room temperature for 30 min. A solution of aldehyde (1.54 mmol) in dry THF (5 ml) was then added dropwise to the mixture and the resulting solution was stirred for 16 h. The mixture was treated with water and extracted with diethyl ether. The combined organic layer was washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel using AcOEt-*n*-hexane (2/1) as the eluent.

12a: 311.4 mg (71%) colorless syrup; ^{1}H NMR (400 MHz, $CDCl_3$) a mixture of isomers: δ = 7.21–7.65 (m, 10H, aromatic H), 4.06 (d, J = 4.0 Hz, 0.1H), 3.58 (d, J = 2.0 Hz, 0.9H), 3.15–3.19 (m, 0.1H), 2.90–2.93 (m, 0.9H), 2.76–2.87 (m, 1.8H), 2.63–2.68 (m, 0.2H), 1.45–1.94 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) trans isomer: δ = 21.99, 25.13, 31.88, 57.01, 58.52, 62.48, 123.99, 125.51, 128.11, 128.48, 129.25, 130.98, 137.51, 143.92, cis isomer: δ = 21.72, 25.20, 26.25, 56.84, 57.35, 58.90, and aromatic carbons; IR (neat) 1090, 1040 cm^{-1}; MS (70 eV, EI) *m/z*: 300 (M^+); HRMS: Found, *m/z* 300.1166, Calcd. for $C_{18}H_{20}O_2S$: M^+, 300.1182.

12b: 315.0 mg (81%) colorless syrup; ^{1}H NMR (90 MHz, $CDCl_3$) a mixture of isomers: δ = 7.44–7.72 (m, 5H, aromatic H), 2.50–2.98 (m, 4H), 1.21–2.03 (m, 10H), 0.78–1.11 (m, 3H); ^{13}C NMR (22.49 MHz, $CDCl_3$) major isomer: δ = 13.81, 19.18, 21.99, 25.19, 31.61, 34.02, 57.10, 57.83, 58.21, 124.06, 129.12, 130.75, 144.81; IR (neat) 1090, 1040 cm^{-1}; MS (70 eV, EI) *m/z*: 266 (M^+); HRMS: Found, *m/z* 266.1329, Calcd. for $C_{15}H_{22}O_2S$: M^+, 266.1329.

1:2 adduct **13**: 77.2 mg (13%) white crystals, m.p. 115–116°C; ^{1}H NMR (90 MHz, $CDCl_3$) a mixture of isomers: δ = 7.01–7.75 (m, 15H, aromatic H), 5.28 (brs, 1H), 4.53 (d, J = 1.6 Hz, 1H), 4.06 (d, J = 4.0 Hz, 0.1H), 3.46 (d, J = 2.0 Hz, 0.9H), 2.78–2.87 (m, 1H), 1.24–2.59 (m, 7H); ^{13}C NMR (22.49 MHz, $CDCl_3$) major isomer: δ = 22.45, 23.97, 31.85, 58.55, 62.24, 68.97, 70.58 and aromatic carbons; IR (KBr) 3400, 1080, 1040 cm^{-1}; MS (70 eV, EI) *m/z*: 281 [M^+ − 125(−PhS=O)].

Reaction of a Six-Membered Oxosulfonium Ylide **11** *with 4-Hexen-3-one*

To a solution of a six-membered oxosulfonium salt **4** (0.52 g, 1.53 mmol) in dry THF (15 ml) was added dropwise a solution of sodium bis(trimethylsilyl)amide (1.70 ml, 1.70 mmol in THF 1 M sol.) and the mixture was stirred at room temperature for 30 min. A solution of 4-hexen-3-one (0.15 g, 1.53 mmol) in dry THF (5 ml) was then added dropwise to the mixture and the resulting solution was stirred for 15 h. The mixture was treated with water and extracted with diethyl ether. The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel using AcOEt-*n*-hexane (2/1) as the eluent to give a mixture of isomers of **15**.

15: 272.9 mg (61%) colorless syrup; ^{1}H NMR (90 MHz, $CDCl_3$) a mixture of isomers: δ = 7.35–7.72 (m, 5H, aromatic H), 2.39–2.82 (m, 5H), 0.95–1.80 (m, 14H); ^{13}C NMR (22.49 MHz, $CDCl_3$) major isomer: δ = 9.72, 19.75, 23.01, 25.12, 27.65, 30.10, 35.24, 35.35, 39.50, 58.62, 125.87, 13.61, 132.44, 145.45, 210.66; IR (neat) 1710, 1060 cm^{-1}; MS (70 eV, EI) *m/z*: 292 (M^+); HRMS: Found, *m/z* 292.1492, Calcd. for $C_{17}H_{24}O_2S$: M^+, 292.1495.

Reaction of a Six-Membered Oxosulfonium Ylide **11** *with 4-Hexen-3-one (2 eq.) in the Presence of Two Equimolar Amounts of NaHMDS*

To a solution of a six-membered oxosulfonium salt **4** (0.52 g, 1.53 mmol) in dry THF (15 ml) was added dropwise a solution of sodium bis(trimethylsilyl)amide (3.21 ml, 3.21 mmol in THF 1 M sol.), and the mixture was stirred at room temperature for 30 min. A solution of 4-hexen-3-one (0.33 g,

3.21 mmol) in dry THF (5 ml) was then added dropwise to the mixture and the resulting solution was stirred for 15 h. The mixture was treated with water and extracted with diethyl ether. The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel using AcOEt-*n*-hexane (2/1) as the eluent to give **16** with **15** (6%).

16: 352.6 mg (59%) colorless syrup; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.48$–7.65 (m, 5H, aromatic H), 3.00–3.04 (m, 1H), 2.77–2.87 (m, 2H), 2.44 (q, $J = 7$ Hz, 2H), 1.32–2.04 (m, 12H), 1.05 (t, $J = 7$ Hz, 3H), 0.77–0.89 (m, 6H), 0.73 (d, $J = 7$ Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 7.34$, 10.45, 18.14, 20.32, 22.04, 25.87, 27.68, 32.27, 35.60, 37.69, 38.02, 40.12, 57.05, 59.44, 63.15, 65.91, 124.02, 129.27, 131.00, 143.92, 215.25; IR (neat) 1720, 1090, 1050 cm^{-1}; MS (70 eV, EI) *m/z*: 390 (M^+); HRMS: Found, *m/z* 390.2242, Calcd. for $C_{23}H_{34}O_3S$: M^+, 390.2227.

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