Ethoxy Group Scrambling in the Sterically Restricted Ethoxysulfonium Salts, 1-(Methylethoxysulfonio)-9-(methylthio)dibenzothiophene and Its Analogous Compounds

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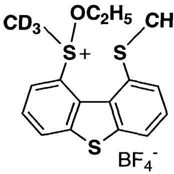
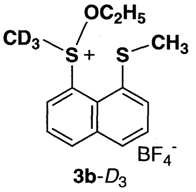
The ethoxy group migration of 1-(methylethoxysulfonio)-9-(methylthio)dibenzothiophene was identified by ^{1}H-NMR at 25 °C. The similar rearrangement of 1-(methylethoxysulfonio)-8-(methylthio)naphthalene was found in identical conditions. The ethoxy scrambling did not proceed in 2-(methylethoxysulfonio)-2'-(methylthio)biphenyl.

It is well known that the two sulfur atoms positioned in close proximity within the van der Waals S-S contact interact strongly each other.[1] Recently, we have reported that the dithia and diselena dications derived from 1,9-bis(arylchalcogeno)-dibenzochalcogenophenes (**1**) are generated in concd H_2SO_4 and react with H_2O to produce the corresponding sulfoxides and selenoxides in high yields.[2] Meanwhile, the photolysis of compound **1** was found to be influenced by the through-space interaction between the two chalcogen atoms at the 1,9-positions.[3] In the course of studies with respect to the through-space interaction of the alkoxysulfonium salts derived from 1-(methylsulfinyl)-9-(methylthio)dibenzothiophene (**2a**), the hydrolysis of 1-(trideuterated methylethoxysulfonio)-9-(methylthio)dibenzothiophene (**3a**-D_3) with aqueous NaOH was performed in CH_2Cl_2 at 25 °C to produce a 1:1 mixture of 1-(trideuterated methylsulfinyl)-9-(methylthio)dibenzothiophene (**2a**-D_3) and 1-(methylsulfinyl)-9-(trideuterated methylthio)-dibenzothiophene (**2a'**-D_3), quantitatively. Though the salt **3a**-D_3 was stable in $CDCl_3$ at -20 °C, the ethoxy group scrambling reaction proceeded at 25 °C. This paper reports the ethoxy group scrambling reaction of the salt **3a**-D_3 and 1-(trideuterated methylethoxysulfonio)-8-(methylthio)naphthalene (**3b**-D_3), and the different results of 2-(trideuterated methylethoxysulfonio)-2'-(methylthio)biphenyl (**3c**-D_3) and 1-(trideuterated methylethoxysulfonio)dibenzothiophene (**3d**-D_3) from the compounds **3a**-D_3 and **3b**-D_3.



3a-D_3



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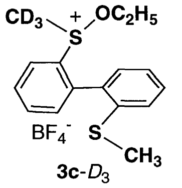

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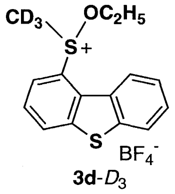
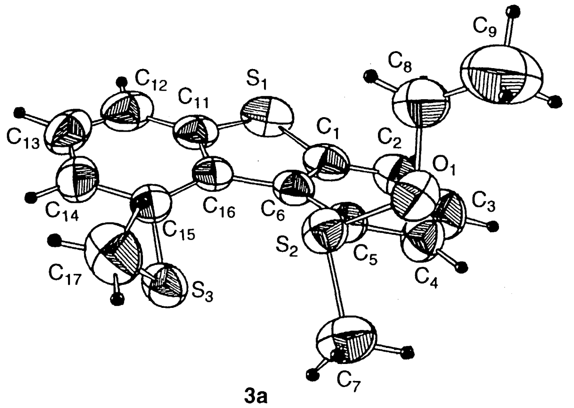


3d-D_3

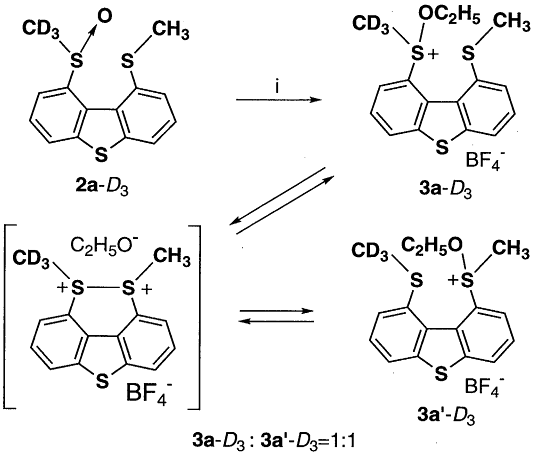


3a

Figure 1. ORTEP drawing of compound **3a** except for BF_4^-.

As a typical procedure for preparation of the alkoxysulfonium salts, the compound **2a** (292 mg, 1.0 mmol) in 2 ml of CH_2Cl_2 was treated with 1 M $(C_2H_5)_3O{\bullet}BF_4$ in CH_2Cl_2 (1.0 ml, 1 mmol) at -20 °C under Ar for 24 h to produce the compound **3a** in 70% yield (285 mg).[4] The salt **3a** was recrystallized from benzene and ether to give the suitable single crystals for measurement of X-ray crystallographic analysis. The structure of the salt **3a** was determined by the crystallographic analysis (Figure 1). In the structure of the compound **3a**, the S_2-O_1 bond lengths are 1.612(2) Å and the bond angles around the sulfonium sulfur atom are 100.2(1)° (O_1-S_2-C_5), 93.9(1)° (O_1-S_2-C_7), and 105.4(2)° (C_5-S_2-C_7), respectively. The S-S distance between S_2 and S_3 atoms and the torsional angle at the C_5-C_6-C_{16}-C_{15} position of the compound **3a** were found to be 2.88 Å and -15.6(5)° which are shorter length and smaller angle than those of the sulfoxide **2a**.[5] Meanwhile, the angle at the O_1-S_2-S_3 position of the sulfonium salt **3a** is 171.2°. These results suggest that the lone pair repulsion between the two sulfur atoms at the 1,9-positions of the compound **2a** decreases by the formation of the salt **3a**, and the two sulfur atoms interact strongly each other by the electric attractive force.

As shown in Figure 1, the sulfonio and sulfenyl sulfur atoms at the 1,9-positions are in close proximity. In order to examine the reactivity of the two sulfur atoms at the 1,9-positions of the sulfonium salt **3a**, the deuterated sulfonium salt **3a**-D_3 was prepared by treatment of the compound **2a**-D_3 with $(C_2H_5)_3O{\bullet}BF_4$ in CH_2Cl_2 at -20 °C (D=99%). The hydrolysis of the sulfonium salt **3a**-D_3 was carried out by hydroxide anion in CH_2Cl_2 at -20 °C to produce the starting sulfoxide **2a**-D_3 quantitatively. When the hydrolysis of the compound **3a**-D_3 with aqueous NaOH was performed in CH_2Cl_2 at 25 °C, the sulfoxide obtained quantitatively was found to be a 1:1 mixture



Scheme 1. Reagent and conditions: i: $(C_2H_5)_3OBF_4$, CH_2Cl_2, -20 °C, Ar.

of the compounds **2a**-D_3 and **2a'**-D_3 by ^{1}H-NMR. Therefore, the salt **3a**-D_3 was dissolved in $CDCl_3$ at -20 °C and its ^{1}H-NMR was measured at -20 °C and 25 °C. The salt **3a**-D_3 was stable in $CDCl_3$ at -20 °C and the ^{1}H-NMR spectrum did not change at all. Interestingly, it was found that the integral ratio of the methylsulfonio protons at the 1-position increased gradually at 25 °C in the ^{1}H-NMR spectrum of the compound **3a**-D_3 and that of the methylsulfenyl protons at the 9-position decreased, revealing that the ethoxy group scrambling reaction in the salt **3a**-D_3 proceeded in $CDCl_3$ at this temperature. The ethoxy group migration equilibrated in a few hours at 25 °C to give a 1:1 mixture of the sulfonium salts **3a**-D_3 and **3a'**-D_3 (Scheme 1). These results suggest that the nucleophilic attack of the hydroxide anion proceeds only on the sulfonium sulfur atom at the 1-position and not on the sulfenyl sulfur atom at the 9-position of the compound **3a**-D_3, and the mixture of the sulfoxides **2a**-D_3 and **2a'**-D_3 was obtained by the hydrolysis of the ethoxysulfonium salt, after scrambling of the ethoxy group in the solution at 25 °C. Apparently, the ethoxy group scrambling reaction should accompany with the oxidation of the sulfenyl sulfur atom at the 9-position and the reduction of the sulfonio sulfur atom at the 1-position.

The ethoxy group migration of the salt **3b**-D_3 (D=95%) which was prepared by treatment of 1-(trideuterated methylsulfinyl)-8-(methylthio)naphthalene (**2b**-D_3) with $(C_2H_5)_3O{\bullet}BF_4$ was found to proceed similarly to produce a 1:1 mixture of the sulfonium salts **3b**-D_3 and **3b'**-D_3. On the other hand, the salts **3c**-D_3 and **3d**-D_3 were derived from 2-(trideuterated methylsulfinyl)-2'-(methylthio)biphenyl (**2c**-D_3) and 1-(trideuterated methylsulfinyl)dibenzothiophene (**2d**-D_3) similarly as described above (**2c**-D_3: D=95%; **2d**-D_3: D=99%). Interestingly, the ethoxy group scrambling of the salt **3c**-D_3 was not observed at all in the identical reaction condition. The ethoxy group scrambling of the salt **3c**-D_3 did not proceed even at 55 °C. Furthermore, though a 1:1 mixture of 1-(methylthio)dibenzothiophene and the salt **3d**-D_3 was dissolved in $CDCl_3$ similarly, the ethoxy group migration could not be observed by ^{1}H-NMR spectroscopy at 25 °C. Therefore, this ethoxy scrambling reaction essentially requires one more sulfur atom in close proximity to initiate the rearrangement reaction. Furthermore, the through-space interaction between the two sulfur atoms was demonstrated to effects the ethoxy group scrambling of the sulfonium salts **3a** and **3b**.

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References and Notes

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4 **3a**: mp. 141-144 °C; ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.18 (t, J=7.0 Hz, 3H), 2.83 (s, 3H), 3.76 (dq, J=9.7, 7.0 Hz, 1H), 4.05 (s, 3H), 4.28 (dq, J=9.7, 7.0 Hz, 1H), 7.63 (t, J=7.8 Hz, 1H), 7.72 (d, J=7.8 Hz, 1H), 7.89 (t, J=7.8 Hz, 1H), 7.91 (d, J=7.8 Hz, 1H), 8.21 (d, J=7.8 Hz, 1H), 8.23 (d, J=7.8 Hz, 1H); FABMS (m/z) 321 $(M\text{-}BF_4)^+$; Anal Found: C, 46.86; H, 4.19%. Calcd for $C_{16}H_{17}OS_3{\bullet}BF_4$: C, 47.06; H, 4.19%. the crystal data: monoclinic, $P2_1/a$, a=8.004(1) Å, b=27.002(0) Å, c=8.587(2) Å, β=91.37(0)°, V=1855.4 Å^3, Z=4, ρ=1.46 g/cm^3, μ(Mo*K*α)=4.2 cm^{-1}, 4173 with $Fo^2>3.0\sigma(Fo^2)$, R=0.051 (R_w=0.052); **3d**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.47 (t, J=7.0 Hz, 3H), 3.74 (s, 3H), 4.51 (dq, J=9.4, 7.0 Hz, 1H, CH_2), 4.28 (dq, J=9.4, 7.0 Hz, 1H), 7.62 (ddd, J=8.1, 7.4, 1.0 Hz, 1H), 7.68 (ddd, J=8.1, 7.4, 0.9 Hz, 1H), 7.85 (t, J=8.0 Hz, 1H), 7.96 (dd, J=7.4, 1.0 Hz, 1H), 8.21 (d, J=8.0 Hz, 1H), 8.30 (dd, J=8.1, 0.9 Hz, 1H), 8.30 (d, J=8.0 Hz, 1H); FABMS (m/z) 275 $(M\text{-}BF_4)^+$.

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