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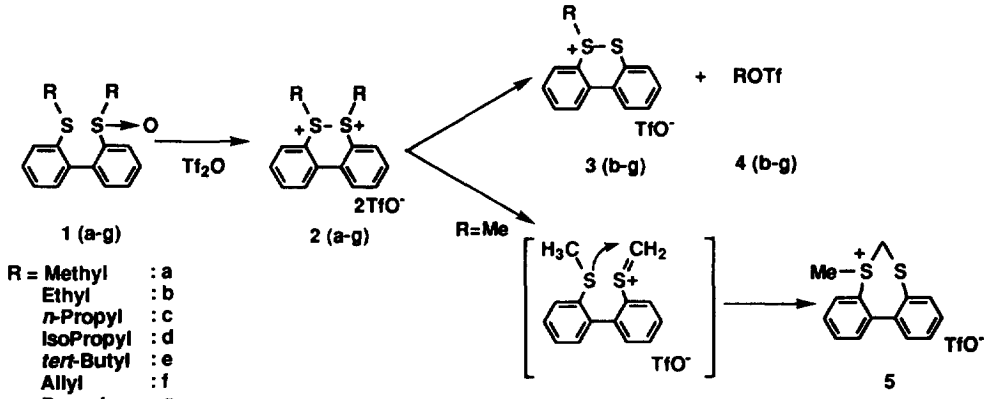
Activation and Facile Dealkylation of Monooxides of 2,2'-Bis(alkylthio)biphenyl with Triflic Anhydride *via* Dithiadications: A New Method for Preparation of Thiasulfonium Salts

Hidetaka Shima, Ryoji Kobayashi, Tatsuya Nabeshima and Naomichi Furukawa*

Tsukuba Advanced Research Alliance Center, Department of Chemistry, University of Tsukuba, Tsukuba, Ibaraki 305, Japan

Abstract: Monooxides of 2,2'-bis(alkylthio)biphenyl undergo facile monodealkylation on treatment with triflic anhydride to afford the corresponding thiasulfonium salts except bis(methylthio) derivative. The reaction proceeds *via* an initial formation of the corresponding dithiadications.

Dications of chalcogens are of considerable current interest in heteroatom chemistry. Monooxides of cyclic bissulfides, i.e., 1,5-dithiacyclooctane[1,2] and dinaphtho[1,8-bc]-1,5-dithiocin[3] undergo deoxygenation on treatment with conc. H_2SO_4 or triflic anhydride (Tf_2O) to afford readily the corresponding *stable* dithiadications *via* through space interaction between the sulfur atoms. Other dithiadications which have an acyclic structure have also been reported but have not been studied well due to its instability.[4] Our attempt here to provide dications of acyclic 2,2'-bis(alkylthio)biphenyl using the corresponding monooxides has been successfully achieved, but unexpectedly, facile monodealkylation of these dithiadications was found to yield the thiasulfonium salts in good yields. In this paper, we report a new facile monodealkylation proceeding *via* the initial formation of highly reactive dithiadications 2 as shown in Scheme 1.



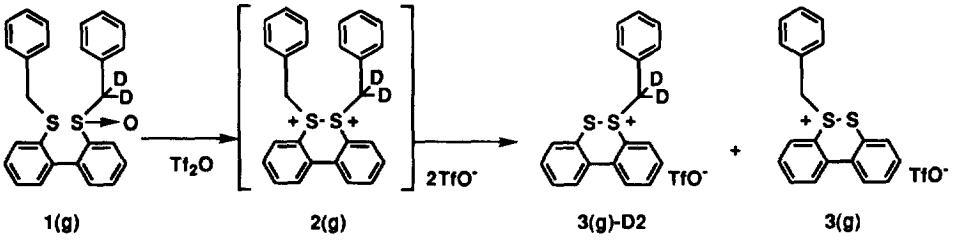
Scheme 1

Monooxides of 2,2'-bis(alkylthio)biphenyl **1(a-g)** were prepared from the corresponding disulfides in good yields. Typically, sulfoxide **1(a)** [R=Me] was treated with Tf_2O which is used as a common reagent to prepare the dithiadications. When **1(a)** was treated with 1 equivalent of Tf_2O in dry CD_3CN at -45°C and its ^1H- and ^{13}C-NMR spectra were measured in situ, no evidence for formation of dithiadication **2(a)** [R=Me] on the NMR spectroscopy was obtained. Instead, in the ^1H-NMR spectrum new two doublet peaks appeared at δ 5.14 and 5.34 ppm (J=14.0 Hz) together with one methyl singlet peak at δ 2.68 ppm. On a preparative scale and after isolation, this product was assigned to the methylsulfonium salt **5** by ^1H-,^{13}C- and ^{19}F-NMR and FAB-MS spectra.[5] In order to determine whether the formation of methylsulfonium salt **5** proceeds *via* dithiadication **2(a)** or not, deuterium-labeling of **1(a)** on the sulfinylmethyl proton was carried out by H-D exchange reaction of **1(a)** under alkaline conditions in THF and deuterated **1(a)-D3** was subjected to the reaction under the same conditions. In the resulting deuterated methylsulfonium salt, the integral ratio of the methyl to the methylene proton was found to be 1:5.1 in the ^1H-NMR.(In the non-deuterated **5**, the ratio of the methyl to the methylene proton is 1:0.67.) This result strongly suggests that dithiadication **2(a)** is produced initially and the deprotonation should be the rate-determining step in the reaction, since proton-distribution in **5** suggests that the isotope effect (k_H/k_D) in the step of proton abstraction is 7.7. A similar isotope effect of proton abstraction was reported in the Pummerer rearrangement of 1,5-dithiacyclooctane (1,5-DTCO) monooxide with Ac_2O (k_H/k_D=1.7).[6] The mechanism of this reaction is shown in Scheme 1.

Similarly, **1(b)** was subjected to react with Tf_2O in an NMR-tube as described above. In this case, however, one set of symmetrical peaks: one triplet at 1.43 ppm of the methyl group and a multiplet peak at 3.80-3.95 ppm of the methylene group were obtained in the ^1H-NMR spectra suggesting the generation of dithiadication **2(b)** at -45°C, which was also supported by the ^{13}C-and ^{19}F-NMR. However, the peaks were found to change gradually to nonsymmetrical peaks: two triplet peaks at 1.41 and 1.56 ppm of the methyl group, a multiplet peak at 3.15-3.85 ppm and a quartet peak at 4.68 ppm of the methylene group in the ^1H-NMR spectra. Since there are few reports about the decomposition of dithiadications,[4] we tried to isolate this decomposition product. On a preparative scale and after removal of CH_3CN, the reaction mixture was washed with dry CH_2Cl_2-Et_2O and the residue was recrystallized from CH_2Cl_2-Et_2O. Pale yellow crystals were obtained and their ^1H-,^{13}C-, ^{19}F-NMR, and FAB-MS spectra and elemental analysis clearly indicate the formation of ethylthiasulfonium salt **3(b)**.[7] It is concluded that **3(b)** is apparently generated *via* the deethylation from one of the two ethyl groups on the sulfur atoms in the dithiadication **2(b)** by *triflate anion* (TfO^-). Actually, ethyl triflate **4(b)** was observed together with **3(b)**. **4(b)** gave the identical peaks with that of the authentic compound[8] on the ^1H-,^{13}C- and ^{19}F-NMR. Similarly, in the reaction of **1(c)** with 1 equivalent of Tf_2O, dithiadication **2(c)** was once generated and then a facile depropylation from one of the propyl groups on the sulfur atoms on **2(c)** occurred to produce propylthiasulfonium salt **3(c)**[9] in good yield, together with propyl triflate **4(c)** which gave identical peaks on the ^1H-,^{13}C- and ^{19}F-NMR with that of the authentic compound prepared independently from iodopropane and silver triflate.[10]

The same reactions using the sulfoxides **1(d-g)** bearing carbonium ion stabilized alkyl groups such as isopropyl, *tert*-butyl, allyl, and benzyl groups on the sulfur atoms were examined. The formation of dithiadications **2(d-g)** was not observed at all even at -45°C; instead, direct formation of thiasulfonium salts

3(d, f and g) and alkyl triflate **4(d, f and g)** was observed by ^{1}H- and ^{13}C-NMR. (The reaction of **1(e)** gave a complex mixture because a large steric hindrance of the two *tert*-butyl groups would prevent the formation of an S-S bond to produce dithiadication **2(e)**.) The dithiadications **2(d, f, and g)** would be very unstable due to the high leaving ability of the substituents as a cation on the sulfur atoms. Since there is no discrete evidence for the formation of dithiadications **3(d, f,** and **g)**, the D-labelled experiment of **1(g)** was carried out. Typically, deuterated **1(g)-D2** prepared by H-D exchange reaction of **1(g)** was allowed to react under the same conditions, and the deuterium content in the benzylthiasulfonium salt was found to be reduced to nearly 50% of the starting **1(g)-D_2**, revealing that the benzylthiasulfonium salt should be a 1:1 mixture of **3(g)-D_2** and **3(g)**. These results can be explained rationally in terms of the initial formation of dithiadication **2(g)** as a highly reactive intermediate in which the two benzyl groups become equivalent. (Scheme 2)



Scheme 2

To obtain further experimental evidence for the formation of dithiadication **2(g)**, the reaction of monosulfoxide **1(g)** with Tf_2O in the presence of 2 equivalents of thiophenol was carried out at -55°C, to produce both the reduced 2,2'-bis(benzylthio)biphenyl and oxidized diphenyl disulfide in 58 and 56% yields respectively, though without Tf_2O no reaction took place at all. Therefore, the present investigation also supports the formation of dithiadication **2(g)** as an intermediate which can accept electrons from highly oxidizable thiophenol.[11]

In conclusion, the reaction of the monooxides of 2,2'-bis(alkylthio)biphenyl **1** with Tf_2O was found to give highly activated dithiadications **2**, from which either deprotonation of the methyl groups on the sulfur atoms to produce ring-contracted methylsulfonium salt **5** in the case of **2(a)** or monodealkylation on the sulfur atoms to produce thiasulfonium salts **3** in the case of **1(b,c,d,f,** and **g)** readily occurs. The reaction mode of the dealkylation of the alkyl groups would be general, except in the case of **2(a)** [R=Me] where the deprotonation should be exclusive due to the lowest pKa value of the methyl group among other alkyl groups. Our present procedure to prepare various thiasulfonium salts is new, as compared to the known methods by the monoalkylation of disulfides with alkyl halides in the presence of heavy metal salts or with trialkyloxonium salts.[12-14] The study of the two reaction modes and the reactions of other monosulfoxides such as 1,8-bis(alkylthio)naphthalenes and 1,3-bis(alkylthio)propanes with Tf_2O is also proceeding in this laboratory.

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5. pale yellow oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 2.68 (s, 3H), 5.14 (d, J=14.0 Hz, 1H), 5.34 (d, J=14.0 Hz, 1H), 7.56 (d, J=7.5 Hz, 1H), 7.61 (t, J=7.5 Hz, 1H), 7.64 (d, J=7.5 Hz, 1H), 7.69 (t, J=7.5 Hz, 1H), 7.72 (t, J=7.5 Hz, 1H), 7.89 (d, J=7.5 Hz, 1H), 7.93 (t, J=7.5 Hz, 1H), 7.96 (d, J=7.5 Hz, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 28.0, 60.7, 120.6, 128.7, 130.1, 130.6, 131.7, 132.6, 133.9, 135.9, 136.2, 136.5, 142.2, 143.4; ^{19}F-NMR (254 MHz) δ -79.7; FABMS m/z 245 $(M\text{-}OTf)^+$. Similar cyclic sulfonium salts such as 1,3-dithiane-1-methyl sulfonium salt were reported. Stahl, I.; Gosselck, J. *Tetrahedron* **1971**, *29*, 2323-2325.
6. Kawada, A.; Furukawa, N. unpublished results.
7. pale yellow crystals. mp. 100-101°C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.41 (t, J=7.2 Hz, 3H), 3.15-3.30 (brs, 1H), 3.70-3.85 (brs, 1H), 7.65 (t, J=7.9 Hz, 1H), 7.69 (t, J=7.9 Hz, 1H), 7.77 (t, J=7.9 Hz, 1H), 7.78 (d, J=7.9 Hz, 1H), 7.92 (t, J=7.9 Hz, 1H), 8.07 (d, J=7.9 Hz, 1H), 8.09 (d, J=7.9 Hz, 1H), 8.28 (d, J=7.9 Hz, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 9.2, 39.5, 118.0, 120.0, 129.0, 129.6, 130.5, 131.3, 132.0, 132.1, 132.3, 132.4, 133.7, 136.0; ^{19}F-NMR (254 MHz) δ -79.4; FABMS m/z 245 $(M\text{-}OTf)^+$; Anal. Calcd for $C_{15}H_{13}F_3O_3S_3$: C,45.68, H, 3.32%. Found: C, 45.38, H, 3.04%.
8. ^{1}H-NMR (270 MHz, $CDCl_3$) δ 1.56 (t, J=7.2 Hz, 3H), 4.68 (q, J=7.2 Hz, 2H); ^{13}C-NMR (68 MHz, $CDCl_3$) δ 15.2, 74.6; ^{19}F-NMR (254 MHz) δ -76.0.
9. pale yellow crystals. mp. 95-96°C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.01 (t, J=7.3 Hz, 3H), 1.73- 1.82 (m, 2H), 3.10-3.25 (brs, 1H), 3.65-3.70 (brs, 1H), 7.66 (t, J=7.9 Hz, 1H), 7.69 (t, J=7.9 Hz, 1H), 7.77 (t, J=7.9 Hz, 1H), 7.78 (d, J=7.9 Hz, 1H), 7.92 (t, J=7.9 Hz, 1H), 8.08 (d, J=7.9 Hz, 1H), 8.10 (d, J=7.9 Hz, 1H), 8.23 (d, J=7.9 Hz, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 12.1, 18.2, 45.4, 118.1, 119.9, 129.0, 129.7, 130.4, 131.3, 131.8, 132.1, 132.3, 132.5, 133.8, 136.0; ^{19}F-NMR (254 MHz) δ -79.5; FABMS m/z 259 $(M\text{-}OTf)^+$; Anal. Calcd for $C_{16}H_{15}F_3O_3S_3$: C, 47.05, H, 3.70%. Found: C, 46.65, H, 3.74%.
10. ^{1}H-NMR (270 MHz, $CDCl_3$) δ 1.05 (t, J=7.5 Hz, 3H), 1.84-1.90 (m, 2H), 4.51 (t, J=6.4 Hz, 2H); ^{13}C-NMR (68 MHz, $CDCl_3$) δ 9.7, 22.7, 79.1; ^{19}F-NMR (254 MHz) δ -76.0. Brian, L. B.; Robert, N. H.; Khosrow, L. *J. Chem. Soc., Perkin 1.* **1980**, 2887-2893.
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