Synthesis and Reaction of Diaminosulfoxonium Salts

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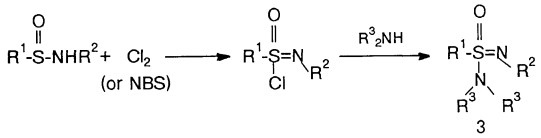
Diaminosulfoxonium salts were prepared by alkylation of sulfonimidamides. Their physical properties were described. Their reaction with bases gave the corresponding ylides and sulfonimidamides. The intramolecular rearrangement of the ylides led to ortho substitution via intermediate cyclohexadienimines. Hydrogen transfer, accompanying rearomatization and the subsequent action of bases gave dihydro-2,1-benzisothiazole derivatives. These ylides were also found to react with aldehydes to afford epoxides in moderate yields.

Heteroatom-substituted sulfonium salts and sulfoxonium salts are interesting compounds because of their anomalous reactivity.[1] We have described the synthesis of diamino-, aminoalkoxy-, and triaminosulfonium salts.[2] In the case of aminoalkoxysulfonium salts, they acted as good alkylating reagents toward nucleophiles. Vilsmeier et al. reported the synthesis of methylmorpholinosuccinimidosulfonium hexachloroantimonate.[3] Wagner and Judelbauer also reported the preparation of methyl-bis(diisopropylamino)sulfonium tetrafluoroborate.[4] Gassman et al. reported the synthesis of aminosulfonium salts and showed that the reaction of these salts with bases gave the rearranged products.[5] However, there is a few reports on the synthesis and reaction of heteroatom substituted sulfoxonium salts. Aminosulfoxonium salts (**1**) were prepared by the alkylation of sulfoximines and acted as methylene-transfer reagents toward carbonyl compounds, α,β-unsaturated ketones to give epoxides and cyclopropanes, respectively.[6] These results prompted us to investigate the synthesis and reaction of diaminosulfoxonium salts (**2**).[7] In this paper, we would like to report the preparation, spectroscopic studies, and reaction of compounds **2**.

Results and Discussion

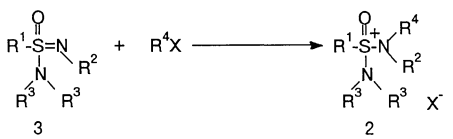
Preparation of Diaminosulfoxonium Salts (2). Since diaminosulfonium salts were prepared by oxidation of sulfenamides with 1-chlorobenzotriazole, *p*-toluenesulfinmorpholide was allowed to react firstly with *N*-chlorosuccinimide or 1-chlorobenzotriazole and then secondary amines.[2] However, these reactions gave only the corresponding ammonium salts quantitatively. We then tried the oxidation of diaminosulfonium salts. A number of oxidizing reagents, such as potassium permanganate, sodium periodate, and *m*-chloroperbenzoic acid were used for this purpose, but sulfoxonium salts **2** could not be obtained.

Johnson and co-workers prepared **1** by the alkylation of sulfoximines.[6] We have also synthesized diaminosulfonium salts by the alkylation of aminosulfilimines.[2] In view of these results, treatment of sulfonimidamides (**3**) with alkylating reagents was investigated as a possible method for the synthesis of **2**. Sulfonimidamides **3** as precursors were prepared by the reaction of sulfinamides with *N*-bromosuccinimide (NBS) or chlorine followed by the addition of secondary amines.[8,9]



Scheme 1.

Treatment of **3a** with triethyloxonium tetrafluoroborate in dichloromethane afforded the corresponding salts (**2b**) in 64% yield. Other diaminosulfoxonium salts **2a—o** summarized in Table 1 were successfully prepared by the reaction of **3** with alkylating reagents in nitromethane or dichloromethane, followed by the addition of sodium tetraphenylborate, if necessary. Compounds **3i** and **3j** could not be alkylated under these conditions, which could be attributed to reduced electron density of the N-atom, because S methyl signal of **3i** was lower than that of **3a** in their NMR spectra. (**3i**, δ=3.10; **3a**, δ=2.89)



Scheme 2.

Recently, we also reported the synthesis and reaction of **3**, which resulted in the preparation of functionalized sulfonimidamides.[9] However, the alkylation of these compounds was unsuccessful because of their low electron density and/or steric hindrance. These results suggested that the electron density of sulfonium cationic center is important on the preparation of sulfoxonium salts. We then compared the spectroscopic results of other sulfonium or sulfoxonium salts

Table 1. Preparation of Diaminosulfoxonium Salts **2**

Sulfonimidamides				Alkylating reagents	Diaminosulfoxonium salts			
3	R^1	R^2	R^3–N–R^3		**2**	R^4	X	Yield/%
3a	Me	*p*-Tol	Morpholino	Me_3O^+ $^-BF_4$	**2a**	Me	$^-BF_4$	81
3a				CF_3SO_3Me	**2a'**	Me	$CF_3SO_3^-$	92
3a				Et_3O^+ $^-BF_4$	**2b**	Et	$^-BF_4$	64
3b	Et	*p*-Tol	Morpholino	CF_3SO_3Me	**2c**	Me	$CF_3SO_3^-$	50
3b				Et_3O^+ $^-BF_4$	**2d**	Et	$^-BF_4$	40
3c	Me	*i*-Pr	Morpholino	$FSO_3Me/NaBPh_4$	**2e**	Me	$^-BPh_4$	42
3d	Et	*i*-Pr	Morpholino	$FSO_3Me/NaBPh_4$	**2f**	Me	$^-BPh_4$	53
3e	*i*-Pr	*i*-Pr	Morpholino	$FSO_3Me/NaBPh_4$	**2g**	Me	$^-BPh_4$	40
3f	*p*-Tol	*i*-Pr	Morpholino	CF_3SO_3Me	**2h**	Me	$CF_3SO_3^-$	60
3g	$ClCH_2CH_2CH_2$	*p*-Tol	Morpholino	Me_3O^+ $^-BF_4/NaBPh_4$	**2i**	Me	$^-BPh_4$	71
3h	*p*-Tol	$PhCH_2$	Morpholino	$FSO_3Me/NaBPh_4$	**2j**	Me	$^-BPh_4$	52
3i	*p*-Tol	*p*-Tosyl	Morpholino	CF_3SO_3Me				0
3j	Me	*p*-Tosyl	Morpholino	CF_3SO_3Me				0
3k	Me	*p*-ClC_6H_4	Morpholino	Me_3O^+ $^-BF_4$	**2l**	Me	$^-BF_4$	81
3l	Me	*p*-ClC_6H_4	*N*-Methylphenyl	Me_3O^+ $^-BF_4$	**2m**	Me	$^-BF_4$	62
3m	Me	*p*-BrC_6H_4	Morpholino	Me_3O^+ $^-BF_4$	**2n**	Me	$^-BF_4$	76
3n	Me	*p*-ClC_6H_4	Dimethylamino	Me_3O^+ $^-BF_4$	**2o**	Me	$^-BF_4$	60

Table 2. IR Spectra ($\nu_{S=O}$ of Sulfoxonium Salts)

Salts	$\nu_{S=O}/cm^{-1}$
2a	1265
2b	1266
2d	1266
2i	1264
2j	1263
$(Me)_3S^+{=}O$ ^-I[10]	1223
$Me_2(p\text{-Tol})S^+{=}O$ $^-HgI_3$[11]	1240
$Me_2(Me_2N)S^+{=}O$ $^-BF_4$[6]	1250

to compounds **2**.

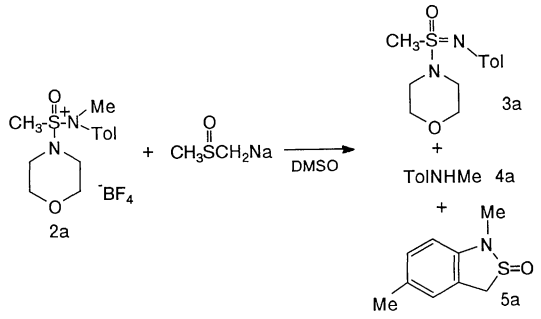
IR Spectra. Compound **2a** shows a strong absorption at 1265 cm^{-1} due to its S–O stretching. ν_{S-O} of normal sulfoxonium salts are 1220—1240 cm^{-1} and ν_{S-O} of dimethylaminosulfoxonium tetrafluoroborate (**1a**) is 1250 cm^{-1}. ν_{S-O} of compounds **2** are much higher than those of **3** and **1**. This result suggests that the double bond character of S–O bond in **2** is much higher than those of **1** and **3**, and the order is **2**>**3**>**1**.

NMR Spectra. The NMR spectra of **2** clearly show that the sulfur bears a high degree of positive charge which significantly deshields the S-methyl protons, thereby shifting the signals downfield to 3.9—4.0 ppm. The downfield shift of S-methyl protons is characteristic of sulfoxonium salts. However, S-methyl signals of **2** are not shifted to lower or higher field than those of aminosulfoxonium salts **1** and trimethylsulfoxonium iodide, which may be attributed to the opposite effects of electronegativity of nitrogen atom and electron-donating effect on N's lone pair. While S-methyl signals of **2** are shifted to lower field by the electron-withdrawing effect of N atom, they are shifted to higher field by the electron-donating effect of N's lone pair.

Reaction of Diaminosulfoxonium Salts. Previously, many sulfoxonium salts and **1** were allowed to react with bases to give the corresponding ylides. However, there is no report on the reaction of **2** with bases. Since Corey and Chaykovsky obtained dimethylsulfoxonium methylide by the reaction trimethylsulfoxonium iodide with sodium methylsulfinylmethanide (abbreviated as dimsylsodium),[11] we first tried the reaction of these sulfoxonium salts with bases. Treatment of **2a** with dimsylsodium in DMSO gave sulfonimidamide **3a**, *N*-methyl-*p*-toluidine (**4a**), and 1-methyl-1,3-dihydro-5-methyl2,1-benzisothiazole 2-oxide (**5a**) were obtained in 6, 38, and 31% yields, respectively. When salt **2b** was allowed to react with dimsylsodium in DMSO at 50 °C, *N*-ethyl-*p*-toluidine (**4b**) and sulfonimidamide **3a**, and 1-ethyl-1,3-dihydro-5-methyl-2,1-benzisothiazole

Table 3. ^1H NMR Spectra (S^+ Methyl Signals of Sulfoxonium and Sulfonium Salts)

Sulfoxonium salts $Me–\overset{\overset{O}{\|}}{\underset{\underset{R^2}{\|}}{S^+}}–R^1$	Me signal/ppm	Sulfonium salts $Me–\overset{\overset{+}{}}{\underset{\underset{R^2}{\|}}{S}}–R^1$	Me signal/ppm
R^1=Me, R^2=Me[12]	3.93 (DMSO-d_6)	R^1=Me, R^2=Me	3.02 (DMSO-d_6)
R^1=Me, $R^2=Me_2N$[6]	4.00 (DMSO-d_6)	R^1=Me, R^2=TsNH[13]	3.44 ($CDCl_3$/DMSO-d_6)
2a'	3.90 (DMSO-d_6)	R^1=Morpholino, R^2=Succinimino[3]	3.77 (CD_3CN)
R^1=Tol(Me)N, R^2=*p*-ClC_6H_4O[14]	4.50 (DMSO-d_6)	$R^1=R^2=(i\text{-Pr})_2N$[4]	3.40 ($CDCl_3$)

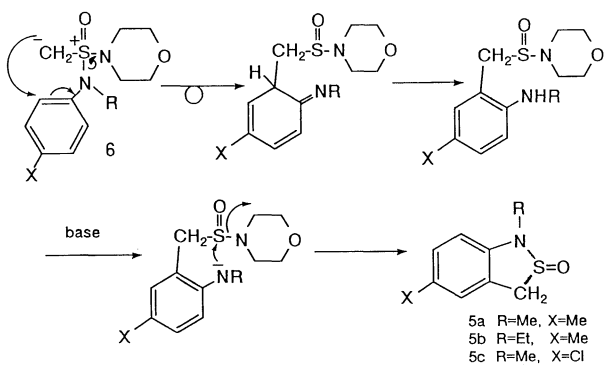


Scheme 3.

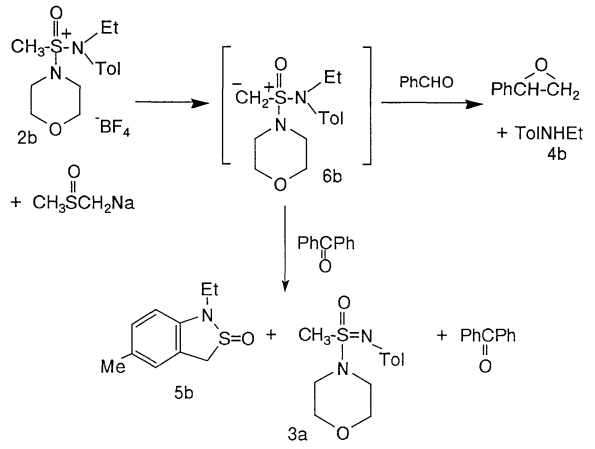
2-oxide (**5b**) were obtained in 40, 10, and 26% yields, respectively.

We then tried this reaction with potassium *t*-butoxide (*t*-BuOK) as a base. Treatment of **2a** with *t*-BuOK in *t*-butyl alcohol afforded **5a** in and 54% yields, respectively. Presumably, diaminosulfoxonium methylide (**6**) was formed first and then was decomposed to give **4**. Compounds **3** were probably formed by abstraction of β-proton from the *N*-ethyl group and/or base attack on *N*-alkyl carbons. As to the formation of **5**, the following mechamism is proposed. The intramolecular [2,3]sigmatropic rearrangement of the ylides **6** led to ortho substitution via intermediate cyclohexadienimines. Hydrogen transfer, accompanying rearomatization, and the subsequent action of a base gave **5**. As shown in Table 4, these compounds were prepared in moderate yields.

To confirm the above ylide formation, the reaction of a mixture of **2b** and dimsylsodium with benzaldehyde was carried out. Treatment of **2b** and dimsylsodium followed by the addition of benzaldehyde afforded styrene oxide and **4b** in 30% and 35% yields, respectively. This fact suggests that **2b** may produce the corresponding ylide **6b** by the reaction with dimsylsodium and **6b** may act as a nucleophilic methylene-transfer reagent. When benzophenone was used as a carbonyl compound, **5b** was obtained in 26% yield and benzophenone was recovered in 70% yield. Johnson et al. stated that the reaction of aminosulfoxonium methylides with aldehydes afforded the corresponding epoxides in 37—62% yields.[6] As to the preparation of epoxides, better yields are obtained than ours. The results of this reaction are summarized in Table 5.



Scheme 4.



Scheme 5.

These results are quite different from those of Gassman et al. and those of Johnson et al. Gassman and co-workers reported that the [2,3]sigmatropic rearrangement occurred as soon as aminosulfonium ylides derived from the treatment of *N*-phenylaminosulfonium salts with bases were formed. They applied the synthesis of indole derivatives starting from aminosulfonium salts by [2,3]sigmatropic reaction followed by reduction of lithium aluminum hydride.[5,14] Johnson and co-workers reported that the reaction of **1** with bases yielded the corresponding ylides, which reacted with aldehydes to give only the corresponding epoxides and they did not confirm the formation of products derived from attack on *N*-alkyl group.[6] However, the present observation has led to the conclusion that the reaction of ylides **6** with carbonyl compounds gives not only rearranged products but also

Table 4. Reaction of Diaminosulfoxonium Salts **2** with Bases

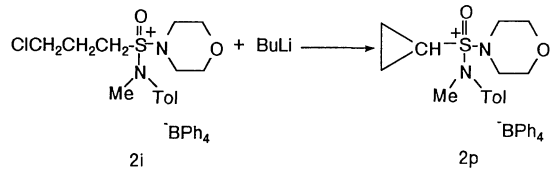
Salts **2**	Conditions			Products (%)		
	Base	Solvent	Temp/°C	**5**	**4**	**3**
2a	CH_3SOCH_2Na	DMSO	50	**5a** (31)	**4a** (38)	**3a** (6)
2a	*t*-BuOK	*t*-BuOH	60	**5a** (54)		
2b	CH_3SOCH_2Na	DMSO	50	**5b** (26)	**4b** (40)	**3a** (10)
2l	*t*-BuOK	*t*-BuOH	60	**5c** (55)		

Table 5. Reaction of Salts **2** with Bases Followed by the Addition of Aldehyde

Salts **2**	Conditions			Aldehyde	Epoxide yield/%	
	Base	Solvent	Temp/°C			
2a	BuLi	THF	0	PhCHO	PhCH(O)CH$_2$	42
2a	BuLi	THF	0	*p*-ClC$_6$H$_4$CHO	*p*-ClC$_6$H$_4$CH(O)CH$_2$	31
2a	BuLi	THF	0	*p*-NO$_2$C$_6$H$_4$CHO	*p*-NO$_2$C$_6$H$_4$CH(O)CH$_2$	55
2a	BuLi	THF	0	Heptanal	CH$_3$(CH$_2$)$_5$CH(O)CH$_2$	31
2b	CH$_3$SOCH$_2$Na	DMSO	60	PhCHO	PhCH(O)CH$_2$	30
2e	CH$_3$SOCH$_2$Na	DMSO	60	PhCHO	PhCH(O)CH$_2$	43
2e	*t*-BuOK	*t*-BuOH	50	PhCHO	PhCH(O)CH$_2$	54

methylene-transferred products.

Cyclopropylaminosulfoxonium salts and cyclopropylsulfonium salts were prepared by treatment of the corresponding 3-chloropropyl derivatives and their reactions with carbonyl compounds gave cyclobutanone derivatives, which have been widely applied to the synthesis of natural products.[15] We also tried the synthesis of cyclopropyldiaminosulfoxonium salt. Treatment of **2i** with butyllithium afforded the corresponding cyclopropyldiaminosulfoxonium tetraphenylborate (**2p**) in 60% yield.



Scheme 6.

In summary, diaminosulfoxonium salts **2** are prepared by alkylation of **3**. Their physical properties are described. Their reaction with bases gave the corresponding ylides and sulfonimidamides. These ylides react with aldehydes to afford epoxides in moderate yields. These ylides also undergo rearrangement to give dihydro-2,1-benzisothiazole derivatives.

Experimental

Melting points are uncorrected. ^{1}H NMR spectra were determined with a JEOL MH-60, a JEOL PMX-60 or a JEOL FX-90 spectrometer. IR spectra were determined with a Hitachi IR 345 spectrometer.

Preparation of *N*-(*p*-Tolyl)-3-chloro-1-propanesulfinamide. To a solution of sodium thiosulfate pentahydrate (27.3 g, 0.11 mol) in 70 ml of water was added a solution of 1-bromo-3-chloropropane (15.8 g, 0.1 mol) in 70 ml of ethanol. After refluxing for 1 h, 0.15 mol of iodine (38.1 g) was added portionwise to this solution. After stirring for 2 h, the reaction mixture was condensed to 50 ml, poured into 100 ml of water, and extracted three times with 30 ml portions of dichloromethane. The combines extracts were washed with water, dried over MgSO$_4$, and evaporated to give 3-chloropropyl disulfide (10.6 g, 0.048 mol, 96%). To a solution of this sulfide (10.6 g, 0.048 mol) and acetic acid (6.0 g, 0.1 mol) in 80 ml of dichloromethane was added dropwise a solution of sulfuryl chloride (20.3 g, 0.15 mol) in 40 ml of dichloromethane at 0 °C. After stirring for 3 h, this solution was evaporated to give crude 3-chloropropanesulfinyl chloride (15.1 g, 0.094 mol). This sulfinyl chloride in dichloromethane (50 ml) was added to a solution of *p*-toluidine (10.7 g, 0.1 mol) and triethylamine (11.1 g, 0.11 mol) in dichloromethane (100 ml) at 0 °C. After stirring for 3 h, the mixture was washed with water (30 ml) for three times, dried over MgSO$_4$, and evaporated to give pale brown crystals. This residue was recrystallized from dichloromethane-hexane to yield 19.7 g (0.085 mol, 90%) of *N*-*p*-tolyl-3-chloropropylsulfinamide; mp 148—149 °C. Anal. Calcd for C$_{10}$H$_{14}$ClNOS: C, 51.84; H, 6.05; N, 6.05%. Found: C, 52.04; H, 6.35; N, 5.85%. ^{1}H NMR (CDCl$_3$) δ=2.33 (m, 2H), 2.27 (s, 3H), 3.10 (m, 2H), 3.58 (t, 2H), 6.95 (q, 4H). Other sulfinamides were prepared in a similar manner.

Preparation of *N*-Benzyl-*p*-toluenesulfonimidomorpholide (3h). To a solution of 2.5 g (10 mmol) of *N*-benzyl-p-toluenesulfinamide in 85 ml of carbon tetrachloride cooled to 0—5 °C was added 1.8 g (10 mmol) of *N*-bromosuccinimide. The resulting solution was stirred for 30 min at 0 °C, during which time an orange color developed. To this solution was added 2.4 g (14 mmol) of morpholine with a pipette and the mixture was stirred for 3 h at 0 °C and 6 h at r. t. Washed with water and dried over MgSO$_4$, the reaction mixture was chromatographed on 30 g of silica gel by elution with 30% ether-hexane. The resulting eluant was evaporated to give a pale yellow oil of **3h**, which crystallized upon standing. Mp 89—90 °C; ^{1}H NMR (CDCl$_3$) δ=2.34 (s, 3H, TolMe), 2.56—2.92 (m, 4H, N-CH$_2$), 3.40—3.75 (m, 4H, O-CH$_2$), 4.23—4.56 (q, 2H), 7.05—7.75 (m, 9H, Ar). Anal. Calcd for C$_{18}$H$_{22}$N$_2$O$_2$S: C, 65.43; H, 6.71; N, 4.75%. Found:

C, 65.63; H, 6.60; N, 4.62%.

Other sulfonimidamides were prepared by the method as mentioned before.[9]

3a: Yield 74%; mp 109—110 °C (lit, [9] 109.5—110 °C). **3b**: Yield 45%; pale brown oil; ^{1}H NMR ($CDCl_3$) δ=1.40 (t, 3H, CH_3CH_2), 2.25 (s, 3H, TolMe), 2.80—3.25 (m, 6H, N-CH_2 and CH_3CH_2), 3.35—3.65 (m, 4H, O-CH_2), 6.80 (s, 4H, Ar). **3c**: Yield 60%; pale orange oil; ^{1}H NMR ($CDCl_3$) δ=1.14 (dd, 6H, $(CH_3)_2CH$-), 2.74 (s, 3H, Me), 3.05—3.25 (m, 4H, N-CH_2), 3.53—3.82 (O-CH_2). **3d**: Yield 42%; pale orange oil; ^{1}H NMR ($CDCl_3$) δ=1.09—1.56 (m, 9H), 2.70—3.36 (m, 6H), 3.48—3.90 (m, 5H). **3e**: Yield 57%; pale yellow oil; ^{1}H NMR ($CDCl_3$) δ=1.00—1.40 (m, 12H), 3.13—3.43 (m, 4H), 3.50—3.77 (m, 6H). **3f**: Yield 39%; mp 101—102 °C; ^{1}H NMR ($CDCl_3$) δ=1.21 (dd, 6H), 2.20 (s, 3H, TolMe), 2.80—2.96 (m, 4H, N-CH_2), 3.68—3.85 (m, 5H, O-CH_2 and $CH(CH_3)_2$), 7.08 (q, 4H, Ar). **3g**: Yield 89%; pale brown oil; ^{1}H NMR ($CDCl_3$) δ=2.30 (s, 3H, TolMe), 2.30—2.70 (m, 4H, CH_2), 3.00—3.45 (m, 6H, N-CH_2 and CH_2), 3.55—3.90 (m, 4H, O-CH_2), 7.06 (s, 4H, Ar). **3i**: Yield 75%; mp 113—114 °C (lit,[9] 113—114 °C). **3j**: Yield 50%; mp 113—114 °C (lit,[9] 113—114 °C). **3k**: Yield 60%; mp 109—110 °C (lit,[9] 109—110 °C). **3l**: Yield 45%; mp 85—86 °C (lit,[9] 85—86 °C). **3m**: Yield 75%; mp 128—129 °C; (lit,[9] 129.1—129.4 °C). **3n**; Yield 52%; mp 118—119 °C (lit,[9] 118—119 °C).

Preparation of Methylmorpholino(*N*-methyl-*p*-tolylamino)-sulfoxonium Trifluoromethanesulfonate (2a'). To a solution of **3a** (7.8 g, 30 mmol) in dichloromethane (30 ml) was added a solution of methyl trifluoromethanesulfonate (5.0 g, 30 ml) in dichloromethane (30 ml). After refluxing for 1.5 h, the solution was evaporated to give pale brown crystals, which were recrystallized from methanol-ether to give colorless crystals. (11.54 g, 27.6 mmol, 92%); mp 132—133 °C; ^{1}H NMR (CD_3SOCD_3) δ=2.20 (s, 3H, TolMe), 3.31 (s, 3H, NMe), 3.29—3.55 (m, 4H, NCH_2), 3.64—3.88 (m, 4H, OCH_2), 3.90 (s, 3H, SMe), 7.42 (q, 4H, Ar). ^{1}H NMR ($CDCl_3$) δ=2.41 (s, 3H, TolMe), 3.44 (s, 3H, NMe), 3.50—3.66 (m, 4H, NCH_2), 3.71 (s, 3H, SMe), 3.70—3.80 (m, 4H, OCH_2), 7.40 (q, 4H, Ar). ^{13}C NMR ($CDCl_3$) δ=21.25 (TolMe), 36.82 (SMe), 39.59 (NMe), 46.14 (NCH_2), 65.80 (OCH_2), 127.65 (Ar), 131.66 (Ar), 134.78 (Ar), 143.05 (Ar). IR (KBr) 2998, 2900, 2865, 1505, 1453, 1430, 1415, 1397, 1370, 1322, 1305, 1265 (S=O), 1223, 1160, 1130, 1105, 1080, 1050, 1030, 990, 950, 927, 898, 850, 820, 784, 755, 710, 698, 635 cm^{-1}. Anal. Calcd for $C_{14}H_{21}N_2O_5S_2F_3$: C, 56.47; H, 7.45; N, 10.98%. Found: C, 56.72; H, 7.23; N, 11.44%.

Compounds **2c** and **2h** were prepared in a similar manner. **2c**: Yield 50%; mp 116—117 °C; ^{1}H NMR ($CDCl_3$) δ=1.41 (t, 3H, J=7.0 Hz, CH_3CH_2-), 2.38 (s, 3H, TolMe), 3.38 (s, 3H, NMe), 3.45—3.75 (m, 10H, CH_2), 7.15—7.35 (q, 4H, Ar). Anal. Calcd for $C_{15}H_{23}N_2O_5S_2F_3$: C, 41.66; H, 5.36; N, 6.48%. Found: C, 41.24; H, 5.31; N, 6.46%. **2h**: Yield 60%; mp 109.5—110.5 °C; Anal. Calcd for $C_{16}H_{25}F_3N_2O_5S_2$: C, 43.04; H, 5.64; N, 6.27%. Found: C, 42.64; H, 5.98; N, 5.96%.

Preparation of 2b. Compound **3a** (7.8 g, 30 mmol) was refluxed with triethyloxonium tetrafluoroborate (6.4 g, 35 mmol) in dichloromethane (200 ml) for 3 h. The resulting mixture was evaporated to give crude **2b** as pale brown crystals in 80% yield. Recrystallization from ethanol gave colorless crystals (7.0 g, 19.2 mmol); mp 153—154 °C; yield 60%; ^{1}H NMR ($CDCl_3$: CD_3SOCD_3=4:1) δ=1.22 (t, 3H, J=7.5 Hz, CH_3), 2.44 (s, 3H, TolMe), 3.48—3.65 (m, 4H, NCH_2), 3.70—3.82 (m, 5H, CH_2 and OCH_2), 3.86 (m, 1H, CH_2), 7.33 (br s, 4H, Ar); IR (KBr) 3020, 2930, 2880, 1510, 1470, 1455, 1395, 1370, 1340, 1315, 1265 (S=O), 1225, 1160, 1140, 1115, 1075, 1025, 1015, 990, 950, 855, 830, 795, 780, 725, 690 cm^{-1}. Anal. Calcd for $C_{14}H_{23}BF_4N_2O_2S$: C, 45.42; H, 6.26; N, 7.57%. Found: C, 45.09; H, 6.52; N, 7.65%.

Compound **2d** was prepared in a similar manner: Yield 40%; mp 134—135 °C; IR (KBr) 2980, 2925, 2870, 1504, 1446, 1384, 1300, 1264 (S=O), 1220, 1110, 1085, 1038, 962, 825, 795, 745, 720, 680, 555, 532, 520 cm^{-1}. Elemental analysis was carried out as a tetraphenylborate. Calcd for $C_{39}H_{47}N_2O_2SB$: C, 75.49; H, 7.45; N, 4.54%. Found: C, 75.22; H, 7.57; N, 5.03%.

Preparation of 2e. To a solution of 6.2 g (30 mmol) of compound **3c** in dichloromethane (100 ml) was added 3.7 g of FSO_3Me (33 mmol). The solution was stirred for 2 h and then concentrated to 20 ml. The resulting solution was added to a solution of 10.3 g (30 mmol) of sodium tetraphenylborate in acetone (50 ml) and stirred for 30 min. A white precipitate formed (FSO_3Na) was filtered off and the filtrate was concentrated to 50 ml. Addition of ether to this solution gave colorless crystals of **2e** (6.5 g, 12 mmol); Mp 181.5—182.5 °C; yield 40%: IR (KBr) 3040, 2966, 2910, 1467, 1415, 1302, 1270 (S=O), 1255, 1215, 1141, 1100, 1074, 970, 930, 840, 743, 733, 707, 625, 600 cm^{-1} Anal. Calcd for $C_{33}H_{41}BN_2O_2S$: C, 73.32; H, 7.65; N, 5.18%. Found: C, 73.49; H, 7.32; N, 5.31%.

2f, **2g**, and **2j** were prepared in a similar manner. **2f**: Mp 134—135 °C; yield 53%: Anal. Calcd for $C_{34}H_{43}BN_2O_2S$: C, 73.63; H, 7.81; N, 5.05%. Found: C, 73.72; H, 7.55; N, 5.06%. **2g**: Yield 40%; mp 134.5—135 °C; Anal: Calcd for $C_{35}H_{45}BN_2O_2S$: C, 73.93; H, 7.98; N, 4.93%. Found: C, 74.21; H, 7.99; N, 4.64%. **2j**: Yield 52%; mp 134—135 °C; Anal. Calcd for $C_{43}H_{46}BN_2O_2S$: C, 77.71; H, 6.78; N, 4.22%. Found: C, 78.15; H, 7.24; N, 3.96%.

Preparation of 2i. To a solution of 3.2 g (10 mmol) of **3g** in 50 ml of dichloromethane was added 1.9 g (13 mmol) of trimethyloxonium tetrafluoroborate. The reaction mixture was refluxed for 6 h, and was concentrated to 20 ml. This solution was added to a solution of 3.4 g (10 mmol) of sodium tetraphenylborate in 50 ml of acetone (20 ml) and stirred for 30 min. A white precipitate formed ($NaBF_4$) was filtered off and the filtrate was concentrated to 20 ml. Addition of ether to this solution gave colorless crystals of **2i**: Mp 147—147.5 °C; yield 71%: ^{1}H NMR (CD_3COCD_3) δ= 2.25—2.55 (m, 2H, CH_2), 2.37 (s, 3H, TolMe), 3.40 (s, 3H, NMe), 3.50—4.00 (m, 12H, CH_2), 6.65—7.50 (m, 24H, Ar). IR (KBr) 3054, 3000, 2980, 2925, 2870, 1575, 1500, 1472, 1445, 1422, 1390, 1300, 1280, 1264 (S=O), 1180, 1150, 1128, 1112, 1080, 1034, 1008, 960, 895, 848, 825, 800, 752, 745, 738, 708, 612 cm^{-1}. Anal. Calcd for $C_{39}H_{44}BN_2O_2SCl$: C, 71.46; H, 6.94; N, 4.36%. Found: C, 71.52; H, 6.88; N, 4.34%.

Preparation of 2a. To a solution of **3a** (3.81 g, 15 mmol) in dichloromethane (100 ml) was added trimethyloxonium tetrafluoroborate (2.94 g, 20 mmol) in portionwise. After refluxing for 3 h, the reaction mixture was evaporated to give pale yellow crystals, which were recrystallized from methanol to afford colorless crystals of **2a** (3.96 g, 11.1 mmol): Yield 74%; mp 160—161 °C; ^{1}H NMR (CD_3NO_2) δ=2.40 (s, 3H, TolMe), 3.40 (s, 3H, NMe), 3.53 (s, 3H, SMe), 3.45—3.67 (m, 4H, NCH_2), 3.70—3.97 (m, 4H, OCH_2), 7.43 (s, 4H, Ar).

Anal. Calcd for $C_{13}H_{21}BF_4N_2O_2S$: C, 43.82; H, 5.90; N, 7.87%. Found: C, 43.84; H, 5.89; N, 7.84%.

Compounds **2l**, **2m**, **2n**, and **2o** were prepared in a similar manner. **2l**: Yield 81%; mp 154—155 °C; ^{1}H NMR ($CDCl_3$: CD_3SOCD_3=1:1) δ=3.45 (s, 3H, NMe), 3.50—3.95 (m, 8H, CH_2), 3.90 (s, 3H, SMe), 7.57 (s, 4H, Ar). IR (KBr) 3100, 3015, 2925, 2870, 1495, 1460, 1410, 1375, 1340, 1290, 1270 (S=O), 1140, 1055, 1015, 985, 960, 925, 895, 840, 785, 745, 720, 600 cm^{-1}. Anal. Calcd for $C_{12}H_{18}BClF_4N_2O_2S$: C, 38.24; H, 4.78; N, 7.42%. Found: C, 38.20; H, 4.36; N, 7.53%. **2m**: Yield 62%; mp 141—142 °C; ^{1}H NMR ($CDCl_3$: CD_3SOCD_3=1:1) δ=3.57 (s, 6H, NMe), 3.88 (s, 3H, SMe), 7.47 (br s, 5H, Ar), 7.55 (br s, 4H, Ar). Anal. Calcd for $C_{15}H_{18}BClF_4N_2OS$: C, 45.34; H, 4.53; N, 7.05%. Found: C, 45.11; H, 4.24; N, 7.18%. **2n**: Yield 76%; mp 139—140 °C; ^{1}H NMR (CD_3SOCD_3) δ=3.41 (s, 3H, NMe), 3.54—3.68 (m, 8H, CH_2), 4.02 (s, 3H, SMe), 7.66 (q, 4H, Ar). IR (KBr) 3085, 2995, 2910, 2860, 1485, 1455, 1405, 1370, 1335, 1285, 1265 (S=O), 1133, 1047, 1010, 980, 965, 950, 920, 890, 850, 835, 780, 730, 710 cm^{-1}. Anal. Calcd for $C_{12}H_{18}BBrF_4N_2O_2S$: C, 34.20; H, 4.28; N, 6.65%. Found: C, 33.86; H, 4.34; N, 6.39%. **2o**: Yield 60%; mp 101—102 °C; ^{1}H NMR (CD_3COCD_3) δ=3.85 (s, 9H, NMe), 3.95 (s, 3H, SMe), 7.14 (q, 4H, Ar). Anal. Calcd for $C_{10}H_{16}BClF_4N_2O$: C, 35.82; H, 4.78; N, 8.36%. Found: C, 35.41; H, 4.85; N, 8.44%.

Reaction of Salt 2b with Dimsylsodium in DMSO. Sodium hydride (0.28 g, 6 mmol, 50% dispersion) in 100 ml of a three-necked flask was washed with 10 ml of hexane for three times, and DMSO (10 ml) was added and warmed at 50 °C. After stirring for 30 min, salt **2b** (1.85 g, 5 mmol) in DMSO (5 ml) was added to this solution at 60 °C. After stirring for 6 h, the reaction mixture was poured into 50 ml of water. The suspension was extracted with hexane (15 ml×3) and dichloromethane (15 ml×3). The combined extracts were washed with water, dried over $MgSO_4$, and evaporated to give pale brown oil. The resulting oil was chromatographed over alumina by elution of hexane, dichloromethane–hexane (1:1), and then dichloromethane. The hexane eluant was evaporated to give *N*-ethyl-*p*-toluidine (**4b**) (0.27 g, 2 mmol, 40%). The dichloromethane–hexane eluant was evaporated to give **5b** (0.25 g, 1.3 mmol); yield 26%, mp 94.5—95.5 °C, ^{1}H NMR ($CDCl_3$) δ=1.46 (t, 3H, N-CH_2CH_3), 2.29 (s, 3H, $ArCH_3$), 3.70 (d, 1H, J=16 Hz, CH_2) 4.05 (d, 1H, J=16 Hz, CH_2), 6.53—7.05 (m, Ar). IR (KBr) 3010, 2925, 2875, 2825, 2730, 1600, 1480, 1440, 1390, 1365, 1345, 1338, 1295, 1285, 1265, 1192, 1160, 1146, 1120, 1083, 1072, 1058, 912, 895, 870, 857, 816, 770, 740, 706, 690, 652 cm^{-1}. Anal. Calcd for $C_{10}H_{13}NOS$: C, 61.55; H, 6.67; N, 7.18%. Found: C, 61.87; H, 6.94; N, 7.33%. The dichloromethane eluant was evaporatd to give **3a** (0.11 g, 0.5 mmol, 10%).

The reaction of **2a** (1.78 g, 5 mmol) was carried in a similar manner. Compound **4a** (0.23 g, 1.9 mmol, 38%), **5a** (0.28 g, 1.5 mmol, 31%), and **3a** (0.07 g, 0.3 mmol, 6%) were obtained. **5a**: Mp 82—83 °C; ^{1}H NMR ($CDCl_3$) δ=2.30 (s, 3H, $ArCH_3$), 3.25 (s, 3H, NMe), 3.82 (d, 1H, J=15 Hz, CH_2), 4.13 (d, 1H, J=15 Hz, CH_2), 6.47—7.17 (m, 3H, Ar). IR (KBr) 3046, 2970, 2960, 2915, 2820, 1605, 1486, 1450, 1438, 1382, 1320, 1290, 1275, 1180, 1138, 1105, 1068, 940, 900, 880, 824, 815, 742, 718, 695, 658 cm^{-1}. Anal. Calcd for $C_9H_{11}NOS$: C, 59.53; H, 5.68; N, 7.66%. Found: C, 59.67; H, 6.08; N, 7.77%.

Reaction of Salt 2a with Potassium *t*-Butoxide in *t*-Butyl Alcohol. The solution of **2a** (0.75 g, 2 mmol) in *t*-butyl alcohol (15 ml) was added a solution of potassium *t*-butoxide (0.22 g, 2.0 mmol) in *t*-butyl alcohol (10 ml) at 50 °C. After stirring for 5 h, 25 ml of water was added to this suspension and concentrated to 20 ml. The resulting mixture was extracted with dichloromethane (15 ml×3). The combined extracts were washed with 1 M(=mol dm^{-3}) HCl (*N*-methyl-*p*-toluidine was separated), dried over $MgSO_2$, and evaporated to give the crude **5a**, which was recrystallized from ethanol to give colorless crystals of **5a** (0.20 g, 1.1 mmol). Yield 54%. The reaction of **2l** with *t*-BuOK (0.77 g, 2 mmol) was carried out in a similar manner. 1-Methyl-1,3-dihydro-5-chloro-2,1-benzisothiazole 2-oxide (**5c**) was obtained in 55% yield (0.23 g, 1.1 mmol): Mp 90—91.5 °C; ^{1}H NMR ($CDCl_3$) δ=3.28 (s, 3H, NMe), 3.87 (d, 1H, J=16 Hz, CH_2), 4.20 (d, 1H, J=16 Hz, CH_2), 6.57—7.40 (m, 3H, Ar). Anal. Calcd for C_8H_8ClNOS: C, 47.64; H, 3.97; N, 6.95%. Found: C, 47.51; H, 3.82; N, 6.99%.

Reaction of 2a with Butyllithium Followed by the Addition of Benzaldehyde. To a solution of **2a** (1.78 g, 5 mmol) in THF (50 ml) was added a solution of butyllithium (10% w/v, 3.5 ml, 5.5 mmol) in hexane was added at 0 °C. After stirring for 1 h, benzaldehyde (0.54 g, 5 mmol) in THF (10 ml) was added to this solution at this temperature. After stirring for 6 h, the reaction mixture was warmed up to room temperature and poured into water (100 ml) and extracted with hexane (20 ml×3). The combined extracts were washed with 0.5 M of aq HCl (10 ml×2) and water (10 ml×2). The solution was dried over $MgSO_4$ and filtered. The resulting filtrate was evaporated to give pale yellow oil, which was distilled under reduced pressure (60—70 °C/5 mmHg, 1 mmHg=133.322 Pa) to give styrene oxide (0.25 g, 2.1 mmol); yield 40%. Other reaction was carried out in a similar manner. When *p*-nitrobenzaldehyde (0.76 g, 5 mmol) was used as an aldehyde, *p*-nitrostyrene oxide was obtained in 55% yield. (0.45 g, 2.75 mmol); mp 83—84 °C (lit,[17] mp 84—85 °C), *p*-Chlorostyrene oxide (0.23 g, 1.5 mmol, 31%) and 1-octene oxide (0.19 g, 1.5 mmol, 30%) were obtained in a similar manner.[6]

Reaction of 2b with Dimsylsodium Followed by the Addition of Benzaldehyde. Sodium hydride (0.28 g, 6 mmol, 50% dispersion) in 50 ml of three necked flask was washed with 10 ml of hexane for three times, and DMSO (8 ml) was added and warmed at 50 °C. After stirring for 30 min, salt **2b** (0.75 g, 2.0 mmol) in DMSO (5 ml) was added to this solution at 60 °C. After stirring for 30 min, benzaldehyde (0.53 g, 5 mmol) was added by syringe to this solution at this temperature. After stirring for 6 h, the reaction mixture was poured into 100 ml of water and extracted with ether (20 ml) for three times. The combined extracts were washed with water (10 ml×2) and dried over $MgSO_4$. The resulting mixture was filtered and evaporated to give a orange-red oil. This oil was distilled under reduced pressure to afford styrene oxide (0.18 g, 1.5 mmol, 60—70 °C/5 mmHg) and 4b (0.24 g, 1.75 mmol, 80—90 °C/5 mmHg) in 30 and 35% yields, respectively.

Reaction of 2e with Potassium *t*-Butoxide Followed by the Addition of Benzaldehyde. To a solution of **2e** (2.5 g, 4.6 mmol) in *t*-butyl alcohol (30 ml) was added a solution of potassium *t*-butoxide (0.60 g, 5.5 mmol) in *t*-butyl alcohol (10 ml) at 60 °C. After stirring for 1 h at this temperature, a solution of benzaldehyde (0.5 g, 4.6 mmol) in *t*-butyl alcohol (8 ml) was added to this solution. After stirring for 2 h at this

temperature, the reaction mixture was condensed to 10 ml, poured into water (100 ml). The resulting mixture was extracted with hexane (20 ml×3). The combined extracts were washed with water (10 ml×2), dried over $MgSO_4$, and evaporated to give 0.44 g of crude styrene oxide (3.7 mmol, 75%). This oil was distilled under reduced pressure to afford 3.0 g of pure styrene oxide (bp 66—68 °C/7 mmHg); 2.5 mmol, yield 54%.

Reaction of 2b with Dimsylsodium Followed by the Addition of Benzophenone. Sodium hydride (0.28 g, 6 mmol, 50% dispersion) in 50 ml of three-necked flask was washed with 10 ml of hexane for three times, and DMSO (8 ml) was added and warmed at 50 °C. After stirring for 30 min, salt **2b** (1.85 g, 5.0 mmol) in DMSO (8 ml) was added to this solution at 60 °C. After stirring for 30 min, a solution of benzophenone (0.91 g, 5 mmol) in DMSO (5 ml) was added to this solution at this temperature. After stirring for 6 h, the reaction mixture was poured into 100 ml of water and extracted ether (20 ml) for three times. The combined extracts were washed with water (10 ml×2) and dried over $MgSO_4$. The mixture was filtered and evaporated to give a reddish brown oil. The resulting oil was chromatographed over alumina by elution with dichloromethane–hexane to give benzophenone (0.64 g, 3.5 mmol), **4b** (0.27 g, 2 mmol), sulfonimidamide **3b** (0.25 g, 0.5 mmol), and **5b** (0.25 g, 1.3 mmol) in 70, 40, 10, and 26% yields, respectively.

Reaction of 2i with Butyllithium. To a solution of compound **2i** (3.25 g, 5 mmol) in 50 ml of THF was added 5 mmol of BuLi (10% w/v in hexane) in 3.3 ml of hexane. After the stirring for 2 h at r.t, 100 ml of water was added to this solution. The resulting mixture was extracted with dichloromethane and then dried over $MgSO_4$. The combined extracts were evaporated to give crude **2p** (2.58 g, 4.2 mmol) in 84% yield. Recrystallization from methanol gave colorless crystals (1.84 g, 3 mmol). Mp 134—135 °C; yield 60%: ^1H NMR (CD_3SOCD_3) δ=1.08—1.52 (m, 4H, CH_2CH_2), 2.36 (s, 3H, TolMe), 3.41 (s, 3H, NMe), 3.50—3.65 (m, 5H, CH and NCH_2), 3.65—3.80 (m, 4H, OCH_2), 6.70—7.25 (m, 20 H, Ar), 7.40 (br dd, 4H, Tol). IR (KBr) 3050, 2870, 1590, 1515, 1485, 1460, 1430, 1405, 1345, 1310, 1275, 1200, 1120, 1090, 1075, 1040, 1025, 970, 915, 880, 855, 830, 740, 720, 615 cm^{-1}. Anal. Calcd for $C_{39}H_{43}BN_2O_2S$: C, 75.74; H, 7.19; N, 4.65%. Found: C, 76.22; H, 7.41; N, 4.58%.

References

1) S. Oae, T. Numata, and T. Yoshimura, "The Chemistry of Sulphonium Group," ed by C. J. M. Stirling, John-Wiley & Sons, Chichister-New York-Brisbane-Toronto (1981), pp. 571—672.

2) H. Minato, K. Okuma, and M. Kobayahi, *J. Org. Chem.*, **43**, 652 (1978).

3) E. Vilsmeier, R. Schneider, and E. Hader, *Liebigs Ann. Chem.*, **1980**, 1046.

4) H-U. Wagner and A. Judelbauer, *Angew. Chem., Int. Ed. Engl.*, **17**, 460 (1978).

5) P. G. Gassman and C. D. Gruetzmacher, *J. Am. Chem. Soc.*, **96**, 5487 (1974).

6) C. R. Johnson and P. E. Rogers, *J. Org. Chem.*, **38**, 1793 (1973). C. R. Johnson, J. J. Rigau, M. Haake, D. McCants, Jr., J. E. Keiser, and A. Gertsema, *Tetrahedorn Lett.*, **1968**, 3719. C. R. Johnson, E. R. Janiga, and M. Haake, *J. Am. Chem. Soc.*, **90**, 3890 (1968).

7) In preceding communication; K. Okuma, N. Higuchi, H. Ohta, and M. Kobayashi, *Chem. Lett.*, **1980**, 1503.

8) E. U. Johnson, C. C. Bacon, and C. R. Johnson, *J. Am. Chem. Soc.*, **93**, 5306 (1971). R. E. Booms and D. J. Cram, *J. Am. Chem. Soc.*, **94**, 5438 (1972).

9) K. Okuma, T. Koike, and H. Ohta, *J. Org. Chem.*, **53**, 4190 (1988).

10) "The Aldrich Library of Infrared Spectra," p. 469.

11) M. Kobayashi, K. Kamiyama, H. Minato, Y. Oishi, T. Takeda, and Y. Hattori, *Bull. Chem. Soc. Jpn.*, **45**, 3703 (1972).

12) "The Aldrich Library of NMR Spectra," Vol. X. 2b.

13) A. D. Dawson and D. Swern, *J. Org. Chem.*, **42**, 592 (1977).

14) K. Okuma, Y. Tanaka, and H. Ohta, *J. Am. Chem. Soc.*, **103**, 5976 (1981).

15) P. G. Gassman, D. P. Gilbert, and T. J. van Bergen, *J. Chem. Soc., Chem. Commun.*, **1974**, 201.

16) B. M. Trost and M. J. Bogdanowicz, *J. Am. Chem. Soc.*, **93**, 3773 (1971). C. R. Johnson, C. F. Katekar, R. F. Huxol, and E. R. Janiga, *ibid.*, **93**, 3771 (1971). C. R. Johnson and E. R. Janiga, *ibid.*, **95**, 7692 (1973).

17) E. J. Corey and M. Chaykovsky, *J. Am. Chem. Soc.*, **84**, 867 (1962). *ibid.*, **87**, 1353 (1965).

18) F. Arndt, B. Eistert, and W. Ender, *Ber.*, **62**, 44 (1929).