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Through-bond interaction between sulfonium and sulfenyl sulfur atoms having anthracene and naphthalene spacers

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Abstract

The reaction of 9-(methylsulfinyl)-10-(methylthio)anthracene with trifluoroacetic anhydride followed by quenching with aqueous $NaHCO_3$ gives 9,9-bis(methylthio)-10-anthraquinone. The dithia dication and/or the corresponding carbodication via through-bond interaction between sulfonium and sulfenyl sulfur atoms is proposed as an intermediate. © 1999 Elsevier Science Ltd. All rights reserved.

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In the past two decades the study of σ-bonded dithia dications formed by intramolecular through-space interaction between sulfur atoms in close proximity has been of considerable interest.[1] Recently, Nenajdenko and we have extended this chemistry to intermolecular reactions.[2,3] The Pummerer reaction of mono-sulfoxides of *p*-bis(methylthio)-aromatics (aromatics=benzene, biphenyl, diphenyl sulfide, etc.) with trifluoroacetic anhydride (TFAA) gives a mixture of the corresponding mono-Pummerer product, bis-Pummerer product, and bis-sulfide in an *n*:1:1 ratio ($n \geq 2$), wherein intermolecular interaction between sulfonium and sulfenyl sulfur atoms is much more favorable than the through-bond interaction between them (Scheme 1).[3] In the course of the search for aromatic spacers, we have noticed the distinctive behavior of 9-(methylsulfinyl)-10-(methylthio)anthracene (**1**) and 1-(methylsulfinyl)-4-(methylthio)naphthalene (**8**). Herein, we report the reactions of **1** and **8** with acids or acid anhydrides, which proceed via the dithia dication **B** and/or the corresponding carbodication **C** as a result of through-bond interaction between sulfonium and sulfenyl sulfur atoms.[4]

The reaction of the mono-sulfoxide **1** with 5 equiv. of TFAA in CH_2Cl_2 at −20°C for 5 min followed by quenching with aqueous $NaHCO_3$ gave 9,9-bis(methylthio)-10-anthraquinone (**3**),[5] together with 9,10-anthraquinone (**4**) and 9,10-bis(methylthio)anthracene (**5**), in 79, 5, and 6% isolated yields, respectively (Scheme 2). This reaction is independent of the concentration of **1**. In marked contrast to other mono-sulfoxides of *p*-bis(methylthio)-aromatics,[3] it is noted that the reaction of **1** with TFAA does not afford

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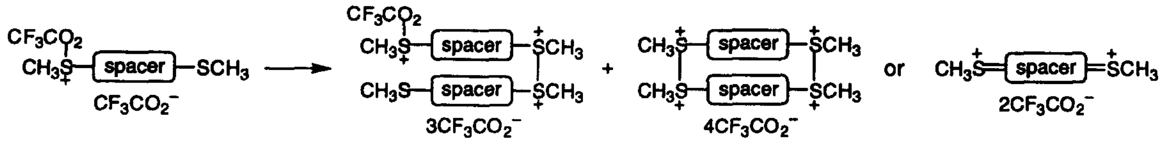
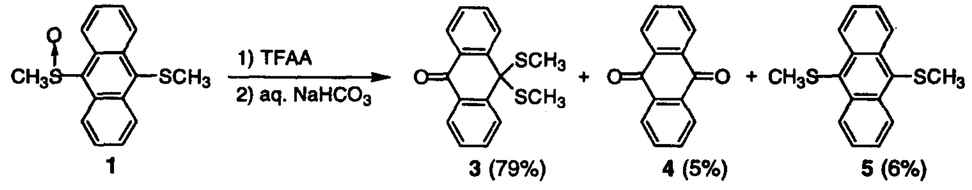


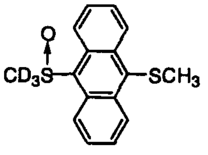
Scheme 1.

any Pummerer products. The ^{13}C NMR spectrum of **3** showed two characteristic peaks at δ 57.61 and 182.53 due to the quaternary carbon of dithio acetal and the carbonyl carbon, respectively. Furthermore, the molecular structure of **3** was confirmed by the X-ray diffraction analysis (Fig. 1).[6]

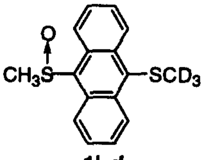


Scheme 2.

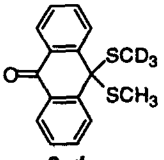
The reaction of **1** with TFAA in $CDCl_3$ at −20°C was monitored by NMR spectroscopy. The ^{1}H NMR spectrum exhibited only two singlet peaks at δ 2.28 and 7.54, and the ^{13}C NMR spectrum showed a peak at δ 87.98 which is characteristic of the quaternary carbon attached with methylthio and trifluoroacetate groups. These data are in good agreement with the structure of 9,10-bis(methylthio)-9,10-bis(trifluoroacetoxy)anthracene (**2**) (Scheme 3).[5,7] The reaction of a 1:1 mixture of 9-(trideuteriomethylsulfinyl)-10-(methylthio)anthracene (**1**-d_3) and 9-(methylsulfinyl)-10-(trideuteriomethylthio)anthracene (**1'**-d_3) with TFAA followed by quenching with aqueous $NaHCO_3$ afforded 9-(methylthio)-9-(trideuteriomethylthio)-10-anthraquinone (**3**-d_3) as a sole product for **3**, indicating that the conversion of **2** into **3** is an intramolecular rearrangement.



1-d_3



1'-d_3



3-d_3

The formation of **2** from **1** and TFAA strongly suggests through-bond interaction between two sulfur atoms during the course of the reaction. The plausible mechanism is as follows (Scheme 3). The reaction of **1** with TFAA gives the trifluoroacetoxysulfonium salt **A**, which could be converted into the transient

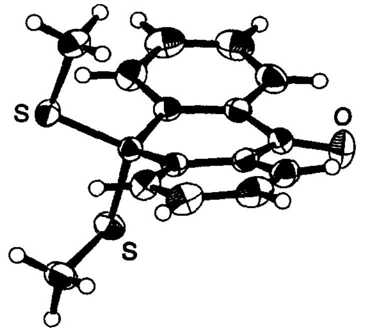
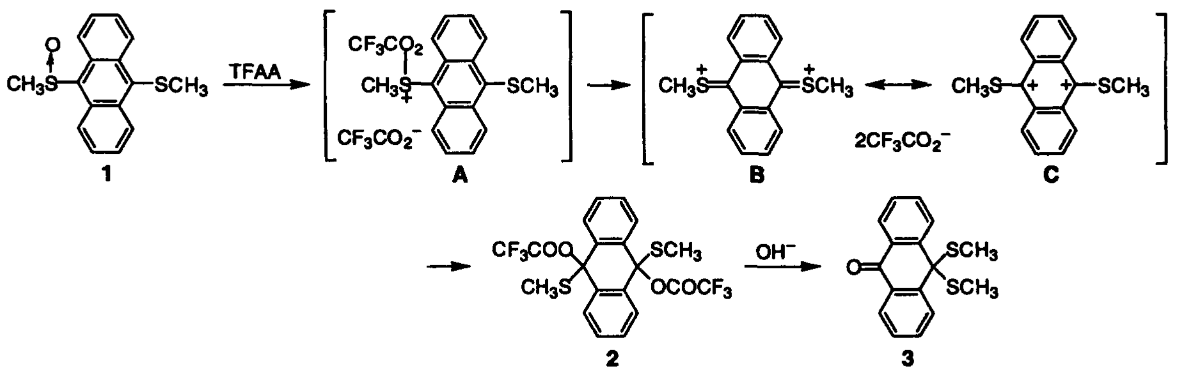


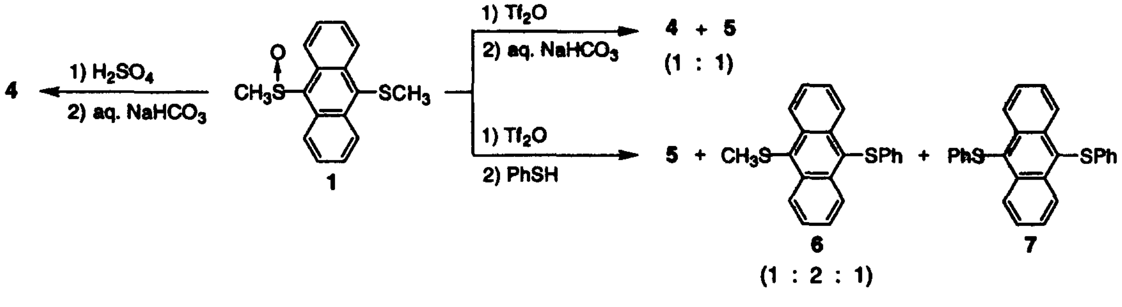
Figure 1. Molecular structure of **3** (35% probability ellipsoids)



Scheme 3.

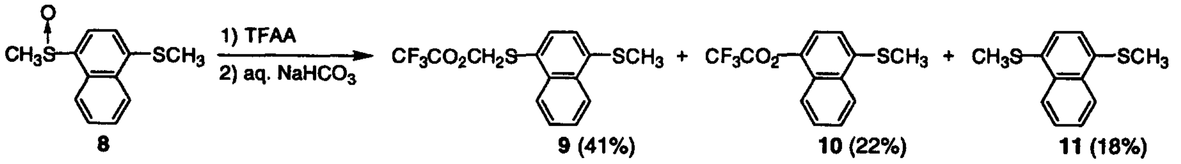
quinoid-like dithia dication **B** and/or the corresponding carbodication $C^{8,9}$ via through-bond interaction between sulfonium and sulfenyl sulfur atoms. It is known that, in 9,10-disubstituted anthracene dications, substantial positive charge is localized at the C9 and C10 positions.[9] Double addition of trifluoroacetates to **B** and/or **C** could produce **2**. Hydrolysis of the trifluoroacetate group in **2** followed by intramolecular rearrangement of the methylthio group from C9 to C10 affords **3**.

Further evidence for the formation of **B** and/or **C** via through-bond interaction comes from the reactions of **1** with H_2SO_4 and trifluoromethanesulfonic anhydride (Tf_2O),[8] wherein the neucleophilicity of these counter ions generated is lower than that of trifluoroacetate. Treatment of **1** with H_2SO_4 at room temperature for 5 min followed by quenching with $NaHCO_3$ quantitatively gave 9,10-anthraquinone (**4**) and dimethyl disulfide (Scheme 4), in marked contrast to 1-(methylsulfinyl)-4-(methylthio)benzene.[10] This result supports the formation of **B** and/or **C** followed by the attack of H_2O on the carbocations to afford **4**. The reaction of **1** with 1 equiv. of Tf_2O in CH_2Cl_2:CH_3CN (v/v 2:3) at –20°C for 5 min followed by quenching with aqueous $NaHCO_3$ quantitatively afforded a 1:1 mixture of **4** and 9,10-bis(methylthio)anthracene (**5**) (Scheme 4). When quenched with 2 equiv. of thiophenol, a mixture of **5**, 9-(methylthio)-10-(phenylthio)anthracene (**6**), and 9,10-bis(phenylthio)anthracene (**7**) was exclusively obtained in a 1:2:1 ratio together with diphenyl-, methylphenyl-, and dimethyl disulfides.



Scheme 4.

The reaction of 1-(methylsulfinyl)-4-(methylthio)naphthalene (**8**) with TFAA under the same conditions as Scheme 2 afforded the normal mono-Pummerer product **9**, 1-(methylthio)-4-(trifluoroacetoxy)naphthalene (**10**), and the bis-sulfide **11** in 41, 22, and 18% yields, respectively (Scheme 5). A bis-Pummerer product which would be produced via intermolecular through-space interaction was detected in only trace amounts. The formations of **10** and **11** could result from through-bond interaction between sulfur atoms. Single addition of trifluoroacetate to a type **B** and/or **C** of naphthalene followed by the attack of another trifluoroacetate on the sulfur atom of the resulting cationic *O,S*-acetal could give **10** and methylsulfenyl trifluoroacetate, which could be reacted with **8** to afford **11**.[4c]



Scheme 5.

In summary, we have demonstrated through-bond interaction between sulfonium and sulfenyl sulfur atoms having anthracene and naphthalene spacers. This result could be attributed to the stability of the dication of polycyclic arenes.[8b,9] Thus, the interchange of intramolecular through-bond and intermolecular through-space interactions between sulfur atoms of *p*-bis(methylthio)-aromatics can be controlled by the nature of the aromatic spacers.[3,10]

Acknowledgements

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5. Spectral data for **2**: ^{1}H NMR ($CDCl_3$, –20°C) δ 2.28 (s, 6H), 7.54 (s, 8H); ^{13}C NMR ($CDCl_3$, –20°C) δ 15.17, 87.98, 118.34 (q, $^1J_{CF}$=287.5 Hz), 124.40, 129.56, 131.07, 154.17 (q, $^2J_{CF}$=43.9 Hz); ^{19}F NMR ($CDCl_3$, –20°C) δ –76.88. Data for **3**: mp 91–92°C; ^{1}H NMR ($CDCl_3$, rt) δ 1.62 (s, 6H), 7.47 (t, J=7.4 Hz, 2H), 7.71 (t, J=7.0 Hz, 2H), 8.27 (d, J=8.1 Hz, 2H), 8.35 (d, J=8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, rt) δ 13.96, 57.61, 126.22, 128.03, 129.96, 131.95, 134.20, 143.58, 182.53; EI-MS *m/z* 287 (M^++1). Anal. calcd for $C_{16}H_{14}OS_2$: C, 67.10; H, 4.93. Found: C, 67.17; H, 5.10.
6. Crystal data for **3**: $C_{16}H_{14}OS_2$, M=286.41, 0.50×0.50×0.60 mm, triclinic, space group $P\bar{1}$, a=8.296(3), b=12.406(3), c=7.424(4) Å, α=90.97(3), β=112.47(3), γ=102.62(2)°, V=684.7(5) Å^3, Z=2, D_c=1.389 g cm^{-3}, μ(Mo-Kα)=3.76 cm^{-1}, T=296 K, $2\theta_{max}$=55.0°, 3365 reflections measured, 3150 unique (R_{int}=0.009). The refinement (215 variables) based on F converged with R=0.033, R_w=0.031, and GOF=1.23 using 2604 unique reflections (I>3.0$\sigma(I)$).
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10. Treatment of 1-(methylsulfinyl)-4-(methylthio)benzene with H_2SO_4 causes an oxygen migration reaction to give a mixture of the mono-sulfoxide, the bis-sulfoxide, and the bis-sulfide, but not benzoquinone. Kobayashi, K.; Obinata, T.; Furukawa, N. *Chem. Lett.* **1997**, 1175.