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Generation of α-Radicals of Acetic Acid Derivatives from α-Stannyl Ester and Amide and Their Reactions with Electron-Rich Olefins

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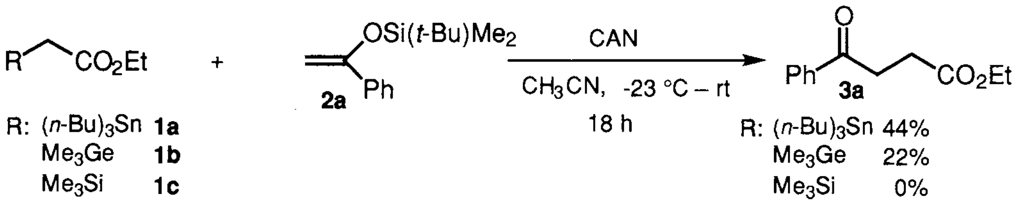
Oxidation of α-tributylstannyl ester and amide with Ce^{IV} compounds generates α-radicals of acetic acid derivatives with the elimination of the stannyl group. The radicals thus generated react with various electron-rich olefins to give the corresponding addition products in good yield.

Oxidative coupling of silyl enol ethers or ketene silyl acetals is a useful synthetic method for the preparation of 1,4-dicarbonyl compounds.1) However, for the cross coupling of silyl enol ethers, one of the silyl enol ethers has to be employed in large excess.1a,d) In addition, ketene silyl acetals have been generally utilized to synthesize symmetrical succinic acid derivatives2) and only one example was recently reported for the cross-coupling reaction.1e)

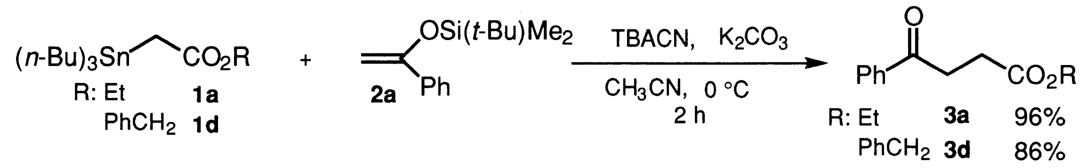
It seemed to be difficult to prevent the self-coupling reaction when the radical species are generated from enol derivatives such as silyl enol ethers by the oxidation,1d) because such substrates also have a property to act as radical acceptors. It is known that α-stannyl acetates exist in equilibrium with the *O*-metallated (enol) forms but predominantly in *C*-metallated(α-stannyl) forms.3) Recently we reported that the one-electron oxidation of α-stannyl sulfides and *N*-(1-stannylalkyl) amides gives the corresponding carbocations with the cleavage of the stannyl-carbon bonds.4) Accordingly, it was expected that the oxidation of α-stannyl acetates may give α-radicals or cations of acetates with the elimination of the stannyl group and then would react with olefinic compounds.

Actually, the reaction of ethyl 2-(tributylstannyl)acetate (**1a**) and α-(*t*-butyldimethylsiloxy)styrene (**2a**, 2 molar amounts) in the presence of 2 molar amounts of ammonium hexanitratocerate(IV) (CAN) gave the addition product **3a** in 44% yield.5) It was also noted that ethyl 2-(trimethylsilyl)acetate (**1c**)6) was hard to be oxidized under the same reaction conditions and the oxidation of a mixture of 2-trimethylgermyl derivative **1b**7) and **2a** with CAN afforded the addition product **3a** in 22% yield (Eq. 1).8)



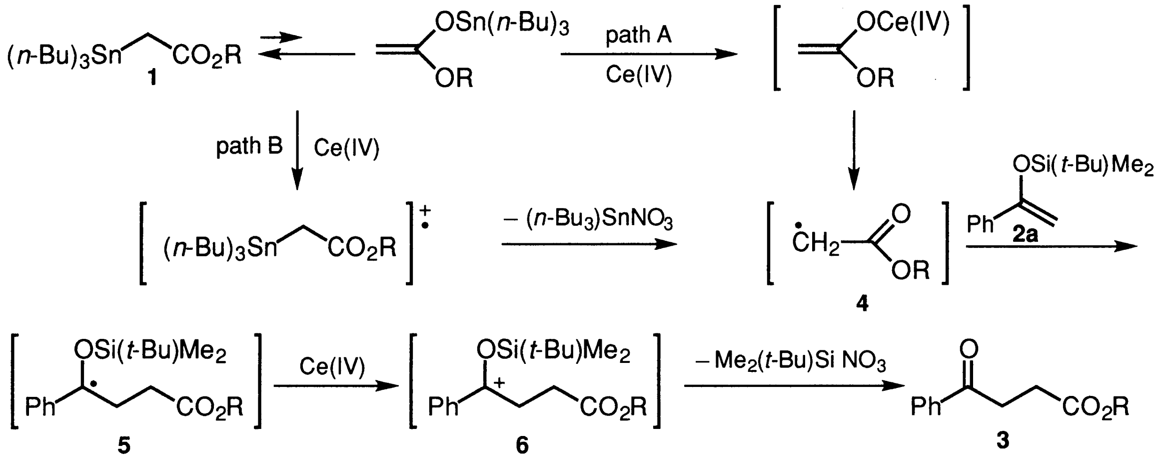
(1)

As the result of examining the reaction conditions, the addition product **3a** or **3d** was obtained in 96% or 86% yield, respectively, by the treatment of a mixture of 1.3 molar amounts of the stannyl ester **1a** or **1d** and the enol ether **2a** with 2 molar amounts of tetrabutylammonium hexanitratocerate(IV) (TBACN)[9] as an oxidant in the presence of K_2CO_3 at 0 °C (Eq. 2). The treatment of **1d** with TBACN in the absence of the acceptor **2a** afforded the homo-coupling product, dibenzyl succinate, in 46% yield, but the above reactions gave the crossed addition products exclusively and none of the succinate was detected.



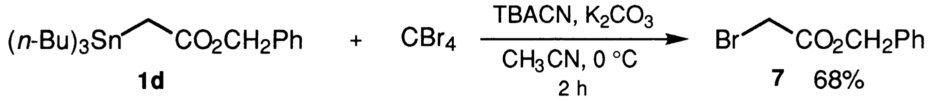
(2)

The reaction is supposed to proceed via the α-radical of acetate **4**. That is, the α-stannyl acetate **1** is oxidized to generate the radical **4** with Ce(IV) through either the path A or B, which adds to the silyl enol ether **2a**. The resulting α-siloxy radical **5** is further oxidized with Ce(IV) to the cation **6**, and the γ-keto ester **3** is formed eventually with the elimination of the silyl nitrate (Scheme 1).



Scheme 1.

Formation of the α-radical **4** was confirmed by the following experiments. The oxidation of **1d** with TBACN in the presence of CBr_4 as a radical trapping reagent[10] gave benzyl 2-bromoacetate (**7**) in 68% yield (Eq.3). The reaction of **1d** and **2a** was also tried in the presence of CBr_4, and the adduct **3d** was obtained in 70% yield along with **7** in 14% yield but not with α-bromoacetophenone.

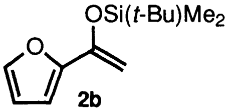
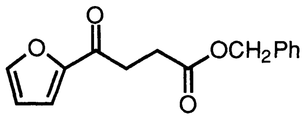
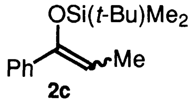
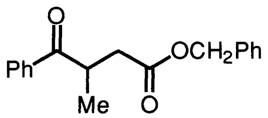
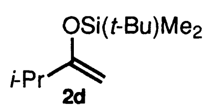
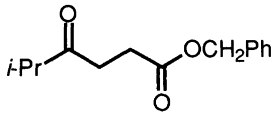
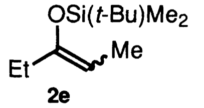
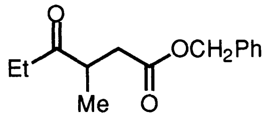
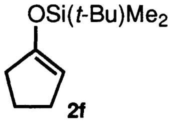
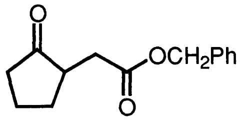
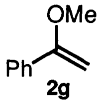
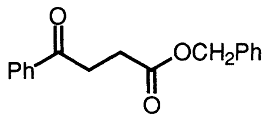
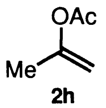
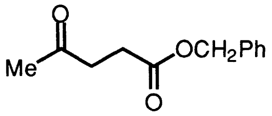
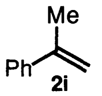
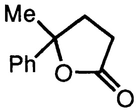
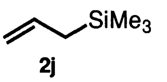
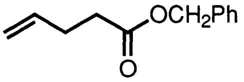


(3)

The reactions of the α-stannyl ester **1d** and various electron-rich olefins **2** were illustrated in Table 1. In addition to aryl substituted silyl enol ethers **2a-c**, aliphatic silyl enol ethers **2d** and **2e**, trisubstituted silyl enol ethers **2e** and **2f**, a vinyl ether **2g** and vinyl acetate **2h** also reacted with **1d** and the addition products were isolated in good yield. Moreover, the reaction of **1d** with α-methylstyrene (**2i**) also proceeded, giving 4-pheny-4-methyl-γ-butyrolactone in moderate yield.

The typical experimental procedure is as follows: To an acetonitrile (20 ml) solution of TBACN (2.25 g, 2.26 mmol) and K_2CO_3 (0.78 g, 5.65 mmol) was added an acetonitrile (5 ml) solution of **1d** (0.50 g, 1.13 mmol) and **2d** (0.20 g, 0.87 mmol) at 0 °C under an argon atmosphere. After stirring for 2 h, aq. $NaHCO_3$ was addeed

Table 1. The Reactions of **1d** with Olefins **2**

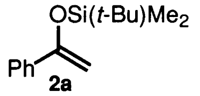
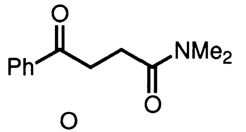
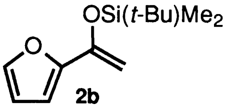
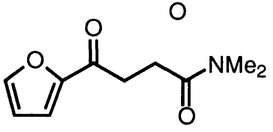
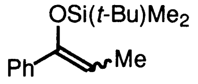
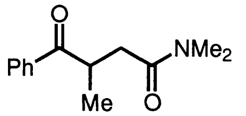
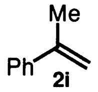
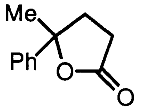
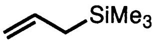
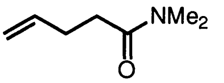
Olefin	Product	Yield/%
 **2b**		87
 **2c**		72
 **2d**		79
 **2e**		72
 **2f**		70
 **2g**		61
 **2h**		61
 **2i**		52
 **2j**		48

to the reaction mixture. Usual work-up and purification by column chromatography (ethyl acetate : hexane = 1 : 5, v/v) gave benzyl 5-methyl-4-oxohexanoate (0.16 g, 79%).

This method was also applied to the generation of a radical from an α-stannyl acetoamide. When *N*,*N*-dimethyl-2-tributylstannylacetamide (**8**)[11] was treated with TBACN in the presence of olefins **2** under the same reaction conditions described above, the addition products were obtained as shown in Table 2.

Thus the α-radicals of acetate and acetamide are readily generated from the α-tributylstannyl acetates **1a,d** and the acetamide **8** by the oxidation with Ce(IV), and the intermolecular addition reaction of these radicals occurs selectively with electron-rich olefins under mild reaction conditions.

Table 2. The Reactions of **8** with Olefins **2**

Olefin	Product	Yield/%
 **2a**		89
 **2b**		79
 **2c**		70
 **2i**		70
 **2j**		48

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8) By the cyclic voltammogram measurements, **1a** exhibited oxidation peaks at about 0.9 V and 2.7 V (*vs*. Ag/Ag$^+$, CH_3CN, irreversible), while **1b,c** showed no oxidation peaks up to 3 V.

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