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Reactivities of Bis(2-bromoethyl)selenium Dibromide and Its Related Compounds: Formation of Hypervalent T-shaped Coordinated Selenium Compounds by Reaction with Pyridine and Its Derivatives

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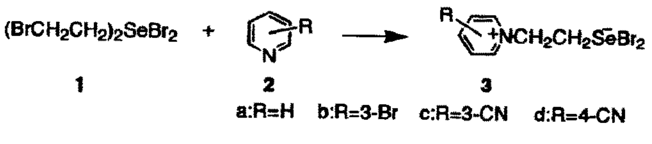
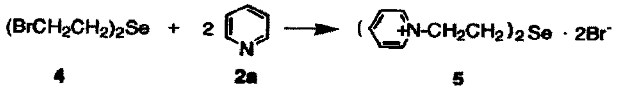
Abstract: The reaction of bis(2-bromoethyl)selenium dibromide **1** with pyridine **2a** and its derivatives **2b**-**2d** gave hypervalent T-shaped coordinated selenium compounds **3a**-**3d** with two halogen atoms in the trans positions in moderate to good yields. Also, 2-pyridiniumethylselenol bromide **10** was obtained by the reaction of (2-bromoethyl)phenyl selenium dibromide **9** with **2a** in 9.8% yield. The X-ray analysis of **10** revealed that the two conformers about the CH_2-CH_2 bond existed in one crystal unit, although the ^{1}H-NMR spectra at room temperature showed relatively free rotation about the CH_2-CH_2 bond.

The linear, three-centered system of selenium atoms has been already known for the complexes of triselenocyanate[1] or tris(selenourea) ion.[2] In these ions, a linear Se-Se-Se chain exists and the central selenium atom has a T-shaped coordination. Organic compounds having a T-shaped coordinated selenium, in which there is an almost linear halogen-selenium-halogen sequence instead of Se-Se-Se chain, were also reported. We have previously reported the various reaction abilities of dialkylselenium dihalides such as the selective reduction of tertiary amides to the corresponding amines,[3-5] the one-pot preparation of 2,5-bis(alkoxymethyl)tetrahydroselenophenes[6] by cycloaddition of bis(2-bromoethyl)selenium dibromide (**1**) to 1,5-hexadiene and the alkoxyselenation of cyclohexene.[7] In connection with the above investigations, we report herein the reactivities of **1** and its related selenium compounds with pyridine and its derivatives as nucleophiles.

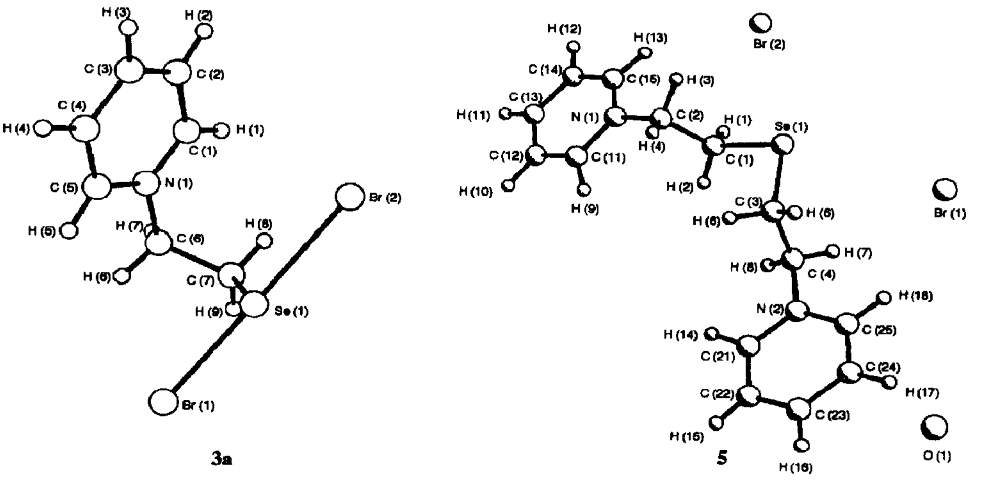
The reaction of **1** with pyridine **2a** as a nucleophile gave pyridiniumethylselenoate dibromide **3a** as an unexpected product in 63% yield,[8] although the reaction of bis(2-bromoethyl)selenide **4** with **2a** gave bis(2-pyridiniumethyl)selenide dibromide **5** as a normal substituted product in 42% yield. Similar reactions of **1** with **2b**, **2c** and **2d** afforded the corresponding **3b**, **3c** and **3d** in moderate to good yields, respectively.





We first thought that the resulting product **3a** was a normal disubstituted compound, bis(2-pyridiniumethyl)selenide dibromide *5*. It is known that the reaction of 2-substituted selenide with some anionic nucleophiles gave substituted products, and in the ^{1}H-NMR spectra of **3a**, the integrated ratio between two triplets due to the ethylene protons appeared at δ 5.09 and 3.95 as the A_2B_2 pattern and the multiplet peaks of the pyridine moiety at δ 8.79-7.97 was 4:4:10.

To determine the structures of **3a** and *5*, an X-ray analysis was carried out.[9] The perspective views with the atomic numbering scheme for **3a** and **5** are illustrated in Fig. 1. The selenium atom in **3a** was three coordinated with a carbon and two bromine atoms in a T-shaped structure. The Br-Se-Br angles is 176.8(1)° which are almost 180°. The two Br-Se-C bond angles are 90.7(6)° and 92.1(6)°, both nearly 90°. Therefore, the Br-Se-Br sequence is nearly linear and the Se-C bond is nearly perpendicular to the Br-Se-Br chain. The average bond length (2.59 Å) of the two Se-Br bonds extremely similar to the sum (2.60 Å) of the "half p-orbital" radius (1.46 Å)[10] of divalent selenium and the covalent radius (1.14 Å)[11] of Br. The result suggests that the linkage form of the Br-Se-Br sequence was a straight three center, four electron (3c-4e) bond based on the p-orbital of Se atom.



3a **5**

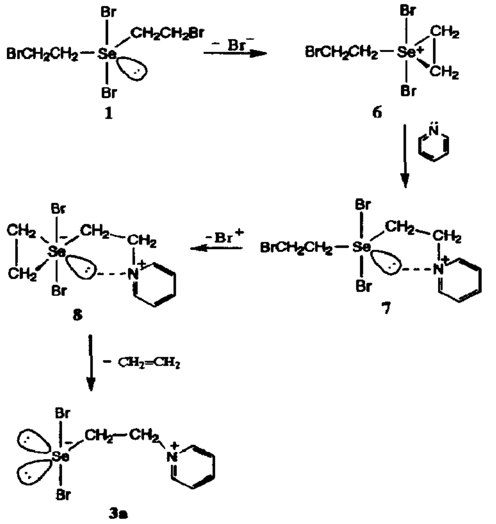
Fig.1. Perspective views of 3a and 5 with the atomic numbering scheme

The ammonium salts of similar T-shaped coordinated selenium molecules with a linear halogen-selenium-halogen sequence have been reported.[11-14] These salts have completely discrete cations of the ammonium part and separate anions of the selenium moiety. On the other hand, the crystal structure of **3a** showed the coexistence of a cation and an anion in a molecule. That is, the nitrogen atom of the pyridinium moiety serves as a cation and the Br-Se-Br sequence may probably act as an anion in a molecule.

Some T-shaped compounds have been reported without the above salts.[14-16] These T-shaped salts and compounds were synthesized from phenylselenenyl halide,[11] ammonium selenocyanate,[11-14] alkyl or arylselenium trihalide[14,16] and carbon diselenide[15] as the corresponding starting materials. Hence, it is the first reported example of organoselenium compounds in which the Se atom has a T-shaped configuration possessing two halogen atoms in the trans position from the dialkylselenium dihalide as a starting substance to our knowledge.

As Petragnani et al. theorized that the T-shaped molecule of selenium and tellurium atoms resulted from the disposition of three bonding and two nonbonding electron pairs,[17,18] it was anticipated that the configuration about the Se atom consists of two lone-pair electrons occupying each of the two equatorial sites, a bond to a carbon on another equatorial and two Br-Se bonds on axial sites in the compound **3a**. Consequently, the products **3** should be hypervalent compounds of selenium.

The plausible formation mechanism of **3a** is shown in Scheme 1. It was proposed that the three membered episelenonium ion as a intermediate was formed in the reaction of the 2-halogen substituted selenide with nucleophilic reagents.[19] There is a known equilibrium[20] between **1** and **4**. Hence the product **5** would be produced from even **1** if the reaction proceeded along **4** given by the debromination of **1**. Isolation of **3a** was presumed that the reaction should go forward without debromination and through a different pathway. Therefore, it seems a novel pathway for the formation of T-shaped compounds. Thus the bromine adduct of the episelenonium ion **6** was expected to be formed. An ordinary attack of **2a** on the three-membered carbon atom of **6** might give mono substituted product **7** where a lone-pair electron on the selenium atom would be attracted to the positive charge on the nitrogen atom of the pyridine part proceeded by the formation of the coordinate bond. Thus, elimination of the bromine cation from **7** consequently produced the intermediate **8** having five coordination and a lone-pair electron. An ethylene is probably then eliminated from **8** and **3a** was produced.



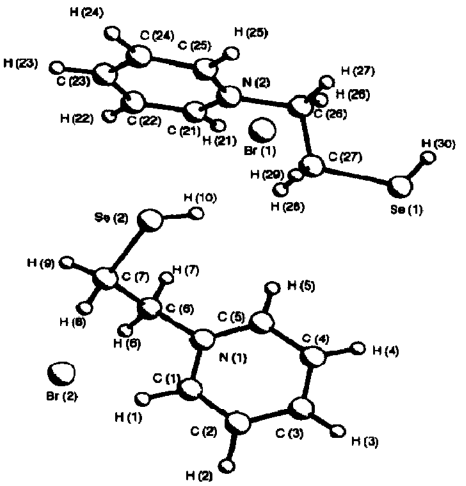
Scheme 1. The plausible formation mechanism of 3a

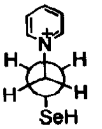
Next, compound **9** was allowed to react with **2a** and the structure of the product **10** was determined by X-ray analysis.[8,9] It was pointed out that not only the substitution of pyridine **2a** against bromine but cleavage between the Se-Ph bond of **9** occurred during the reaction. Furthermore, there existed two crystal

9 **2a** **10**

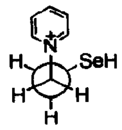
forms in the crystal lattice. The perspective views with the atomic numbering scheme is illustrated in Fig. 2. The fundamental difference between the two molecules was the dihedral angle of N-C-C-Se. One was anti-type and the dihedral angle was 172(2)°, and the other was the gauche type with the dihedral angle of 65(2)°. Since the ^{1}H-NMR spectra for the two methylene moieties of **10** appeared as two triplets at δ 4.04 and 5.15, therefore so that the ethylene bond seems to have relatively free rotation about the C-C bond at room temperature in the solution.

The more detailed reaction mechanism of **1** with **2** and the thermodynamic investigation of **10** are in progress.





anti-10



gauche-10

Fig.2. Perspective views of **10** with the atomic numbering scheme

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8) **3a**: yield 63%, m.p. 108-110°C, **3b** yield 59%, m.p. 131-133°C, **3c**: yield 61%, m.p. 129-130°C, **3d**: yield 46%, m.p. 150-151°C. **5**: yield 42%, m.p. 140-141°C. **10**: yield 9.8%, m.p. 119-121°C. All new compounds were characterized by ^{1}H-NMR spectra and gave satisfactory elemental analysis.
9) X-Ray Crystallography of **3a**, **5** and **10**. For **3a**: $C_7H_9Br_2NSe$, M 345.92, crystal dimensions 0.450x0.100x0.100mm, orthorhombic, space group $P2_12_12_1$, a=9.695(3) Å, b=14.441(5) Å, c=7.478(6) Å, V=1047(2) Å^3, Z=4, DC=2.195g/cm^3, μ(MoKα)=110.56cm^{-1}; R=0.050, Rw=0.034. For **5**: $C_{14}H_{18}Br_2N_2SeO$, M469.08, crystal dimensions 0.400x0.400x0.100mm, monoclinic, space group $P2_1/a$, a=7.840(6) Å, b=14.781(6) Å, c=15.555(5) Å, β=103.08(4)°, V=1756(2) Å^3, Z=4, DC=1 774g/cm^3, μ(MoKα)=66.22cm^{-1}; R=0.047, Rw=0.039. For **10** $C_7H_{10}NSeBr$, M 267.03, crystal dimensions 0.250x0.250x0.370mm, monoclinic, space group $P2_1/c$, a=11.182(7) Å, b=12.330(4) Å, c=13.633(3) Å, β=96.07(3)°, V=1869(2) Å^3, Z=8, DC=1.898g/cm^3, μ(MoKα)=81.45cm^{-1}, R=0.056, Rw=0.045. The structure parameters have been deposited at the "Cambridge Crystallographic Data Centre", U K
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