N-((S)-α-Phenylethyl)-4-phenylazetidin-2-one (20) from 1 and 11: yield 74.0%; IR (film) cm^{-1} 1740 (C=O); M^+, 251. Anal. Calcd for $C_{17}H_{17}NO$: C, 81.27; H, 6.77; N, 5.58. Found: C, 81.38; H, 6.68; N, 5.52. In this case the absolute configuration has the opposite sign at C_4.

20 (epimer 4(R)): $[\alpha]^{20}_D$ 28.1; ^1H NMR (CCl_4) δ 1.82 (d, 3 H, NCHCH_3 J = 7.5 Hz), 2.72 (d, d 1 H, C_3, J = 2.5 Hz, J = 15 Hz), 3.23 (dd, 1 H, C_3, J = 5.0 Hz, J = 15 Hz), 4.15 (q, 1 H, NC*H*CH_3, J = 7.5 Hz), 4.25 (dd, 1 H, C_4, J = 2.5 Hz, J = 5.0 Hz).

20 (epimer 4(S)): $[\alpha]^{20}_D$ +28.5; ^1H NMR (CCl_4) δ 1.35 (d, 3 H, NCHCH_3, J = 7.5 Hz), 2.72 (dd, 1 H, C_3, J = 2.5 Hz, J = 15.0 Hz), 3.18 (dd, 1 H, C_3, J = 5.0 Hz, 15.0 Hz), 4.22 (dd, 1 H, C_4, J = 2.5 Hz, J = 5.0 Hz), 4.95 (q, 1 H, NC*H*CH_3, J = 7.5 Hz).

N-((S)-α-Phenylethyl)-3,3,4-trimethyl-4-phenylazetidin-2-one (21) from 2 and 10: yield 63.0%; mp 116-118 °C; IR (KBr) cm^{-1} 1740 (C=O); M^+, 293. Anal. Calcd for $C_{20}H_{23}NO$: C, 81.91; H, 7.85; N, 4.78. Found: C, 81.82; H, 7.80; N, 4.71.

21 (epimer 4(S)): $[\alpha]^{20}_D$ +10.2; ^1H NMR (CCl_4) δ 0.65 (s, 3 H, Me C_3), 1.18 (s, 3 H, Me C_3), 1.25 (s, 3 H, Me C_4), 1.99 (d, 3 H, NCHCH_3, J = 7.5 Hz), 4.05 (q, 1 H, NC*H*CH_3, J = 7.5 Hz).

21 (epimer 4(R)): $[\alpha]^{20}_D$ +43.5; ^1H NMR (CCl_4) δ 0.65 (s, 3 H, Me C_3), 1.30 (s, 3 H, Me C_3), 1.75 (d, 3 H, NCHCH_3, J = 7.5 Hz), 1.85 (s, 3 H, Me C_4), 4.13 (q, 1 H, NC*H*CH_3, J = 7.5 Hz).

N-((S)-1-Phenyl-2-propyl)-3,3-dimethyl-4-phenylazetidin-2-one (22) from 4 and 10: yield 53.0%; IR (film) cm^{-1} 1740 (C=O); M^+, 293; $[\alpha]^{20}_D$ +74.8. The mixture of epimers was not separated by HPLC. Anal. Calcd for $C_{20}H_{23}NO$: C, 81.91; H, 7.85; N, 4.78. Found: C, 81.28; H, 7.78, N, 4.70. The ^1H NMR spectrum of the mixture of epimers consisted of a series of overlapping signals and did not allow for full differentiation of isomers. However, the ratio of epimers was determined by integration of the signals for H at C_4: **22** epimer (ca. 65%), ^1H NMR (CCl_4) δ 3.98 (s, 1 H, C_4). **22** epimer (ca. 35%), ^1H NMR (CCl_4) δ 3.82 (s, 1 H, C_4).

N,3-Dimethyl-4-phenylazetidin-2-one (33) from 27 and 23: yield 57.0%; IR (film) cm^{-1} 1750 (C=O); M^+, 175. Anal. Calcd for $C_{11}H_{13}NO$: C, 75.42; H, 7.42; N, 8.00. Found: C, 75.31; H, 7.38; N, 8.08.

***cis*-10**: $[\alpha]^{20}_D$ +2.2 (*c* 2.4, CCl_4); ^1H NMR (CCl_4) δ 0.83 (d, 3 H, Me C_3, J = 7.5 Hz), 2.88 (s, 3 H, NMe), 3.55 (dq, 1 H, C_3, J = 5.0 Hz, J = 7.5 Hz), 4.62 (d, 1 H, C_4, J = 5.0 Hz).

***trans*-33**: $[\alpha]^{20}_D$ +9.2 (*c* 2.6, CCl_4); ^1H NMR (CCl_4) δ 1.47 (d, 3 H, Me C_3), 2.80 (s, 3 H, NMe), 3.02 (dq, 1 H, C_3, J = 2.0 Hz, J = 7.5 Hz), 4.02 (d, 1 H, C_4, J = 2.0 Hz).

33 from 30 and 23: yield 69.0%; cis isomer, $[\alpha]^{20}_D$ +9.2 (*c* 2.6, CCl_4); trans isomer, $[\alpha]^{20}_D$ +7.2 (*c* 2.0, CCl_4); ^1H NMR data as above.

N,3-Dimethyl-4-*tert*-butylazetidin-2-one (34) from 24 and 27: yield 50.0%; IR (film) cm^{-1} 1750 (C=O); M^+, 155. Anal. Calcd for $C_9H_{17}NO$: C, 69.68; H, 10.97; N, 9.03. Found: C, 69.57; H, 10.85; N, 9.13.

***trans*-11**: $[\alpha]^{20}_D$ +11.0; ^1H NMR (CCl_4) δ 1.00 (s, 9 H, *t*-Bu), 1.25 (d, 3 H, Me C_3, J = 7.5 Hz), 2.8 (s, 3 H, NMe), 2.85 (dq, 1 H, C_3, J = 2.5 Hz, J = 7.5 Hz), 2.95 (d, 1 H, C_4, J = 2.5 Hz).

N-Methyl-4-phenylazetidin-2-one (35) from 29 and 23: yield 82.0%; IR (film) cm^{-1} 1750 (C=O); M^+, 161; $[\alpha]^{20}_D$ -6.0 (*c* 1.9, CCl_4). Anal. Calcd for $C_{10}H_{11}NO$: C, 74.53; H, 6.83; N, 8.69. Found: C, 74.41; H, 6.78; N, 8.76. ^1H NMR (CCl_4) δ 2.78 (s, 3 H, NMe), 3.40 (dd, 1 H, C_3, J = 5.0 Hz, J = 12.5 Hz), 4.50 (dd, 1 H, C_4, J = 2.5 Hz, J = 5.0 Hz).

35 from 8 and 1: yield 50%; $[\alpha]^{20}_D$ +19.0 (*c* 1.9, CCl_4); spectral data as above.

N,3,3-Trimethyl-4-phenylazetidin-2-one (36) from 28 and 23: yield 60.0%; IR (film) cm^{-1} 1750 (C=O); M^+, 189; $[\alpha]^{20}_D$ +118.0 (*c* 2.6, CCl_4). Anal. Calcd for $C_{12}H_{15}NO$: C, 76.19; H, 7.94; N, 7.41. Found: C, 76.27; H, 7.86; N, 7.57. ^1H NMR (CCl_4) δ 0.77 (s, 3 H, C_3 Me), 1.43 (s, 3 H, Me C_3), 2.85 (s, 3 H, NMe), 4.25 (s, 1 H, C_4).

36 from 32 and 23: yield 30.0%; $[\alpha]^{20}_D$ -63.3 (*c* 2.2, CCl_4); spectral data as above.

Reactions of (Aryloxy)oxosulfonium Ylides with Carbonyl Compounds

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Received July 7, 1983

Reactions of (aryloxy)oxosulfonium salts with alkyllithium followed by the addition of carbonyl compounds gave β-aryloxy sulfones, β-aroyloxy sulfones, and α,β-unsaturated or β,γ-unsaturated sulfones in 1.4-17.9%, 1.2-7.2%, and 4.5-13.5% yields, respectively. Ylides obtained by treatment of these sulfonium salts with *n*-BuLi reacted with carbonyl compounds to give betaines, which formed unusual four-membered cyclic alkoxyoxosulfonium salts. The aryloxy anions thus formed attacked β-carbons of these salts to afford β-aryloxy sulfones. The aroyloxy anion that might be formed by autoxidation also attacked β-carbons of these salts to afford β-aroyloxy sulfones. When these anions attacked the α- or γ-protons of these satls, unsaturated sulfones were obtained. This is the first example that the reaction of ylide with carbonyl compounds gave sulfone derivatives via four-membered cyclic alkoxyoxosulfonium salts that were produced by the intramolecular S_N2 mechanism. The yields of unsaturated sulfones were raised up to 35-60% by a one-pot reaction.

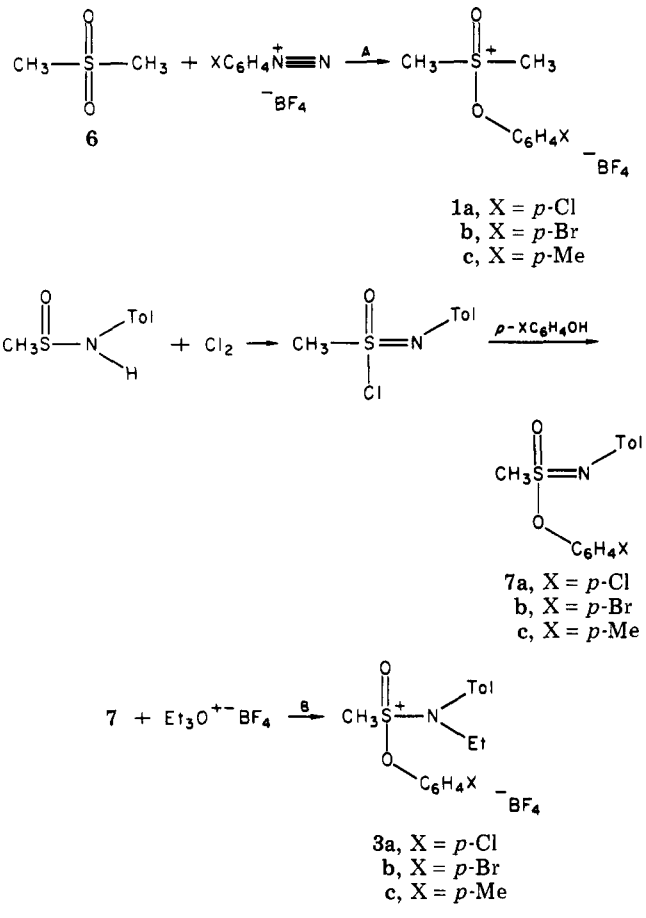
It is well-known that sulfonium and oxosulfonium salts react with bases to give the corresponding ylides, which act as methylene transfer reagents toward carbonyl compounds.[1] However, there is no report that sulfur ylides react with carbonyl compounds to give unsaturated sulfones via four-membered cyclic intermediates. Whiting et al., Still et al., and Oishi et al. reported that the reactions of (aryloxy)oxosulfonium salts **1** with nucleophiles gave not only the corresponding ylides but also the corresponding sulfoxides.[2] We are interested in this anomalous reactivity. If ylides are formed by the reaction of these salts with bases, betaines derived from carbonyl compounds may afford the S^+-attacked products (i.e., sulfurane oxides

(1) Corey, E. J.; Chaykovsky, M. *J. Am. Chem. Soc.* **1965**, *87*, 1353. For reviews, see: Trost, B. M.; Melvin, L. S., Jr. "Sulfur Ylides"; Academic Press: New York, 1975. Block, E. "Reactions of Organosulfur Compounds"; Academic Press: New York, 1978. Stirling, C. J. M., Ed. "The Chemistry of The Sulphonium Group"; Wiley: New York, 1981.

(2) (a) Chalkley, G. R.; Snodin, D. J.; Stevens, G.; Whiting, M. C. *J. Chem. Soc. C* **1970**, 682. Chalkley, G. R.; Snodin, D. J.; Stevens, G.; Whiting, M. C. *J. Chem. Soc., Perkin Trans. 1* **1978**, 1580. (b) Shimagaki, M.; Tsuchiya, H.; Ban, Y.; Oishi, T. *Tetrahedron Lett.* **1978**, *3435*. (c) Still, I. W. J.; Szilagyi, S. *Synth. Commun.* **1979**, *9*, 923. Still, I. W. J.; Ablenas, F. J. *J. Org. Chem.* **1983**, *48*, 1617.

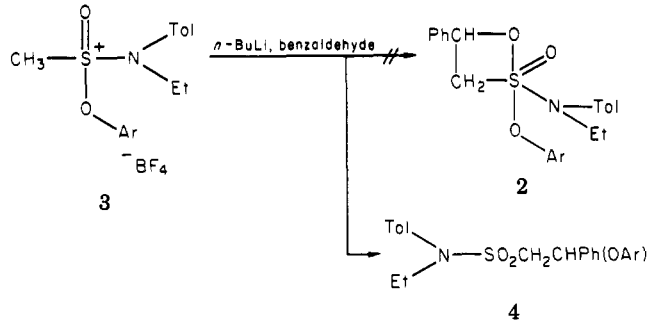
0022-3263/84/1949-1402$01.50/0

Scheme I



or cyclic alkoxyoxosulfonium salts).

In a previous paper, we reported the preparation of sulfurane oxides **2** by the reaction of an amino(aryloxy)-oxosulfonium salts **3** with benzaldehyde in the presence



of base and discussed the difference in stabilities of cyclic sulfurane oxides.[3] However, these compounds were shown by crystallographic analysis not to be **2** but to be β-aryloxy sulfonamides **4**.[4] In this paper, we report that the reactions of these (aryloxy)oxosulfonium ylides **5** with carbonyl compounds gave β-aryloxy sulfone derivatives and α,β- or β,γ-unsaturated sulfone derivatives via four-membered cyclic intermediates.

Results and Discussion

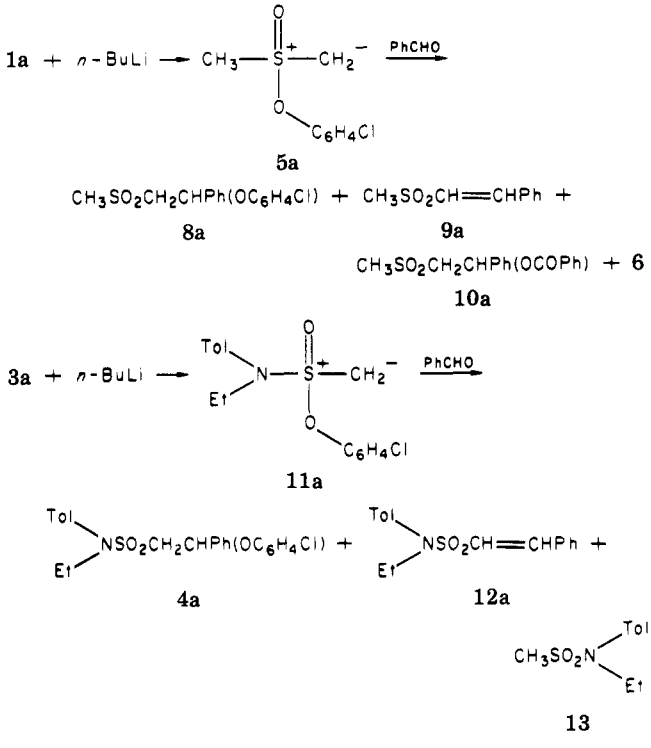
Dimethyl(aryloxy)oxosulfonium salts **1a–c** were prepared by the reaction of dimethyl sulfone (**6**) with para-substituted benzenediazonium salts (Scheme I, method A).[2] Amino(aryloxy)oxosulfonium salts **3a–c** were prepared by refluxing a dichloromethane solution of the corresponding sulfonimidates **7** with Meerwein reagents (method B)[3,5] (Table I).

Table I. Preparation of (Aryloxy)oxosulfonium Salts

method	salts	mp, °C	yield, %	^{1}H NMR
A	**1a**	124–125[a]	50.1	4.39 (s, 6), 7.65 (s, 4)
A	**1b**	106–107	47.2	4.34 (s, 6), 7.63 (q, 4)
A	**1c**	130–131	47.1	2.40 (s, 3), 4.32 (s, 6), 7.30 (q, 4)
B	**3a**	117–119	76.2	1.17 (t, 3), 2.39 (s, 3), 3.85–4.30 (m, 2), 4.11 (s, 3), 7.24 (s, 9), 7.49 (s, 4)
B	**3b**	122–123	43.9	1.13 (t, 3), 2.24 (s, 3), 3.65–4.20 (m, 2), 4.09 (s, 3), 7.18 (s, 4), 7.50 (q, 4)
B	**3c**	116–117	52.6	1.13 (t, 3), 2.24 (s, 3), 2.31 (s, 3), 3.90–4.15 (m, 2), 4.02 (s, 3), 7.19 (s, 4), 7.31 (s, 4)

[a] Lit. mp 127 °C.

Scheme II



Treatment of a solution of **1a** with *n*-BuLi resulted in the formation of ylide **5a**, which was allowed to react with benzaldehyde at room temperature to give β-aryloxy sulfone **8a**, α,β-unsaturated sulfone **9a**, β-benzoyloxy sulfone **10a**, and **6** (Scheme II). Treatment of amino(aryloxy)-oxosulfonium ylide **11a** with benzaldehyde at room temperature or 50 °C resulted in β-aryloxy sulfonamide **4a**, α,β-unsaturated sulfonamide **12a**, and *N*-ethyl-*N*-*p*-tolylmethanesulfonamide **13**. On the other hand, the reaction of **11c** with benzophenone afforded only **13** and the benzophenone was recovered. Ylides **5** and **11** might be less reactive than other sulfur ylides (aminooxosulfonium ylide, dimethyloxosulfonium ylide, etc.). **6** and **13** might be produced by the hydrolysis of **5** and **11**[2a,c] (Table II). As the yields of the products were low, we then tried these reactions at −60 °C. Treatment of a solution of ylide **5a**

(3) Okuma, K.; Tanaka, Y.; Ohta, H. *J. Am. Chem. Soc.* **1981**, *103*, 5976.
(4) Okuma, K.; Tanaka, Y.; Ohta, H. *J. Am. Chem. Soc.* **1982**, *104*, 7385. Yokomori, Y.; Okuma, K., unpublished results.
(5) Johnson, C. R.; Wambsgans, A. *J. Org. Chem.* **1979**, *44*, 2278.

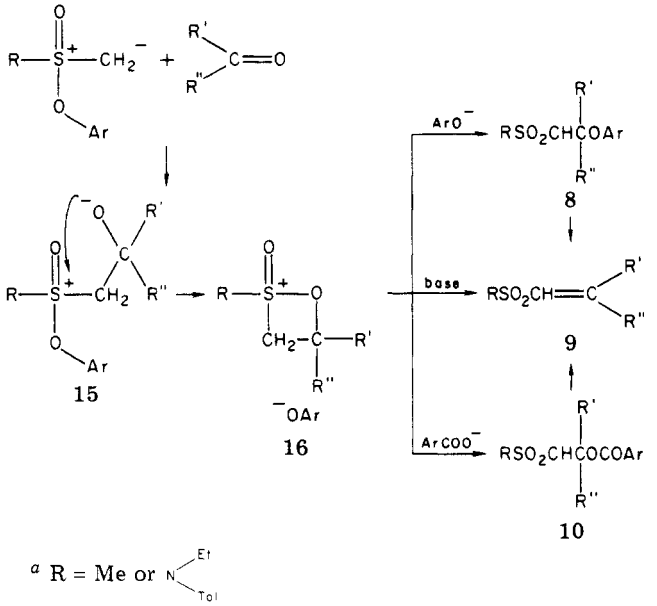
Table II. Reaction of 5 or 11 with Carbonyl Compounds at Room Temperature

oxosulfonium salt	carbonyl compound	reaction time, h	excess ylide, mol %	products, %				recovered carbonyl compound, %	para-substituted phenol, %
				8 or 4	9, 12, or 14	10	6 or 13		
1a	PhCHO	3	0	4.5	6.0	6.6	30	28	70
1c	PhCHO	3	0	1.4	5.1	7.2	32	28	74
3a	PhCHO	3	20	17.9	18.0	0	15	13	62
3b	PhCHO	3	10	16.8	10.5	0	17	12	50
3c	PhCHO	3	10	0	13.5	0	19	18	72
1a	*p*-ClC_6H_4CHO	3.5	0	5.1	4.5	1.2	25	22	74
1a	PhCOPh	5	10	0	0	0	76	90	78
3c	PhCOPh	5	10	0	0	0	73	88	75

Table III. Reactions of 5 or 11 with Carbonyl Compounds at -60 °C

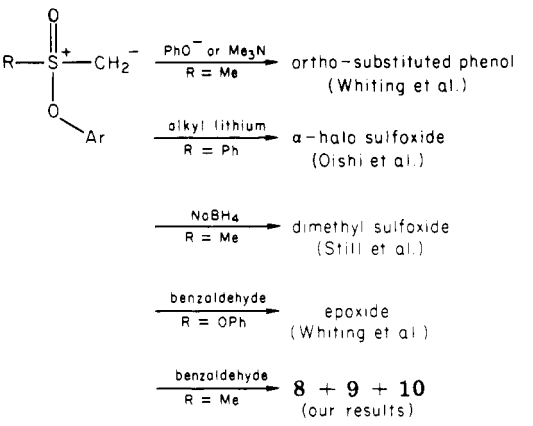
entry	oxosulfonium salt	carbonyl compound	reaction time, h	excess ylide, mol %	products, %			recovered carbonyl compound, %	para-substituted phenol, %
					8 or 4	9, 12, or 14	6 or 13		
1	1a	PhCHO	3	0	16.1	19.8	16	10	52
2	1a	PhCHO	3	50	21.3	25.3	43	5	105
3	1a	PhCHO	3	80	22.0	27.5	65	2	130
4	1b	PhCHO	3	50	15.8	33.6	46	3	84
5	1c	PhCHO	3	50	8.2	20.7	49	3	101
6	3a	PhCHO	3	0	12.0	33.0	10	18	48
7	3a	PhCHO	3	50	15.0	36.0	50	5	88
8	1a	*p*-ClC_6H_4CHO	3	50	15.1	19.4	53	4	120
9	1a	*p*-MeC_6H_4CHO	3	50	12.3	30.6	51	4	102
10	1a	acetone	3	0	0	22.0	23		78
11	1a	acetone	3	50	0	31.0	48		110
12	1a	PhCH=CHCHO	3	0	11.9	28.0	21	22	65
13	1b	PhCH=CHCHO	3	50	13.7	30.7	52	2	110
14	1b	4-*tert*-butyl-cyclohexanone	3	50	3.7	42.0	64	30	123

Scheme III. Mechanism[a]

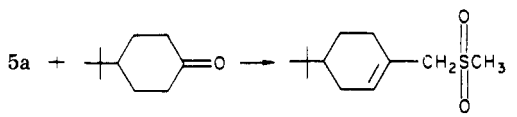


[a] R = Me or

Scheme IV



with benzaldehyde at −60 °C gave **8a**, **9a**, and **6** in 21.3%, 25.3%, and 43.0% yield, respectively (entry 2, Table III). On the other hand, the reaction of **5a** with 4-*tert*-butylcyclohexanone afforded β,γ-unsaturated sulfone **14b** and **6** in 42.0% and 64.0% yields, respectively (entry 14). In general, the best results were obtained by using a 50% excess of ylide at −60 °C.



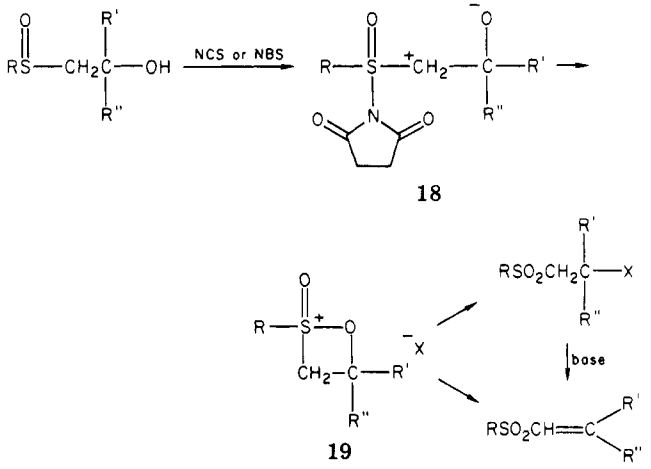
14b

The reaction can be rationalized by an intramolecular mechanism; ylide **5** can attack carbonyl compounds to give betaine **15**, forming an unusual four-membered cyclic oxosulfonium salts **16**. Aryloxy anion and benzoyloxy anion further attack the β-carbon of **16** to give **8** and **10**, respectively. Unsaturated sulfones **9** or **14** were obtained by abstraction of the α- or γ-proton of salt **16** or by abstraction of the α-proton of **8** or **10** (Scheme III). α,β-Unsaturated sulfones are known to be generally thermodynamically less stable than the β,γ-isomers.[6] Benzoyloxy anion was formed by autoxidation of benzaldehyde, which might be suggested by the following two results: the reaction of benzaldehyde with *n*-BuLi did not afford benzyl alcohol and benzoic acid, and autoxidation of benzaldehyde in THF gave about 3% of benzoic acid.

Whiting et al. showed that the reaction of (diaryloxy)-oxosulfonium ylide with benzaldehyde gave styrene oxide,

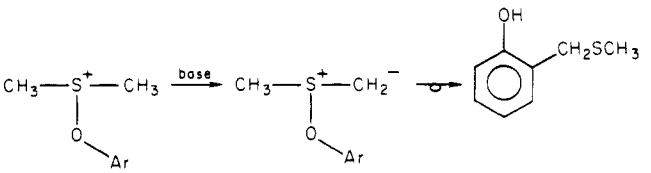
(6) Broaddus, C. D. *Acc. Chem. Res.* **1968**, *1*, 231.

Scheme V



which acted as a methylene transfer reagent (Scheme IV). They also pointed out that the reaction of (aryloxy)oxosulfonium salts with sodium phenoxide or trimethylamine gave ortho-substituted phenols.[2a] Oishi and co-workers found that treatment of (aryloxy)oxosulfonium salts with alkyllithium afforded α-halogenomethyl phenyl sulfoxides.[2b] Recently, Still et al. reported the synthesis of a sulfoxide by the reaction of an (aryloxy)oxosulfonium salt with sodium borohydride or by the reaction of this salt with *n*-BuLi followed by the addition of the hydride.[2c] Since these results are quite different from ours, we explain these differences as follows. Phenoxide ion and alkyl anions attacked α-protons of **1** forming corresponding ylides, which rearranged to give α-halo sulfoxide or ortho-substituted phenols. Sulfoxide was produced by further addition of hydride ion. Methylene transfer reaction might occur in the presence of carbonyl compounds. The differences in the reactivity of a (diaryloxy)oxosulfonium ylide and **5a–c** is a reflection of differences in the "leaving group" ability, because the (diaryloxy)oxosulfonium ylide might be more stable than **5a–c** as seen in ref 2a.

(Aryloxy)oxosulfonium salts **1** are a relatively unknown class of compounds having chemical properties that are different considerably from those (aryloxy)sulfonium salts **17**. Whereas **17** are quite unstable and cannot be isolated



17

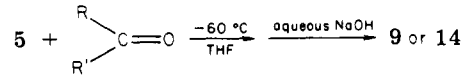
at room temperature, **1** are stable and can be isolated.[7] Alkali immediately convert **17** to ortho-substituted phenols by the Sommelet–Hauser type rearrangement, whereas **1a–c** with *n*-BuLi and carbonyl compounds afford **8** and **9** (or **14**).[8] The difference in the reactivity of **1** and **17** may be attributed to the difference of electron density on the respective sulfur atoms.

Previously, unsaturated sulfones and β-halo sulfones were obtained by the reactions of β-hydroxy sulfoxides with NBS or NCS[9] (Scheme V). Betaine **18** is structurally related to betaine **15** and the structure of cyclic alkoxyoxosulfonium salts **19** is the same with our **16**. This result suggests that this reaction is quite similar to ours.

Table IV. Preparation of Trans Sulfones from 1a

carbonyl compounds	products, % 9 or 14		6
PhCHO	9a	52.3	52
p-ClC_6H_4CHO	9b	60.0	55
p-MeC_6H_4CHO	9c	53.0	61
acetone	14a	35.0	61
4-*tert*-butylcyclohexanone	14b	50.2	63
PhCH=CHCHO	14e	44.0	55

Since β-aryloxy sulfones could be converted to unsaturated sulfones in quantitative yields by refluxing the sulfones with aqueous NaOH, we let ylide **5** react with carbonyl compounds followed by the addition of aqueous NaOH, by refluxing 2 h. As shown in Table IV, yields of



9 or **14** were raised up to 35.0–60.0%. This is another approach to the synthesis of unsaturated sulfones from carbonyl compounds and **1** by a one-pot reaction.

Experimental Section

General Methods. Melting points are uncorrected. NMR spectra were obtained by using JEOL JNM-PMX-60 and FX-200 spectrometers. IR spectra were recorded on a Hitachi IR-345 spectrometer.

Materials. *N*-*p*-Tolylmethanesulfinamide was prepared from methanesulfinyl chloride, *p*-toluidine, and triethylamine[10] (mp 114–115 °C, lit. mp 115–116 °C). Diazonium salts were prepared from para-substituted aniline, sodium nitrite, and fluroboric acid.[11] Dimethyl sulfone, Sephadex LH-20, and SiO_2 were purchased from Aldrich, Pharmacia, and Merck, respectively.

Preparation of Dimethyl(*p*-chlorophenoxy)oxosulfonium Fluoborate (1a) (Method A). In a 100-mL round-bottomed flask was placed 8.46 g (90 mmol) of dimethyl sulfone, which was warmed up to 130 °C. To this flask was added portion-wise 6.49 g (30 mmol) of *p*-chlorobenzenediazonium fluoborate in 15 min. After being stirred for 30 min, the reaction mixture was cooled to room temperature. Recrystallization from acetone–ether gave colorless crystals of **1a**. **1b** and **1c** were prepared in a similar manner. **1b**. Anal. Calcd for $C_8H_{10}BBrF_4O_2S$: C, 28.57; H, 2.97. Found: C, 28.49; H, 2.57. **1c**. Anal. Calcd for $C_9H_{13}BF_4O_2S$: C, 39.85; H, 4.80. Found: C, 39.75; H, 4.90.

Preparation of *p*-Chlorophenyl *N*-*p*-Tolylmethanesulfonimidate (7a). To a dichloromethane solution (200 mL) of *N*-*p*-tolylmethanesulfinamide (8.6 g, 50 mmol) was added chlorine gas (80 mmol) at −50 °C in 1 h. After stirring 2 h, this pale yellow suspension was warmed up to room temperature, filtered, and concentrated to 30 mL. The resulting solution was added dropwise to a dichloromethane (300 mL) solution of *p*-chlorophenol (6.4 g, 50 mmol) and triethylamine (5.0 g. 50 mmol) at −10 °C. After stirring 2 h, the suspension was poured into water and extracted three times with dichloromethane. The combined dichloromethane solution was dried over $MgSO_4$ and evaporated to give a pale orange oil, which solidified on standing. Recrystallization from methanol gave colorless crystals of **7a**: yield 77.8%; mp 76–77 °C. Anal. Calcd for $C_{14}H_{14}ClNO_2S$: C, 56.85; H, 4.74; N, 4.74. Found: C, 56.86; H, 4.85; N, 4.63. **7b** and **7c** were prepared in a similar manner. **7b**: mp 90–91 °C; yield 72.0%. Anal. Calcd for $C_{14}H_{14}BrNO_2S$: C, 49.41; H, 4.21; N, 4.21. Found: C, 49.62; H, 4.27; N, 4.22. **7c**: mp 101–102 °C; yield 76.8%. Anal. Calcd for $C_{15}H_{17}NO_2S$: C, 64.98; H, 6.86; N, 5.05. Found: C, 65.08; H, 6.46; N, 5.45.

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Preparation of Methyl(ethyltolylamino)(*p*-tolyloxy)oxosulfonium Fluoborate (3c) (Method B). To a dichloromethane solution of **7c** (2.0 g, 7.3 mmol) was added triethyloxonium fluoborate (1.9 g, 10 mmol).[12] After refluxing 1.5 h, the reaction mixture was evaporated to give a pale brown oil. Isolation of **3c** was carried out by gel chromatography over Sephadex LH-20 (80% crude yield). Recrystallization from methanol gave colorless crystals. Anal. Calcd for $C_{17}H_{22}BF_4NO_2S$: C, 52.17; H, 5.67; N, 3.58. Found: C, 52.36; H, 5.49; N, 3.19. **3a** and **3b** were prepared in a similar manner. **3a**. Anal. Calcd for $C_{16}H_{19}BClF_4NO_2S$: C, 46.69; H, 4.65; N, 3.40. Found: C, 46.56; H, 4.87; N, 3.52. **3b**. Anal. Calcd for $C_{16}H_{19}BBrF_4NO_2S$: C, 42.14; H, 4.20; N, 3.07. Found: C, 42.36; H, 4.49; N, 3.19.

Reaction of 11a with Benzaldehyde at Room Temperature. To a THF solution (30 mL) of **3a** (4.94 g, 12 mmol) was added dropwise a hexane solution of *n*-BuLi (6.4 mL, 10% w/v) at room temperature. After being stirred for 30 min, a THF solution (15 mL) of benzaldehyde (1.06 g, 10 mmol) was added dropwise to this solution at room temperature (or 50 °C) in 10 min. After being stirred 3 h, the dark red solution was washed with water and extracted with ether (30 mL × 3); the ethereal solution was dried over $MgSO_4$ and evaporated. The resulting dark red oil was subjected to medium-pressure column chromatography (Merck, pre-packed column size B, SiO_2). Five components were obtained. (a) Benzaldehyde (0.14 g, 1.3 mmol) was eluted first (eluant, hexane). (b) *p*-Chlorophenol (0.80 g, 6.2 mmol) was eluted second (eluant, 80% hexane–dichloromethane). (c) *N*-Ethyl-*N*-tolyl-2-(*p*-chlorophenoxy)-2-phenylethanesulfonamide (**4a**,[3] 0.60 g, 1.79 mmol) was further eluted (eluant, 50% hexane–dichloromethane): mp 125–126 °C. Anal. Calcd for $C_{23}H_{24}ClNO_3S$: C, 64.26; H, 5.59; N, 3.26. Found: C, 64.66; H, 5.96; N, 3.51. (d) *N*-Ethyl-*N*-*p*-tolyl-*trans*-styrenesulfonamide (**12**, 0.54 g, 1.8 mmol) was then eluted (eluant, 25% hexane–dichloromethane): mp 82–83 °C; ^1H NMR ($CDCl_3$) δ 1.13 (t, 3 H), 2.35 (s, 3 H), 3.63 (q, 2 H), 6.74 (d, 1 H, J = 15.0 Hz), 7.16 (s, 4 H), 7.21 (d, 1 H, J = 15.0 Hz), 7.38 (s, 5 H, Ph); IR (KBr) $\nu_{S=O}$ 1135, 1335 cm^{-1}. Anal. Calcd for $C_{17}H_{19}NO_2S$: C, 67.77; H, 6.31; N, 4.65. Found: C, 67.56; H, 6.41; N, 4.47. (e) **13** (0.32 g, 1.5 mmol) was eluted last (eluant, dichloromethane).

Other reactions were carried out in a similar manner.

Reaction of 5c with Benzaldehyde. **1c** (1.36 g, 5 mmol), *n*-BuLi (3.2 mL, 10% w/v, 5 mmol), and benzaldehyde (0.53 g, 5 mmol) were used. After workup, six components were obtained. (a) Benzaldehyde (0.15 g, 1.4 mmol). (b) *p*-Cresol (0.48 g, 3.7 mmol). (c) 2-(*p*-Tolyloxy)-2-phenylethyl methyl sulfone (**8c**, 0.02 g, 0.069 mmol): mp 121–122 °C; ^1H NMR ($CDCl_3$) δ 2.21 (s, 3 H), 3.06 (s, 3 H), 3.22 (dd, 1 H, J = 15.3 Hz, J = 1.8 Hz), 3.71 (dd, 1 H, J = 10.4 Hz, J = 15.3 Hz), 5.70 (dd, 1 H, J = 10.4 Hz, J = 1.8 Hz), 6.87 (q, 4 H), 7.35 (s, 5 H); ^{13}C NMR ($CDCl_3$) δ 19.8 (TolMe), 42.4 (SMe), 61.9 (SCH_2), 75.4 (CH), 115.6, 116.9, 126.7, 129.7, 129.8, 130.8, 138.9 (Ar); IR (KBr) $\nu_{S=O}$ 1125, 1297 cm^{-1}. Anal. Calcd for $C_{16}H_{18}O_3S$: C, 66.21; H, 6.21. Found: C, 66.12; H, 6.35. (d) 2-(Benzoyloxy)-2-phenylethyl methyl sulfone (**10a**, 0.11 g, 0.36 mmol): mp 146–147 °C; ^1H NMR ($CDCl_3$) δ 2.89 (s, 3 H, SMe), 3.46 (dd, 1 H, SCH_2, J = 3.7 Hz, J = 15.1 Hz), 3.86 (dd, 1 H, SCH_2, J = 9.3 Hz, J = 15.1 Hz), 6.25 (dd, 1 H, PhCH, J = 9.3 Hz, J = 3.7 Hz), 7.35–8.09 (m, 10 H, Ar); ^{13}C NMR ($CDCl_3$) δ 42.4 (SMe), 60.5 (SCH_2), 71.2 (CH), 125.6, 128.6, 129.2, 129.8, 133.6, 133.7 (Ar); IR (KBr) $\nu_{S=O}$ 1143, 1295 cm^{-1}, $\nu_{C=O}$ 1710 cm^{-1}. Anal. Calcd for $C_{16}H_{16}O_4S$: C, 63.16; H, 5.26. Found: C, 62.88; H, 5.33. (e) *trans*-Styryl methyl sulfone (**9a**, 0.05 g, 0.27 mmol): mp 80–81 °C; ^1H NMR ($CDCl_3$) δ 3.03 (s, 3 H, SMe), 6.84 (d, 1 H, SCH, J = 15.4 Hz), 7.48 (s, 5 H, Ph), 7.66 (d, 1 H, PhCH, J = 15.4 Hz); IR (KBr) $\nu_{S=O}$ 1110, 1305 cm^{-1}. Anal. Calcd for $C_9H_{10}O_2S$: C, 59.34; H, 5.49. Found: C, 58.94; H, 5.76. (f) **6** (0.15 g, 1.6 mmol).

Reaction of 5a with Benzaldehyde. **1a** (1.46 g, 5 mmol), *n*-BuLi (3.2 mL, 10% w/v, 5 mmol), and benzaldehyde (0.53 g, 5 mmol) were used. After workup, six components were obtained. (a) Benzaldehyde (0.15 g, 1.4 mmol). (b) *p*-Chlorophenol (0.45 g, 3.5 mmol). (c) 2-(*p*-Chlorophenoxy)-2-phenylethyl methyl sulfone (**8a**, 0.07 g, 0.23 mmol): mp 110–111 °C; ^1H NMR ($CDCl_3$) δ 3.04 (s, 3 H, SCH_3), 3.25 (dd, 1 H, SCH_2, J = 2.2 Hz, J = 15.3 Hz), 3.74 (dd, 1 H, SCH_2, J = 10.1 Hz, J = 15.3 Hz), 5.70 (dd, 1 H, PhCH, J = 10.1 Hz, J = 2.2 Hz); ^{13}C NMR ($CDCl_3$) δ 43.2 (SMe), 62.0 (SCH_2), 76.1 (PhCH), 119.0, 126.5, 129.5, 129.8, 130.1, 138.0 (Ar); IR (KBr) $\nu_{S=O}$ 1115, 1305 cm^{-1}. Anal. Calcd for $C_{15}H_{15}ClO_3S$: C, 57.79; H, 4.83. Found: C, 57.79; H, 5.05. (d) **10a** (0.09 g, 0.30 mmol). (e) **9a** (0.06 g, 0.33 mmol). (f) **6** (0.14 g, 1.5 mmol).

Reaction of 11b with Benzaldehyde. **3b** (2.0 g, 4.4 mmol), *n*-BuLi (3.0 mL, 10% w/v, 4.5 mmol), and benzaldehyde (0.43 g, 4.0 mmol) were used. After workup, five components were obtained. (a) Benzaldehyde (0.51 g, 0.48 mmol). (b) *p*-Bromophenol (0.43 g, 2.5 mmol). (c) *N*-ethyl-*N*-*p*-tolyl-2-(*p*-bromophenoxy)-2-phenylethanesulfonamide (**4b**, 0.32 g, 0.67 mmol): mp 131–132 °C. Anal. Calcd for $C_{23}H_{24}BrNO_3S$: C, 58.23; H, 5.10; N, 2.95. Found: C, 58.61; H, 5.29; N, 2.94. (d) **12** (0.13 g, 0.43 mmol). (e) **13** (0.15 g, 0.68 mmol).

Reaction of 11c with Benzaldehyde. **3c** (2.15 g, 5.5 mmol), *n*-BuLi (3.8 mL, 10% w/v, 6.0 mmol), and benzaldehyde (0.53 g, 5.0 mmol) were used. After workup, four components were obtained. (a) Benzaldehyde (0.10 g, 0.9 mmol). (b) *p*-Cresol (0.39 g, 3.6 mmol). (c) **12** (0.21 g, 0.68 mmol). (d) **13** (0.20 g, 0.95 mmol).

Reaction of 5a with *p*-Chlorobenzaldehyde. **1a** (3.50 g, 12 mmol), *n*-BuLi (8.4 mL, 10% w/v, 13 mmol), and *p*-chlorobenzaldehyde (1.69 g, 12 mmol) were used. After workup, six components were obtained. (a) *p*-Chlorobenzaldehyde (0.35 g, 2.6 mmol). (b) *p*-Chlorophenol (1.0 g, 7.8 mmol). (c) 2-(*p*-Chlorophenoxy)-2-(*p*-chlorophenyl)ethyl methyl sulfone (**8d**, 0.21 g, 0.61 mmol): mp 142–143 °C; ^1H NMR ($CDCl_3$) δ 3.06 (s, 3 H, SMe), 3.23 (dd, 1 H, SCH_2, J = 2.2 Hz, J = 15.3 Hz), 3.72 (dd, 1 H, SCH_2, J = 10.7 Hz, J = 15.3 Hz), 5.68 (dd, 1 H, PhCH, J = 2.2 Hz, J = 10.7 Hz), 6.98 (q, 4 H, *p*-ClC_6H_4O), 7.32 (s, 4 H, *p*-ClC_6H_4); ^{13}C NMR ($CDCl_3$) δ 43.2 (SMe), 61.9 (SCH_2), 75.7 (Ar CH), 117.7, 127.4, 129.5, 136.0 (Ar); IR (KBr) $\nu_{S=O}$ 1135, 1295 cm^{-1}. Anal. Calcd for $C_{15}H_{14}Cl_2O_3S$: C, 52.17; H, 4.06. Found: C, 51.75; H, 4.13. (d) 2-(*p*-Chlorophenyl)-2-[(*p*-chlorobenzoyl)oxy]ethyl methyl sulfone (**10b**, 0.05 g, 0.13 mmol). Since the yield of **10b** was quite low, analytically pure product could not be obtained. Both **10b** is spectroscopically pure: ^1H NMR ($CDCl_3$) δ 2.90 (s, 3 H, SCH_3), 3.39 (dd, 1 H, SCH_2, J = 3.8 Hz, J = 14.7 Hz), 3.79 (dd, 1 H, SCH_2, J = 9.2 Hz, J = 14.7 Hz), 6.43 (dd, 1 H, Ar CH, J = 9.2 Hz, J = 3.8 Hz), 7.13–8.14 (m, 8 H, Ar). (e) *p*-Chlorostyryl methyl sulfone (**9b**, 0.12 g, 0.55 mmol): mp 127–128 °C; ^1H NMR ($CDCl_3$) δ 3.03 (s, 3 H, SMe), 6.90 (d, 1 H, J = 15.2 Hz), 7.10 (s, 4 H, Ar), 7.61 (d, 1 H, J = 15.2 Hz); IR (KBr) $\nu_{S=O}$ 1125, 1295 cm^{-1}. Anal. Calcd for $C_9H_9ClO_2S$: C, 49.88; H, 4.16. Found: C, 49.63; H, 4.33. (f) **6** (0.28 g, 3.0 mmol).

Reaction of 5a with Benzophenone. **1a** (1.61 g, 5.5 mmol), *n*-BuLi (3.8 mL, 10% w/v, 6 mmol), and benzophenone (0.91 g, 5.0 mmol) were used. After workup, three components were obtained. (a) Benzophenone (0.82 g, 4.5 mmol). (b) *p*-Chlorophenol (0.48 g, 3.8 mmol). (c) **6** (0.36 g, 3.8 mmol).

Reaction of 11a with Benzophenone. **3a** (2.26 g, 5.5 mmol), *n*-BuLi (3.8 mL, 10% w/v, 6.0 mmol), and benzophenone (0.91 g, 5 mmol) were used. After workup, three components were obtained. (a) Benzophenone (0.80 g, 4.4 mmol). (b) *p*-Chlorophenol (0.48 g, 3.75 mmol). (c) **13** (0.78 g, 3.7 mmol).

Reaction of 5c with Benzaldehyde at −60 °C. To a solution of 4.05 g (15 mmol) of **1c** in 25 mL of THF was added dropwise a solution of 10% w/v *n*-BuLi (7.5 mL, 17 mmol) in hexane over a period of 10 min at −60 °C. After being stirred 30 min, a THF solution of benzaldehyde (1.06 g, 10 mmol) was added dropwise to this solution. The mixture was stirred for 3 h at this temperature and warmed up to room temperature. A 50-mL volume of water and 40 mL of dichloromethane were added. The organic layer was separated and the water layer was extracted twice with dichloromethane. The combined extract was dried over $MgSO_4$ and evaporated. The resulting brown oily crystals were subjected to medium-pressure column chromatography (Merck, pre-packed column size A, SiO_2). Five components were obtained. Benzaldehyde (0.03 g, 0.3 mmol) was eluted first (eluant, hexane). *p*-Cresol (1.09 g, 10.1 mmol) was eluted second (eluant 80% hexane–dichloromethane). **8c** (0.24 g, 0.82 mmol) was further eluted (eluant 50% hexane–dichloromethane). **9a** (0.38 g, 2.1 mmol) was then eluted (eluant 25% hexane–dichloromethane). **6** (0.46 g, 4.9 mmol) was lastly eluted (eluant dichloromethane).

Other reactions were carried out in a similar manner.

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Reaction of 5a with Benzaldehyde at −60 °C. 1a (2.19 g, 7.5 mmol), *n*-BuLi (4.8 mL, 10% w/v, 7.5 mmol), and benzaldehyde (0.53 g, 5 mmol) were used. After workup, five components were obtained. (a) Benzaldehyde (0.03 g, 0.03 mmol). (b) *p*-Chlorophenol (0.67 g, 5.0 mmol). (c) **8a** (0.33 g, 1.1 mmol). (d) **9a** (0.23 g, 1.3 mmol). (e) **6** (0.20 g, 2.1 mmol).

Reaction of 5b with Benzaldehyde. 1b (4.03 g, 12 mmol), *n*-BuLi (7.7 mL, 10% w/v, 12 mmol), and benzaldehyde (0.85 g, 8.0 mmol) were used. After workup, five components were obtained. (a) Benzaldehyde (0.03 g, 0.03 mmol). (b) *p*-Bromophenol (1.16 g, 6.7 mmol). (c) 2-(*p*-Bromophenoxy)-2-phenylethyl methyl sulfone (**8b**, 0.45 g, 1.3 mmol): mp 127–128 °C; ^{1}H NMR ($CDCl_3$) δ 3.04 (s, 3 H, SMe), 3.24 (dd, 1 H, SCH_2, J = 15.3 Hz, J = 2.1 Hz), 3.72 (dd, 1 H, SCH_2, J = 10.4 Hz, J = 15.3 Hz), 5.70 (dd, 1 H, PhCH, J = 2.1 Hz, J = 10.4 Hz), 7.02 (q, 4 H, *p*-BrC_6H_4), 7.34 (s, 5 H, Ph); ^{13}C NMR ($CDCl_3$) δ 43.1 (SMe), 62.2 (SCH_2), 76.2 (PhCH), 114.6, 118.2, 126.0, 129.0, 129.3, 132.5, 137.6, 155.7 (Ar); IR (KBr) $\nu_{S=O}$ 1133, 1304 cm^{-1}. Anal. Calcd for $C_{15}H_{15}BO_3S$: C, 50.70; H, 4.23. Found: C, 50.79; H, 4.09. (d) **9a** (0.49 g, 2.7 mmol). (e) **6** (0.35 g, 3.7 mmol).

Reaction of 11a with Benzaldehyde at −60 °C. 3a (3.09 g, 8.1 mmol), *n*-BuLi (5.1 mL, 10% w/v, 8.0 mmol), and benzaldehyde (0.53 g, 5.0 mmol) were used. After workup, five components were obtained. (a) Benzaldehyde (0.027 g, 0.025 mmol). (b) *p*-Chlorophenol (0.57 g, 4.4 mmol). (c) **4a** (0.32 g, 0.75 mmol). (d) **12** (0.54 g, 1.8 mmol). (e) **13** (0.53 g, 2.5 mmol).

Reaction of 5a with *p*-Chlorobenzaldehyde at −60 °C. 1a (2.19 g, 7.5 mmol), *n*-BuLi (4.8 mL, 10% w/v, 7.5 mmol), and *p*-chlorobenzaldehyde (0.71 g, 5.0 mmol) were used. After workup, five components were obtained. (a) *p*-Chlorobenzaldehyde (0.028 g, 0.02 mmol). (b) *p*-Chlorophenol (0.77 g, 6.0 mmol). (c) **8d** (0.26 g, 0.75 mmol). (d) **9b** (0.21 g, 0.97 mmol). (e) **6** (0.25 g, 2.7 mmol).

Reaction of 5a with *p*-Methylbenzaldehyde at −60 °C. 1a (0.35 g, 12 mmol), *n*-BuLi (7.7 mL, 10% w/v, 12 mmol), and *p*-methylbenzaldehyde (0.96 g, 8.0 mmol) were used. After workup, four components were obtained. (a) *p*-Methylbenzaldehyde (0.038 g, 0.036 mmol). (b) *p*-Chlorophenol (1.05 g, 8.2 mmol). (c) 2-(*p*-Chlorophenoxy)-*p*-tolylethyl methyl sulfone (**8e**, 0.32 g, 0.99 mmol): colorless oil: ^{1}H NMR ($CDCl_3$) δ 2.30 (s, 3 H, TolCH$_3$), 3.00 (s, 3 H, SMe), 3.17 (dd, 1 H, SCH_2, J = 2.6 Hz, J = 14.8 Hz), 3.73 (dd, 1 H, SCH_2, J = 14.8 Hz, J = 9.6 Hz), 5.62 (dd, 1 H, TolCH, J = 2.6 Hz, J = 9.6 Hz), 6.93 (q, 4 H, *p*-ClC_6H_4), 7.16 (s, 4 H, Tol). Analytically pure product could not be obtained. (d) *p*-Methylstyryl methyl sulfone (**9c**, 0.48 g, 2.4 mmol): mp 113–114 °C; ^{1}H NMR ($CDCl_3$) δ 2.39 (s, 3 H, TolMe), 3.03 (s, 3 H, SMe), 6.88 (d, 1 H, J = 15.3 Hz), 7.32 (d, 4 H, Tol), 7.59 (d, 1 H, J = 15.3 Hz); IR $\nu_{S=O}$ (KBr) 1145, 1315 cm^{-1}. Anal. Calcd for $C_{10}H_{12}O_2S$: 61.22; H, 6.12. Found: C, 61.21; H, 6.46. (e) **6** (0.38 g, 4.0 mmol).

Reaction of 5a with Acetone at −60 °C. 1a (1.46 g, 5.0 mmol), *n*-BuLi (3.2 mL, 10% w/v, 5.0 mmol), and acetone (0.29 g, 5.0 mmol) were used. After workup, three components were obtained. (a) *p*-Chlorophenol (0.50 g, 3.9 mmol). (b) 2-Methyl-2-propenyl methyl sulfone (**14a**, 0.15 g, 1.1 mmol):[13] colorless oil; ^{1}H NMR ($CDCl_3$) δ 1.97 (m, 3 H, Me), 2.93 (s, 3 H, SMe), 3.70 (s, 2 H, SCH_2), 5.10 (m, 1 H). (c) **6** (0.11 g, 1.15 mmol).

Reaction of 5a with *trans*-Cinnamaldehyde. 1a (1.46 g, 5.0 mmol), *n*-BuLi (3.2 mL, 10% w/v, 5.0 mmol), and *trans*-cinnamaldehyde (0.66 g, 5.0 mmol) were used. After workup, five components were obtained. (a) *trans*-Cinnamaldehyde (0.15 g, 1.1 mmol). (b) *p*-Chlorophenol (0.42 g, 3.3 mmol). (c) 2-(*p*-Chlorophenoxy)-4-phenyl-3-butenyl methyl sulfone (**8f**, 0.20 g, 0.59 mmol): colorless oil; ^{1}H NMR ($CDCl_3$) δ 3.03 (s, 3 H, SMe), 3.19 (dd, 1 H, SCH_2, J = 15.2 Hz, J = 3.6 Hz), 3.60 (dd, 1 H, SCH_2, J = 15.2 Hz, J = 9.0 Hz), 5.34 (ddd, 1 H, SCH_2CH, J = 9.0 Hz, J = 3.6 Hz, J = 6.8 Hz), 6.15 (dd, 1 H, PhCH=CH, J = 16.2 Hz, J = 6.8 Hz), 6.63 (d, 1 H, PhCh, J = 16.2 Hz), 7.11 (q, 4 H, *p*-ClC_6H_4), 7.31 (s, 5 H, Ph). Analytically pure product could not be isolated. (d) 4-Phenyl-1,3-butadienyl methyl sulfone (**9d**, 0.30 g, 1.4 mmol): mp 95–96 °C; ^{1}H NMR ($CDCl_3$) δ 2.99 (s, 3 H, SMe), 6.50 (d, 1 H, SCH, J = 14.7 Hz), 6.82 (dd, 1 H, PhCH=C*H*, J = 10.4 Hz, J = 15.5 Hz), 7.00 (d, 1 H, PhCH, J = 15.5 Hz), 7.40–7.45 (m, 6 H, SCH=CH, and Ph); IR (KBr) $\nu_{S=O}$ 1130, 1270 cm^{-1}. Anal. Calcd for $C_{11}H_{12}O_2S$: C, 58.93; H, 5.36. Found: C, 59.33; H, 5.31. (e) **6** (0.10 g, 1.1 mmol).

Reaction of 5a with 4-*tert*-Butylcyclohexanone at −60 °C. 1a (1.31 g, 4.5 mmol), *n*-BuLi (4.2 mL, 10% w/v, 4.5 mmol), and 4-*tert*-butylcyclohexanone (0.46 g, 3.0 mmol) were used. After workup, five components were obtained. (a) 4-*tert*-Butylcyclohexanone (0.14 g, 0.90 mmol). (b) *p*-Chlorophenol (0.47 g, 3.7 mmol). (c) [1-[(Methylsulfonyl)methyl]-1-(*p*-chlorophenoxy)-4-*tert*-butyl]cyclohexane (**8g**, 0.04 g, 0.11 mmol): mp 126–127 °C; ^{1}H NMR ($CDCl_3$) δ 0.82 (s, 9 H, *t*-Bu), 0.77–2.50 (br, 9 H), 3.11 (s, 3 H, SMe) 3.43 (s, 2 H, SCH_2), 7.11 (q, 4 H, *p*-ClC_6H_4); IR (KBr) $\nu_{S=O}$ 1125. 1305 cm^{-1}. Anal. Calcd for $C_{18}H_{27}ClO_3S$: C, 60.25; H, 7.53. Found: C, 60.37; H, 7.86. (d) (4-*tert*-Butyl-1-cyclohexenyl)methyl methyl sulfone (**14b**, 0.28 g, 1.25 mmol): mp 99–100 °C; ^{1}H NMR ($CDCl_3$) δ 0.88 (s, 9 H, *t*-Bu), 0.92–2.62 (br, 7 H), 3.65 (s, 2 H, SCH_2), 5.88 (m, 1 H, olefinic); IR (KBr) $\nu_{S=O}$ 1135, 1300 cm^{-1}. Anal. Calcd for $C_{12}H_{22}O_2S$: C, 62.61; H, 9.57. Found: C, 62.61; H, 9.93. (e) **6** (0.18 g, 1.9 mmol).

Preparation of 9a from 8a. To a solution of 0.62 g (2.0 mmol) of **8a** in 15 mL of THF was added 10% aqueous NaOH (20 mL). This solution was refluxed for 2 h, then concentrated to 25 mL, and extracted three times with 10 mL of ether. The combined extract was washed with water, then dried over $MgSO_4$, and evaporated to give pale yellow crystals of **9a** (0.36 g, 2.0 mmol). Recrystallization from MeOH gave colorless crystals; mp 80–81 °C.

One-Pot Synthesis of Unsaturated Sulfone 9a. To a solution of 6.50 g (15 mmol) of **1a** in 40 mL of THF was added dropwise a solution of 10% (w/v) *n*-BuLi in hexane (11.5 mL, 18 mmol) over a period of 10 min at −60 °C. After being stirred 30 min, a THF solution of benzaldehyde (1.06 g, 10 mmol) was added dropwise to this solution. The mixture was stirred for 3 h at this temperature and warmed up to room temperature. A 30-mL volume of 10% aqueous NaOH was added and refluxed for 3 h, and the resulting suspension was then extracted three times with 20 mL of ether. The combined extract was washed with water and then dried over $MgSO_4$ and evaporated. The resulting brown oil was chromatographed in 60 g of SiO_2 by elution with hexane–dichloromethane (50%) mixture to give unsaturated sulfone **9a** (0.95 g, 5.2 mmol) and **6** (0.50 g, 5.2 mmol). Other unsaturated sulfones were obtained in a similar manner.

Reaction of Benzaldehyde with *n*-BuLi. To a THF solution (30 mL) of benzaldehyde (0.53 g, 5 mmol) was added dropwise a hexane solution of *n*-BuLi (3.2 mL, 10% w/v, 5 mmol). After being stirred 12 h, the reaction mixture was washed with 1 N HCl and extracted with dichloromethane (30 mL × 3). The dichloromethane layer was dried over $MgSO_4$ and evaporated. The NMR spectra of resulting pale yellow oil did not show those of benzoic acid and benzyl alcohol.

Autoxidation of Benzaldehyde. A solution of benzaldehyde (0.53 g, 5 mmol) in 30 mL of THF was stirred for 12 h. This solution was evaporated and washed with water and extracted with hexane (30 mL × 3). The water layer was titrated with 0.1 N NaOH, which showed the formation of about 3% of benzoic acid.[14]

Acknowledgment. This work was partly supported by the Ministry of Education, Japanese Government (Grant-In-Aid 56740220), and the Central Research Institute of Fukuoka University.

(13) **15a** was identified by its authentic sample, which was produced by the reaction of 2-methyl-2-hydroxypropyl methyl sulfoxide with *N*-bromosuccinimide at −60 °C:[9] yield 20%; bp 85–95 °C/0.6 mmHg; IR $\nu_{S=O}$ 1135, 1315 cm^{-1}.

(14) Pasto, D. J.; Johnson, C. R. "Laboratory Text for Organic Chemistry"; Prentice-Hall, Inc.: New Jersey, 1979; p 431.