Formation and Stability of New Hybrid Dichalcogena Dications(S-Se, S-Te and Se-Te) Bearing (2-Methylchalcogenomethyl)phenyl Skeleton

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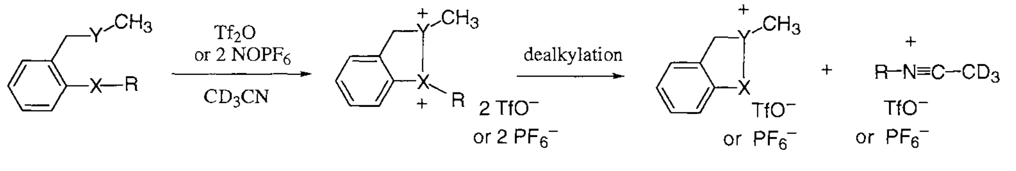
Ethyl 2-(methylthiomethyl)phenyl selenide **1a**, telluride **1b** and ethyl 2-(methylselanylmethyl)phenyl telluride **1c** were prepared and treated with 1 equivalent of triflic anhydride (Tf$_2$O) or 2 equivalents of nitrosonium salts (NOBF$_4$ or NOPF$_6$) at low temperature to generate the corresponding selenathia, tellurathia and telluraselena dications(**2a, 2b** and **2c**), the structures of which were determined by NMR spectroscopy and **2b** was successfully isolated.

Organo-chalcogena dications are an unusual chemical species, whose stability and reactivity are of current interests in heteroatom chemistry.[1] Cyclic dichalcogena dications of the 1,5-dichalcogenocyclooctane skeleton prepared by reacting monooxides with trifluoromethanesulfonic anhydride (Tf$_2$O) or bischalcogenides with 2 equivalents of NOBF$_4$ are stable, and their structures were determined by X-ray crystallographic analysis.[2] However, acyclic analogues were found to be unstable and decomposed easily to form the corresponding thiasulfonium salts on dealkylation.[3] We report here the first formation of hybrid-type selenathia, tellurathia and telluraselena dications bearing a 2–(methylchalcogenomethyl) phenyl structure.

Ethyl 2-(methylthiomethyl)phenyl selenide **1a**, telluride **1b** and ethyl 2-(methylselenomethyl)phenyl telluride **1c** were prepared. **1a** was treated directly with 1 equivalent of Tf$_2$O[4] or 2 equivalents of NOPF$_6$ in CD$_3$CN at –40 °C and its ^{1}H, ^{13}C and ^{77}Se NMR spectra were measured *in situ*. A set of AB quartet peaks at 5.20 and 5.52 ppm (J = 16.8 Hz) and a singlet at 3.25 ppm due to the methyl group were obtained in the ^{1}H NMR spectrum and a signal at 852.0 ppm in the ^{77}Se NMR spectrum suggesting the generation of the selenathia dication **2a** at –40 °C, which is confirmed by the ^{13}C NMR spectra. These peaks were observed at the lower field than those of the starting selenide **1a**; especially, 580 ppm of the downfield shift in ^{77}Se NMR strongly supports the generation of **2a**. However, above 0 °C, the peaks began to shift gradually to the set of AB quartet peaks at 4.92 and 5.14 ppm (J = 16.4 Hz) and a methyl singlet at 3.07 ppm in the ^{1}H NMR spectrum and a shift to signal at 810.9 ppm in the ^{77}Se NMR spectrum. The AB quartet and the methyl singlet peaks indicate the formation of methyl selenasulfonium salt **3a**.

To compare the stability between **2a** and 1-ethyl-2-ethyl-*3H*-1,2-benzodithioledium bis(trifluoromethanesulfonate) **2f** which has been described in the previous paper[3b], a kinetic study for the thermolysis was carried out using the variable temperature ^{1}H NMR method. The plot of ln([a]/[a-x]) vs. time, where [a] was the initial concentration and [a–x] was the concentration of **2a** as a function of time, gave a straight line with a good correlation coefficient (r^2 = 0.995 – 0.997), indicating that the reaction obeys the first order equation with respect to the concentration of dication **2a**. The rate constant of deethylation from **2a** is $(5.072 \pm 0.279) \times 10^{-4}$ sec^{-1} (0 °C) which is ca. one-half of the corresponding dithia–analog **2f** $(9.808 \pm 0.035) \times 10^{-4}$ sec^{-1} (0 °C). This result indicates that **2a** is more stable than the sulfur analog at 0 °C.

Similarly, **1b** and **1c** were treated under the same reaction conditions. Each reaction showed typical downfield shift for formation of dications in the ^{1}H and ^{77}Se or ^{125}Te NMR spectra. The ^{1}H, ^{77}Se and ^{125}Te NMR chemical shifts of these dications and the starting materials are summarized in Table 1. In contrast to **2a** and **2f**, no significant changes in the ^{1}H NMR spectrum from –40 °C to 50 °C were observed, indicating that **2b** and **2c** are stable even at 50 °C. Therefore, the stability among the chalcogenides has been determined to be Te >> Se > S. Indeed, the tellurathia dication **2b** was isolated by treatment of **1b** with 1 equivalent of Tf$_2$O in anhydrous CH$_3$CN at –40 °C. After crystallization from CH$_3$CN-Et$_2$O, dication **2b** was obtained in 42% yield as pale yellow crystals. The ^{1}H NMR spectrum of **2b**, measured in CD$_3$CN at room temperature, exhibits the same signals as those obtained in the reaction of **1b** with Tf$_2$O *in situ*. However, because of its high hygroscopicity, X-ray



1 **2** **3** **4**

Compd	X	Y	R	Compd	X	Y	R
a	Se	S	Et	**d**	Te	S	^{i}Pr
b	Te	S	Et	**e**	Te	Se	^{i}Pr
c	Te	Se	Et	**f**	X^a	S	Et

^{a} **1f**: X = SO, **2f** and **3f**: X = S

Scheme 1.

Table 1. NMR and MS data for **1-3** which have TfO$^-$ as a counter anion

Compd	^{1}H (δ)		^{77}Se (δ)	^{125}Te (δ)	^{19}F (δ)	MS
	Ar–(C$\underline{H}_2$)–Y	Y–C$\underline{H}_3$	($J_{\mathrm{Se–Te}}$)	($J_{\mathrm{Te–Se}}$)		
1a	3.86 (s)	2.03 (s)	271.7			246 (EI, M$^+$)
2a	5.20, 5.52 (ABq, J = 16.8 Hz)	3.25 (s)	852.0			
3a	4.92, 5.12 (ABq, J = 16.4 Hz)	3.07 (s)	810.9		–75.5	217 (EI, M$^+$)
1b	3.86 (s)	1.99 (s)		418.8		296 (EI, M$^+$)
2b	4.86, 5.04 (ABq, J = 16.8 Hz)	2.89 (s)		1367.9	–75.4	445 [(FAB, (M–TfO$^-$)$^+$]
1c	3.95 (s)	1.91 (s)	165.3	415.8		342 (EI, M$^+$)
2c	4.94, 5.14 (ABq, J = 16.0 Hz)	2.97 (s)	375.0	1313.9	–79.3	491 [(FAB, (M–TfO$^-$)$^+$]
1d	3.89 (s)	1.93 (s)		581.0		310 (EI, M$^+$)
2d	4.87, 5.11 (ABq, J = 16.9 Hz)	3.00 (s)		1447.0		
3d	4.71, 4.84 (ABq, J = 16.1 Hz)	3.04 (s)		1585.4	–79.7	263 (EI, M$^+$)
1e	3.89 (s)	1.91 (s)	171.7	573.8		356 (EI, M$^+$)
2e	4.96, 5.20 (ABq, J = 15.2 Hz)	3.07 (s)	369.7	1375.6		
			(247.0 Hz)	(247.0 Hz)		
3e	4.73, 4.93 (ABq, J = 14.8 Hz)	2.99 (s)	337.2	1445.9	–79.8	313 (EI, M$^+$)
1f	3.73, 3.78 (ABq, J = 12.8 Hz)	2.04 (s)				214 (EI, M$^+$)
2f	5.51, 5.82 (ABq, J = 16.8 Hz)	3.52 (s)				
3f	5.00, 5.29 (ABq, J = 16.4 Hz)	3.00 (s)			–75.7	169 [(FAB, (M–TfO$^-$)$^+$]

crystallographic analysis has not been achieved.

Next, we prepared isopropyl 2-(methylthiomethyl)phenyl telluride **1d** and isopropyl 2-(methylselenomethyl)phenyl telluride **1e** and treated them under the same reaction conditions. The ^{1}H NMR spectra of these reactions indicate the generation of tellurathia dication **2d** and telluraselena dication **2e** at –40 °C (Table 1). The formation of dication **1e** was confirmed by ^{77}Se-^{125}Te NMR coupling as shown in Table 1. However, on elevating the temperature above 20 °C, dealkylation proceeded to form tellurasulfonium salt **3b** or telluraselenonium salt **3c** and *N*-isopropylacetamide was obtained after hydrolysis in high yield. The tellurasulfonium salt **3c** was isolated by treatment of the **1e** with 1 equivalent of Tf_2O in anhydrous CH_3CN at –40 °C to 20 °C. After isolation from CH_3CN-Et_2O, tellurasulfonium salt **3c** was obtained in 55% yield as brown crystals. The ^{1}H NMR spectrum of **3c**, measured in CD_3CN at room temperature, exhibits the same signals as those obtained after dealkylation from **2e**. The molecular structure of **3c** except for its counter anion part was characterized by the parent peaks in its MS spectrum.[5]

To obtain information on the stability of these dications (**2a**, **2b**, **2c** and **2f**), *ab initio* calculations were carried out at the RHF/3-21G$^{(*)}$ level using Spartan 4.1.2.[6] The atomic charges were calculated by the natural population analysis.[7]

The atomic charges on the central chalcogen atom in these dications were calculated to be +0.86 (S, **2f**), +1.06 (Se, **2a**), +1.54 (Te, **2b**) and +1.44 (Te, **2c**). The bond order of X-CH_2CH_3 in **2f**, **2a**, **2b** and **2c** are 0.773, 0.816, 0.909 and 0.910, respectively. This order agrees with the stability of the dications obtained by the experimental results. The dications become more stable as the electronegativity of the central chalcogen atom becomes smaller.

In conclusion, the preparation and stability of a new type of hybrid dications formed from the acyclic chalcogenides *via* transannular bond formation were studied. The dications become more stable as the electronegativity of the central chalcogen atom becomes smaller.

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5 **3e**: reddish brown crystals. mp 119.5–120.5 °C; ^{1}H NMR (400 MHz, CD_3CN, -35 °C) δ 2.99 (s, 3H), 4.73, 4.93 (ABq, J = 14.8 Hz, 2H), 7.32 (t, J = 8.0 Hz, 1H), 7.33 (t, J = 8.0 Hz, 1H), 7.46 (d, J = 8.0 Hz, 1H), 7.74 (d, J = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, CD_3CN) δ 19.7, 48.0, 122.9, 129.3, 130.1, 131.3, 135.3, 142.3; ^{77}Se NMR (76 MHz, CD_3CN) δ 337.2 (relative to Me_2Se); ^{125}Te NMR (126 MHz, CD_3CN) δ 1445.9 (relative to Me_2Te); ^{19}F NMR (254 MHz, CD_3CN) δ –79.8 (relative to $CFCl_3$); EI–MS (m/z) 313 (M–TfO$^-$)$^+$; Anal. Calcd for $C_9H_9F_3O_3SSeTe$: C, 23.46; H, 1.97%. Found: C, 23.23; H, 2.15%.

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