Syntheses of Some Alkoxy-, Dialkoxy-, and Alkoxyamino-sulfonium Ions and Their *O*-Methylene and *N*-Methylene PMR Chemical Shifts

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Alkylation of sulfenates proved to be a good method for synthesis of alkoxysulfonium ion not obtainable by alkylation of sulfoxides. Dialkoxy- and alkoxyamino-sulfonium ions were prepared by alkylation of sulfinates and sulfinamides. Ethoxy- and methoxymorpholinophenylsulfonium tetraphenylborates were obtained as high-melting crystals, which almost quantitatively alkylated amines at room temperature. PMR spectra of $RR'\overset{\oplus}{S}$–OCH_AH_BR'' and $RR'\overset{\oplus}{S}$–$N(R'')CH_AH_BR'''$ were determined, and the relationship between $\delta_A-\delta_B$ and (R,R') were examined.

Sulfonium ions containing hetero atom substituents are interesting compounds, and some of them have been investigated in our laboratoris.[1-3] The two hydrogens of *O*-methylene and *N*-methylene groups in alkoxy- and amino-sulfonium ions are expected to be magnetically non-equivalent if the other two substituents on the sulfonium sulfur atom are different. It seems to be of interest to determine the PMR spectra of $RR'\overset{\oplus}{S}$–OCH_AH_BR'' and $RR'\overset{\oplus}{S}$–$N(R'')CH_AH_BR'''$ and to study the relationship between $\delta_A-\delta_B$ and (R,R'). Some new alkoxy-, dialkoxy-, and alkoxyamino-sulfonium ions were synthesized, and their PMR spectra were examined.

Results and Discussion

Alkoxysulfonium ions were prepared by two different methods. The first method used was alkylation of sulfoxides.[4,5] Ethoxysulfonium trifluoromethanesulfonates (triflates) **1a—c** were prepared by ethylation of the corresponding sulfoxides with ethyl triflate in CD_3NO_2. Alkoxysulfonium salts have been studied by various groups, but few papers described ethoxysulfonium salts.[6-8] In these papers, PMR data were not shown.

$$\underset{\underset{\downarrow}{O}}{R\text{–}S\text{–}R'} + CF_3SO_3Et \longrightarrow \underset{\underset{O\text{–}Et}{|}}{R\text{–}\overset{\oplus}{S}\text{–}R'}\ CF_3SO_3^{\ominus}$$

1 {**a**: R=Me, R'=*p*-Tol; **b**: R=$PhCH_2$, R'=Ph; **c**: R=Et, R'=Bu

Since neopentylation of sulfoxides is not possible, neopentyloxysulfonium ions cannot be prepared from sulfoxides. Although alkylation of sulfenates has not been described in the literature, it is expected to be a possible method for producing alkoxysulfonium salts. Hogg and Robertson[9] treated sodium arenesulfenate with a 10-fold excess of FSO_3Me in 30% aq. dioxane, but a methoxysulfonium ion was not formed. When an equimolar mixture of neopentyl benzenesulfenate and methyl triflate in nitromethane was allowed to stand for 10 min at 34 °C, its PMR spectrum showed that the sulfenate was quantitatively converted to methylphenylneopentyloxysulfonium triflate **1d**. Thus, alkylation of a sulfinate appears to be a good method for producing an alkoxysulfonium ion.

$$Ph\text{–}S\text{–}O\text{–}CH_2CMe_3 + CF_3SO_3Me \longrightarrow Ph\text{–}\overset{\oplus}{S}(Me)\text{–}OCH_2CMe_3\ CF_3SO_3^{\ominus}$$

1d

Compared with **1a—c**, the neopentyloxysulfonium salt **1d** is less stable. When a nitromethane solution of **1d** was allowed to stand at 34 °C, about 10% decomposed in 2 days. When a nitromethane solution of **1d** was evaporated and the residue was treated with an acetone solution of $NaBPh_4$, the corresponding anion-exchanged salt was not obtained, and decomposition products were found. When a CD_3NO_2 solution of **1d** was heated at 75 °C for 18 h, it completely decomposed, and neopentyl alcohol was one of the main product. Apparently a *neopentyloxy*arylalkylsulfonium ion is unstable. Among dialkoxyarylsulfonium ions (**3**) (discussed later), methoxy*neopentyloxy*-*p*-tolylsulfonium triflate (**3a**) and methoxy*benzyloxy*-*p*-tolylsulfonium triflate (**3b**) are found to decompose in solution whereas dimethoxy-*p*-tolylsulfonium triflate (**3c**) is stable in solution.

Dialkoxysulfonium ions were synthesized by alkylation of sulfinates.[1] From alkyl ethanesulfinates and alkyl triflate dialkoxyethylsulfonium triflates **2a—c** were prepared.

$$\underset{\underset{\downarrow}{O}}{Et\text{–}S\text{–}OR} + CF_3SO_3R' \xrightarrow{CD_3NO_2} \underset{\underset{O\text{–}R'}{|}}{Et\text{–}\overset{\oplus}{S}\text{–}OR}\ CF_3SO_3^{\ominus}$$

2 {**a**: R=CH_2CMe_3, R'=Et; **b**: R=CH_2CMe_3, R'=Me; **c**: R=Et, R'=Me

PMR spectra showed that sulfinates were completely converted to dialkoxysulfonium ions.

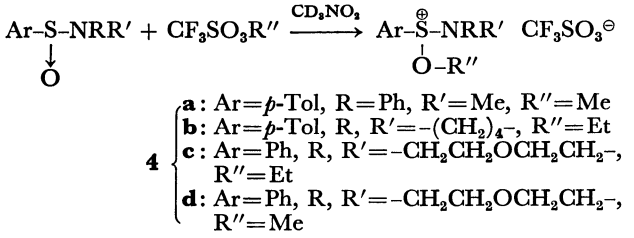
When benzyl and neopentyl *p*-toluenesulfinates were treated with methyl triflate, the solution became viscous suggesting the occurrence of polymerization, and the corresponding dialkoxysulfonium ions **3a** and **3b** were not obtained. In the case of methyl *p*-toluenesulfinate, the corresponding dimethoxy-*p*-tolylsulfonium salt **3c** was successfully prepared in solution.[1] It is worth

$$\underset{\underset{\downarrow}{O}}{p\text{-Tol–S–OR}} + CF_3SO_3Me \xrightarrow{CD_3NO_2} \underset{\underset{O\text{–}Me}{|}}{p\text{-Tol–}\overset{\oplus}{S}\text{–OR}}\ CF_3SO_3^{\ominus}$$

3 {**a**: R=CH_2Ph; **b**: R=CH_2Me_3; **c**: R=Me

noting that alkoxyneopentyloxyethylsulfonium ions are stable in solution, whereas methoxyneopentyloxy-*p*-tolylsulfonium ion is unstable in solution.

Alkoxyaminosulfonium salts were prepared by alkylation of sulfinamides.[2]

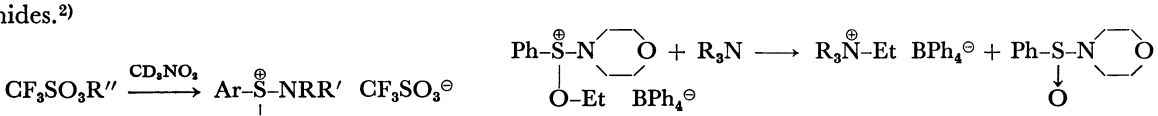


4 { **a**: Ar=*p*-Tol, R=Ph, R′=Me, R″=Me; **b**: Ar=*p*-Tol, R, R′=-$(CH_2)_4$-, R″=Et; **c**: Ar=Ph, R, R′=-$CH_2CH_2OCH_2CH_2$-, R″=Et; **d**: Ar=Ph, R, R′=-$CH_2CH_2OCH_2CH_2$-, R″=Me

When *N*-phenyl-*N*-methyl-*p*-tolylsulfinamide was treated with methyl triflate in CD_3NO_2 at −20 °C, decomposition took place and the corresponding sulfonium salt **4a** was not found. This apparent instability of a methoxy-*N*-phenylaminosulfonium ion may be related with the low electron density on the nitrogen atom due to the resonance with the phenyl ring. Methoxypyrrolidino-*p*-tolylsulfonium triflate (**4b**) was stable so long as it was kept in solution but decomposed upon evaporation of the solvent. This decomposition may be related with the greater nucleophilicity of the dialkylamino nitrogen atom which attack the alkoxy alkyl group of **4b** itself (pyrrolidinium salts were found to be products of decomposition). The pK_a of morpholine (8.36)[10] is between that of *N*-methylaniline (4.85)[10] and that of pyrrolidine (11.27),[10] and it appeared that alkoxymorpholinosulfonium salts may be stable enough for isolation as solids, since the electron-density on the morpholine nitrogen is not too great nor too small.

When *N*-benzenesulfinylmorpholine was mixed with an equimolar amount of CF_3SO_3R'' (R″=Et or Me) in CD_3NO_2 at room temperature, **4c** or **4d** was formed, which was isolated as stable solids and converted into high-melting crystals by exchanging its anion with $NaBPh_4$.

The reaction of ethoxymorpholinophenylsulfonium tetraphenylborate with pyridine or triethylamine gave ethylated amine (91—95%) and the original sulfinamide (94—98%).



This is in quite a contrast with the reaction of methyl-*p*-tolylmethoxysulfonium ion with nucleophiles which yielded a mixture of various products.[5] If optically-active **4** is prepared (either by resolution of diastereomers with optically-active anions or by alkylation of optically-active sulfinamides derivable from optically-active sulfinates,[11] it can be used as asymmetric alkylating agents, and optically-active sulfinamides can be recovered which can be used again by alkylating it with alkyl triflate. Among various sulfonium salts, **4** is the best alkylating agent.

The PMR spectra of these sulfonium ions were determined, and their *O*-methylene and *N*-methylene chemical shifts are compared in Table 1. Magnetic non-equivalence of methylene protons in sulfinates (RSO_2CH_2R')[12] and sulfinamides ($RSONR'CH_2R''$)[13,14] has been described in the literature, but that in alkoxy-, dialkoxy-, and alkoxyamino-sulfonium ions is described here for the first time.

The relationship between $\delta_A-\delta_B$ and R,R′ in $RR'\overset{\oplus}{S}-OCH_AH_BR''$ and $RR'\overset{\oplus}{S}-N(R'')CH_AH_BR''$ are summarized in Table 2. The pairs of R and R′ always giving rise to different δ_A and δ_B are 1) aryl and alkyl, 2) aryl and alkoxy, and 3) aryl and $-O^{\ominus}$, and those giving rise to equal δ_A and δ_B are 1) aryl and alkylamino, and 2) aryl and benzyl.

The non-equivalence of the methylene protons shown in Table 1 is due to the difference in the magnetic environments caused by the chiral sulfur atom.[15] Although N–$\overset{\oplus}{S}$ and O–$\overset{\oplus}{S}$ bonds may have some partial

Table 1. Comparison of O-CH_2 and N-CH_2 ^{1}H-NMR absorptions in $RR''\overset{\oplus}{S}-OCH_2R''$ and $RR'\overset{\oplus}{S}-N(R'')CH_2R'''$

	Ph-S-CH_2Ph	Bu-S-Et	p-Tol-S-N	Ph-S-N O	Et-S-O	Et-S-OMe	Et-S-OCH_2CMe_3	Tol-S-Me	Tol-S-O
	CH_AH_B Me	CH_AH_B Me	CH_AH_B Me	CH_AH_B Me	CH_AH_B Me	CH_AH_B Me	CH_AH_B Me	CH_AH_B Me	CH_AH_B Me
$(\delta_A+\delta_B)/2$ (ppm)	4.33 (q)	4.36 (q)	4.57 (q)	4.55 (q)	3.94 (q)	4.66 (q)	4.68 (q)	4.16-4.48 (m)	3.36-4.32 (m)
$\delta_A-\delta_B$ (ppm)	0	0	0	0	≒0	≒0	≒0	>0	>0
J_{AB} (Hz)	0	0	0	0	≒0	≒0	≒0	>0	>0
Solvent	CD_3NO_2	CD_3NO_2	CD_3NO_2	$(CD_3)_2CO$	CD_3NO_2	CD_3NO_2	CD_3NO_2	CD_3NO_2	neat

Et-S-O	Et-S-OEt	Et-S-OMe	Ph-S-Me	Tol-S-O	Ph-S-OEt	Ph-S-O	Tol-S-OEt	Tol-S-O	Me-S-O
CH_AH_B CMe_3	CH_AH_B CMe_3	CH_AH_B CMe_3	CH_AH_B CMe_3	CH_AH_B CMe_3	N CH_AH_B O	N CH_AH_B O	N CH_AH_B	N CH_AH_B	N-Et CH_AH_B Me
3.90 (q)	4.26 (q)	4.29 (q)	3.92 (q)	3.36 (q)	3.20-3.50 (m)	2.16-3.32 (m)	3.10-3.90 (m)	2.57-3.41 (m)	(m)[a]
0.067	0.067	0.065	0.23	0.40	>0	>0	>0	>0	0.35[a]
9.4	8.8	9.0	9.1	9.1	>0	>0	>0	>0	10[a]
CCl_4	CD_3NO_2	CD_3NO_2	CD_3NO_2	CD_3NO_2	$(CD_3)_2CO$	$(CD_3)_2CO$	CD_3NO_2	CD_3NO_2	$CDCl_3$

(a) The data by R. M. Moriarty, *J. Org. Chem.* **30**, 600 (1965): Chemical shifts are not described.

Table 2. Relationship between $\delta_A-\delta_B$ and (R,R') in $RR'\overset{\oplus}{S}-OCH_AH_BR''$ and $RR'\overset{\oplus}{S}-N(R'')CH_AH_BR'''$

	R, R'		
	in $RR'\overset{\oplus}{S}-OCH_AH_B-Me$	in $RR'\overset{\oplus}{S}-OCH_AH_BCMe_3$	in $RR'\overset{\oplus}{S}-N(R'')CH_AH_BR'''$
$\delta_A-\delta_B=0$	(Ph, CH_2Ph) (Bu, Et) (p-MeC_6H_4,) (Ph,)		
$\delta_A-\delta_B\fallingdotseq0$	(Et, OMe) (Et, OCH_2CMe_3) (Et, $-O^{\ominus}$)	(Et, $-O^{\ominus}$) (Et, OEt) (Et, OMe)	
$\delta_A-\delta_B>0$	(p-MeC_6H_4, Me) (p-MeC_6H_4, $-O^{\ominus}$)	(Ph, Me) (p-MeC_6H_4, $-O^{\ominus}$)	(Ph, $-O^{\ominus}$) (Ph, OEt) (p-MeC_6H_4, OEt) (p-MeC_6H_4, $-O^{\ominus}$) (Me, $-O^{\ominus}$)

double bond character, the rotations around the N–$\overset{\oplus}{S}$ and O–$\overset{\oplus}{S}$ bonds are not restricted, since 2p-3d π overlaps in sulfur compounds are not much affected by S–N rotation.[13,14] Even under conditions of rapid rotation or in the absence of unequal populations of several conformers, methylene hydrogens α or β to a chiral sulfur atom can be non-equivalent.[12–15] Interpretation of the data shown in Tables 1 and 2 is not easy; accumulation of more data is necessary before one can reasonably explain these phenomena.

Experimental

PMR spectra were determined with a Hitachi Perkin-Elmer NMR Spectrometer R-20 (60 MHz) at 34 °C with CH_2Cl_2 (δ 5.30) as an internal standard.[16] The concentrations were about 10 wt %.

Neopentyl benzenesulfenate[17] was prepared by the reaction among benzenesulfenyl chloride (10.4 mmol), neopentyl alcohol (10.4 mmol), and pyridine (10.4 mmol) at −5 °C. Yield, 1.6 g (80%), bp, 80 °C/2 mmHg.

Alkyl triflates were prepared according to the methods described in the literature. CF_3SO_3Me, bp 100 °C (lit,[18] 99 °C). CF_3SO_3Et, bp 119 °C (lit,[19] 115 °C).

Sulfinates (or sulfinamides) were prepared either by the reaction between sulfinyl chlorides and alcohols (or amines) or by the condensation between sulfinic acids and alcohols (or amines) with *N,N'*-dicyclohexylcarbodiimide.[21] *N*-*p*-Toluenesulfinylpyrrolidine was prepared from pyrrolidine and *p*-toluenesulfinyl chloride in ether at 0°, and recrystallized from hexane; yield, 31%; mp 52—53 °C; NMR (CD_3NO_2) δ= 1.55—1.86 (m, 4, N-$CH_2C\underline{H}_2$–), 2.27 (s, 3, $C\underline{H}_3$–C_6H_4), 2.57—3.41 (m, 4, N–$C\underline{H}_2$), 7.10—7.53 (q, 4, –$C_6\underline{H}_4$–); Found: C, 62.77; H, 7.12; N, 6.36%. Calcd for $C_{11}H_{15}ONS$: C, 63.14; H, 7.23; N, 6.69%.

Ethoxysulfonium Triflates ***1a—c.*** They were prepared by mixing equimolar amounts of the corresponding sulfoxides and ethyl triflate in CD_3NO_2. Since they are oils which cannot be distilled, their elemental analyses were not carried out. *p*-TolMe$\overset{\oplus}{S}$–OEt $\overset{\ominus}{BF_4}$ was described in the literature,[6–8] but its PMR data were not shown. PMR: **1a**, δ=1.27 (t, 3, $C\underline{H}_3CH_2$–), 2.39 (s, 3, $C\underline{H}_3C_6H_4$–), 3.60 (s, 3, $C\underline{H}_3$–S), 4.16—4.48 (m, 2, CH_2), 7.40—8.10 (q, 4, –$C_6\underline{H}_4$–); **1b**, δ=1.22 (t, 3, $C\underline{H}_3CH_2$), 4.33 (q, 2, $CH_3C\underline{H}_2$), 5.05 (q, 2, S–CH_AH_B–Ph, $\Delta\delta_{AB}$=0.23 ppm, J_{AB}=12.8 Hz), 6.95—8.00 (m, 10, Ph); **1c**, δ=1.31 (t, 3, $C\underline{H}_3CH_2$–S), 1.39 (t, 3, $C\underline{H}_3CH_2$–O), 0.60—2.20 (m, 7, $C\underline{H}_3C\underline{H}_2C\underline{H}_2$–), 3.26—3.71 (m, 4, $C\underline{H}_2$–S–$C\underline{H}_2$), 4.36 (q, 3, CH_3–S), 3.92 (q, O–CH_AH_B–, J_{AB}=9.1Hz), 7.64—8.20 (m, 5, C_6H_5–).

Neopentyloxymethylphenylsulfonium Triflate ***1d.*** When an equimolar mixture of neopentyl benzenesulfenate and methyl triflate in nitromethane was allowed to stand for 10 min at 34 °C, its PMR spectrum showed that the sulfenate was converted to **1d**. After the solvent was evaporated, the residue was dissolved in a small amount of acetone, and an equimolar amount of $NaBPh_4$ was added. However, the corresponding anion-exchanged salt was not obtained, and only decomposition products were found.

When a CD_3NO_2 solution of **1d** was heated at 75 °C for 18 h, it completely decomposed. Its PMR spectrum showed absorptions at δ=0.85 (s, 9.0H, $(CH_3)_3C$–), 2.35 (s, 0.54H, $PhSC\underline{H}_3$), 2.44 (s, 0.64H, ?), 3.19 (s, 1.29H, ?), 3.63 (s, 1.94H, $Me_3CC\underline{H}_2\overset{\oplus}{O}H_2$), and 7.16—7.83 (m, Ar–H). When an equimolar amount of pentadeuteriopyridine was added, the absorptions of neopentyl alcohol was shifted to δ=0.75 ($(CH_3)_3C$–) and δ=3.12 (CH_2).

PMR of **1d** (CD_3NO_2), δ=0.80 (s, 9, $(CH_3)_3C$–), 3.57 (s, 3, CH_3–S), 4.92 (q, CH_AH_B–CMe_3), 7.64—8.20 (m, 5, Ph).

Alkoxyneopentyloxyethylsulfonium Triflates ***2a,b.*** They were prepared by the reaction of an equimolar mixture of neopentyl ethanesulfinate and ethyl or methyl triflate in CD_3NO_2 at 34 °C for 1 h. They were stable only in solution, and decomposed when the solvent was evaporated. PMR: **2a**, δ=0.92 (s, 9, $(CH_3)_3C$–), 1.41 (t, 3, $C\underline{H}_3CH_2S$–), 1.43 (t, 3, $C\underline{H}_3CH_2O$–), 3.66 (q, 2, $CH_3C\underline{H}_2S$–), 4.26 (q, 2, –OCH_AH_B–CMe_3, J_{AB}=8.8 Hz), 4.68 (q, 2, $OC\underline{H}_2CH_3$); **2b**, δ=0.90 (s, 9, $(CH_3)_3C$–), 1.37 (t, 3, $C\underline{H}_3CH_2S$–), 3.68 (q, 2, $CH_3C\underline{H}_2S$–), 4.29 (s, 3, CH_3O–), 4.29 (q, 2, OCH_AH_B, J=9.0 Hz); **2c**, δ=1.35 (t, 3, $C\underline{H}_3CH_2S$–), 1.42 (t, 3, $C\underline{H}_3CH_2O$–), 3.63 (q, 2, $CH_3C\underline{H}_2S$–), 4.25 (s, 3, CH_3O–), 4.66 (q, 2, $CH_3C\underline{H}_2O$–).

Alkoxyaminosulfonium Triflates ***4b—d.*** They were prepared by the reaction of an equimolar mixture of an arenesulfinamide and alkyl triflate in CD_3NO_2 at 34 °C for 1 h. Upon evaporation of the solvent, **4b** decomposed, whereas **4c** and **4d** could be isolated as oils. PMR(CD_3NO_2) of **4b**; δ= 1.49 (t, 3, $C\underline{H}_3CH_2O$–), 1.85—2.14 (m, 4, $-CH_2CH_2N$), 2.39

(s, 3, $C\underline{H}_3C_6H_4$–), 3.10—3.90 (m, 4, –$C\underline{H}_2N$), 4.57 (q, 2, –OCH_2–), 7.32—7.80 (q, 4, –C_6H_4–).

Ethoxymorpholinophenylsulfonium Tetraphenylborate. After a mixture of *N*-benzenesulfinylmorpholine (7.6 mmol), ethyl triflate (7.6 mmol) and nitromethane (20 ml) was allowed to stand overnight at room temperature, the solvent was evaporated. The residue was dissolved in a small amount of acetone, and sodium tetraphenylborate (7.6 mmol) was added. Ether was added till the solution became turbid, and in 1 h white crystals were formed; yield, 4.2 g (99%), mp 143 °C. Found: C, 77.57; H, 6.96; N, 2.53%. Calcd for $C_{36}H_{38}O_2$-NB: C, 77.27; H, 6.84; N, 2.50%. PMR (CD_3COCD_3), δ=1.49 (t, 3, CH_3), 3.20—3.50 (m, 4, –CH_2N–), 3.50—3.80 (m, 4, –$CH_2C\underline{H}_2O$–), 4.55 (q, 2, $CH_3C\underline{H}_2O$–), 6.60—8.00 (m, 5, Ph–).

Methoxymorpholinophenylsulfonium tetraphenylborate was prepared in a similar manner. Yield, 94%; mp 139 °C. Found: C, 78.68; H, 7.06; N, 2.71%. Calcd for $C_{35}H_{36}O_2$-NB: C, 77.06; H, 6.65; N, 2.57%. PMR(CD_3COCD_3), δ=3.38—3.71 (m, 4, –CH_2N), 3.71—4.05 (m, 4, –CH_2O), 4.37 (s, 3, CH_3O–), 6.75—8.12 (m, 5, Ph).

Reaction between Ethoxymorpholinophenylsulfonium Tetraphenylborate and Amines. An equimolar mixture of the reactants in CD_3COCD_3 was allowed to stand for 2.5 h at 34 °C, and its PMR spectrum showed the completion of the reaction. Ether was added, and the precipitates formed were filtered. The filtrate was concentrated, and the sulfinamide obtained was dissolved in CCl_4 and its amount was determined by PMR with tetrachloroethane as the internal standard. From triethylamine, $Et_4\overset{\oplus}{N}B\overset{\ominus}{Ph}_4$ (94.8%) and *N*-benzenesulfinylmorpholine (94.3%) were obtained. From pyridine, $C_5H_5\overset{\oplus}{N}$–Et $B\overset{\ominus}{Ph}_4$ (91.0%) and *N*-benzenesulfinylmorpholine (98.2%) were obtained.

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