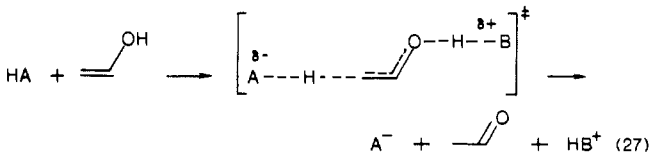


that a change in reaction medium from pure water to 60–70 mol % aqueous dimethyl sulfoxide produced a 50-fold depression in n the rate of hydrolysis of ethyl vinyl ether, which is reminiscent of the behavior of A-1 reactions, whereas the same solvent change produced a much smaller, only 4-fold, depression in the rate of ketonization of acetaldehyde enol, reminiscent of the behavior of A-2 reactions.

Such a difference in solvent effect, however, might be expected even if ketonization and vinyl ether hydrolysis were both occurring by the same stepwise mechanism. The difference in behavior of A-1 and A-2 reactions[30] has been rationalized in tt erms of differential solvation of reactants and transition state,[30b] using arguments similar to those now employed to explain differences in various concentrated-acid acidity functions. In both A-1 and A-2 reactions, rapid protonation of the substrate by hydronium ion is followed by rate-determining reaction of the substrate conjugate acid, but in the A-1 process this rate-determining step is unimolecular, whereas in the A-2 process it is a bimolecular attack of water in which the water molecule is taking on positive charge. There is thus a greater difference in the number of positively charged O–H bonds, which are the principle sites for solvational stabilization, between the initial-state hydronium ion and the rate-determining transition state in the A-1 process than in the A-2 process; the A-1 process will consequently experience the greater solvent effect. A similar difference in the balance of positively charged O–H bonds between initial and transition states exists for vinyl ether hydrolysis and enol ketonization proceeding by a stepwise mechanism, for the enol has an O–H bond not present in the vinyl ether. The solvent effect on vinyl ether hydrolysis should therefore be stronger than the solvent effect on enol ketonization, even if both reactions occur by the same stepwise mechanism.

A concerted reaction mechanism for the ketonization of enols of course implies a concerted mechanism for the reverse process, the enolization of carbonyl compounds. It has been known for some time that the rate law for the enolization of acetone contains a third-order term[18a,c,d,31] and that this third-acid term very probably represents a concerted reaction path; a similar term has recently been detected in the enolization of cyclohexanone.[32] It is believed, however, that, at least in the case of acetone, the concerted mechanism is of minor importance.[1b,18a,c,e,33]

Acknowledgment. We are grateful to the Natural Sciences and Engineering Research Council of Canada and to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for their financial support of this research.

Registry No. $Me_2C{=}CHOTMS$, 6651-34-9; $Me_2C{=}CHOH{\cdot}Li$, 32970-42-6; $Me_2C{=}CHOH{\cdot}K$, 103818-01-5; $Me_2C{=}CHOH$, 56640-70-1; Me_2CHCHO, 78-84-2; $Me_2C{=}CHO^-$, 77212-99-8; F^-, 16984-48-8; HCl, 7647-01-0; DCl, 7698-05-7; NaOH, 1310-73-2; $CNCH_2CO_2H$, 372-09-8; HCO_2H, 64-18-6; AcOH, 64-19-7; $CH_2ClPO_3H^-$, 54947-16-9; $H_2PO_4^-$, 14066-20-7; H_2O, 7732-18-5; H^+, 12408-02-5; D^+, 14464-47-2; D, 16873-17-9; MeLi, 917-54-4; KH, 7693-26-7.

Supplementary Material Available: Tables S1–S5 of rate constants (11 pages). Ordering information is given on any current masthead page.

(30) (a) Tommila, E.; Murto, M.-J. *Acta Chem. Scand.* **1963**, *17*, 1957–1970. (b) Cox, B. G.; McTigue, P. T. *Aust. J. Chem.* **1967**, *20*, 1815–1822. (c) McTigue, P. T.; Watkins, A. R. *Aust. J. Chem.* **1972**, *25*, 777–783.

(31) Dawson, H. M.; Spivey, E. *J. Chem. Soc.* **1930**, 2180–2189.
(32) Hand, E. S.; Jencks, W. P. *J. Am. Chem. Soc.* **1975**, *97*, 6221–6230.
(33) Bell, R. P. *The Proton in Chemistry*, 2nd ed.; Cornell University: New York, 1973; pp 148–154.

Transannular Bond Formation between the Amino and the Sulfonio Groups in 6,7-Dihydro-6-methyl-5*H*-dibenzo[*b*,*g*][1,5]thiazocinium Salts. The First Example of a Sulfurane with an Apical Alkyl Group

Kin-ya Akiba,* Kohichi Takee, Yasuko Shimizu, and Katsuo Ohkata

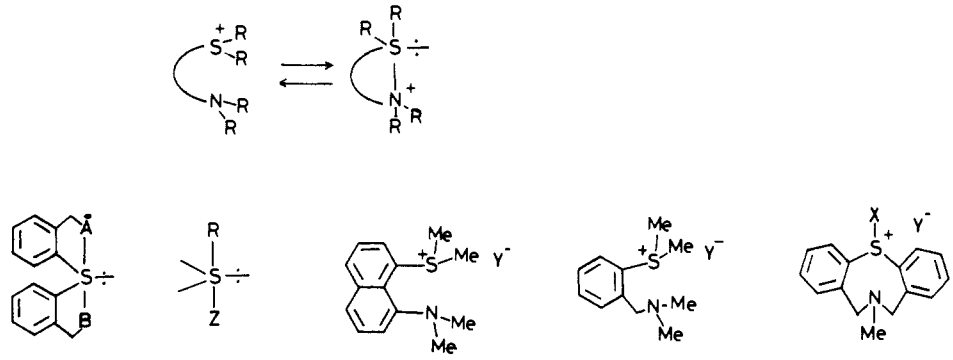
Contribution from the Department of Chemistry, Faculty of Science, Hiroshima University, Higashisenda-machi, Naka-ku, Hiroshima 730, Japan. *Received March 27, 1986*

Abstract: A series of S-substituted *N*-methyl-6,7-dihydro-5*H*-dibenzo[*b*,*g*][1,5]thiazocinium salts (**5a–e**) have been prepared from the *S*-chloro derivative (**5e**), which was obtained from the corresponding sulfoxide (**6**) and thionyl chloride. An excellent linear relationship is observed between the ^1H and the ^{13}C NMR chemical shifts of the *N*-methyl group and Hammett's σ_m substituent constants at the sulfur. The structures of **5a–e** have been shown to be ammoniosulfuranes with a distorted trigonal-bipyramidal geometry around the sulfur atom. The nitrogen atom lies well within the sum of the van der Waals radii of N and S, and the N–S distance (2.10–2.50 Å) shortens according to the increase of electron-withdrawing character of the substituent on the sulfur atom. Additional evidence for (methylammonio)sulfurane (**5a**) came from the low reactivity (1/1300) of transmethylation to pyridine compared with its related diphenylmethylsulfonium tetrafluoroborate (**11**). In connection with transmethylation of *S*-adenosylmethionine, intramolecular interactions between the amino and sulfonio groups are discussed for some methylsulfonium salts (**5a**, **13**, **14**, and **16**) in which the nitrogen base (amino or pyridyl group) is substituted at the side chain.

In the last decade, many kinds of sulfuranes (**1**) have been synthesized and most of the stable isolable ones share the feature of a five-membered ring linking an apical electronegative group and an equatorial aromatic ring carbon on the sulfur.[1] Not-

0002-7863/86/1508-6320$01.50/0

Scheme I[a]



1 2 3 4 5a-e, 6

[a] For **5**: **a**, X = Me, Y = PF_6; **b**, X = Et, Y = PF_6; **c**, X = MeO, Y = $SbCl_6$; **d**, X = EtO, Y = $SbCl_6$; **e**, X = Cl, Y = Cl, $SbCl_6$, PF_6. For **6**: X = O.

withstanding, less attention has been paid to alkylsulfuranes such as **2** where an electropositive group is attached at an apical position in the trigonal-bipyramidal structure. An (alkylammonio)sulfurane as a category of this type has been suggested as an intermediate in the conversion of sulfoxides into aminosulfonium salts.[2] Very recently, a four-membered (alkylammonio)sulfurane was claimed to have been observed by ^1H NMR in the reaction of various sulfoxides with *N*-sulfinylalkanaminium salts by Kresze et al.[3]

During the course of our investigation on selective alkylation of the amino and the sulfide groups within a molecule, it came to our attention that there may be direct interaction between the amino and the sulfonio groups. This expectation, however, could not be supported decisively even if the two groups were placed in close proximity such as **3** and **4** (see Scheme I). This failure was ascribed to the frontal congestion among four methyl groups.[4]

In order to get around the congestion surrounding the sulfur and the nitrogen atoms and to evaluate the minimum interaction energy between them, the 6,7-dihydro-*N*-methyl-5*H*-dibenzo[*b*,*g*][1,5]thiazocinium system (**5**) was chosen as a model compound. The reason for this is the conformational analysis of the eight-membered ring in thiazocine and its related compounds was investigated in detail by the Ollis group and some others and also we noticed definite interaction between the sulfinyl and the amino groups of **6** as described in the preceding paper.[5,7] In this paper, we wish to describe the transannular interaction between the sulfonio and the amino groups and consequently to demonstrate the first example for an isolable sulfurane with an alkyl group at the apical position.[6]

Results and Discussion

Synthetic Considerations. 6,7-Dihydro-6-methyl-5*H*-dibenzo[*b*,*g*][1,5]thiazocine 12-oxide (**6**) is available in considerably large quantities by the known procedure.[7,8] Alkylation of **6** with Meerwein's reagents ($Me_3O^+SbCl_6^-$ and $Et_3O^+SbCl_6^-$) produced the O-alkylated compound (**5c**,**d**) in moderate yield. Although simple diarylmethoxysulfonium derivatives were converted into the corresponding alkylsulfonium compounds by treatment with organometallic reagents,[9] attempts to prepare the *S*-methylsulfonium derivative (**5a**) by reaction of the *S*-methoxysulfonium derivative (**5c**) with dimethylcadmium or methyl Grignard reagent were all in vain.

Treatment of the sulfoxide **6** with thionyl chloride in benzene solution afforded a colorless crystalline product (**5e**, Y = Cl) in quantitative yield, but the chloride was very hygroscopic and labile under a moist atmosphere.[7] When the counteranion was converted into the hexachloroantimonate (**5e**, Y = $SbCl_6$) or the hexafluorophosphate (**5e**, Y = PF_6), the compound became considerably stable under the usual handling conditions.

Reaction of **5e** (Y = Cl) with lithium dimethylcuprate at −78 °C furnished a colorless solid (mp 195–197 °C) which was isolated by using the hexafluorophosphate as a counteranion. The structure was characterized as the *S*-methyl derivative (**5a**) on the basis of its spectral data as well as its chemical behavior. Elemental analysis gave a satisfactory result for $C_{16}H_{18}NSPF_6$. In the ^1H NMR spectrum in CD_3CN solution are observed the characteristic signals δ 2.53 (s, 3 H), 3.30 (s, 3 H), and 4.06 (s, 4 H), together with signals for eight aromatic hydrogens. The proton-decoupled carbon spectrum features only nine lines which reveals the presence of symmetry in the molecule and the existence of a single conformer.[5-8] In addition, the methyl group substituted at the sulfur atom was smoothly transferred into a nucleophile (pyridine) to give back 6,7-dihydro-6-methyl-5*H*-dibenzo[*b*,*g*][1,5]thiazocine (**10**) together with an N-methylated nucleophile. The *S*-methyl derivative (**5a**) was converted to the *S*-ethyl derivative (**5b**, mp 195–198 °C) by way of methylation of the sulfonium ylide, which was generated from **5a** with butyllithium at −78 °C in THF solution.

The chemical interconversions between **5a–e** are summarized in Scheme II. Structural assignments to ammoniosulfuranes (**5a–e**) rather than sulfonium salts are founded upon NMR spectral data as well as a single-crystal X-ray structural analysis, as discussed elsewhere.[17a]

Structural Considerations. NMR Spectral Analysis. It is interesting to consider some problems concerning the conformation of the eight-membered ring from the standpoint of transannular interaction between an electron-deficient sulfur atom and an amino moiety.[5] *N*-Benzylthiazocine **8** (see Scheme III) has been shown

(1) (a) Kapovits, I.; Kálmán, A. *J. Chem. Soc., Chem. Commun.* **1971**, 649. (b) Perozzi, E. F.; Martin, J. C. *J. Am. Chem. Soc.* **1972**, *94*, 5519. (c) Adzima, L. J.; Chiang, C. C.; Paul, I. C.; Martin, J. C. *J. Am. Chem. Soc.* **1978**, *100*, 953. (d) Kapovits, I.; Rabai, J.; Ruff, F.; Kucsman, A. *Tetrahedron*, **1979**, *35*, 1869; *Ibid.* **1979**, *35*, 1875. (e) Perozzi, E. F.; Martin, J. C. *J. Am. Chem. Soc.* **1979**, *101*, 1591. (f) Michalak, R. S.; Martin, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 1683. (g) Martin, J. C. *Science* **1983**, *221*, 509, and references cited therein.

(2) Drabowicz, J.; Bujnicki, B.; Mikolajczyk, M. *J. Org. Chem.* **1981**, *46*, 2788.

(3) Schwöbel, A.; Pérez, M. A.; Rössert, M.; Kresze, G. *Liebigs Ann. Chem.* **1982**, 723.

(4) Ohara, Y.; Akiba, K-y.; Inamoto, N. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 1508.

(5) (a) Gellatly, R. P.; Ollis, W. D.; Sutherland, I. O. *J. Chem. Soc., Perkin Trans. 1*, **1976**, 913. (b) Renaud, R. N.; Bovenkamp, J. W.; Franser, R. R.; Roustan, J. L. A. *Can. J. Chem.* **1977**, *55*, 3456. (c) Brieaddy, L. E.; Hurlbert, B. S.; Mehta, N. B. *J. Org. Chem.* **1981**, *46*, 1630. (d) Leonard, N. J.; Oki, M.; Chiavarelli, S. *J. Am. Chem. Soc.* **1955**, *77*, 6234.

(6) Preliminary reports: Akiba, K-y.; Takee, K.; Ohkata, K.; Iwasaki, F. *J. Am. Chem. Soc.* **1983**, *105*, 6965. (b) Ohkata, K.; Takee, K.; Akiba, K-y. *Tetrahedron Lett.* **1983**, *24*, 4859.

(7) Akiba, K-y.; Takee, K.; Ohkata, K. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 1946.

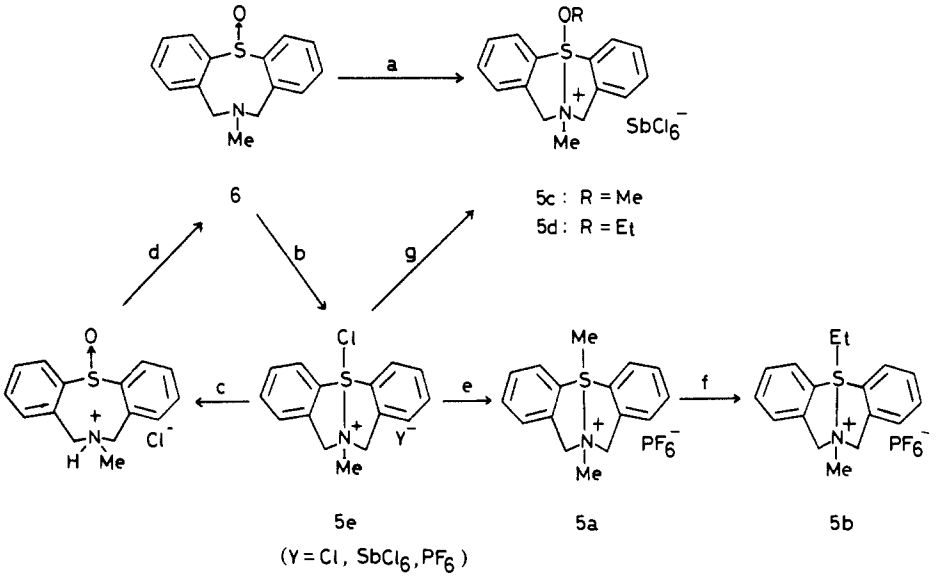
(8) Tanaka, S.; Watanabe, H.; Ogata, Y. *Yakugaku Zasshi* **1973**, *93*, 997.

(9) (a) Andersen, K. K.; Cinquini, M.; Papanikolaou, N. E. *J. Org. Chem.* **1970**, *35*, 706. (b) LaRochelle, R. W.; Trost, B. M. *J. Am. Chem. Soc.* **1971**, *93*, 6077.

Table I. Selected ^1H and ^{13}C NMR Chemical Shifts of Ammoniosulfuranes **5a–e**

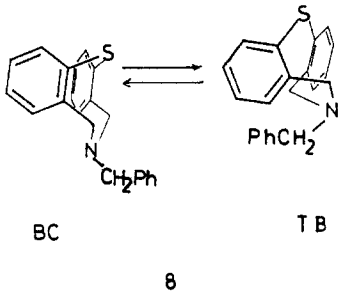
compd	X	Y^-	substit const, σ_m	^1H NMR (CD_3CN) δ		^{13}C NMR (CD_3CN) δ	
				N-Me	$N-CH_2$	N-Me	$N-CH_2$
5a	Me	PF_6^-	−0.07	2.53	4.06	39.8	56.4
5b	Et	PF_6^-	−0.07	2.54	4.03	40.1	56.7
5c	MeO	$SbCl_6^-$	0.12	2.77	4.25	41.7	57.5
5d	EtO	$SbCl_6^-$	0.10	2.77	4.24	41.8	57.6
5e	Cl	PF_6^-	0.37	3.13	4.65	43.8	59.8

Scheme II[a]



[a] Reagents and conditions: (a) $Me_3O^+SbCl_6^-$ or $Et_3O^+SbCl_6^-$; (b) $SOCl_2$; (c) H_2O; (d) aqueous $NaHCO_3$; (e) $LiMe_2Cu$; (f) *n*-BuLi, MeI; (g) MeOH or EtOH.

Scheme III



to possess two stable conformations, the boat-chair (BC) and the twist-boat (TB), whose ratio (BC/TB) is 3:1 at −14 °C.[5a,10] This fact indicates that the BC form is more stable than the TB form to the extent of 0.57 kcal/mol.

On the other hand, the *S*-chloro derivative (**5e**) exists solely as a single conformer from −30 °C to 43 °C as judged from ^1H NMR spectral data. In the ^1H NMR spectrum in CD_3CN solution are the characteristic signals δ 3.13 (s, 3 H), 4.59, 4.65 (ABq, J = 15.6 Hz, 4 H), and 8.3–8.6 (m, 2 H), together with a multiplet for the other aromatic protons, 7.2–8.0 (m, 6 H). The most reasonable structure of **5e** was ammonio-*S*-chlorosulfurane rather than **5e′**, **5e″**, and **5e‴** for the following reasons: (i) The chemical shift of the *N*-methyl protons of the sample is close to that of the *N*,*N*-dimethylthiazocinium derivative (**9**: δ 3.16) of the TB form.[7] (ii) The ^1H NMR spectrum of the sample is independent of the exchange of counteranions (Y = Cl, $SbCl_6$, PF_6). (iii) It is accepted as a characteristic feature of the ^1H NMR spectrum of diarylsulfuranes of type **1** that the aromatic ortho protons appear at lower field by 1–3 ppm (δ 8.0–9.7) than the other aromatic protons, probably due to the effect of the polarizable apical bond.[11] This is the case for **5e** (δ 8.23–8.63 (m, 2 H), indicating that the chlorine atom attached to the sulfur atom occupies the favorable apical position due to apicophilicity of an electronegative group in a sulfurane.[1g]

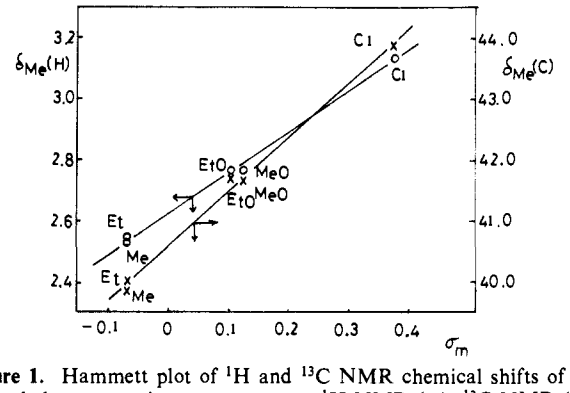
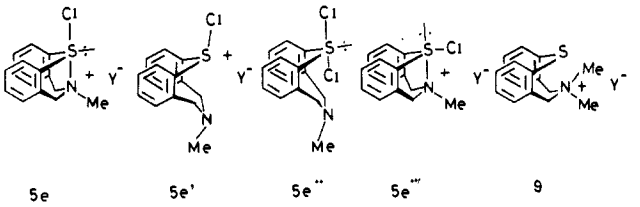


Figure 1. Hammett plot of ^1H and ^{13}C NMR chemical shifts of the *N*-methyl group against σ_m constants: ^1H NMR (○), ^{13}C NMR (×).

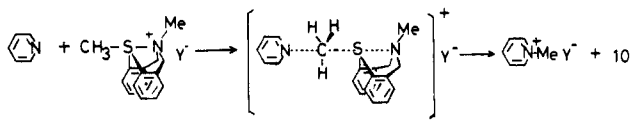


^1H NMR spectra of the other derivatives (**5a–d** and **6**) also indicate that these compounds exist preferentially in a single conformer from −30 to 43 °C. The *S*-methoxy derivative **5c** was

(10) In accord with the nomenclature used in the literature, the description "BC", "TB", and "BB" refer to "boat chair", "twist boat", and "boat boat" conformations in an eight-membered ring.[5c]

(11) (a) Astrologes, G. W.; Martin, J. C. *J. Am. Chem. Soc.* **1977**, *99*, 4390. (b) Granoth, I.; Martin, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 2711.

Scheme IV



5a Transition State

observed to be in the TB geometry as the sole conformer, even in the presence of hydrochloric acid. The fact that **5c** (Y = PF_6) is not protonated by hydrochloric acid indicates that the electron pair of the nitrogen is absorbed by the sulfonio group making the interaction strong enough to fix a TB form. Selected chemical shifts of the ^1H and ^{13}C NMR spectra are collected in Table I.

Examination of ^1H and ^{13}C NMR chemical shifts of **5a–e** reveals the existence of excellent linear relationships of signals for *N*-methyl groups, $\delta_{Me}(H)$ and $\delta_{Me}(C)$, and methylene groups, $\delta_{CH_2}(H)$ and $\delta_{CH_2}(C)$, against Hammett's σ_m substituents constants at the sulfur atom (Figure 1).

$$\delta_{Me}(H) = 1.35\sigma_m + 2.63 \quad (r = 0.994, n = 5)$$

$$\delta_{CH_2}(H) = 1.36\sigma_m + 4.12 \quad (r = 0.993, n = 5)$$

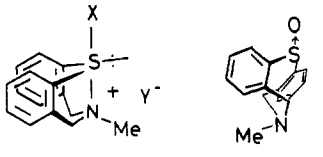
$$\delta_{Me}(C) = 8.80\sigma_m + 40.7 \quad (r = 0.993, n = 5)$$

$$\delta_{CH_2}(C) = 7.48\sigma_m + 56.95 \quad (r = 0.983, n = 5)$$

Furthermore, one expects correlation between the ^{13}C NMR shifts and the local electron density in a series of closely related compounds,[12] although complications are introduced by several factors that influence ^{13}C chemical shifts in different types of compounds. In fact, the existence of a linear relationship of the ^1H NMR chemical shifts of *N*-methyl signals for **5a–e** against those of ^{13}C NMR, $\delta_{Me}(H) = 0.151\delta_{Me}(C) - 3.52$ ($r = 0.994$, $n = 5$), clearly reflects the change of electron density around the amino group with the substituent at the sulfur atom.

Such linear relationships suggest that these compounds maintain at least an analogous conformation in solution, which can be characterized as the TB and/or BB form on the basis of ^1H NMR spectral data,[5b] and that the electron-withdrawing effect of the substituent at the sulfur atom is transmitted to the *N*-methyl group, probably through space or directly. An almost equivalent value of the slope of the methyl signals compared with that of the methylene signals supports the existence of direct interaction between the sulfonio and the amino groups. An analogous phenomenon has been also observed in monocyclic or bicyclic sulfuranes by Martin et al.[13]

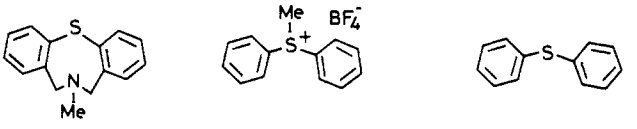
It is noteworthy in ^1H NMR spectra data that the *N*-methyl protons of **5a** are less shielded than in its parent amino sulfide (**10**), while the chemical shift of the *N*-methyl signal of **4** are almost the same as that of *N*,*N*-dimethyl-2-(methylthio)-benzylamine.[7] Therefore, it can be considered that electron density around the *N*-methyl group of **5a** is decreased as a consequence



TB or BB form 5a-e TB form 6

of N–S transannular interaction or bond formation. Accordingly, ammoniosulfurane rather than the sulfonium salt is the most reasonable structure. Since there appears to be no more than 1–2% (actually unobservable) of the BC form in ^1H NMR spectrum of **5a** at 35 °C, the N–S attractive interaction in the BB or TB form must be at least 2–3 kcal/mol. Additional supportive evidence for the (methylammonio)sulfurane such as **5a** came from kinetic studies of transmethylation.

Kinetic Studies of Transmethylation of Some Methylsulfonium Salts. In order to confirm the formation of hypervalent S–N bond in **5a**, kinetic studies of transmethylation of **5a** and methyldiphenylsulfonium salt (**11**) to pyridine-d_5 were undertaken.[6b,14]



10 11 12

Each reaction afforded the corresponding sulfide (**10** or **12**) along with the *N*-methylpyridinium salt in spectroscopically quantitative yield.

Rate determinations of the reaction of **5a** and **11** were carried out ^1H NMR spectrometrically in pyridine-d_5 solution at various temperatures under pseudo-first-order conditions in which the nucleophile was present by ca. 50 times excess as the solvent.

The reactions were conducted in pyridine-d_5 in the probe of a Hitachi R-90H FT NMR spectrometer. Close attention was paid to keeping the experimental conditions such as spinning rate and solution volume as rigorously identical as possible in all runs. The transmethylations were found to follow nicely first-order kinetics for more than 3 half-lives in all cases. For each kinetic determination, at least 10 points were taken. Pseudo-first-order rate constants (k_{obsd}) at different temperatures and extrapolated ones for 25 °C, which were obtained by standard least-squares procedures using the $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values, are collected in Table II.

In the present system, the exceptionally low reactivity of **5a** is revealed by direct comparison with **11**. It is particularly instructive to consider that **5a** was decelerated by a factor of 1300 relative to **11**. The enthalpy of activation for **5a** ($\Delta H^{\ddagger}$ = 23.1 kcal/mol) is considerably larger than that of **11** ($\Delta H^{\ddagger}$ = 18.1 kcal/mol). Transmethylations by methylsulfonium salts proceed via an S_N2 mechanism and are generally decelerated with electron-releasing substituents.[14c] The present deceleratain in **5a** can be mainly attributable to the ground-state stabilization due to the N–S attractive interaction or electron transfer from the nitrogen to the sulfonio moiety. Furthermore, the entropy of activation (−7.82 eu) for **5a** is less negative compared with that (−10.3 eu) for **11**.[15] Although the activation entropy depends upon various factors, the less negative entropy may reflect a constraint of the ground state of **5a** due to N–S bonding. In other words, this constraint is released at the transition state due to weakening of N–S bonding during the progress of the transmethylation, as illustrated in Scheme IV.

Thus, kinetic studies also support that there is a considerable degree of N–S bonding in **5a**, thus decreasing the positive charge and increasing the electron density at the sulfonium group. If the nucleophilic displacement of **5a** and **11** proceeded via a similar transition state around the reaction center as pictured in Figure 2, it is estimated that the N–S interaction of **5a** is attractive to the extent of about 5 kcal/mol.

There may be such an interaction between amine and sulfonio moieties in transmethylation of biochemically interesting substrates

(12) (a) Olah, G. A.; Mateescu, G. D. *J. Am. Chem. Soc.* **1970**, *92*, 1430. (b) Fliszár, S.; Cardinal, G.; Bēraldin, M.-T. *J. Am. Chem. Soc.* **1982**, *104*, 5287.

(13) (a) Adzima, L. J.; Martin, J. C. *J. Am. Chem. Soc.* **1977**, *99*, 1657. (b) Lam, W. Y.; Duesler, E. N.; Martin, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 127.

(14) (a) Coward, J. K.; Sweet, W. D. *J. Org. Chem.* **1971**, *36*, 2337. (b) Young, T. E.; Oyler, A. R. *J. Org. Chem.* **1976**, *41*, 2753. (c) Hughes, E. D.; Whittingham, D. J. *J. Chem. Soc.* **1960**, 806. (d) Badet, B.; Julia, M.; Lefebvre, C. *Bull. Soc. Chim. Fr.* **1984**, II-431.

(15) Although transmethylation of methylsulfonium salt generally obeys second-order kinetics (S_N2), the present study was analyzed by means of the pseudo-first-order approximation due to the difficulty of determining the concentration of substrate precisely.

Table II. Kinetic Data for Transmethylation of Methylsulfonium Salts (**5a**, **11**, and **13–16**) to Pyridine-d_5

compd	T,[a] °C	k_{obsd}, s^{-1}	corr coeff	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu	k_{obsd}^{ref}/k_{obsd}
5a[b]	45.0	1.82×10^{-5}	0.999			
	45.0	1.82×10^{-5}	0.999			
	35.0	4.72×10^{-6}	0.999			
	35.0	4.62×10^{-6}	0.997			
	25.0	1.38×10^{-6}	0.998	23.1	−7.82	1.0
	25.0	1.58×10^{-6}	0.999			
11	35.0	5.09×10^{-3}	0.999			
		5.41×10^{-3}	0.999			
	25.0[c]	1.90×10^{-3}		18.1	−10.3	1.3×10^{3}
	22.5	1.43×10^{-3}	0.999			
	16.5	7.20×10^{-4}	0.997			
	13.8	5.60×10^{-4}	0.999			
13	35.0	9.52×10^{-5}	0.999			
		9.58×10^{-5}	0.999			
	25.0	3.58×10^{-5}	0.998	19.1	−16.7	1.0
		3.49×10^{-5}	0.999			
	15.0	1.08×10^{-5}	0.999			
		1.12×10^{-5}	0.999			
15	46.6	1.81×10^{-3}	0.999			
	46.5	1.67×10^{-3}	0.999			
	42.4	9.64×10^{-4}	0.999			
	42.3	9.79×10^{-4}	0.999			
	32.3	4.00×10^{-4}	0.996			
	32.3	4.78×10^{-4}	0.998			
	25.0[c]	2.02×10^{-4}		17.6	−16.2	5.71
14	74.5	5.44×10^{-4}	0.998			
	72.9	4.90×10^{-4}	0.999			
	65.3	1.84×10^{-4}	0.999			
	63.3	1.63×10^{-4}	0.999			
	56.6	7.85×10^{-5}	0.998			
	55.0	7.86×10^{-5}	0.999			
	25.0[c]	1.80×10^{-6}		23.1	−7.44	1.00
16	55.9	8.52×10^{-4}	0.998			
	54.9	7.01×10^{-4}	0.999			
	46.8	2.44×10^{-4}	0.999			
	46.5	2.56×10^{-4}	0.997			
	32.9	4.15×10^{-5}	0.999			
	32.3	4.22×10^{-5}	0.999			
	25.0[c]	1.40×10^{-5}		25.0	3.12	7.78

[a] Measured at the probe of NMR instrument (±0.3 °C). [b] Measured in a constant-temperature bath (±0.01 °C). [c] Extrapolated value based upon the activation parameters.

Table III. Selected Bond Lengths (Å) and Angles (deg) for Ammoniosulfuranes (**5a**, **5c**, and **5e**) and Aminosulfoxide (**6**)[a]

compd	X	counteranion, Y^-	$\angle X_{ap}SN_{ap}$, deg	$\angle C_{eq}SX_{ap}$, deg	l(N–S), Å	bond energy,[b] D_{NS}, kcal/mol	bond order,[c] n
5a	Me	PF_6^-	176.9	101.9	2.466	1.8	0.06
5c	MeO	$SbCl_6^-$	175.3	95.7	2.206	5.8	0.17
5e	Cl	PF_6^-	176.9	96.6	2.091	9.5	0.34
6[d]	O	–	179.4	104.0	2.609	1.0	0.04

[a] Reference 17a. [b] Reference 20. [c] Reference 21. [d] Reference 7.

such as *S*-adenosylmethionine and its related compounds,[14a,16] if the moieties can be arranged appropriately for the interaction. In connection with this problem, some investigations on transmethylation in open-chain models (**13–16**) were carried out by the same method as that mentioned above.

The kinetic data are summarized in Table II. A preparative scale reaction of **13–16** in pyridine solution also afforded the precursor sulfides (**17–20**) and *N*-methylpyridinium salt in high yields.

Compared with reactivity of **5a** relative to **11**, the open-chain systems (**13** and **14**) transferred the methyl group only ca. $^1/_6$–$^1/_8$

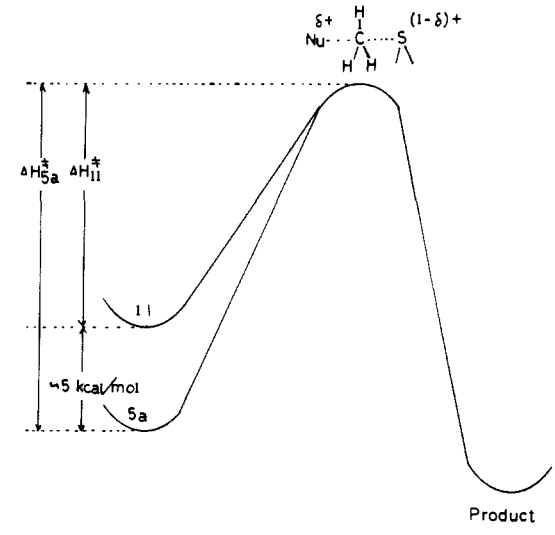
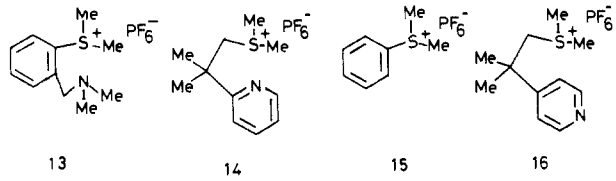
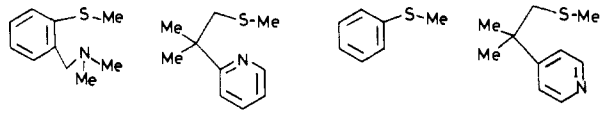


Figure 2. Stabilization of the ground state in **5a** relative to **11**.

(16) (a) Greenberg, D. A. *Adv. Enzymol. Relat. Subj. Biochem.* **1963**, *25*, 395. (b) Coward, J. K. *The Biochemistry of S-Adenosyl Methionine* Salvatore, F., Borek, E., Zappia, V., Williams-Ashman, H. G., Schlenk, F., Eds.: Columbia University: New York, 1977; p 127. (c) Cantoni, G. L. *Ann. Rev. Biochem.* **1975**, *44*, 435. (d) Maw, G. A. "The Chemistry of the Sulfonium Group" *The Chemistry of Functional Groups*; Stirling, C. J. M., Ed.; Wiley: New York, 1981; Part 2, p 703. (e) Hegazi, M. F.; Borchardt, R. T.; Schowen, R. L. *J. Am. Chem. Soc.* **1979**, *101*, 4359. (f) Golding, B. T.; Nassereddin, I. K. *J. Am. Chem. Soc.* **1982**, *104*, 5815. (g) Carey, P. R.; Storet, A. C. *Acc. Chem. Res.* **1983**, *16*, 455.



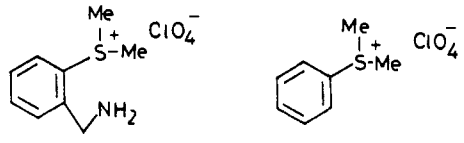
13 14 15 16



17 18 19 20

as fast as the corresponding reference compounds (**15** and **16**). Judging from the relative reactivity, it seems that very weak interaction between the sulfonio and amino groups might decelerate the trans-methylation reaction of the sulfonium salts (**13** and **14**). However, a pronounced feature for the attractive interaction in the consideration of activation parameters ($\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$) is not found.

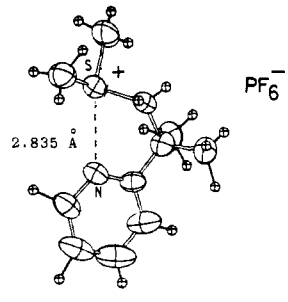
Notwithstanding, it is notable that the rate depression of **13** is the reverse direction of Coward's finding in which the *o*-CH_2NH_2-substituted compound (**21**) was hydrolyzed ca. 1.5 times as fast as the corresponding reference compound (**22**).[14a] The



21 22

conflict may be ascribed into the difference of the medium where the kinetics was investigated. The explanation is consistent with the fact that S_N2 reactivity of sulfonium salts was decreased as solvent polarity increased owing to the solvation of the initial state.[18]

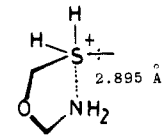
The conformation of **14** in the solid state was determined by an X-ray structure analysis on a single crystal.[17c] The sulfur and



14

nitrogen are oriented face to face as expected by Thorpe–Ingold effect of dimethyl groups and also due to intramolecular N–S interaction. But the N–S distance is 2.835 Å, and the sulfur has a tetrahedral configuration.

The ab initio Hartree–Fock calculation (4-31G) with sulfur d orbitals using $H_2NCH_2OCH_2SHX^+$ (X = H and Cl) model systems (**23**) gave an S–N bonded cyclic structure as ammoniosulfurane, while the calculation without the d orbital caused breaking of the S–N bond. The origin of the S–N bond stability is attributed to both electrostatic and charge-transfer interactions.[17b]



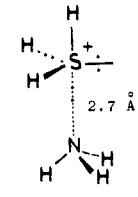
23

On the basis of the kinetic and structural data, we believe that such an N–S interaction may be present in the model compounds as well as in biological systems.[16]

Geometry around the Sulfur and Nitrogen Atoms of 5a–e. In order to clarify the geometry around the sulfur atom in **5a**, **5c**, and **5e**, X-ray structural analysis was performed on single crystals of these compounds.[17a] Figure 3 shows structures of **5a**, **5c**, and **5e**. The selected bond lengths and bond angles are summarized in Table III.

The angle $C_{eq}SX_{ap}$ (95.7° in **5c** and 96.6° in **5e**) is close to a right angle, which indicates a nearly planar structure about the sulfur atom. The distortion from trigonal bipyramid is somewhat pronounced in **5a** (101.9°) and **6** (104.1°) relative to **5c** and **5e**. The nitrogen atom in **5e** is along the axis of the S–X_{ap} bond and at a distance of 2.091 Å from the sulfur atom. The other N–S distances are determined to be 2.446 Å for **5a** and 2.206 Å for **5c**, respectively. Thus the crystal structures of **5a**, **5c**, and **5e** reveal a slightly distorted trigonal bipyramidal geometry about the sulfur atom.

Moreover, these N–S distances are very much shorter than the sum of the van der Waals radii (3.35 Å), which also indicates that there is definite transannular interaction between sulfur and nitrogen atoms. Indeed, ab initio calculation (4-31G) with d orbitals in S and N in a model system (**24**) showed the existence of a potential energy minimum near 2.7 Å enough to create substantial binding between them.[17b]



24

The N–S bond distances become gradually shorter according to the increase of electron-withdrawing character of the substituent at apical position.[17,19] On the basis of the results, the bond order and energy of these polarized hypervalent S–N bonds are evaluated roughly by applying Pauling's[20] and Huggins'[21] equations as shown in Table III. The S–N binding energy in (methylammonio)-sulfurane **5a** is calculated to be about 1.8 kcal/mol, which corresponds well to the minimum value (2–3 kcal/mol) estimated from the conformation analysis by means of the ^1H NMR spectrum.

In conclusion, each thiazocinium salt (**5a–e**) has been shown to exist preferentially in the ammoniosulfurane rather than the aminosulfonium on the basis of ^1H NMR spectral data as well as the single-crystal X-ray structural analyses. It is expected that the hypervalent X_{ap}–S–N bond would become stronger according to the increase of the electron-withdrawing character of the apical substituent, and the binding energy of S–N bond would be more than ca. 2 kcal/mol. The fact that the apical S–N distance

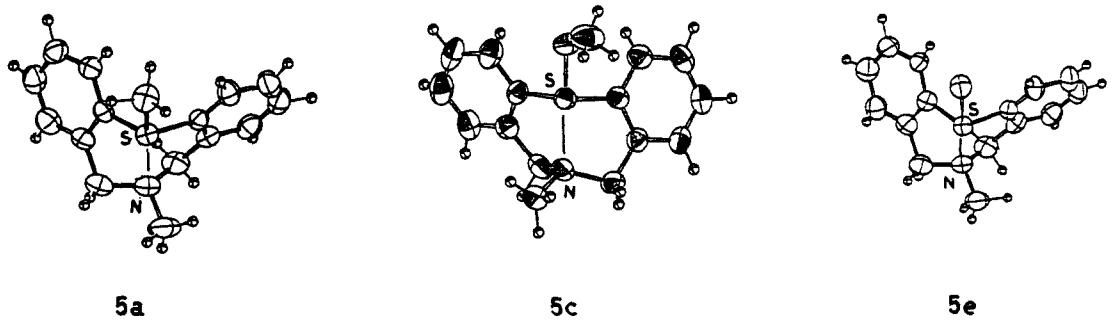
(17) (a) Iwasaki, F.; Akiba, K-y. *Acta Crystallogr., Sect. B: Struct. Sci.* **1985**, *41*, 445. (b) Morokuma, K.; Hanamura, M.; Akiba, K-y. *Chem. Lett.* **1984**, 1557. (c) Iwasaki, F.; Akiba, K-y., to be published.

(18) Reichardt, C. *Lösungsmittel-Effecte in der Organishe Chemie* Verlag Chemie: Weinheim/Bergstr, Germany, 1973; pp 63–65.

(19) Cohen-Addad, C.; Lehmann, M. S.; Becker, P.; Pārkānyi, L.; Kālmān, A. *J. Chem. Soc., Perkin Trans. 2*, **1984**, 191.

(20) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University: Ithaca, NY, 1960; pp 260 and 221–228.

(21) (a) Huggins, M. L. *J. Am. Chem. Soc.* **1953**, *75*, 4126. (b) Leung, F.; Nyburg, S. C. *Can. J. Chem.* **1972**, *50*, 324.



5a 5c 5e

Figure 3. Molecular structure of ammoniosulfurane (**5a**, **5c**, and **5e**).

shortens and the configuration at the sulfur approaches trigonal bipyramidal as the degree of electron-withdrawing character (σ_m) of the other apical group increases for a series in Table III suggests that the tetrahedral sulfur distorts toward the trigonal bipyramid according to the nucleophilic attack at the sulfonium center.[22] This tendency is also reflected in the ^1H and ^{13}C NMR spectral data of **5a–e**. Several investigations of such an interaction between an electron-deficient sulfur and an electron-donating group have been made;[3,4,23,24] however, **5a,b** are the first examples of an alkylsulfurane with an apical alkyl group. Moreover, **5e** can be regarded as an intermediate which is in accord with the explanation of the large acceleration in oxidation of amino sulfides such as **10** with halogens.[7,24]

Experimental Section

Infrared spectra were recorded on a Hitachi 215 grating IR spectrophotometer. The ^1H NMR spectra were determined with Varian T-60 and Hitachi R-90H instruments. The ^{13}C spectra were also run on the Hitachi R-90H spectrometer. All the melting points are uncorrected.

6,7-Dihydro-12-ethoxy-6-methyl-5*H*-dibenzo[*b*,*g*][1,5]thiazocinium Hexachloroantimonate (5d). A mixture of 6,7-dihydro-6-methyl-5*H*-dibenzo[*b*,*g*][1,5]thiazocine 12-oxide (**6**)[7] (648 mg, 2.52 mmol) and triethyloxonium hexachloroantimonate (1.105 g, 2.53 mmol) in dry dichloromethane (10 mL) was stirred at room temperature for 10 h under an argon atmosphere. The mixture was filtered and the filtrate was concentrated to give 478 mg (31%) of **5d**. A pure sample of the salt was obtained by recrystallization from ether–acetonitrile: mp 176–178 °C; ^1H NMR (CD_3CN) δ 1.48 (t, J = 7.0 Hz, 3 H), 2.77 (s, 3 H), 4.23 (q, J = 7.0 Hz, 2 H), 4.24 (s, 4 H), 7.30–7.85 (m, 6 H), and 7.90–8.26 (m, 2 H); ^{13}C NMR (CD_3CN) δ 16.0, 41.8, 57.6, 68.2, 128.7, 131.7, 133.9, and 138.4.

Anal. Calcd for $C_{17}H_{20}NOSSbCl_6$: C, 32.89; H, 3.25; N, 2.26. Found: C, 33.07; H, 3.08; N, 2.22.

6,7-Dihydro-12-methoxy-6-methyl-5*H*-dibenzo[*b*,*g*][1,5]thiazocinium Hexachloroantimonate (5c). **5c** (mp 148–151 °C, 22%) was obtained from **6** and trimethyloxonium hexachloroantimonate:[7] ^1H NMR (CD_3CN) δ 2.77 (s, 3 H), 3.92 (s, 3 H), 4.25 (s, 4 H), 7.35–7.80 (m, 6 H), and 7.92–8.15 (m, 2 H); ^{13}C NMR (CD_3CN) δ 41.7 (q, N–Me), 57.5 (t, N–CH_2), 57.4 (q, OMe), 128.4 (d), 128.6 (d), 130.9 (s), 131.6 (d), 133.8 (d), and 138.1 (s, S–C).

12-Chloro-6,7-dihydro-6-methyl-5*H*-dibenzo[*b*,*g*][1,5]thiazocinium Chloride (5e, Y = Cl). To a solution of **6** (639 mg, 2.49 mmol) in dry benzene (14 mL) was added dropwise a solution of thionyl chloride (1 mL) in the same solvent (2 mL) under a nitrogen atmosphere. The mixture was stirred at room temperature for 2.5 h and filtered. The yellowish solids were washed with dry benzene and ether successively before drying under an inert gas. There was obtained a colorless hygroscopic chloride (**5e**, Y = Cl; 739 mg, 95%): ^1H NMR ($CDCl_3$) δ 3.13 (s, 3 H), 4.70 (s, 4 H), 7.22–8.02 (m, 6 H), and 8.23–8.63 (m, 2 H).

12-Chloro-6,7-dihydro-6-methyl-5*H*-dibenzo[*b*,*g*][1,5]thiazocinium Hexachloroantimonate (5e, Y = $SbCl_6$). To a stirred suspension of the chloride (**5e**, Y = Cl) in anhydrous dichloromethane (10 mL) prepared from sulfoxide (**6**) (607 mg, 2.36 mmol) and excess thionyl chloride was added dropwise a solution of pentachloroantimony (0.3 mL, 2.36 mmol) in the same solvent (5 mL). The mixture was stirred at 0 °C for 5 min and at room temperature for 1.5 h before filtration. The solids were dried under a nitrogen atmosphere to yield 822 mg (57%) of a pure sample (**5e**, Y = $SbCl_6$): mp 170–173 °C; IR ν_{max} (KBr) 1455 and 1015 cm^{-1}; ^1H NMR (CD_3CN) δ 3.13 (s, 3 H), 4.65 (s, 4 H), 7.23–8.02 (m, 6 H), and 8.31–8.69 (m, 2 H).

Anal. Calcd for $C_{15}H_{15}NSSbCl_7$: C, 29.47; H, 2.47; N, 2.29. Found: C, 29.58; H, 2.26; N, 2.15.

12-Chloro-6,7-dihydro-6-methyl-5*H*-dibenzo[*b*,*g*][1,5]thiazocinium Hexafluorophosphate (5e, Y = PF_6).[7] To a stirred suspension of **5e** (Y = Cl) in anhydrous dichloromethane (10 mL) prepared from **6** (517 mg, 2.01 mmol) and excess thionyl chloride was added ammonium hexafluorophosphate (1.31 g, 8.04 mmol). The mixture was stirred at room temperature for 17 h prior to filtration. The filtrate was diluted with dry ether to afford 288 mg (34%) of **5e** (Y = PF_6) as a colorless solid: mp 145–155 °C dec; ^1H NMR (CD_3CN) δ 3.13 (s, 3 H), 4.59 and 4.72 (AB q, J = 15.6 Hz, 4 H), 7.30–8.05 (m, 6 H), and 8.27–8.65 (m, 2 H); ^{13}C NMR (CD_3CN) δ 43.8, 59.9, 127.7, 130.7 (×2), 131.9, 134.6, and 137.7.

6,7-Dihydro-6,12-dimethyl-5*H*-dibenzo[*b*,*g*][1,5]thiazocinium Hexafluorophosphate (5a). To a suspension of cuprous iodide (293 mg, 1.54 mmol) in dry ether (2 mL) was added dropwise 4.1 mL (3.08 mmol) of ethereal methyllithium solution (0.75 M) at −10–0 °C under argon atmosphere. The mixture was stirred at the same temperature for 1 h to give a colorless solution. The solution of lithium dimethylcuprate was added dropwise to a stirred suspension of the chloride (**5e**, Y = Cl; 400 mg, 1.28 mmol) in tetrahydrofuran (40 mL) at −78 °C under a nitrogen atmosphere. The mixture was stirred at −78 °C for 4 h before quenching with an aqueous solution of potassium hexafluorophosphate (10 g) and ammonium chloride (2.9 g) and ice. The product was extracted into dichloromethane, and the organic layers were dried with anhydrous magnesium sulfate. Evaporation of the solvent yielded a colorless oil (533 mg). Trituration with dichloromethane (5 mL) and ether (100 mL) afforded a colorless solid. Recrystallization of the solid from acetonitrile and ether furnished 80 mg (16%) of **5a** as a pure sample: mp 195–197 °C; IR ν_{max} (KBr) 1438 and 820 cm^{-1}; ^1H NMR (CD_3CN) δ 2.53 (s, 3 H), 3.30 (s, 3 H), 4.06 (s, 4 H), and 7.26–7.92 (m, 8 H); ^{13}C NMR (CD_3CN) δ 23.5 (q), 39.8 (q), 56.4 (t), 126.9 (s), 128.0 (d), 130.2 (d), 130.9 (d), 133.5 (d), and 141.1 (s).

Anal. Calcd for $C_{16}H_{18}NSPF_6$: C, 47.88; H, 4.52; N, 3.49. Found: C, 47.64; H, 4.41; N, 3.42.

6,7-Dihydro-12-ethyl-6-methyl-5*H*-dibenzo[*b*,*g*][1,5]thiazocinium Hexafluorophosphate (5b). To a stirred suspension of **5a** (50 mg, 0.13 mmol) in dry THF (5 mL) was added dropwise *n*-butyllithium in hexane (1.6 M, 3.2 mmol) at room temperature under a nitrogen atmosphere to yield an orange solution (sulfur ylide). After the mixture was stirred for 30 min, methyl iodide (0.08 mL, 1.6 mmol) was added at −78 °C to the solution. The reaction mixture was stirred at the same temperature for 2 days prior to the quenching with aqueous potassium hexafluorophosphate (2.5 g) and ammonium chloride (0.8 g) solution and ice. Workup in the presdescribed manner gave 59.5 mg of a greenish oil. The residual material was triturated and recrystallized from acetonitrile and ether to give 18.5 mg (35%) of **5b**: mp 195–198 °C; ^1H NMR (CD_3CN) δ 1.46 (t, J = 7.5 Hz, 3 H). 2.54 (s, 3 H), 3.85 (q, J = 7.5 Hz, 2 H), 4.03 (s, 4 H), and 7.14–7.90 (m, 8 H); ^{13}C NMR (CD_3CN) δ 18.8, 33.0, 40.1, 56.7, 125.7, 128.1, 130.6, 131.0, 133.6, and 141.7.

Anal. Calcd for $C_{17}H_{20}NSPF_6$: C, 49.16; H, 4.85; N, 3.37. Found: C, 49.43; H, 4.91; N, 3.16.

Dimethyl[2-((*N*,*N*-dimethylamino)methyl)phenyl]sulfonium Hexafluorophosphate (13). By predescribed method,[7] **13** was obtained from 2-((*N*,*N*-dimethylamino)methyl)phenyl methyl sulfide.

Dimethylphenylsulfonium Hexafluorophosphate (15). Treatment of thioanisole (1.24 g, 10 mmol) with methyl iodide (11.36 g, 80 mmol) and silver tetrafluoroborate (1.95 g, 10 mmol) in 10 mL of acetonitrile afforded the sulfonium salt. Recrystallization of the salt from ether–ace-

(22) Kikuchi, K.; Furukawa, N.; Moriyama, M.; Oae, S. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 1934.

(23) (a) Johnson, C. R.; Rigau, J. J. *J. Am. Chem. Soc.* **1969**, *91*, 5398. (b) Hirschon, A. S.; Olmstead, M. M.; Doi, J. T.; Musker, W. K. *Tetrahedron Lett.* **1982**, *23*, 317. (c) Hirschon, A. S.; Beller, J. D.; Olmstead, M. M.; Doi, J. T.; Musker, W. K. *Tetrahedron Lett.* **1981**, *22*, 1195.

(24) Doi, J. T.; Musker, W. K. *J. Am. Chem. Soc.* **1981**, *103*, 1159.

tonitrile gave a pure tetrafluoroborate (1.46 g, 64%): mp 146–146.5 °C; ^{1}H NMR (Me_2SO-d_6) δ 3.27 (s, 6 H) and 7.68–8.19 (m, 5 H).

To a stirred suspension of the tetrafluoroborate (1.27 g, 5.62 mmol) in anhydrous dichloromethane (10 mL) was added ammonium hexafluorophosphate (2.75 g, 16.9 mmol). The mixture was stirred at room temperature for 24 h prior to filtration. The filtrate was diluted with ether to afford 0.64 g (40%) of **15** as a colorless solid: mp 115.5–116.5 °C; ^{1}H NMR (Me_2SO-d_6) δ 3.27 (s, 6 H) and 7.67–8.17 (m, 5 H).

Anal. Calcd for $C_8H_{11}SPF_6$: C, 33.81; H, 3.91. Found: C, 33.79; H, 3.91.

2-(1,1-Dimethyl-2-(methylthio)ethyl)pyridine (18) and 4-(1,1-Dimethyl-2-(methylthio)ethyl)pyridine (20). To a cooled mixture of diisopropylamine (5.02 mL, 37.3 mmol) at 0 °C was added butyllithium (19 mL of 1.6 M hexane solution). After 30-min stirring of the mixture, 10.8 mL (62.2 mmol) of hexamethylphosphoramide and 3.76 g (31.1 mmol) of 2-isopropylpyridine were added into the solution. The solution was cooled at −78 °C followed by addition of chloromethyl methyl sulfide (2.63 mL, 31 mmol). The reaction mixture was stirred at the same temperature for 12 h. The mixture was poured onto ice and extracted with dichloromethane. The organic layers were washed with water, dried over anhydrous magnesium sulfate, and evaporated to yield a yellow oil. Distillation of the residue gave a colorless oil (**18**, 2.59 g, 46%).

By the same procedure, **20** was obtained from 3.80 g (31.4 mmol) of 4-isopropylpyridine in 62% yield as a colorless oil.

For **18**: bp 82.5–83.5 °C/1.5 mmHg; IR ν_{max} (neat) 3050, 2960, 2920, 1585, and 1470 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.44 (s, 6 H), 1.89 (s, 3 H), 2.96 (s, 2 H), 6.98–7.97 (m, 3 H), and 8.69–8.82 (m, 2 H); mass spectrum, *m/e* 181 (M^+).

For **20**: bp 108–109 °C/1.5 mmHg; IR ν_{max} (neat) 3040. 2960, 2920, 1595, and 1405 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.39 (s, 6 H), 1.91 (s, 3 H), 2.78 (s, 2 H), 7.19–7.29 (m, 2 H), and 8.47–8.59 (m, 2 H); mass spectrum, *m/e* 181 (M^+).

Dimethyl[2-methyl-2-(2-pyridyl)propyl]sulfonium Hexafluorophosphate (14) and Dimethyl[2-methyl-2-(4-pyridyl)propyl]sulfonium Hexafluorophosphate (16). By a method similar to the preparation of **13**, each pyridinium BF_4 salt of the sulfonium tetrafluoroborate was obtained. Neutralization of the salt by aqueous sodium carbonate followed by extraction with dichloromethane in the presence of potassium hexafluorophosphate and ammonium chloride gave a colorless crystalline product. Recrystallization of the solid from acetonitrile–ether–dichloromethane afforded a pure sample in 30–80% yield.

For **14**: mp 115.5–116.5 °C; ^{1}H NMR (CD_3CN) δ 1.49 (s, 6 H), 2.90 (s, 6 H), 3.63 (s, 2 H), 7.23–7.85 (m, 3 H), and 8.46–8.53 (m, 1 H).

Anal. Calcd for $C_{11}H_{18}NSPF_6$: C, 38.71; H, 5.32; N, 4.10. Found: C, 38.94; H, 5.32; N, 3.92.

For **16**: mp 123.5–124.5 °C; ^{1}H NMR (CD_3CN) δ 1.54 (s, 6 H), 2.64 (s, 6 H), 3.61 (s, 2 H), 7.61–7.68 (m, 2 H), and 8.54–8.61 (m, 2 H).

Anal. Calcd for $C_{11}H_{18}NSPF_6$: C, 38.71; H, 5.32; N, 4.10. Found: C, 38.93; H, 5.26; N, 3.94.

Kinetic Measurements on Transmethylation. General Procedure. A solution of **5a** (29.7 mg, 0.074 mmol) in pyridine-d_5 (0.3 mL) was placed in a 5-mm NMR tube. The tube was immersed in a constant-temperature bath maintained at 45 °C (±0.01 °C). After a measured amount of time, the tube was removed from the bath and immediately cooled in an ice-water bath. At each time interval, the ^{1}H NMR spectra of the methyl region were recorded and the relative integrated area of the peak was used to calculate the percent composition of the starting material and the resulting pyridinium salt. The values of the pseudo-first-order rate constant, k_{obsd}, for the transmethylation were calculated by using the method of least squares. By a similar methodology, kinetics at other temperatures and of other substrates were carried out. But, the rate constants for **11** and **13–16** were measured in a probe (±0.3 °C) in the ^{1}H NMR spectral instrument. A least-squares treatment of the Eyring equation where the transmission coefficient was taken to be unity gave the apparent values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$.[15] The results are summarized in Table II.

Product Analyses of Transmethylation. General Procedure. A solution of **5a** (22.6 mg, 0.056 mmol) in 0.25 mL of pyridine-d_5 was heated at 45 °C for 50 h. The solution was concentrated under reduced pressure, and the resulting suspension was subjected to preparative thin-layer chromatography on silica gel (elution with ethyl acetate). There were isolated 10.9 mg (80%) of sulfide (**10**, mp 65–66 °C) and 9.4 mg (68%) of methylpyridinium-d_5 hexafluorophosphate (mp 205–208 °C). For **10**: ^{1}H NMR ($CDCl_3$) δ 2.11 (s, 3 H), 3.31–5.07 (br s, 4 H), 6.90–7.30 (m, 6 H), and 7.41–7.72 (m, 2 H). By a similar procedure, reaction of **11** and **13–16** gave the corresponding sulfide (**12** and **17–20**) along with methylpyridinium salt in 66–85% yield.

Acknowledgment. We are indebted partially to a Grant-in-Aid for Scientific Research (No. 57430006 and 60303004), administered by the Ministry of Education, Science, and Culture of the Japanese Government. We also acknowledge helpful discussions with Professors K. Morokuma (The Institute for Molecular Science), F. Iwasaki (The University of Electro-Communications), and J. C. Martin (Vanderbilt University).

Registry No. 5a, 89027-69-0; **5b**, 103905-22-2; **5c**, 103905-16-4; **5d**, 103905-14-2; **5e** (Y = Cl), 103905-17-5; **5e** (Y = $SbCl_6$), 103905-19-7; **5e** (Y = PF_6), 103905-20-0; **6**, 87532-42-1; **11**, 10504-60-6; **13**, 89027-71-4; **14**, 103905-26-6; **15**, 76470-18-3; **16**, 103905-28-8; **18**, 103905-23-3; **20**, 103905-24-4; triethyloxonium hexachloroantimonate, 32646-67-3; trimethyloxonium hexachloroantimonate, 54075-76-2; pentachloroantimony, 7647-18-9; ammonium hexafluorophosphate, 16941-11-0; methyl lithium, 917-54-4; potassium hexafluorophosphate, 17084-13-8; methyl iodide, 74-88-4; thioanisole, 100-68-5; silver tetrafluoroborate, 14104-20-2; dimethylphenyl sulfonium tetrafluoroborate, 33613-52-4; 2-isopropylpyridine, 644-98-4; chloromethyl methyl sulfide, 2373-51-5; 4-isopropylpyridine, 696-30-0.