A Facile Preparation of Rubidium and Caesium Selenocarboxylates

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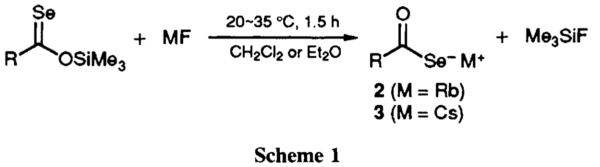
Treatment of *O*-trimethylsilyl selenocarboxylates with rubidium and caesium fluorides affords rubidium and caesium selenocarboxylates in good yields.

Alkali metal selenocarboxylates are one of the most important class of compounds for the synthesis of selenocarboxylic acid derivatives. In these salts, the preparation of lithium, sodium, and potassium selenocarboxylates has been established by the reaction of acyl chlorides with the corresponding metal selenides[1] or of diacyl selenide with potassium methanolate.[1c–e] However, until this work, the rubidium **2** and caesium selenocarboxylates **3** have remained elusive, though synthetically and spectroscopically interesting compounds. The above two methodologies cannot be applied to the preparation of **2** and **3**, because of the difficulty of the synthesis of the starting metal selenides (Rb_2Se and $C2_2Se$) and alcoholates (RO^-M^+, M = Rb, Cs). Furthermore, the salt-exchange reaction, which has been employed for the preparation of the sulfur analogues, rubidium and caesium thio-[2] and dithio-carboxylates,[3] is also unsuitable owing to the extreme instability of selenocarboxylic acids themselves. We now report the facile and general preparation and isolation of **2** and **3**.

The preparation of **2** and **3** was achieved by the reaction of *O*-trimethylsilyl selenocarboxylates **1**[4] (hereafter referred to as the *O*-silyl selenoester) with rubidium and caesium fluorides, respectively (Scheme 1). For example, when rubidium fluroide and a slight excess of *O*-silyl selenoester **1** (R = 4-MeC_6H_4) were stirred in dichloromethane at room temp., the red–violet colour of the ester gradually disappeared. After stirring for 1.5 h, filtration of the resulting precipitates and recrystallization from a mixed solvent of methanol and ethanol (1:2) afforded 80% of rubidium 4-methylbenzene-



Scheme 1

Table 1 Yields and νC=O bands of rubidium **2** and caesium selenocarboxylates **3**

Compound	RCOSe$^-$M$^+$ R	M	Yield[a] (%)	M.p.[b] /°C	νC=O[c] /cm^{-1}	Colour
2a	Bu^t	Rb	71	86–108	1560	Pale yellow
2b	Ph	Rb	74	141–159	1545	Yellow
2c	4-MeC$_6$H$_4$	Rb	80	143–167	1546	Yellow
2d	4-MeOC$_6$H$_4$	Rb	75	101–123	1542	Yellow
3a	Bu^t	Cs	74	95–104	1558	Pale yellow
3b	Ph	Cs	79	173–198	1547	Yellow
3c	4-MeC$_6$H$_4$	Cs	80	138–145	1547	Yellow
3d	4-MeOC$_6$H$_4$	Cs	68	151–158	1538	Yellow

[a] Isolated yield. [b] Decomposition. [c] KBr.

carboselenoates **2c**.†‡ Similarly, the reaction with other aliphatic and aromatic *O*-trimethylsilyl selenoesters **1** (R = akyl, aryl) gave the corresponding rubidium salts **2a–d**‡ in good yields. Under the same conditions using diethyl ether as a solvent, the reaction with caesium fluoride provided the high yields of the expected caesium salts **3a–d**.‡§ In contrast to the fluorides, it is noted that the reactions with other rubidium and caesium halogenides did not occur even under refluxing conditions of tetrahydrofuran.

The obtained rubidium **2** and caesium salts **3** are pale-yellow to yellow plate crystals. They are insoluble in common aprotic solvents, but dissolve in protic solvents and can be readily recrystallized from methanol, ethanol or a mixed solvent of the alcohols and diethyl ether. The aromatic salts (**2**, **3**, R = aryl) are more stable thermally and towards oxygen than the aliphatics. For example, the appreciable change of the 4-methylbenzene derivatives **2c** and **3c** in the solid state are not observed even after being left to stand at room temp. for 3 h or in the case instance described below 0 °C for over a week. However, the most simple aliphatic derivatives, rubidium and caesium selenoacetates (**2** and **3**, R = Me) are highly unstable and quickly decompose even at −20 °C with liberation of red selenium.

In conclusion, the first selenocarboxylic acid rubidium **2** and caesium salts **3** have been isolated from the reaction of *O*-silyl selenoesters **1** with the corresponding metal fluorides. We believe that this simple synthetic approach will stimulate further investigation of not only these salts, but also many other chalcogeno-carboxylic, -carbamic, and -carbon acid heavy metal salts.

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† *Spectroscopic data* for **2c**: IR ν/cm^{-1} (KBr): 3050, 1606, 1579, 1546 (νC=O), 1291, 1200, 1158, 1107, 1011, 903, 820, 789, 762, 717, 628, 615, 740, 454; ^{1}H NMR (270 MHz, CD$_3$OD): δ 2.31 (s, 3H, CH$_3$), 7.1–8.1 (m, 4H, Ar); ^{13}C NMR (67.8 MHz, CD$_3$OD): δ 21.4 (CH$_3$), 128.9, 129.5, 142.3, 145.2 (Ar), 215.1 (CO); ^{77}Se NMR (51.5 MHz, CD$_3$OD): δ 357.3.

‡ Satisfactory spectral data and elementary analyses have been obtained for all new compounds.

§ *Spectroscopic data* for **3c**: IR ν/cm^{-1} (KBr): 3050, 1607, 1580, 1547 (νC=O), 1407, 1295, 1200, 1161, 1110, 903, 824, 792, 632, 472; ^{1}H NMR (270 MHz, CD$_3$OD): δ 2.32 (s, 3H, CH$_3$), 7.1–8.1 (m, 4H, Ar); ^{13}C NMR (67.8 MHz, CD$_3$OD): δ 21.4 (CH$_3$), 128.8, 129.5, 142.1, 145.3 (Ar), 215.2 (CO); ^{77}Se NMR (51.5 MHz, CD$_3$OD): δ 361.9.