

The First Example of the Generation of Acylselenenyl Halides from *Se*-Arsanyl Selenoesters: Application to the Synthesis of *Se*- β -Oxoalkyl Selenoesters

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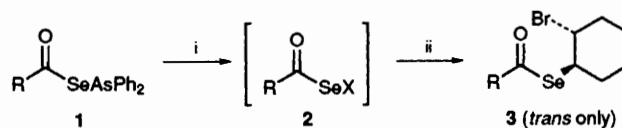
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Acylselenenyl halides **2** (X = Cl, Br) have been generated from RC(O)SeAsPh₂ **1** and *N*-halogenosuccinimide, and the chlorides **2** (X = Cl) have been treated with enol silyl ethers to give *Se*- β -oxoalkyl selenoesters **5** in good yields.

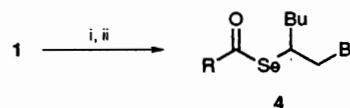
Selenocarboxylic acid esters are of increasing importance in view of their synthetic utility.^{1,2} The conventional methods for the introduction of RC(O)Se moieties have been limited to acylation or alkylation of nucleophilic selenium species such as RSeM and RC(O)SeM (M = Li, Na, K, AlMe₂, etc.).²⁻⁴ On the other hand, no precedent has been reported for an electrophilic selenocarboxylating agent, although sulfur counterparts have been well studied.⁵ We report here the first example of the generation of acylselenenyl halides **2** (X = Cl, Br) and their application to the synthesis of *Se*- β -oxoalkyl selenoesters **5**.

A variety of selenoesters [RC(O)SeM, M = Sn, Pb, etc.]⁶ were treated with *N*-bromosuccinimide (NBS), and to the resulting mixture was added cyclohexene. Interestingly, when the *Se*-arsanyl ester **1**† was employed as the starting material at -70 °C, the reaction gave the selenoester **3** in 62% yield as the *trans*-isomer (Scheme 1). Similarly, the reaction with *N*-chlorosuccinimide (NCS) gave the adduct, but as a stereoisomeric mixture. In trapping with hex-1-ene, the correspond-

ing adduct **4** was obtained regioselectively (Scheme 2). These results clearly indicated that **2** (X = Br) was generated *in situ* and then underwent addition to cyclohexene and hex-1-ene *via* an epi-selenonium ion intermediate.⁷ Unfortunately, attempts to isolate acylselenenyl halides **2** (X = Cl, Br) have failed and gave [RC(O)Se]₂. This instability of **2** is in sharp



Scheme 1 Reagents and conditions: i, **1**, NBS, CH₂Cl₂, -70 °C, 1 h; ii, cyclohexene, -70 to 20 °C, 1 h, 62% (X = Br)



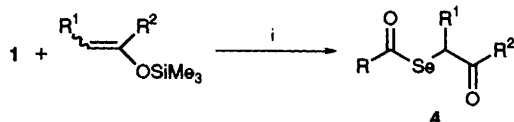
Scheme 2 Reagents and conditions: i, **1**, NBS, CH₂Cl₂, -70 °C, 1 h; ii, hex-1-ene, -70 to 20 °C, 1 h, 41%

† Compounds RC(O)SeAsPh₂ **1** were prepared from the corresponding RC(O)SeNa and Ph₂AsCl.

Table 1 Synthesis of β -oxoalkyl selenoesters from *Se*-arsanyl selenoesters **1**, NCS and enol silyl ethers^a

Entry	Product 5			Yield (%) ^b
	R	R ¹	R ²	
1	4-MeC ₆ H ₄	Me	Et	65
2		-[CH ₂] ₃ CHMe-		52 ^c
3		-[CH ₂] ₄ -		67
4	Ph			50
5	4-MeOC ₆ H ₄			60
6	4-ClC ₆ H ₄			62
7	Me ₂ N			55

^a All reactions were carried out under argon atmosphere. ^b Isolated yields. ^c *cis-trans*-Mixture (1:1).

**Scheme 3** Reagents and conditions: i, **1**, NCS, enol silyl ether (5 equiv.), CH₂Cl₂, 20 °C, 1 h

contrast to that of the sulfur analogues for which even iodide derivatives can be isolated.⁵

In order to obtain further proof of the generation of **2** (X = Cl), a variety of olefins were examined as the trapping reagent. Addition to olefins having electron-donating groups proceeded smoothly. The results of the reaction of **1** and NCS with enol silyl ethers are summarised in Table 1 (Scheme 3). The use of excess amounts (5.0 equiv.) of enol silyl ethers gave *Se*- β -oxoalkyl esters **5**‡ in good yields (entries 1–6), compounds which are not easy to prepare by other methods.⁸ The addition of the RC(O)Se moiety took place regioselectively at the carbon atom remote from the Me₃SiO group accompanied with the elimination of Me₃Si. This is again indicative of the occurrence of the electrophilic introduction of the RC(O)Se moiety analogous to the reaction of PhSeBr.⁹ Substitution of the aromatic ring with methoxy and chloro groups did not affect the product yields (entries 5 and 6). The reaction of *Se*-arsanyl carbamoselenoate also proceeded in a similar manner to yield the selenoester in 55% yield (entry 7),

‡ All new compounds gave satisfactory spectral and/or analytical data.

whereas the reaction of aliphatic selenoesters gave rise only to [RC(O)Se]₂ as the sole product.

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