olefin. On the other hand, the TMM complexes bearing electron-withdrawing groups are more ambiguous. No clear preferences exist for the trifluoromethyl substituent, but the cyanide appears analogous to the methyl substituent in its positional selectivity. These latter predictions await experimental scrutiny.

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Novel Reaction Course of Oxosulfonium Ylides to Sulfurane Oxides

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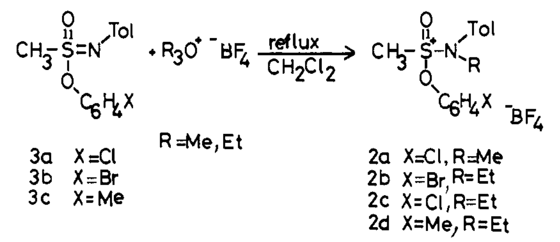
Five-membered dialkoxyspirosulfurane oxides have been prepared by oxidation of the corresponding sulfuranes.[1] Since the original work of Corey and Chaykovsky,[2] many reactions of oxosulfonium ylides have been reported. But no attempt to synthesize sulfurane oxides from oxosulfonium ylides has yet been made. In this communication we report the synthesis of aminodioxysulfurane oxides **1**, which are the first reported four-membered cyclic sulfurane oxides, by the reaction of oxosulfonium ylides with benzaldehyde.

Aminoaryloxyoxosulfonium salts **2** as starting materials were prepared by refluxing (2 h) a dichloromethane solution of the corresponding sulfoximines **3**[3] with 1.2 equiv of Meerwein reagent.[4] Isolation of **2** was carried out by gel chromatography over Sephadex LH-20 (80% crude yield). Recrystallization from methanol gave colorless crystals, identified as **2** by ^{1}H NMR spectra.



To a refluxing THF solution of **2a** (10 mmol) was added dropwise a *n*-hexane solution of *n*-BuLi (10 mmol). After 15 min, a THF solution of benzaldehyde (10 mmol) was added to the above solution at 50 °C in 10 min, and the resulting dark red solution was washed with water and extracted with ether; the ethereal solution was dried over $MgSO_4$. After evaporation of ether, sulfurane oxide **1a** was obtained by SiO_2 chromatography in 20% yield (solvent and eluant; dichloromethane–*n*-hexane).

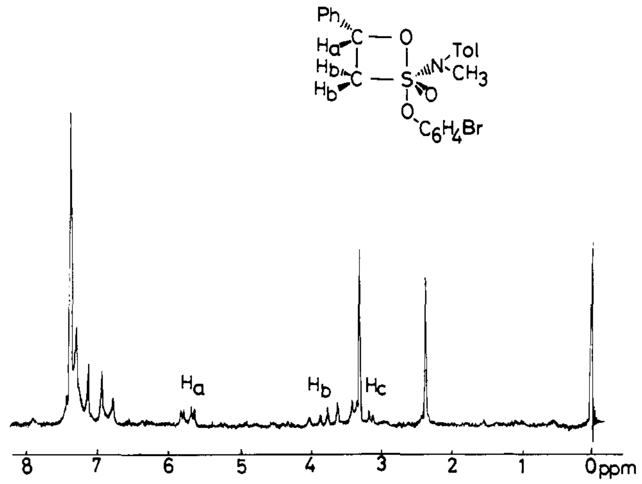
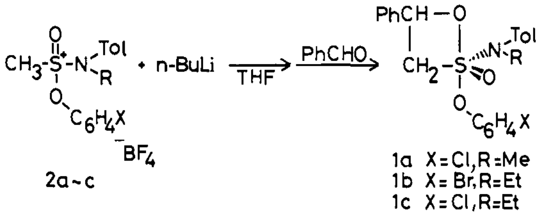


Figure 1. 60-MHz ^{1}H NMR spectrum of compound **1a**.

Recrystallization from methanol gave colorless crystals, mp 118–119 °C. Sulfurane oxides **1b** and **1c** were also obtained by the above method, mp 131–132 °C and 125–126 °C, respectively.[5,6]



The three quartet peaks of **1a** at 3.10, 3.68, and 5.66 ppm show a typical AMX pattern assigned to four-membered cyclic structure (Figure 1). But the peaks of **1b** to be assigned to the ring methylene and N–Et methylene are slightly different; this difference may be caused by the nonequivalence of the diastereotopic methylene protons of the N–Et group (Figure 2). The nonequivalence of geminal proton groups seen in the ^{1}H NMR spectra of **1** is consistent with a four-membered structure. Four-membered cyclic dioxyphosphoranes also show similar spectral patterns.[7] Since all known sulfurane oxides have trigonal-bipyramidal geometries, compounds **1** may also have the same ones.[1]

The reaction can be rationalized by an intramolecular mechanism; the ylides **4** obtained by treatment of **2** with *n*-BuLi attacked benzaldehyde to give betaines **5** in which the negatively charged O entered into bonding with the positively charged S,

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(4) **2a**: ^{1}H NMR ($CDCl_3$) δ 2.30 (s, 3, tol–Me), 3.63 (s, 3, N–Me), 4.11 (s, 3, S^+–Me), 7.15 (s, 4, tol), 7.50 (s, 4, OC_6H_4Cl). **2b**: ^{1}H NMR ($CDCl_3$) δ 1.15 (t, 3, J = 8.0 Hz, N–CH_2CH_3), 2.37 (s, 3, N–tol–Me), 3.83–4.37 (m, 2, N–CH_2CH_3), 4.09 (s, 3, S^+–Me), 7.20 (s, 4, N–tol), 7.51 (q, 4, OC_6H_4Br). **2c**: ^{1}H NMR ($CDCl_3$) δ 1.15 (t, 3, J = 7.0 Hz, N–CH_2CH_3), 2.40 (s, 3, N–tol–Me), 3.87–4.33 (m, 2, N–CH_2CH_3), 4.09 (s, 3, S^+–Me), 7.20 (s, 4, N–tol), 7.46 (s, 4, OC_6H_4Cl). **2d**: ^{1}H NMR ($CDCl_3$) δ 1.11 (t, 3, J = 7.0 Hz, N–CH_2CH_3), 2.33 (s, 3, N–tol–Me), 2.38 (O–tol–Me), 3.83–4.20 (m, 2, N–CH_2CH_3), 4.02 (s, 3, S^+–Me), 7.20 (s, 4, N–tol), 7.30 (s, 4, O–tol).

(5) **1a**: ^{1}H NMR ($CDCl_3$) δ 2.40 (s, 3, tol–Me), 3.24 (dd, 1, J_{ac} = 14.3 Hz, J_{bc} = 3.1 Hz, H_c), 3.27 (s, 3, N–Me), 3.68 (dd, 1, J_{ab} = 8.8 Hz, J_{bc} = 14.3 Hz, H_b), 5.66 (dd, 1, J_{ab} = 8.8 Hz, J_{ac} = 3.1 Hz, H_a), 6.83–7.33 (m, 13, aromatic); ^{13}C NMR, ($CDCl_3$) δ 20.97 (tol–Me), 38.87 (N–Me), 57.14 (S–CH_2–), 76.34 (PhCH–), 117.96, 126.13, 126.74, 128.25, 129.12, 129.44, 130.02, 137.49, 138.68, 155.71 (aromatic). M_r (vapor pressure osmometer), calcd 415.5; obsd 384 (solvent; benzene, at 45 °C). This result implies that the structure of sulfurane oxide is monomeric. **1b**: ^{1}H NMR ($CDCl_3$) δ 1.07 (t, 3, J = 7.3 Hz, N–CH_2CH_3), 2.36 (s, 3, tol–Me), 3.26 (dd, 1, J_{bc} = 14.7 Hz, J_{ac} = 1.5 Hz, H_c), 3.55, 3.79 (d, 2, J = 13.7 Hz, H_α and H_β), 3.75 (dd, 1, J_{bc} = 14.7 Hz, J_{ab} = 8.3 Hz, H_b), 5.71 (dd, 1, J_{ab} = 8.3 Hz, J_{ac} = 1.5 Hz, H_a), 6.80–7.35 (m, 13, aromatic). ^{13}C NMR ($CDCl_3$) δ 14.72 (N–CH_2CH_3), 21.02 (tol–Me), 46.80 (N-CH_2CH_3), 57.97 (S–CH_2–), 76.41 (PhCH–), 117.88, 126.10, 126.83, 128.68, 129.12, 129.41, 130.07, 136.08, 138.75, 155.71 (aromatic). **3c**: ^{1}H NMR ($CDCl_3$) δ 1.07 (t, 3, J = 7.1 Hz, N–CH_2CH_3), 2.36 (s, 3, tol–Me), 3.27 (dd, 1, J_{bc} = 15.0 Hz, J_{ac} = 2.4 Hz), 3.55, 3.78 (d, 2, J = 13.7 Hz, H_α and H_β), 3.74 (dd, 1, J_{bc} = 15.0 Hz, J_{ab} = 8.3 Hz, H_b), 5.70 (dd, 1, J_{ab} = 8.3 Hz, J_{ac} = 2.4 Hz, H_a), 6.81–7.34 (m, 13, aromatic). ^{13}C NMR ($CDCl_3$) δ 14.74 (CH_2CH_3), 21.04 (tol-Me), 46.83 (CH_2CH_3), 57.99 (S-CH_2–), 76.48 (PhCH–), 117.90, 126.13, 126.83, 128.92, 129.12, 129.44, 130.09, 136.12, 138.12, 138.78, 155.76 (aromatic).

(6) A new chiral center with the possible formation of two diastereoisomers of **1** will be generated by these reactions. But only one isomer was obtained, and the other was not observed in the ^{1}H NMR spectra of crude reaction mixtures.

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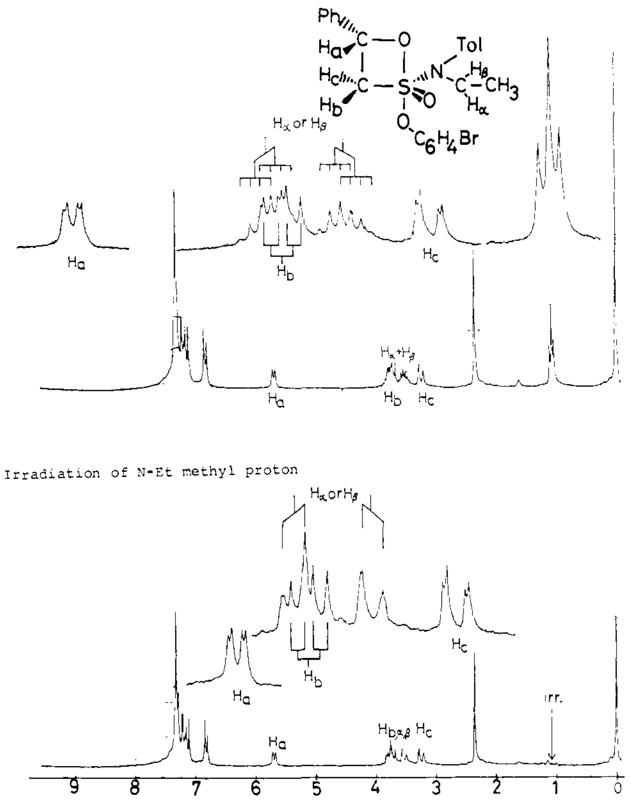
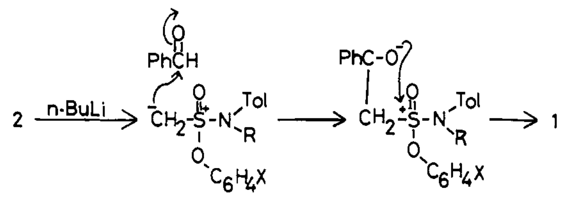


Figure 2. 200-MHz ^{1}H NMR spectra of compound **1b**.

forming unusual four-membered cyclic compounds resembling the intermediates of the Wittig reaction.



Gassman and Amick found that the reaction of aryloxysulfonium salts with bases at low temperature gave ortho-substituted phenols via [2,3]-sigmatropic rearrangement.[8] We recently synthesized diaminooxosulfonium salts by alkylation of the corresponding sulfoximines.[9] Their reaction with dimsylsodium gave the corresponding ylides, whose negatively charged parts rearranged to the ortho positions of the arylamino substituents to give dihydrobenzoisothiazole derivatives. On the other hand, Johnson and Rogers reported that the reaction of aminooxosulfonium ylides with carbonyl compounds in presence of bases yielded the corresponding epoxides and sulfinamides.[10] The present result differs entirely from the results cited above. We could thus find a new reaction pathway of oxosulfonium ylides.

According to Martin et al., the incorporation of the sulfurane function into a five-membered heterocyclic ring has a dramatic effect on its rates of reaction (reactivity order: acyclic, monocyclic, spirobicyclic).[11] We examined the reaction of **2d** with sodium phenoxide, intending to obtain an acyclic sulfurane oxide. Treatment of **2d** with sodium phenoxide afforded not an expected sulfurane oxide but only a mixture of decomposition products. And sulfurane oxide was not obtained by the benzaldehyde reaction of **2d**. The above results suggest that an acyclic aminodioxysulfurane oxide is ordinarily unstable, and a halogeno group in an aryloxy substituent is necessary to stabilize a sulfurane oxide. An additional factor in the stability of **1** might be the interaction between the lone pair of electrons of the nitrogen with the sulfurane oxide function. Law and Martin found evidence for such interaction between the sulfurane oxide functional group and the lone pair on carbon of an anion derives by the deprotonation of a methyl group attached to sulfur.

In summary, we have shown that aminodioxysulfurane oxides **1** were prepared by the reaction of aminoaryloxyoxosulfonium ylides with benzaldehyde via intramolecular addition of corresponding betaines. Although the general applicability of our results remains to be proved, it is clear that this is the first reaction pathway of oxosulfonium ylides to sulfurane oxides.

We are currently investigating the exact structure of **1** in greater detail.

Acknowledgment. We thank the Ministry of Education of Japan for financial assistance (Grant-in-Aid for Scientific Research, 56740220).

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(12) Satisfactory values of elemental analysis were obtained for new compounds except for **2a** and **2d**. Compound **2a** is a glassy substance, and **2d** is easily decomposed. M.p.: **2b**, 122–123; **2c**, 117–119; **2d**, 116–117 dec; **3a**, 76–77; **3b**, 90–91; **3c**, 101–102 °C.

Vibronic Spectra of Naphthalene and Naphthalene-d_8 Cations in Solid Argon

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There has been considerable recent research on optical spectroscopy of molecular cations in noble gas matrices. These studies have involved both stable and photosensitive cations such as hexafluorobenzene,[1] other fluorine-substituted benzene cations,[2] and diacetylene cation[3] on one hand and toluene[4] cycloheptatriene,[5] halotoluene,[6] and styrene cations[7] on the other. Naphthalene has been studied extensively by photoelectron spectroscopy,[8-11] and the absorption spectrum of naphthalene cation (hereafter N$^+$) has been observed in a variety of glassy matrices.[12-14] The absorption spectrum of N$^+$ in noble gas matrices provides both vibrational and electronic data, which may be compared to photoelectron spectra in order to better understand the ion itself and the ion-matrix interaction.

The cryogenic apparatus and photoionization source have been described previously.[15,16] After suitable outgassing, naphthalene

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