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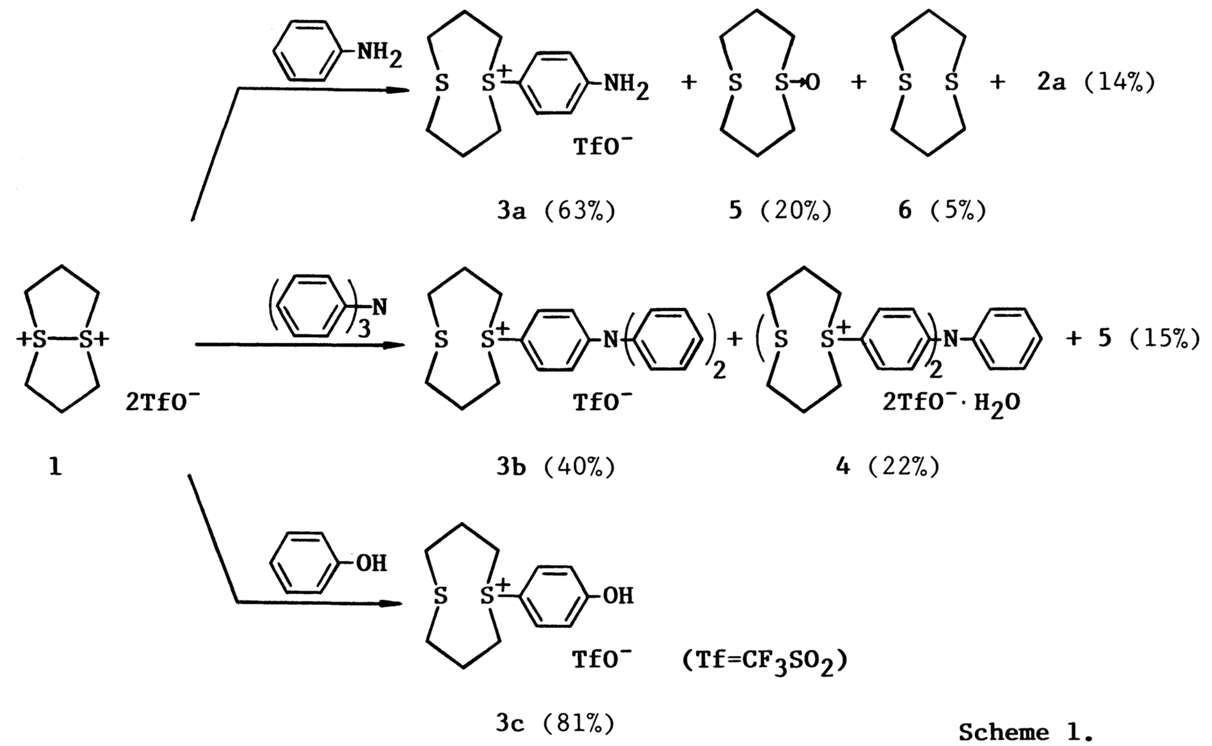
A New Mode of Aromatic Substitution and Redox Reaction of Substituted Benzenes with Disulfide Dication: 1,5-Dithioniabicyclo[3.3.0]octane Bis(trifluoromethanesulfonate)

Hisashi FUJIHARA, Ryouichi AKAISHI, and Naomichi FURUKAWA*
Department of Chemistry, University of Tsukuba, Tsukuba, Ibaraki 305

Disulfide dication was found to react with several aromatics to give either the substitution or redox products. The reaction mode depends remarkably on the oxidation potential of the aromatics.

The dications with adjacent two positively charged heteroatoms are quite rare and their structures and reactivities are of considerable interest. As such an example, recently disulfide dications have been prepared.[1,2] However, the reactions using the disulfide dication have not been well explored because of the difficulties to obtain stable compounds. Recently, we succeeded in preparation of disulfide dication, 1,5-dithioniabicyclo[3.3.0]octane bis(trifluoromethanesulfonate) (**1**) as a remarkably stable crystalline salt which was first characterized by X-ray crystallographic analysis.[3] We report here the first observation of aromatic substitution and redox reaction in the reaction of disulfide dication salt **1** with various substituted benzenes having different oxidation potentials.[4]

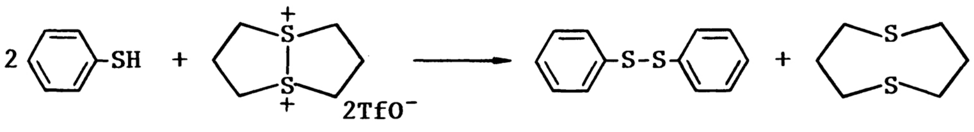
To a stirred solution of dication salt **1**[3] (0.54 mmol) in anhydrous acetonitrile (12 mL) was added a solution of aniline (**2a**) (0.54 mmol) in anhydrous acetonitrile (8 mL) under an Ar atmosphere at 0 °C and the whole mixture was stirred for 3 h. Then the reaction mixture was treated with aqueous sodium hydrogen carbonate solution. After usual work-up, the residue was chromatographed on silica-gel to afford the corresponding p-substituted sulfonium salt **3a**[5] was obtained in 63%, together with 1,5-dithiacyclooctane 1-oxide (**5**) in 20%, 14% recovery of **2a**, and 1,5-dithiacyclooctane (**6**) in 5% yields, respectively. Similar treatments of triphenylamine (**2b**) with **1** led to the corresponding monosulfonium salt **3b**[6] in 40%, together with an interesting disubstituted product **4**[7] in 22%, and **5** in 15% yields, respectively.



Scheme 1.

When phenol (**2c**) was similarly treated with dication **1**, the sulfonium salt **3c**[8] was obtained in 81% yield. These results are shown in Scheme 1. Structures of **3a**, **3b**, **3c**, and **4** were assigned based on the spectral data. Apparently, these substitution reactions of **2a**, **2b**, and **2c** with **1** occur only at the para-positions of the aromatic rings. On the other hand, anisole (**2d**) did not react with **1**, though it is well known that **2d** reacts with heterosulfonium cations to produce the corresponding aryl sulfonium salts.[9] The unreactivity of **2d** toward **1** seems to be due to the higher oxidation potential of **2d** than those of **2a**, **2b**, and **2c**.[4] These observations are quite different from those of the reactions of aromatic sulfide cation radical such as thianthrene cation radical ($Th^{+\cdot}$) with **2a** and **2d**. Namely, $Th^{+\cdot}$ reacts with **2d** to give the p-substituted product,[10,11] whereas, the reaction of $Th^{+\cdot}$ with **2a** affords the oxidation products instead of the substitution product.[11] This distinct difference in reactivity between **1** and $Th^{+\cdot}$ is probably due to the difference in the oxidation potentials of their precursors.[12]

In contrast to the above aromatics, treatments of thiophenol (**2e**) (2 equiv.) with dication **1** under the conditions described above gave diphenyl disulfide (**7**) as the oxidation product in 86% yield and sulfide **6** as the reduction product in 84% yield (Scheme 2). Several other thiols react with **1** to afford the corresponding disulfides and **6**.



2e **1** **7** (86%) **6** (84%)

Scheme 2.

On the other hand, the reactions of p-substituted aromatic amines such as 4-methoxyaniline (**8**) and tris(4-bromophenyl)amine (**9**) with dication **1** were carried out as follows. When a solution of **8** (2 equiv.) in anhydrous CH_3CN was added to a solution of **1** in anhydrous CH_3CN at 0 °C, the solution became immediately purple. Its UV spectrum exhibits λ_{max} 530 nm which is consistent with that of **8** obtained from one-electron anodic oxidation.13) This phenomenon shows that **8** was oxidized to its cation radical by **1**, since the oxidation potential of **8** is lower than that of the dication precursor.12a) Treatment of this solution with H_2O afforded sulfide **6** as the reduction product (50%) and the recovered **8** in 51% yield, whereas the other products could not be characterized.14) However, **1** did not react with **9** which is more difficult to be oxidized than **8**, since the oxidation potential of **9** is much higher than that of **8**.

The results described herein show first examples of the substitution and the redox reaction of dication **1** with several aromatics. Thus, disulfide dication **1** acts both as an electrophile and an oxidant toward aromatics.

References

1) W. K. Musker, T. L. Wolford, and P. B. Roush, J. Am. Chem. Soc., 100, 6416 (1978).
2) H. Fujihara, A. Kawada, and N. Furukawa, J. Org. Chem., 52, 4254 (1987).
3) H. Fujihara, R. Akaishi, and N. Furukawa, J. Chem. Soc., Chem. Commun., 1987, 930. The X-ray crystallographic analysis of dication **1** indicates that the S-S distance is 2.121 Å which is only slightly longer than the normal S-S single bond (2.08 Å); the details will be reported elsewhere.
4) The oxidation potentials (E/V vs. SCE) for used aromatics are as follows: **2e**(0.5),a) **8**(0.55),b) **2a**(0.87),b) **2b**(0.92),c) **2c**(1.35),c) **9**(1.32),c) and **2d**(1.77).b) a) F. Magno, G. Bontempelli, and G. J. Pilloni, Electroanal. Chem. 30, 375 (1971); b) K. Sasaki, A. Kitani, and M. Tsuboi, Nippon Kagaku Kaishi, 1973, 2269 ; c) N. L. Weinberg and H. R. Weinberg, Chem. Rev., 68, 449 (1968) and references cited therein.
5) **3a**: mp 167 °C(decomp); IR (KBr) 3454, 3356 (NH_2) and 1310-1229 (CF_3SO_3) cm^{-1}; ^1H NMR (CD_3CN) δ 7.47 (d, J=9 Hz, 2H, ArH), 6.78 (d, J=9 Hz, 2H, ArH), 5.19-4.81 (br s, 2H, NH_2), 3.97-3.33 (m, 4H, S^+CH_2), 2.95-2.67 (m, 4H,

SCH_2), and 2.51-2.24 (m, 4H, CH_2); ^{13}C NMR (CD_3CN) δ 154.1, 132.4, 116.7, 116.0, 47.6, 31.0, and 26.6. Found: C, 39.84; H, 4.64; N, 3.51%. Calcd for $C_{13}H_{18}F_3NO_3S_3$: C, 40.09; H, 4.66; N, 3.60%.

6) **3b**: colorless oil; IR (neat) 1334 (Ar-N) and 1310-1225 (CF_3SO_3) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.68 (d, J=9 Hz, 2H, ArH), 7.50-6.86 (m, 12H, ArH), 4.64-4.26 (m, 2H, S^+CH_2), 3.68-3.27 (m, 2H, S^+CH_2), and 3.10-2.21 (m, 8H, SCH_2CH_2); ^{13}C NMR ($CDCl_3$) δ 152.9, 145.4, 131.1, 129.9, 126.3, 125.8, 120.5, 119.7, 47.6, 31.0, and 26.5. MS(m/z) 392 (M^+-CF_3SO_3).

7) **4**: mp 199-201 °C (decomp); IR (KBr) 3438 (OH), 1322 (Ar-N) and 1310-1230 (CF_3SO_3) cm^{-1}; ^1H NMR (CD_3CN) δ 7.71 (d, J=9 Hz, 4H, ArH), 7.60-7.05 (m, 9H, ArH), 4.07-3.44 (m, 8H, S^+CH_2), 3.10-2.59 (m, 8H, SCH_2), and 2.55-2.22 (m, 8H, CH_2); ^{13}C NMR (CD_3CN) δ 151.9, 132.4, 131.3, 128.2, 126.0, 124.9, 47.2, 31.2, and 26.7. Found: C, 44.68; H, 4.34; N, 1.63%. Calcd for $C_{32}H_{39}F_6NO_7S_6$: C, 44.90, H, 4.59, N, 1.64%.

8) **3c**: mp 160 °C; IR (KBr) 3463 (OH) and 1350-1199 (CF_3SO_3) cm^{-1}; ^1H NMR (CD_3CN) δ 8.56-8.38 (br s, 1H, OH), 7.67 (d, J=9 Hz, 2H, ArH), 7.07 (d, J=9 Hz, 2H, ArH), 4.04-3.41 (m, 4H, S^+CH_2), 3.10-2.59 (m, 4H, SCH_2), and 2.55-2.21 (m, 4H, CH_2); ^{13}C NMR (CD_3CN) δ 162.6, 132.7, 122.3, 118.5, 47.3, 31.0, and 26.5. Found: C, 39.57; H, 4.46%. Calcd for $C_{13}H_{17}F_3O_4S_3$: C, 39.99; H, 4.38%.

9) J. P. Marino, "Topics in Sulfur Chemistry, Vol. 1," ed by A. Senning, Georg Thieme Publishers, Stuttgart (1976), p. 1.

10) Shine(11) proposed that the reaction of $Th^{+\cdot}$ with **2d** involved a disproportionation to the reactive dication (Th^{2+}), while Parker(10a) proposed that its reaction involved a direct electrophilic reaction of $Th^{+\cdot}$. a) U. Svanholm, O. Hammerich, and V. D. Parker, J. Am. Chem. Soc., 97, 101 (1975).

11) H. J. Shine, "The Chemistry of the Sulfonium Group," ed by C. J. M. Stirling and S. Patai, John Wiley & Sons, New York (1981), Chap. 14.

12) a) The oxidation potential (E/V vs. SCE) of **6** as precursor of **1** is 0.7 (dication stage) which is converted from V vs. Ag/0.1 M-Ag^+ by addition of 0.3 V: M. D. Ryan, D. D. Swanson, R. S. Glass, and G. S. Wilson, J. Phys. Chem., 85, 1069 (1981); b) The oxidation potential (E/V vs. SCE) of Th is 1.26 and 1.77.(11) The sulfides, **6** and Th show reversible redox behavior.

13) a) J. Bacon and R. N. Adams, J. Am. Chem. Soc., 90, 6596 (1968); b) M. Masui and H. Ohmori, J. Chem. Soc., Perkin Trans 2, 1972, 1882.

14) The controlled potential electrolysis of **8**, one electron per molecule give the complex products which are not identified.(13b)

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