CHEMISTRY LETTERS, pp. 393-396, 1990.

Reactivity of Diselenide Dication Salt, 1,5-Diselenoniabicyclo[3.3.0]octane Bis(hexafluorophosphate) toward Aromatics. A New Mode of Aromatic Substitution and Redox Reaction

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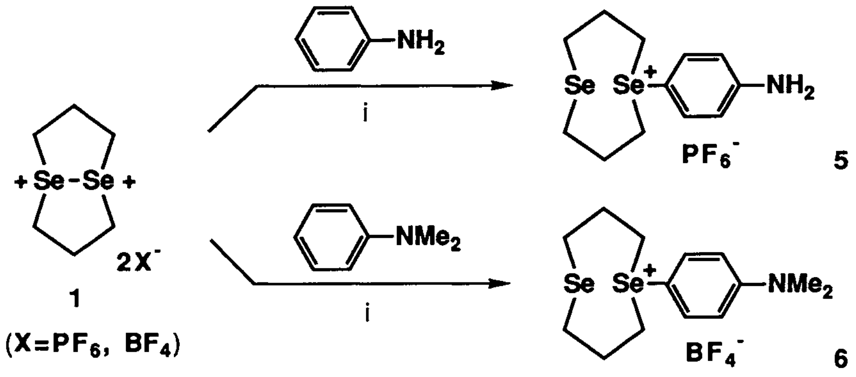
A new diselenide dication salt, 1,5-diselenoniabicyclo[3.3.0]-octane bis(hexafluorophosphate) was reacted with several aromatics to afford either the substitution or redox products. The reaction mode depends on the oxidation potential of aromatics.

Dications bonded by two positively charged heteroatoms are a little known, and study of their structures and reactivities is of great interest.[1,2] However, the investigation of reactivity of dications has received less attention, because of the difficulties to obtain stable compounds. Recently, we reported the first characterization of the crystal structure and the reactivity of disulfide dication salt, 1,5-dithioniabicyclo[3.3.0]octane bis-(trifluoromethanesulfonate).[3] In contrast, tetra-alkyl substituted diselenide dication salt $[R_2Se^{+}\text{-}^{+}SeR_2 \cdot 2X^{-}]$ has never been isolated except our recent result.[5] Namely, we found that the two-electron oxidation of a new cyclic bis-selenide, 1,5-diselenacyclooctane (**2**)[4] with nitrosonium hexafluorophosphate ($NOPF_6$) gave the diselenide dication, 1,5-diselenoniabicyclo[3.3.0]octane bis(hexafluorophosphate) (**1**) as a stable crystalline salt.[5] We now present here the first observation of aromatic substitution and redox reaction of the diselenide dication salt **1** with several substituted benzenes and heterocyclic compounds having different oxidation potentials.[6]

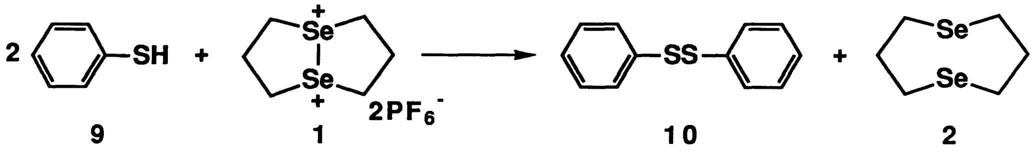
A new diselenide dication salt **1** ($X^{-}=PF_6$, BF_4) was prepared by a reaction of bis-selenide **2** with two equivalents of $NOPF_6$ or $NOBF_4$ in CH_2Cl_2-CH_3CN. A typical run is as follows. To a stirred solution of dication salt **1**[5] (411 mg, 0.77 mmol) in anhydrous acetonitrile (2 mL) was added a solution of aniline (**3**) (143 mg, 1.54 mmol) in anhydrous acetonitrile (3 mL) under an Ar atmosphere at



Scheme 1. Conditions: i; CH_3CN, room temp., Ar.

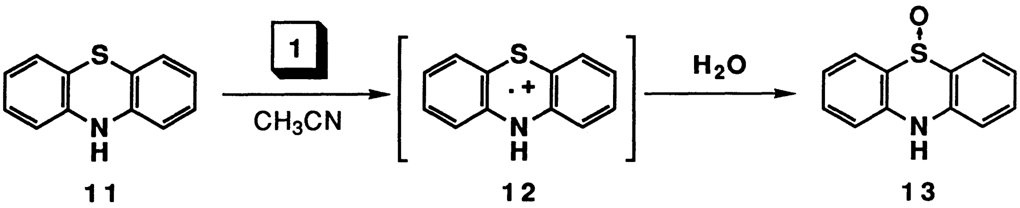
room temperature and the whole mixture was stirred for 6 h. The mixture was then treated with H_2O, and after usual work-up, the residue was chromatographed on silica-gel (eluent: $CHCl_3$-MeOH) to afford the corresponding para-substituted selenonium salt, 1-(4-aminophenyl)-5-selena-1-selenoniacyclooctane hexafluorophosphate (**5**) as white crystal in 55% yield.[7] Similar treatment of N,N-dimethylaniline (**4**) with dication **1** led to the corresponding selenonium salt **6** in 68% yield[8] (Scheme 1). Structures of **5** and **6** were assigned based on the spectral data.[7,8] Apparently, these substitution reactions of **3** and **4** with **1** occur only at the para-position of the aromatic ring. While the alkylamine such as diisopropylamine did not react with the dication **1**. Interestingly, a new type of selenonium salt bearing bifunctional groups, **6**, shows an unusual property in the electrochemical oxidation, namely the cyclic voltammogram of **6** shows one reversible oxidation peak at +0.88 V vs. Ag/Ag^+. Simple selenonium salts, selenides, and N,N-dimethylaniline show irreversible oxidation wave by itself; the details will be reported elsewhere. On the other hand, the reaction of triphenylamine (**7**) or phenol (**8**) with dication **1** did not give the corresponding substituted product. The unreactivity of **7** and **8** toward **1** might depend on their higher oxidation potentials than those of **3** and **4**.[6] In contrast, the aromatic substitutions of normal selenonium salts with aromatics have not been reported in our knowledge.

The redox reaction was found to take place in the treatment of diselenide dication **1** with thiophenol (**9**) which gave diphenyl disulfide (**10**) (92%) as the oxidation product and the bis-selenide **2** as the reduction product (Scheme 2). These distinct differences in reactivity between **1** and the aromatics described above seem to be due to the difference in the oxidation potentials of the aromatics.[6]



Scheme 2.

When a solution of phenothiazine (**11**) (1 equiv.) in anhydrous CH_3CN was added to a solution of diselenide dication **1** (1 equiv.) in anhydrous CH_3CN under an Ar atmosphere at -20 °C, the solution became yellowish-brown. Its UV-visible spectrum exhibits absorptions at λ_{max} 436 and 515 nm which are consistent with the spectrum previously reported for the phenothiazine cation radical.[9] This phenomenon shows that phenothiazine was oxidized to its mono cation radical (**12**) by dication **1**, since the oxidation potential of **11** is lower than that of the dication precursor.[4] Treatment of this solution with H_2O gave phenothiazine 5-oxide (**13**)[10] in 65% yield, and none of the substituted product was obtained (Scheme 3). These results indicate that **11** undergoes one-electron oxidation to form the cation radical **12** which reacts with H_2O to produce the sulfoxide **13**.



Scheme 3.

Thus, a new diselenide dication salt **1** acts both as an electrophile and an oxidant toward aromatics. The reaction mode depends remarkably on the oxidation potential of aromatics.

This work was supported by a Grant-in-Aid for Scientific Research (No. 01740293) from the Ministry of Education, Science, and Culture of Japan.

References

1) R. W. Alder, R. B. Sessions, J. O. Gmünder, and C. A. Grob, J. Chem. Soc., Perkin Trans. 2, 1984, 411; W. K. Musker, T. L. Wolford, and P. B. Roush, J. Am. Chem. Soc., 100, 6416 (1978).

2) H. Fujihara and N. Furukawa, J. Mol. Struct. (Theochem), 186, 261, (1989); H. Fujihara, J.-J. Chiu, and N. Furukawa, J. Am. Chem. Soc., 110, 1280 (1988).

3) H. Fujihara, R. Akaishi, and N. Furukawa, J. Chem. Soc., Chem. Commun., 1987, 930; F. Iwasaki, N. Toyoda, R. Akaishi, H. Fujihara, and N. Furukawa, Bull. Chem. Soc. Jpn., 61, 2563 (1988); H. Fujihara, R. Akaishi, and N. Furukawa, J. Chem. Soc., Chem. Commun., 1989, 147.

4) The cyclic voltammogram of bis-selenide **2** shows reversible oxidation peak at +0.25 V vs. Ag/Ag^+.

5) H. Fujihara, R. Akaishi, T. Erata, and N. Furukawa, J. Chem. Soc., Chem. Commun., in press.

6) The oxidation potentials (E/V vs. $Ag/AgNO_3$) for aromatics used are as follows. **3** (+0.54 V): S. Wawzonek and T. W. McIntyre, J. Electrochem. Soc., 114, 1025 (1967). **4** (+0.40 V) and **7** (+0.61 V): E. T. Seo, R. F. Nelson, J. M. Fritsch, L. S. Marcoux, D. W. Leedy, and R. N. Adams, J. Am. Chem. Soc., 88, 3498 (1966). **8** (+1.04 V): C. Parkanyi and R. Zahradnik, Coll. Czech. Chem. Commun., 30, 4287 (1965). **9** (+0.2 V): F. Magno, G. Bontempelli, and G. J. Pilloni, Electroanal. Chem., 30, 375 (1971). **11** (+0.22 V): J. P. Billon, Bull. Soc. Chim. Fr., 1960, 1784.

7) Compound **5**: mp 151-152 °C; FT-IR (KBr, cm^{-1}) 3483, 840; ^1H NMR (CD_3CN) δ 7.37 (d, J=8.8 Hz, 2H, ArH), 6.75 (d, J=8.8 Hz, 2H, ArH), 3.80-3.31 (m, 4H, Se^+-CH_2), 3.16-2.69 (m, 4H, Se-CH_2), and 2.66-2.20 (m, 4H, CH_2); ^{13}C NMR (CD_3CN) δ 152.9, 132.1, 119.8, 116.2, 46.3, 27.0, and 25.0. Anal. Calcd for $C_{12}H_{18}F_6NPSe_2$: C, 30.08; H, 3.79; N, 2.92%. Found: C, 30.24; H, 4.05; N, 2.87%.

8) Compound **6**: mp 141-142 °C; ^1H NMR (CD_3CN) δ 7.47 (d, J=9.3 Hz, 2H, ArH), 6.81 (d, J=9.3 Hz, 2H, ArH), 3.84-3.34 (m, 4H, Se^+-CH_2), 3.19-2.74 (m, 4H, Se-CH_2), 3.01 (s, 6H, Me), and 2.72-2.28 (m, 4H, CH_2); ^{13}C NMR (CD_3CN) δ 153.7, 131.7, 119.2, 113.8, 46.3, 40.3, 27.0, and 25.0. Anal. Calcd for $C_{14}H_{22}BF_4NSe_2$: C, 37.45; H, 4.93; N, 3.19%. Found: C, 36.99; H, 4.79; N, 3.14%.

9) a) H. J. Shine and E. E. Mach, J. Org. Chem., 30, 2130 (1965); b) C. Bodea and I. Silberg, Adv. Heterocyclic Chem., Academic Press, 9, 321 (1968).

10) Compound **13**: mp 265 °C; FT-IR (KBr, cm^{-1}) 1076, 976 (SO)$^{9b)}$; MS (m/z): 215 (M^+); ^1H NMR (500 MHz, CD_3OD) δ 7.92 (d, J=7.9 Hz, 2H), 7.64-7.60 (m, 2H), 7.38 (d, J=8.3 Hz, 2H), and 7.26-7.21 (m, 2H); ^{13}C NMR (CD_3OD) δ 138.5, 134.4, 132.2, 122.7, 120.3, and 118.1.

(Received December 20, 1989)