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Reactivity of Alkaneselenenyl Bromide: Conversion of Alcohols into the Corresponding Alkyl Bromides with Dialkylselenium Dibromide

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Synopsis. The reaction of alcohols with dialkylselenium dibromide gave the corresponding bromides in moderate to high yields. Alkaneselenyl bromide, produced by the thermal decomposition from dialkylselenium dibromide, acts as a brominating agent. The reaction of alcohols with dialkylselenium dichloride also afforded the corresponding chlorides, although the yields were relatively low compared with those of the bromide.

Although organoselenium compounds have been known for a long time, some compounds being described at the end of the last century, the use of selenium reagents or intermediates has only been recent.[1] Although the structures of the organoselenium functions are similar to those of organic sulfur compounds, the use of selenium reagents often facilitates the reaction to proceed under simpler and milder conditions. It is also well known that alkyl halides can be obtained by the reaction of alcohols with many kinds of halogenating agents.[2] For example, hydrogen halide, phosporous halide, thionyl halide, etc. have been used as halogenating agents. Recently, Furukawa et al.[3] also reported the conversion of alcohols to alkyl bromides using the bromine adduct of dimethyl sulfide (Me_2SBr_2). In a previous paper, we reported a new procedure for the highly selective reduction of tertiary amides to the corresponding amines with $NaBH_4$–diethylselenium dibromide **2a** as the reducing agent in tetrahydrofuran.[4] We also reported a convenient one-pot procedure for the synthesis of symmetric tricalcogena[3]metallocenophanes using **2a** as the selenium insertion reagent.[5] In connection with these results we report here a new procedure for the convenient conversion of alcohols to alkyl halides using dialkylselenium dihalide **2** as the halogenating agent.

Results and Discussion

The reaction was carried out as follows. The reaction of **2a** with a large excess of 1-octanol at 80 °C for 7 h afforded 1-bromooctane in 98% yield together with 1,2-dibromoethane (75%). Similar reactions were carried out using **2b**, **2c**, and **2d** as brominating agents. These results are summarized in Table 1. At room temperature this reaction did not proceed, and the starting materials were recovered quantitatively. Furthermore, among the examined dialkylselenium dibromides used as brominating agents **2a**, **2b**, **2c**, and **2d**, **2a** usually gave the best results; the yields of 1-bromooctane using **2b**, **2c**, and **2d** had nearly similar values. These results suggest that the bromine atom in **2a** may act as an electron-attracting group, and the cleavage of the Se–C bond in **2a** occurred more easily compared with those in **2b**, **2c**, and **2d**. The following bromination of several kinds of alcohols was therefore carried out using **2a** as the bromination reagent. These results are summarized in Table 2. Primary alcohols could be converted to the corresponding bromides in much higher yields compared with those of secondary alcohols. The yields of primary bromides **3a**—**c** were also much higher than that obtained by the methods already reported.[2] In contrast with the above bromination reaction, the reaction of the alcohols with bis(2-chloroethyl)selenium dichloride **4** gave the corresponding alkyl chlorides **5a**—**d**, although the yields were relatively low compared with those for bromination (Table 2). This result may be attributed to the strong Se–Cl bond compared to the Se–Br bond.[6] Furthermore, a similar reaction of alcohols was carried out using diethylselenium diiodide **6** as the iodinating reagent. However, the corresponding alkyl iodides could not be obtained in any cases. The differences in the halogenating abilities between the bromine or

$$\underset{\mathbf{1}}{\mathrm{ROH}} \xrightarrow{\mathbf{2}} \underset{\mathbf{3}}{\mathrm{RX}}$$

Table 1. Bromination of 1-Octanol **1a** with Dialkylselenium Dibromides **2**

Brominating agent R_2SeBr_2	Yield (%) of 1-bromooctane **3a**
2a: $R=BrCH_2CH_2-$	98
2b: $R=CH_3CH_2-$	35
2c: $R=(CH_3)_2CH-$	45
2d: $R=C_6H_{13}-$	40

a) Determined by GLC based on **2**.

Table 2. Halogenation of Alcohols with Bis(2-haloethyl)selenium Dihalides **2a** and **4**

Alcohol R=	Reagent	Product X=	Yield/%
1a: $C_8H_{17}-$	**2a**	**3a** (X=Br)	98
1a: $C_8H_{17}-$	**4**	**5a** (X=Cl)	39
1b: $C_5H_{11}-$	**2a**	**3b** (X=Br)	78
1b: $C_5H_{11}-$	**4**	**5b** (X=Cl)	35
1c: C_4H_9-	**2a**	**3c** (X=Br)	96
1c: C_4H_9-	**4**	**5c** (X=Cl)	34
1d: $C_3H_7\underset{\vert}{C}HCH_3$	**2a**	**3d** (X=Br)	52
1d: $C_3H_7\underset{\vert}{C}HCH_3$	**4**	**5d** (X=Cl)	8
1e: $C_2H_5\underset{\vert}{C}HCH_3$	**2a**	**3e** (X=Br)	50
1f: $C_2H_5\underset{\vert}{C}(CH_3)_2$	**2a**	**3f** (X=Br)	52
1g: $(CH_3)_3C-$	**2a**	**3g** (X=Br)	41

a) The yields were determined by GLC.

chlorine adducts and the iodine adduct are attributable to these structures. Indeed, it was reported that the chlorine and bromine adducts of dialkyl selenide are trigonal bipyramidal structures, while the iodine adduct is a molecular complex.[7,8] The iodine adduct could therefore not react with alcohol, while the reaction of the bromine and chlorine adducts with alcohol gave alkaneselenyl halides and an alkyl halide. In fact, Behagel et al.[9] and Edwards et al.[10] reported that the thermal decomposition of dialkylselenium dibromide easily gave alkaneselenenyl bromide and alkyl bromide. This finding was also confirmed by the following experiments. After a solution of diethylselenium diiodide **6** in methanol-d_4 was refluxed for 7 h, the ^{1}H NMR spectrum of the solution was measured. However, no spectral changes were observed.

In order to investigate the chemical species in this reaction, the change conversion of 1-octanol **1a** versus the reaction time in the reaction with **2b** and with ethaneselenenyl bromide **7** (which was obtained by the reaction of diethyl diselenide with bromine in quantitative yield) was measured. Very similar results were obtained (yields ca. 30%) in both reactions. Similar results were also obtained in a comparison of the reactions of 1-butanol with **2b** and **7**. The yields of the alkyl bromide using ethaneselenenyl bromide **7** are comparable with those using **2a**, although the reason cannot be detailed at present. However, these finding suggests that bromination occurred as follows: i) after thermal decomposition of **2b** in alcohol gives **7**, the negatively charged bromine atom of **7** attacks the carbon atom attached to the hydroxyl group; ii) perhaps the initial reaction is the formation of alkaneselnenyl bromide and the resulting alkaneselenenyl bromide rapidly reacts with nucleophile to form HBr and RSeOR′. The next step is a nucleophilic replacement of the hydroxyl group of alcohol by the bromine anion. Support for the reaction mechanism (ii) is, however, based on the following. It is well known that the reaction of alkaneselenenyl bromide with methanol gave HBr and a stable selenium compound.[11,12] Furthermore, the reaction of 1-octanol **1a** with bis(2-bromoethyl)selenium dibromide **2a** in the presence of hydrogen chloride gave 1-chlorooctane **5a** together with 1-bromooctane **3a** in 77% yield. Also, as previously described, the relatively higher reactivity of **2a** in comparison with **2b**—**d** has been ascribed to a facile generation of the corresponding alkaneselenenyl bromide from **2a**. This means that the rate-determining step is the generation of the alkaneselenenyl bromide, rather than the brominating step.

This reaction mechanism is completely different from that of the bromination methanism of alcohol using Me_2SBr_2, in which dimethylbromosulphonium bromide plays an important role as the brominating agent.[3]

Experimental

Gas chromatography was performed on a Shimadzu G. C-8APF gas chromatography with a PEG20M (2.0%) 2m glass column.

Materials. Diethylselenium dibromide **2b**,[13] diethylselenium diiodide **6**,[14] bis(2-bromoethyl)selenium dibromide **2a**,[15] bis(2-chloroethyl)selenium dichloride **4**,[16] dihexylselenium dibromide **2d**,[17] diisopropylselenium dibromide **2c**,[17] diethyl diselenide and ethaneselenenyl bromide **7**[18] were prepared according to methods described in the literature. All of the alcohols and alkyl halides purchased from commercial sources were used without further purification; all solvents were purified by distillation in the usual manner.

General Procedure for the Halogenation of Alcohols with Dialkylselenium Dihalide. The following procedure used for the preparation of the alkyl halides is representative. A mixture of bis(2-bromoethyl)selenium dibromide **2a** (2.25 g, 5 mmol) and alcohol **1a** (10 ml) was stirred for 7 h at 80 °C. The reaction mixture was cooled to room temperature and then the supernatant solution was analyzed by GLC. The yield of 1-bromooctane **3a** was 98%.

All products, thus obtained, were known compounds, and were identified by the bp's as well as by comparisons of the NMR and IR spectra and/or the GLC retention times with those of authentic samples prepared independently.

A similar reaction was also carried out at room temperature. However, the brominating products could not be obtained and the starting materials were recovered in quantitative yields.

Preparation of Ethaneselenenyl bromide 7 in 1-Octanol or Tetrachloromethane. Bromine (0.40 g, 2.5 mmol) was rapidly added to a solution of diethyl diselenide (0.78 g, 2.5 mmol) in 1-octanol **1a** (10 ml). After the solution was stirred for 30 min at 0 °C, ethaneselenenyl bromide **7** was obtained in quantitative yield according to a method described in the literature.[18]

The resulting ethaneselenenyl bromide **7** was used without isolation in the following reaction with alcohols, as described below.

General Procedure for the Bromination of Alcohols with Ethaneselenenyl Bromide 7 in Tetrachloromethane. To a tetrachloromethane solution (10 ml) containing diethyl diselenide (1.56 g, 5 mmol) bromine (0.8 g, 5 mmol) was quickly added at 0 °C. After stirring 30 min at 0 °C, 1-octanol **1a** (1.30 g, 10 mmol) was rapidly added to the resulting tetrachloromethane solution of ethaneselenenyl bromide **7**. The reaction mixture was stirred for a further 7 h at 80 °C. After the reaction mixture was cooled to room temperature, the supernatant solution was analyzed by GLC. The yield of 1-bromooctane **3a** was 35%.

General Procedure for the Bromination of Alcohols with Ethaneselenenyl Bromide 7 in Alcohol. A mixture of diethyl diselenide (0.78 g, 2.5 mmol) and bromine (0.40 g, 2.5 mmol) in 1-octanol **1** (10 ml) was stirred for 30 min at 0 °C and then refluxed for a further 7 h at 80 °C. After the reaction mixture was cooled to room temperature, the supernatant solution was analyzed by GLC. The yield of 1-bromooctane **3a** was 35%.

Reaction of 1-Octanol 1a with 2a in the Presence of HCl. A solution of **2a** (2.25 g, 5 mmol) in 10 ml of 1-octanol **1a** containing dry HCl was stirred at 80 °C for 7 h. The reaction mixture was then analyzed. The GLC analyses revealed the presence of **3a** (3.9 mmol, 77%) and 1-chlorooctane **5a** (1.1 mmol).

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