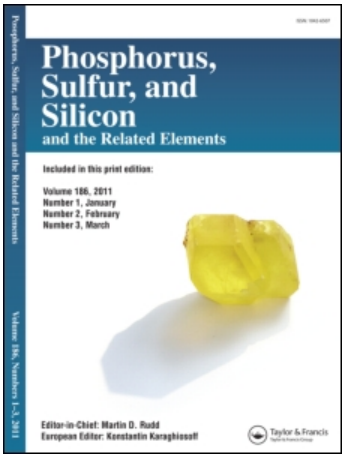

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THERMAL RACEMIZATION OF OPTICALLY ACTIVE AMINOSULFONIUM SALTS

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Optically active *o*-methoxyphenylphenylaminosulfonium salts were synthesized from optically active *o*-methoxyphenylphenyl-*N*-*p*-tosylsulfilimine. The rates of racemization of the salts have been measured and found to follow first-order kinetics. The racemization proceeds through pyramidal inversion on the sulfur atom. The rate and the activation parameters determined for the racemization of *o*-methoxyphenylphenyl-aminosulfonium perchlorate (**1a**) are 1.58×10^{-4} (sec^{-1}), $\Delta H^{\ddagger} = 27$ Kcal · mol^{-1}, and $\Delta S^{\ddagger} = 1$ eu (75°C), respectively. These data show that the aminosulfonium salt racemizes 6–10 times faster than the corresponding sulfilimine.

There have been a number of studies on the thermal racemization of optically active tricoordinate sulfur compounds.[1] However, many of the sulfur compounds used have different substituents, and the measurements of the rates of the racemizations were often carried out under different conditions. Hence, it is difficult to compare the rates of the racemizations of different species on the same basis. A rough estimation can nevertheless be made of the relative rates of the thermal racemization through the pyramidal inversion of sulfur compounds bearing similar substituents, namely, sulfoxide:[2] sulfilimine:[3] sulfonium salt:[4] sulfonium ylide[4d,5] = 5×10^{-8}: 1.0: 3×10^{3}: 3×10^{5}, respectively. One remaining class of tricoordinate sulfur derivative for which the thermal racemization has not been compared is the onium salts which may or may not undergo racemization faster than ylide type compounds. Darwish and his co-workers found that the sulfonium ylide racemized faster than the corresponding sulfonium salt[5] but the aminosulfonium salt was shown to be racemized thermally faster than the corresponding sulfilimine.[3a,b] We have investigated the thermal racemization of sulfilimine[3c,d] and shown that the racemization proceeds unimolecularly through pyramidal inversion. We now have prepared optically active *o*-methoxyphenylphenylaminosulfonium salts, measured their thermal racemization and compared the rates with those of the previous data.[3c,d]

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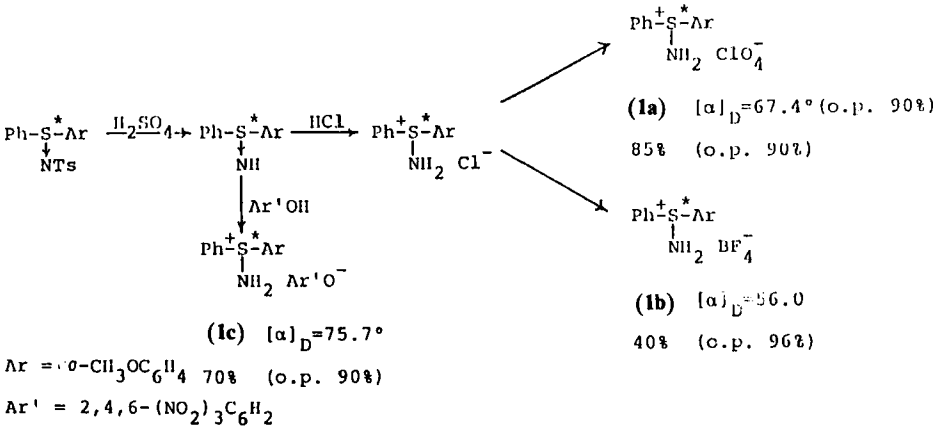
RESULTS AND DISCUSSION

Optically active aminosulfonium salts (**1a–c**) were synthesized from the corresponding optically active sulfilimines as shown in Scheme 1. The racemization was followed with a polarimeter and the rates were found to be nicely correlated with the first-order kinetic equation. The first-order rate constants of (**1a–c**) thus obtained in ethanol and ethyl methyl ketone and summarized in Table I.

The activation parameters obtained from the Arrhenius plots for the racemization of (**1a**) are summarized in Table II.

As shown in Table I, changes of the concentration of (**1a**) and the counteranion had no influence on the rates. Furthermore, change of solvent from aprotic (ethyl methyl ketone) to protic (ethanol) also showed no significant influence on the activation parameters. After heating the optically active sulfonium salts until they racemized completely, either in ethanol or in ethyl methyl ketone, the racemic sulfonium salts were found to be recovered nearly quantitatively.



SCHEME 1 Syntheses of optically active aminosulfonium salts (**1a–c**)

TABLE I

First-order rate constants for the racemization of aminosulfonium salt

	X	Conc/M^{-1}	Temp/°C	$10^4 k/sec^{-1}$	Solvent
1a	ClO_4	0.0164	58.7	0.24 ± 0.07	EtCOMe
1a	ClO_4	0.0164	69.9	1.03 ± 0.02	EtCOMe
1a	ClO_4	0.0164	80.0	2.92 ± 0.32	EtCOMe
1a	ClO_4	0.1064	65.9	0.59 ± 0.01	EtOH
1a	ClO_4	0.0164	74.4	1.58 ± 0.04	EtOH
1a	ClO_4	0.0164	84.9	4.92 ± 0.07	EtOH
1a	ClO_4	0.0255	74.4	1.57 ± 0.05	EtOH
1b	BF_4	0.0164	65.9	0.56 ± 0.01	EtOH
1c	picrate	0.0164	65.9	0.56 ± 0.01	EtOH

TABLE II

Activation parameters of perchlorate

Solvent	$\Delta H^{\neq}$ (75°C) Kcal · mol^{-1}	$\Delta H^{\neq}$ (75°C) eu
EtCOMe	26.7 ± 0.6	0.68 ± 1.87
EtOH	26.1 ± 0.2	−1.21 ± 0.66

Since the activation entropy is nearly zero, there would be no significant conformational change between the ground state and the transition state. All these observations indicate that the thermal racemization of these aminosulfonium salts (**1**) proceeds via an intramolecular process, namely pyramidal inversion. The rate for the pyramidal inversion of these heteroatom-centered compounds is generally influenced by the electronegativity of the heteroatom ligand. When a more electronegative group is substituted on the sulfur atom, the lone electron pair on the sulfur atom is considered to have mainly *s* character and hence to localize around the central sulfur atom; consequently, the greater the *s* character of the lone electron pairs in the ground state, the more the ground state would be stabilized. However, in the transition state, the central sulfur atom should assume an sp^2-*p* planar structure and one of the lone electron pairs would occupy a *p* orbital. Therefore, the barrier to the pyramidal inversion should be increased by substitution of a more electronegative group. For example, the sulfoxide, which has a stronger electronegative S—O bond than the S—N bond of the sulfilimine, undergoes pyramidal inversion much slower than the corresponding sulfilimine. Furthermore, the electron-withdrawing substituent on the heteroatom also increases the *s* character of the lone electron pair on the central sulfur atom by the inductive effect, and hence, the rate of the racemization should become smaller. For example, the rates of the racemization of *o*-methoxyphenylphenyl-(*N*-substituted)benzenesulfonylsulfilimines were found to be correlated with Hammett's σ values and the ρ value obtained was −0.31.[3d] Namely, the rate of racemization became smaller as the substituent became more electron withdrawing. A similar trend has also been observed in the thermal racemizations of the sulfonium ylide and the corresponding sulfonium salt;[5] the electron density on the sulfur should be lower in the sulfonium salt than that in the sulfonium ylide. Darwish *et al.* reported that methyl-*p*-tolyl(*N*-methyl-*p*-tolylsulfonylamino)sulfonium trifluoromethanesulfonate racemizes 50 times faster than the corresponding sulfilimine.[3b] In the present study, the aminosulfonium salt was found to racemize 6–10 times faster than the corresponding sulfilimine. Since the electron density of the nitrogen of the aminosulfonium salt should be lower than that of the sulfilimine, the inductive effect described above cannot alone explain the higher rate of racemization of the aminosulfonium salt than that of the sulfilimine. One conceivable factor might be that the rate of the thermal racemization of the sulfur compounds is influenced markedly by the repulsion between the lone electron pair of the central sulfur atom and those of the ligand heteroatom. Since this repulsion increases in going from the ground state to the transition state, the greater the number of lone electron pairs on the ligand heteroatom, the larger will be the energy barrier to the pyramidal inversion. Thus, the aminosulfonium salt, which has

one lone electron pair on the α-nitrogen, may racemize faster than the sulfilimine which possesses two lone electron pairs on the α-nitrogen.

EXPERIMENTAL

All melting points are uncorrected. IR spectra were recorded on a JASCO A-3 and ^{1}H NMR were recorded on a Hitachi Perkin-Elmer R-600. Optical rotations were measured with a JASCO DIP-140. Product analyses were performed by liquid chromatography on a Yanaco L-1030, packed with Yanako Gel 5510, eluted with methanol.

Optically active (*RF*)-(+) *o-methoxyphenylphenylamino-sulfonium perchlorate* (**1a**). To an acetone solution (15 ml) of optically active (R)-(+) *o*-methoxyphenylphenylsulfilimine[3d] (0.692 g, 2.99 mmol) $[\alpha]_D^{20}$ = 172° (90% o.p.), an acetone solution (2 ml) of concentrated hydrochloric acid (0.3 ml) was added with stirring in an ice bath. When colorless precipitates appeared, the solvent was evaporated and an aqueous solution of sodium perchlorate (0.443 g, 3.62 mmol) was added. The aqueous solution was extracted with dichloromethane and the extract was dried and evaporated under vacuum. Yield was 0.843 g (85%). The oily product was crystallized from dichloromethane-ether. Colorless crystals; mp, 128–129°C; $[\alpha]_D^{20}$ = 67.4° (acetone, c = 1.10). IR (KBr): 3400, 1145, 1115, and 1085 cm^{-1}. ^{1}H NMR ($CDCl_3$-CD_3CN): δ = 3.64 (3 H, s, *o*-CH_3O—), 5.65–6.05 (2 H, br, NH_2—), 7.12–8.09 (9 H, m, aromatic protons). Found: C, 47.09; H, 4.19; N, 4.17%. Calcd for $C_{13}H_{14}ClNO_5S$: C, 47.06; H, 4.25; N, 4.22%.

Optically active (*R*)-(+) *o-methoxyphenylphenylamino-sulfonium tetrafluoroborate* (**1b**). The sulfonium salt (**1b**) was obtained from optically active (R)-(+) *o*-methoxyphenylphenylsulfilimine (0.868 g, 3.75 mmol) $[\alpha]_D^{20}$ = 135° (96% o.p.), concentrated hydrochloric acid (0.15 ml), and sodium tetrafluoroborate (0.233 g, 2.03 mmol) by the same procedure as above. The product was recrystallized from dichloromethane-ether. Yield was 0.243 g (40%). Colorless crystals; mp, 110.5–112.5°C; $[\alpha]_D^{20}$ = 56.0° ($CHCl_3$, c = 0.736). IR (KBr); 3080, 2970, 1480, 1290, and 1080 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 3.74 (3 H, s, *o*-CH_3O—), 6.87–7.95 (11 H, m, aromatic protons and NH_2—). Found: C, 48.77; H, 4.35; N, 4.40%. Calcd for $C_{13}H_{14}BF_4NOS$: C, 48.92; H, 4.42; N, 4.38%.

Optically active (*R*)-(+) *o-methoxyphenylphenylamino-sulfonium picrate* (**1c**). To the benzene solution (5 ml) of optically active (R)-(+) *o*-methoxyphenylphenylsulfilimine (0.48 g, 2.07 mmol) $[\alpha]_D^{20}$ = 172° (90% o.p.), a benzene solution (5 ml) of 85% picric acid (0.568 g, 2.11 mmol) was added and the benzene was evaporated. An oily residue was crystallized from dichloromethane-ether. Yield was 0.663 g (70%). Yellow crystals; mp, 97–99°C; $[\alpha]_D^{20}$ = 75.7° ($CHCl_3$ c = 0.608). IR (KBr): 1630, 1610, 1335, and 1275 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 3.85 (3 H, s, *o*-CH_3O—), 6.75–8.18 (11 H, m, aromatic protons), 8.89 (2 H, s, NH_2—). Found: C, 49.65; H, 3.44; N, 11.87%. Calcd for $C_{19}H_{16}N_4O_8S$: C, 49.56; H, 3.50; N, 12.16%.

Kinetics. Any one of the aminosulfonium salts (**1a–c**) was dissolved in a distilled solvent and the solution was put into ampuls. The ampuls were immersed in a constant temperature oil bath. Each one of these ampuls was picked up periodically, and immediately cooled in a dry ice bath and subjected to the measurement of the optical rotation. After the reaction, liquid chromatography showed that no other product appeared other than the aminosulfonium salt. The first-order rate constants were obtained from the following equation.

$$kt = \ln(\alpha_0/\alpha_t)$$

α_0; initial optical rotation

α_t; optical rotation of time t

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