Oxidative Generation of α-Radicals of Carbonyl Compounds from the α-Stannyl Derivatives and Their Reactions with Electron-Rich Olefins

Yasushi Kohno and Koichi Narasaka*

Department of Chemistry, Graduate School of Science, The University of Tokyo, 7-3-1, Hongo, Bunkyo-ku, Tokyo 113

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The oxidation of α-tributylstannyl alkanoates with tetrabutylammonium hexanitratocerate(IV) generates α-radicals of the alkanoates by eliminating the stannylium ion. The thus-formed radicals react with various electron-rich olefinic compounds, such as silyl enol ethers, giving addition products in good yield. This method formally achieves selective cross coupling between alkanoates and ketones.

The oxidative coupling of carbonyl compounds at their α-positions affords a straightforward method for preparing 1,4-dicarbonyl compounds. To realize this process, the oxidative coupling of silyl enol ethers or ketene silyl acetals has been studied extensively.[1,2] Although symmetrical 1,4-dicarbonyl compounds are readily available by applying the oxidative coupling of silyl enol ethers, this method has not been efficiently applied for preparing unsymmetrical 1,4-dicarbonyl compounds.[1] One of the silyl enol ethers has to be employed in excess amounts to prepare unsymmetrical 1,4-diketones with reasonable selectivity; only 2-siloxypropene has been employed as the acceptor of radical intermediates.[2] The coupling reaction of ketene silyl acetals has been utilized to synthesize symmetrical succinate derivatives.[3] Recently, Hirao et al. succeeded in the selective cross coupling of silyl enol ethers by using an oxovanadium compound as an oxidant, in which each silyl enol ether is used in equal amounts.[4] However, the combination of silyl enol ethers is limited and the silyl enol ethers employed as radical sources are required to be more substituted than the silyl enol ethers employed as radical acceptors, since the former must be oxidized more easily than the latter. In spite of these modifications, it generally seems to be difficult to prevent self-coupling reactions when radical species are generated from enol derivatives, because such derivatives act not only as radical sources, but also as radical acceptors (Scheme 1).

We have reported that the stannyl–carbon bonds of the cation radicals of α-stannyl sulfides and *N*-(1-stannylalkyl) amides and carbamates readily cleave to give the corresponding carbocationic intermediates and the stannyl radical (Scheme 2), and that the thus-formed cationic intermediates are utilized as synthetic intermediates for carbon–carbon bond formation.[5]

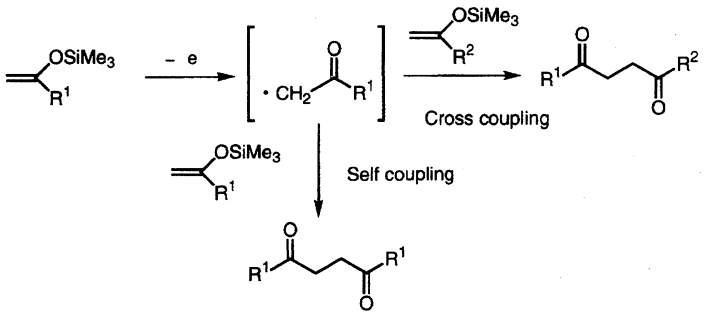
In addition, it was noted that the introduction of a stannyl group lowers the oxidation potential of the original sulfides, amides, and carbamates. This phenomenon had been observed by Yoshida and Glass; the introduction of a stannyl group is apparently more effective to lower the oxidation potential, compared with that of a silyl group.[6]

A cyclic voltammogram measurement was performed on α-stannyl, germyl, and silyl acetates, such as ethyl 2-(tributylstannyl)acetate (**1**), 2-(trimethylgermyl)-acetate (**2**), and 2-(trimethylsilyl)acetate (**3**). Ethyl 2-(tributylstannyl)acetate (**1**) exhibited oxidation peaks at about 0.9 and 2.7 eV (vs. Ag/Ag^+, CH_3CN, irreversible), while 2-trimethylgermyl and 2-trimethylsilyl derivatives **2**, **3** showed no oxidation peaks up to 3 eV. Hence, we intended to use α-stannyl alkanoates as radical sources to carry out cross-coupling reactions selectively in order to prepare unsymmetrical 1,4-dicarbonyl compounds. That is, when a mixture of an α-stannyl alkanoate and a silyl enol ether is oxidized, the α-stannyl alkanoate would be oxidized preferentially, giving an α-radical species along with an elimination of the stannylium ion. The thus-formed radical species would react with the silyl enol ether exclusively, because the α-stannyl alkanoate exists not in the *O*-metallated (enol) form, but predominantly in a *C*-metallated (α-stannyl) form (Scheme 3).[7]

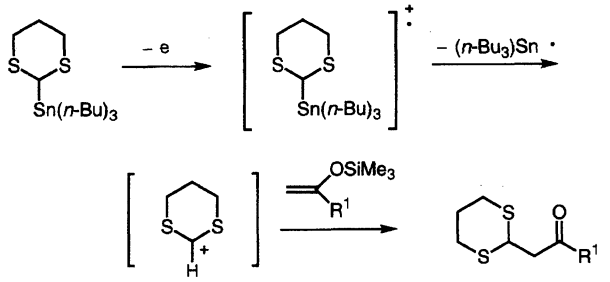
Based on the above consideration, we examined the oxidation of α-stannyl alkanoates with metallic oxidants as well as their addition reaction with olefinic compounds.

Results and Discussion

Preparation of γ-Keto Alkanoates by the Reaction of α-Tributylstannyl Alkanoates with Electron-Rich Olefins.[8] It is known by ^1H NMR

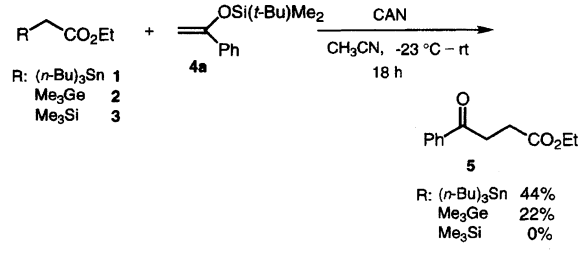


Scheme 1.



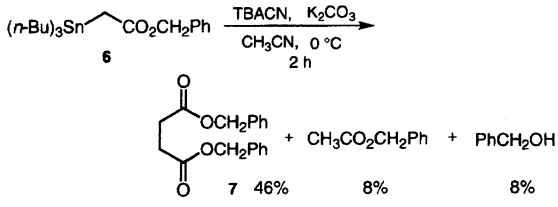
Scheme 2.

measurements that **1** exists as the α-stannyl (*C*-metallated) form, and that no detectable amount of the *O*-metallated tautomer is contained in the $CDCl_3$ solution.[7] The coupling reaction was first tried by using ethyl 2-tributylstannylacetate (**1**) as a radical source. The α-stannyl acetate **1** was oxidized with 2 molar amounts of ammonium hexanitratocerate(IV) (CAN) in the presence of 2 molar amounts of α-(*t*-butyldimethylsiloxy)styrene (**4a**). As expected, the addition product **5** was obtained in 44% yield (Eq. 1). The coupling reaction was also examined by employing the α-germyl acetate **2** and α-silyl acetate **3**;[9] however, these derivatives were found not to be suitable for radical sources, compared to the stannyl derivative **1**.



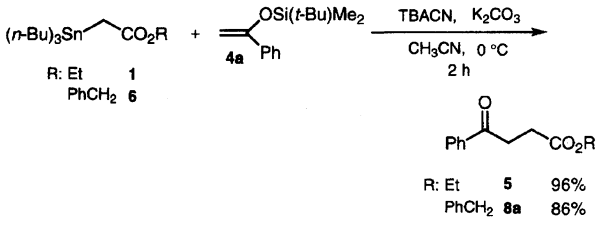
(1)

The reaction of the α-stannyl acetate **1** with α-siloxystyrene **4a** was examined by using various metallic oxidants, such as Mn^{III}, Ag^{II}, Fe^{III}, and Cu^{II} compounds. Among these oxidants, although only $CuCl_2$ could oxidize **1**, ethyl 2-chloroacetate was obtained in moderate yield and no addition product **5** was detected. Then, the reaction conditions were screened by using Ce(IV) compounds as oxidants. To neutralize the reaction medium, a reaction of **1** and **4a** was carried out in the presence of K_2CO_3 by oxidation with tetrabutylammonium hexanitratocerate(IV) (TBACN),[10] increasing the yield of **5** to 67%. Since the yield was not sufficiently increased, benzyl 2-tributylstannylacetate (**6**) was oxidized with TBACN in the absence of the acceptor **4a** in order to examine the degradation pathways of the cation radical of the α-stannyl ester. In addition to dibenzyl succinate (**7**), which is considered to be a self-coupling product of the α-radical(46%), benzyl acetate and benzyl alcohol were isolated in each 8% yield (Eq. 2).



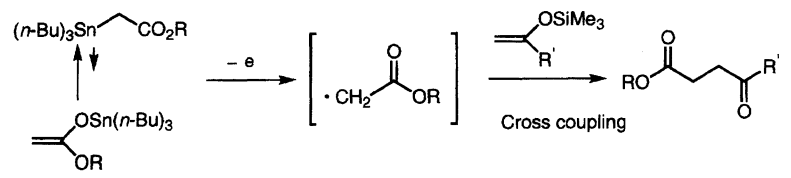
(2)

By the formation of benzyl alcohol, the cation radical of **6** was found to decompose into the formation of alcohol in addition to the generation of the α-radical.[11] The α-stannyl esters, **6** and **1**, were supposed to be slightly consumed due to the degradation to alcohols, even in a reaction with the silyl enol ether; hence, the reaction was attempted by employing small excess amounts of stannyl acetates, **1** or **6**. Thus, the addition product, **5** or **8a**, was obtained in 96 or 86% yield, respectively, by treating a mixture of **4a** and 1.3 molar amounts of **1** or **6** with 2 molar amounts of TBACN in the presence of K_2CO_3 (Eq. 3).



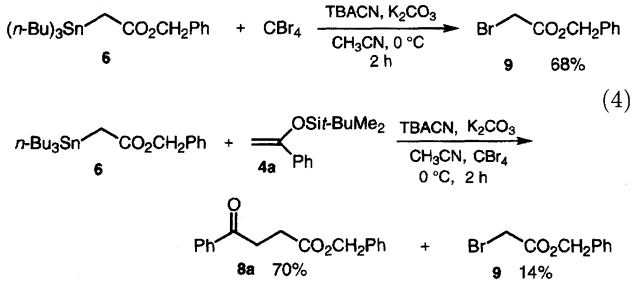
(3)

To ascertain the formation of the α-radicals from the stannylacetates, **6** was oxidized with TBACN in the presence of CBr_4 as a radical trapping reagent.[12] Although benzyl 2-bromoacetate (**9**) was isolated in 68% yield, bromotributyltin was not detected (Eq. 4). The reaction of **6** and **4a** was also tried in the presence of



Scheme 3.

CBr_4 and the adduct **8a** was obtained in 70% yield along with the bromoacetate **9** in 14% yield without the formation of α-bromoacetophenone (Eq. 5). Accordingly, the radical species is apparently generated from α-stannyl acetate **6**, and the oxidation of silyl enol ether **4a** hardly proceeds under these reaction conditions.

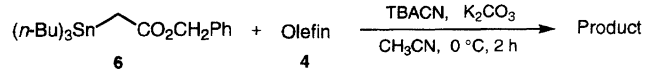


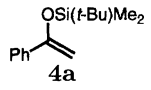
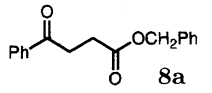
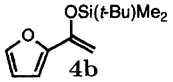
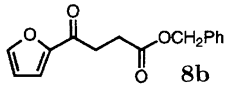
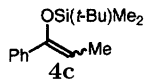
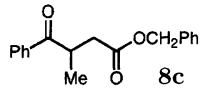
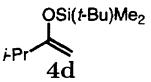
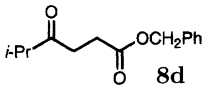
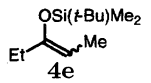
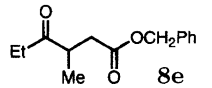
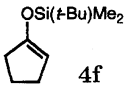
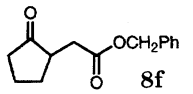
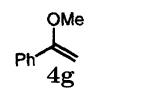
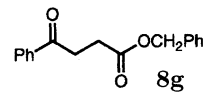
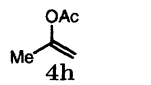
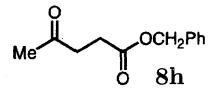
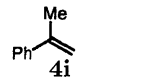
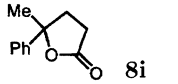
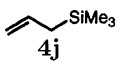
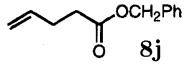
Based on the above-mentioned results, the reaction presumably proceeds as shown in Scheme 4. That is, the α-stannyl acetate **6** is oxidized with Ce(IV) to generate radical **10** via either path A or B, which adds to the silyl enol ether **4a**. The resulting radical-addition intermediate, an α-siloxy radical **11**, is further oxidized with Ce(IV) to a cation **12**, and the γ-keto ester **13** is eventually formed along with the elimination of a silyl nitrate.

The oxidative coupling of the α-stannyl ester **6** and various electron-rich olefins **4** exhibits a wide generality, as shown in Table 1. Silyl enol ethers, such as aromatic silyl enol ethers **4a**—**c**, aliphatic silyl enol ethers **4d**—**f**, and trisubstituted silyl enol ethers **4c**, **e**, and **f**, reacted with **6** to give γ-keto esters **8a-f** in good yield. A vinyl ether **4g**, a vinyl acetate **4h**, and an allylsilane **4j** gave the corresponding addition products in moderate yield. 1-Methylstyrene (**4i**) was also employed as a radical acceptor, giving 4-phenyl-4-methyl-γ-butyrolactone (**8i**).

It was noted that the α-stannyl acetates have been employed successfully as sources of alkoxycarbonylmethyl radicals. Thus, some other α-stannyl alkanoates, such as methyl 2-(tributylstannyl)propionate (**14**), methyl 2-(tributylstannyl)butyrate (**15**), and methyl 2-(tributylstannyl)isobutyrate (**16**), were prepared and provided for the oxidation. The reactions of α-stannyl alkanoates **14**, **15**, and **16** with aromatic silyl enol ethers **4a** and **b** were tried under the same reaction conditions as described above; the results are given in Table 2. The addition products were obtained in good yield in the reactions of α-stannyl alkanoates **14** and **15**. However, the disubstituted derivative **16** reacted with

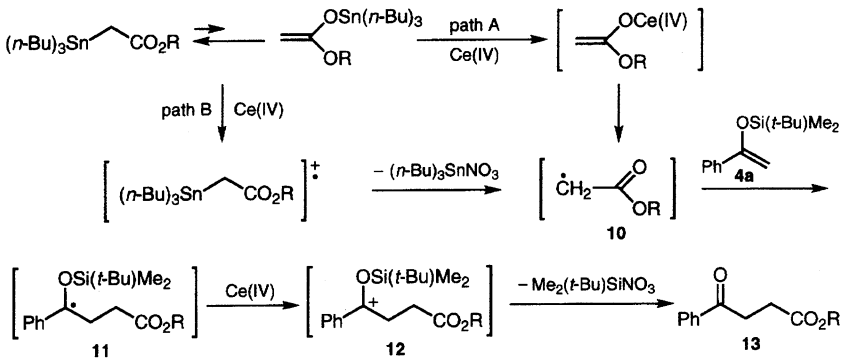
Table 1. Reaction of **6** with Olefinic Compounds **4**



Olefin	Product	Yield/%
 **4a**	 **8a**	86
 **4b**	 **8b**	87
 **4c**	 **8c**	72
 **4d**	 **8d**	79
 **4e**	 **8e**	72
 **4f**	 **8f**	70
 **4g**	 **8g**	61
 **4h**	 **8h**	61
 **4i**	 **8i**	52
 **4j**	 **8j**	48

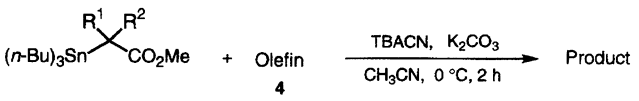
the silyl enol ethers **4** to give mainly the homo coupling product, dimethyl 2,2,3,3-tetramethylsuccinate, instead of the addition products **19a**, **b**, presumably due to a steric hindrance and the radical stability of the resulting tertiary α-radical.

Reaction of α-Tributylstannyl Acetamide with Electron-Rich Olefins. Although α-stannyl acetamides also exist in equilibrium with enol (*O*-stannyl) forms, they are predominantly in α-stannyl (*C*-metallated) forms, similarly to α-stannyl esters.[13] Accordingly, α-stannyl acetamides were expected to be uti-



Scheme 4.

Table 2. Reaction of **14**, **15**, and **16** with Silyl Enol Ethers **4a** and **4b**



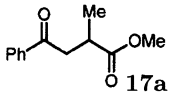
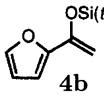
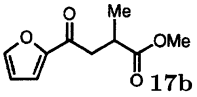
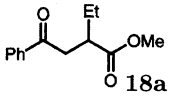
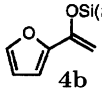
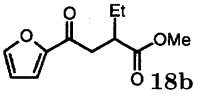
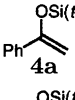
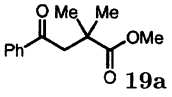
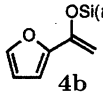
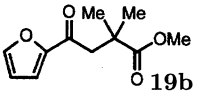
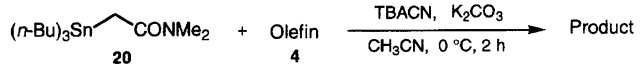
R^1	R^2	Olefin	Product	Yield/%
Me	H	 **4a**	 **17a**	80
14		 **4b**	 **17b**	82
Et	H	 **4a**	 **18a**	80
15		 **4b**	 **18b**	77
Me	Me	 **4a**	 **19a**	14
16		 **4b**	 **19b**	18

Table 3. Reaction of **20** with Olefinic Compounds **4**



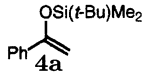
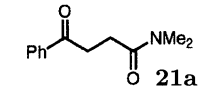
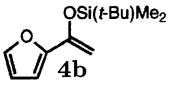
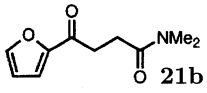
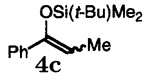
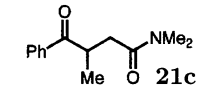
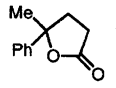
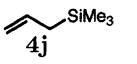
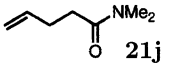
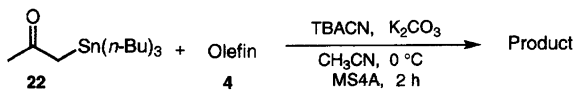
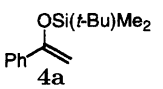
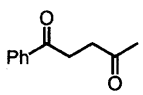
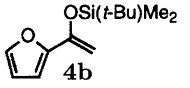
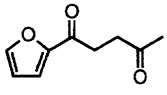
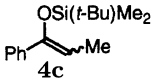
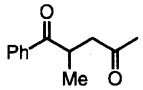
Olefin	Product	Yield/%
 **4a**	 **21a**	89
 **4b**	 **21b**	79
 **4c**	 **21c**	70
 **4i**	 **8i**	70
 **4j**	 **21j**	48

Table 4. Reaction of **22** with Olefinic Compounds **4**



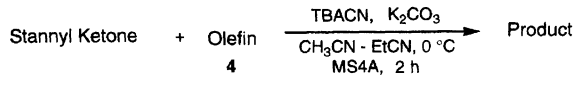
Olefin	Product	Yield/%
 **4a**	 **23a**	63
 **4b**	 **23b**	56
 **4c**	 **23c**	49

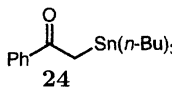
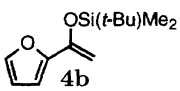
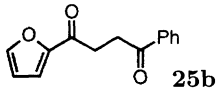
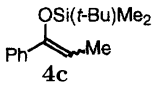
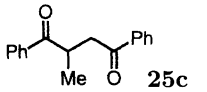
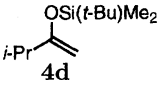
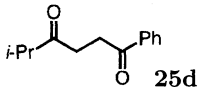
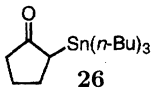
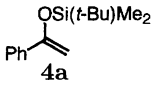
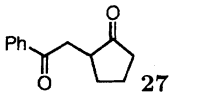
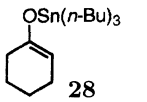
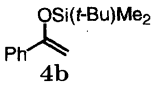
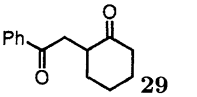
lized as radical sources for oxidative additions to olefins. Thus, *N,N*-dimethyl-2-(tributylstannyl)acetamide (**20**) was treated with TBACN in the presence of several olefins **4** under the same reaction conditions, as shown in Table 3, the reaction generally proceeded to give addition products **21** and **8**.

Reactions of α-Stannyl Ketones with Electron-Rich Olefins. As mentioned above, self coupling is well suppressed by using α-stannyl carboxylic acid derivatives as radical sources. This is mainly because the *C*-stannylated structures are predominant in the α-stannyl esters and amides. In contrast with stannyl esters and amides, it has been reported concerning the structure of α-stannyl ketones that the tautomer ratios of the *O*- and *C*-stannyl forms are widely dependent on the substrates.[14]

α-(Tributylstannyl)acetone (**22**) is known to exist in the *C*-stannyl form predominantly over the *O*-stannyl

Table 5. Reaction of Stannyl Ketones **24**, **26**, and **28** with Olefinic Compounds **4**



Stannyl ketone	Olefin	Product	Yield/%
 **24**	 **4b**	 **25b**	48(18)[a]
	 **4c**	 **25c**	35(28)
	 **4d**	 **25d**	18(30)
 **26**	 **4a**	 **27**	8(28)
 **28**	 **4b**	 **29**	13(39)

a) Yield of the self-coupling products from the stannyl ketones.

tautomer.[15,16] The stannylacetone **22** was generated in situ from isopropenyl acetate and tributylstannyl methoxide,[15] and then oxidized with TBACN in the presence of the silyl enol ether **4a**. Although the cross-coupling product **23a** was obtained in 49% yield, no self coupling product, 2,5-hexanedione, was isolated. When the reaction was performed in the presence of Molecular Sieves 4A, the product yield was increased to 63%. A silyl enol ether of 2-acetylfuran **4b** and a trisubstituted silyl enol ether **4c** were also employed as radical acceptors; however, the yield of the addition products was rather low compared with that in the reactions of the stannyl acetates (Table 4).

The oxidation reactions of some α-stannyl ketones, such as α-(tributylstannyl)acetophenone (**24**),[15,16] 2-(tributylstannyl)cyclopentanone (**26**),[16] and 1-(tributylstannyloxy)cyclohexene (**28**),[16] were examined in the presence of silyl enol ethers (Table 5). It has been reported that, in equilibrium, the ratio of the *C*-stannyl and the *O*-stannyl forms of α-stannylacetophenone **24** is ca. 7 : 3 and that of the cyclopentanone derivative **26** is 1 : 1, while **28** exists almost exclusively in the *O*-stannyl form.[15,16] As depicted in Table 5, the yield of the cross-coupling products of the stannyl ketones and silyl enol ehters decreased as the ratio of the *O*-stannyl form to the *C*-stannyl one increased. When the ratio of the *O*-stannyl form becomes over 0.5, self-coupling reaction products are generated preferentially. Thus, it is apparent that the selectivity of the cross-coupling reaction between the α-stannyl derivatives with olefinic compounds essentially depends on the tautomer ratio of the *C* and *O*-stannyl forms.

In conclusion, the α-radicals of carboxylic acid derivatives are readily generated from the corresponding α-tributylstannyl derivatives by the oxidation with Ce(IV), and the intermolecular addition reaction of these radicals proceeds selectively to electron-rich olefins under mild reaction conditions. This method can be utilized for preparing unsymmetrical 1,4-dicarbonyl compounds, particularly γ-keto carboxylic acid derivatives.

Experimental

General. IR spectra were measured with a Horiba FT 300-S spectrometer. ^{1}H NMR spectra (500 MHz) were recorded on a Bruker AM 500 spectrometer with $CHCl_3$ (δ=7.24) used as an internal standard. High-resolution mass spectra were recorded on a JEOL JMS-SX102A mass spectrometer operating at 70 eV. All melting points are uncorrected.

Cyclic voltammetry was measured with a Hokuto Denko HA-151 potentiostat/galvanostat connected to a Hokuto Denko HA-111 function generator. We used an undivided cell equipped with a platinum disk anode and a platinum wire cathode in 0.1 M Et_4NClO_4/CH_3CN. An Ag/AgI (saturated NaI solution in CH_3CN) electrode was used as a reference. The sweep rate was 100 mV s^{-1}.

Acetonitrile and propiononitrile were distilled from P_2O_5, then CaH_2, and dried over Molecular Sieves 4A (MS 4A). CAN (Kanto Chemical Co., Inc., guaranteed grade) and K_2CO_3 (Kanto Chemical Co., Inc., guaranteed grade) were dried under a vacuum at 80 °C before use. TBACN was prepared by a known method.[10] Silyl enol ethers (**4a**—**4f**),[17] vinyl ether **4g**,[18] and allyltrimethylsilane (**4j**),[19] were synthesized according to the literature. Isopropenyl acetate

(**4h**) and α-methylstyrene (**4i**) were distilled from CaH_2. Ethyl 2-(tributylstannyl)acetate (**1**), benzyl 2-(tributylstannyl)acetate (**6**), methyl 2-(tributylstannyl)propionate (**14**), methyl 2-(tributylstannyl)butyrate (**15**), and methyl 2-(tributylstannyl)isobutyrate (**16**) were prepared according to the literature.[7] Ethyl 2-(trimethylgermyl)acetate (**2**) and ethyl 2-(trimethylsilyl)acetate (**3**) were prepared according to the literature.[9] *N,N*-Dimethyl-2-(tributylstannyl)acetamide (**20**) was prepared by a method reported by Roubineau and Pommier.[13] α-(Tributylstanny)acetone (**22**), α-(tributylstannyl)acetophenone (**24**), 2-(tributylstannyl)cyclopentanone (**26**), and 1-(tributylstannyloxy)cyclohexene (**28**) were prepared by the known methods.[15,16]

The reactions were monitored by thin-layer chromatography (TLC) using precoated silica gel plates (Merck Kieselgel 60 F-254 Art.5715). Silica-gel column chromatography was carried out with Merck Kieselgel 60 Art.7734. Preparative TLC was performed on silica gel (Wakogel B-5F).

All of the reactions were carried out under an argon atmosphere.

General Procedure for the Reaction of 2-Tributylstannylalkanoates with Olefinic Compounds. 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 (5.0 ml) solution of benzyl 2-(tributylstannyl)acetate (**6**) (0.50 g, 1.13 mmol) and the silyl enol ether **4d** (0.20 g, 0.87 mmol) at 0 °C under an argon atmosphere. After stirring for 2 h, saturated aqueous sodium hydrogencarbonate was added to the reaction mixture; the mixture was filtered through Celite. Organic materials were extracted with dichloromethane, and the combined extracts were dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure and the residue was purified by column chromatography (hexane : ethyl acetate=5 : 1, v/v) to afford benzyl 5-methyl-4-oxohexanoate (**8d**) (0.16 g, 79%).

Spectral data and physical properties of the coupling products are as follows.

Ethyl 4-Oxo-4-phenylbutyrate (5):[20] Colorless oil; IR (neat) 1734, 1687, 1369, and 1169 cm^{-1}; ^1H NMR δ=1.21 (3H, t, J=7.2 Hz), 2.70 (2H, t, J=6.6 Hz), 3.25 (2H, t, J=6.6 Hz), 4.10 (2H, q, J=7.2 Hz), 7.39—7.42 (2H, m), 7.49—7.52 (1H, m), and 7.92—7.94 (2H, m). Found: C, 69.60; H, 6.83%. Calcd for $C_{12}H_{14}O_3$: C, 69.89; H, 6.84%.

Benzyl 4-Oxo-4-phenylbutyrate (8a): Colorless oil; IR (neat) 1736, 1687, 1215, and 750 cm^{-1}; ^1H NMR δ=2.81 (2H, t, J=6.6 Hz), 3.32 (2H, t, J=6.6 Hz), 5.14 (2H, s), 7.29—7.35 (5H, m), 7.43—7.46 (2H, m), 7.54—7.57 (1H, m), and 7.96—7.97 (2H, m). Found: C, 76.02; H, 6.06%. Calcd for $C_{17}H_{16}O_3$: C, 76.10; H, 6.01%.

Benzyl 4-(2-Furyl)-4-oxobutyrate (8b): Colorless crystals; mp 59—60 °C (hexane-ethyl acetate); IR (KBr) 1730, 1668, 1468, and 1165 cm^{-1}; ^1H NMR δ=2.78 (2H, t, J=6.8 Hz), 3.17 (2H, t, J=6.8 Hz), 5.12 (2H, s), 6.51 (1H, dd, J=3.4 and 1.6 Hz), 7.19 (1H, d, J=3.4 Hz), 7.28—7.35 (5H, m), and 7.56 (1H, d, J=1.6 Hz). Found: C, 69.78; H, 5.51%. Calcd for $C_{15}H_{14}O_4$: C, 69.76; H, 5.46%.

Benzyl 3-Methyl-4-oxo-4-phenylbutyrate (8c): Colorless oil; IR (neat) 1734, 1684, 1169, and 978 cm^{-1}; ^1H NMR δ=1.21 (3H, d, J=7.1 Hz), 2.50 (1H, dd, J=16.8 and 5.6 Hz), 3.02 (1H, dd, J=16.8 and 8.5 Hz), 3.92—3.99 (1H, m), 5.05 (1H, d, J=12.3 Hz), 5.09 (1H, d, J=12.3 Hz), 7.29—7.32 (5H, m), 7.43—7.46 (2H, m), 7.53—7.56 (1H, m), and 7.95—7.97 (2H, m). Found: C, 76.76; H, 6.55%. Calcd for $C_{18}H_{18}O_3$: C, 76.57; H, 6.43%.

Benzyl 5-Methyl-4-oxohexanoate (8d): Colorless oil; IR (neat) 1738, 1714, and 1163 cm^{-1}; ^1H NMR δ=1.08 (6H, d, J=6.9 Hz), 2.57—2.63 (1H, m), 2.61 (2H, t, J=6.6 Hz), 2.76 (2H, t, J=6.6 Hz), 5.09 (2H, s), and 7.27—7.33 (5H, m). Found: C, 71.73; H, 7.60%. Calcd for $C_{14}H_{18}O_3$: C, 71.77; H, 7.74%.

Benzyl 3-Methyl-4-oxohexanoate (8e): Colorless oil; IR (neat) 1736, 1716, and 1178 cm^{-1}; ^1H NMR δ=1.02 (3H, t, J=7.3 Hz), 1.09 (3H, d, J=7.3 Hz), 2.32 (1H, dd, J=16.8 and 5.2 Hz), 2.42—2.57 (2H, m), 2.82 (1H, dd, J=16.8 and 9.0 Hz), 2.96—3.03 (1H, m), 5.03 (1H, d, J=12.3 Hz), 5.08 (1H, d, J=12.3 Hz), and 7.27—7.34 (5H, m). HRMS Found: m/z 234.1257. Calcd for $C_{14}H_{18}O_3$: M, 234.1256.

Benzyl 2-(2-Oxocyclopentyl)acetate (8f): Colorless oil; IR (neat) 1738, 1263, and 1163 cm^{-1}; ^1H NMR δ=1.54—1.62 (1H, m), 1.74—1.81 (1H, m), 1.97—2.03 (1H, m), 2.08—2.16 (1H, m), 2.23—2.33 (2H, m), 2.40—2.47 (2H, m), 2.73—2.78 (1H, m), 5.10 (2H, s), and 7.28—7.35 (5H, m). Found: C, 72.14; H, 6.95%. Calcd for $C_{14}H_{16}O_3$: C, 72.39; H, 6.94%.

Benzyl 4-Oxopentanoate (8h):[21] Colorless oil; IR (neat) 1732, 1724, and 1157 cm^{-1}; ^1H NMR δ=2.16 (3H, s), 2.61 (2H, t, J=6.4 Hz), 2.74 (2H, t, J=6.4 Hz), 5.10 (2H, s), and 7.28—7.36 (5H, m).

4-Methyl-4-phenyl-γ-butyrolactone (8i):[22] Colorless oil; IR (neat) 1776, 1246, and 1134 cm^{-1}; ^1H NMR δ=1.65 (3H, s), 2.33—2.46 (3H, m), 2.53—2.61 (1H, m), 7.21—7.24 (1H, m), and 7.28—7.36 (4H, m).

Benzyl 4-Pentenoate (8j):[23] Colorless oil; IR (neat) 1738 and 1165 cm^{-1}; ^1H NMR δ=2.37—2.42 (2H, m), 2.44—2.48 (2H, m), 4.97—5.01 (1H, m), 5.02—5.07 (1H, m), 5.12 (2H, s), 5.78—5.86 (1H, m), and 7.29—7.37 (5H, m).

Methyl 2-Methyl-4-oxo-4-phenylbutyrate (17a):[24] Colorless oil; IR (neat) 1736, 1687, 1450, and 1173 cm^{-1}; ^1H NMR δ=1.26 (3H, d, J=7.1 Hz), 3.01 (1H, dd, J=17.7 and 5.5 Hz), 3.08—3.15 (1H, m), 3.46 (1H, dd, J=17.7 and 7.9 Hz), 3.68 (3H, s), 7.43—7.46 (2H, m), 7.53—7.56 (1H, m), and 7.94—7.95 (2H, m).

Methyl 4-(2-Furyl)-2-methyl-4-oxobutyrate (17b): Colorless crystals; mp 52 °C (hexane–ethyl acetate); IR (KBr) 1736, 1678, 1468, and 1227 cm^{-1}; ^1H NMR δ=1.23 (3H, d, J=7.3 Hz), 2.87 (1H, dd, J=17.2 and 5.9 Hz), 3.05—3.13 (1H, m), 3.29 (1H, dd, J=17.2 and 7.9 Hz), 3.66 (3H, s), 6.51 (1H, dd, J=3.5 and 1.5 Hz), 7.17 (1H, d, J=3.5 Hz), and 7.55 (1H, d, J=1.5 Hz). Found: C, 61.40; H, 6.19%. Calcd for $C_{10}H_{12}O_4$: C, 61.22; H, 6.16%.

Methyl 2-Ethyl-4-oxo-4-phenylbutyrate (18a): Colorless oil; IR (neat) 1734, 1685, 1448, and 1169 cm^{-1}; ^1H NMR δ=0.95 (3H, t, J=7.4 Hz), 1.62—1.74 (2H, m), 2.97—3.02 (1H, m), 3.03 (1H, dd, J=17.3 and 4.7 Hz), 3.44 (1H, dd, J=17.3 and 8.6 Hz), 3.68 (3H, s), 7.42—7.45 (2H, m), 7.52—7.55 (1H, m), and 7.93—7.95 (2H, m). HRMS Found: m/z 220.1086. Calcd for $C_{13}H_{16}O_3$: M, 220.1099.

Methyl 2-Ethyl-4-(2-furyl)-4-oxobutyrate (18b): Colorless oil; IR (neat) 1734, 1678, 1468, and 1167 cm^{-1}; ^1H NMR δ=0.92 (3H, t, J=7.4 Hz), 1.58—1.73 (2H, m), 2.89 (1H, dd, J=17.2 and 5.0 Hz), 2.94—2.99 (1H, m), 3.27 (1H, dd, J=17.2 and 8.9 Hz), 3.66 (3H, s), 6.50 (1H, dd, J=3.4 and 1.6 Hz), 7.17 (1H, d, J=3.4 Hz), and 7.55 (1H, d, J=1.6 Hz). HRMS Found: m/z 210.0882. Calcd for

$C_{11}H_{14}O_4$: M, 210.0892.

Methyl 2, 2- Dimethyl- 4- oxo- 4- phenylbutyrate (19a):[25] Colorless oil; IR (neat) 1736, 1689, and 1200 cm^{-1}; ^1H NMR δ=1.30 (6H, s), 3.27 (2H, s), 3.65 (3H, s), 7.41—7.44 (2H, m), 7.51—7.55 (1H, m), and 7.90—7.92 (2H, m).

Methyl 2,2- Dimethyl- 4- (2- furyl)- 4- oxobutyrate (19b): Colorless oil; IR (neat) 1734, 1678, 1469, and 1201 cm^{-1}; ^1H NMR δ=1.26 (6H, s), 3.10 (2H, s), 3.62 (3H, s), 6.48 (1H, dd, J=3.5 and 1.5 Hz), 7.11 (1H, d, J=3.5 Hz), and 7.51 (1H, d, J=1.5 Hz). HRMS Found: m/z 210.0891. Calcd for $C_{11}H_{14}O_4$: M, 210.0892.

The Reaction of Benzyl 2- (Tributylstannyl)- acetate with CBr_4. To an acetonitrile (20 ml) solution of TBACN (1.00 g, 1.00 mmol) and K_2CO_3 (0.35 g, 2.50 mmol) was added an acetonitrile (5.0 ml) solution of benzyl 2-(tributylstannyl)acetate (**6**) (0.25 g, 0.50 mmol) and CBr_4 (1.66 g, 5.00 mmol) at 0 °C under an argon atmosphere. After stirring for 2 h, saturated aqueous sodium hydrogencarbonate was added to the reaction mixture, and the mixture was filtered through Celite. Organic materials were extracted with dichloromethane, and the combined extracts were dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure and the residue was purified by preparative TLC (hexane : ethyl acetate=5 : 1) to give benzyl 2-bromoacetate (**9**) (0.08g, 68%). Colorless oil; IR (neat) 1741 and 1279 cm^{-1}; ^1H NMR δ=3.85 (2H, s), 5.19 (2H, s), and 7.33—7.36 (5H, m).

General Procedure for the Reaction of Tributylstannyl Amide with Olefinic Compounds. To an acetonitrile (20 ml) solution of TBACN (2.15 g, 2.15 mmol) and K_2CO_3 (0.74 g, 5.39 mmol) was added an acetonitrile (5.0 ml) solution of *N,N*-dimethyl-2-(tributylstannyl)acetamide (**20**) (0.41 g, 1.08 mmol) and the silyl enol ether **4a** (0.19 g, 0.83 mmol) at 0 °C under an argon atmosphere. After stirring for 2 h, saturated aqueous sodium hydrogencarbonate was added to the reaction mixture; the mixture was then filtered through Celite. Organic materials were extracted with dichloromethane, and the combined extracts were dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure and the residue was purified by preparative TLC (hexane : ethyl acetate=1 : 1) to afford *N,N*-dimethyl-4-oxo-4-phenylbutanamide (**21a**) (0.15 g, 89%).

Spectral data and physical properties of the addition products **21** are as follows.

***N,N*-Dimethyl-4-oxo-4-phenylbutanamide (21a):**[26] Colorless oil; IR (neat) 1685, 1645, 1496, and 1251 cm^{-1}; ^1H NMR δ=2.75 (2H, t, J=6.6 Hz), 2.93 (3H, s), 3.06 (3H, s), 3.32 (2H, t, J=6.6 Hz), 7.41—7.44 (2H, m), 7.50—7.54 (1H, m), and 7.97—7.99 (2H, m).

***N,N*-Dimethyl-4-(2-furyl)-4-oxobutanamide (21b):** Colorless crystals; mp 52 °C (hexane–ethyl acetate); IR (KBr) 1670, 1639, 1468, and 1144 cm^{-1}; ^1H NMR δ=2.65 (2H, t, J=6.6 Hz), 2.83 (3H, s), 2.96 (3H, s), 3.08 (2H, t, J=6.6 Hz), 6.42 (1H, dd, J=3.5 and 1.5 Hz), 7.12 (1H, d, J=3.5 Hz), and 7.48 (1H, t, J=1.5 Hz). Found: C, 61.41; H, 6.66; N, 7.25%. Calcd for $C_{10}H_{13}NO_3$: C, 61.53; H, 6.71; N, 7.18%.

***N, N*- Dimethyl- 3- methyl- 4- oxo- 4- phenylbutanamide (21c):** Colorless oil; IR (neat) 1684, 1645, 1406, and 1242 cm^{-1}; ^1H NMR δ=1.15 (3H, d, J=7.2 Hz), 2.35 (1H, dd, J=16.3 and 4.6 Hz), 2.84 (3H, s), 2.98 (3H, s), 3.00 (1H, dd, J=16.3 and 9.4 Hz), 4.00—4.05 (1H, m), 7.39—7.42 (2H, m), 7.47—7.50 (1H, m), and 7.97—7.99 (2H, m). HRMS Found: m/z 219.1249. Calcd for $C_{13}H_{17}NO_2$: M, 219.1260.

***N,N*-Dimethyl-4-pentenamide (21j):**[27] Colorless oil; IR (neat) 1647 and 1498 cm^{-1}; ^1H NMR δ=2.31—2.38 (4H, m), 2.90 (3H, s), 2.96 (3H, s) 4.92—4.95 (1H, m), 4.99—5.02 (1H, m), and 5.78—5.86 (1H, m).

General Procedure for the Reaction of Tributylstannyl Ketones with Olefinic Compounds. To an acetonitrile (10 ml) and propiononitrile (10 ml) solution of TBACN (2.25 g, 2.26 mmol), K_2CO_3 (0.78 g, 5.65 mmol) and MS 4A (0.50 g) was added a propiononitrile (5.0 ml) solution of a tributylstannyl ketone (1.30 mmol) and an olefin (1.00 mmol) at 0 °C under an argon atmosphere. After stirring for 2 h, saturated aqueous sodium hydrogencarbonate was added to the reaction mixture; the mixture was then filtered through Celite. Organic materials were extracted with dichloromethane, and the combined extracts were dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure and the residue was purified by preparative TLC (hexane : ethyl acetate=5 : 1) to afford an addition product.

Spectral data and physical properties of the products are as follows.

1-Phenyl-1,4-pentanedione (23a):[2,4] Colorless oil; IR (neat) 1716, 1685, and 1360 cm^{-1}; ^1H NMR δ=2.43 (3H, s), 2.85 (2H, t, J=6.3 Hz), 3.24 (2H, t, J=6.3 Hz), 7.40—7.43 (2H, m), 7.50—7.53 (1H, m), and 7.93—7.95 (2H, m).

1-(2-Furyl)-1,4-pentanedione (23b):[28] Colorless oil; IR (neat) 1716, 1676, and 1469 cm^{-1}; ^1H NMR δ=2.18 (3H, s), 2.81 (2H, t, J=6.6 Hz), 3.08 (2H, t, J=6.6 Hz), 6.48 (1H, dd, J=3.5 and 1.6 Hz), 7.16 (1H, d, J=3.5 Hz), and 7.53 (1H, d, J=1.6 Hz).

1-Phenyl-2-methyl-1,4-pentanedione (23c):[29] Colorless oil; IR (neat) 1714, 1682, and 1452 cm^{-1}; ^1H NMR δ=1.13 (3H, d, J=7.2 Hz), 2.12 (3H, s), 2.51 (1H, dd, J=18.1 and 5.0 Hz), 3.12 (1H, dd, J=18.1 and 8.5 Hz), 3.89—3.95 (1H, m), 7.41—7.44 (2H, m), 7.49—7.53 (1H, m), and 7.93—7.95 (2H, m).

1- (2- Furyl)- 4- phenyl- 1, 4- butanedione (25b):[30] Colorless crystals; mp 88 °C (hexane–ethyl acetate); IR (KBr) 1674, 1466, and 1236 cm^{-1}; ^1H NMR δ=3.29 (2H, t, J=6.5 Hz), 3.43 (2H, t, J=6.5 Hz), 6.53 (1H, dd, J=3.5 and 1.7 Hz), 7.25 (1H, d, J=3.5 Hz), 7.44—7.47 (2H, m), 7.54—7.57 (1H, m), 7.59 (1H, d, J=1.7 Hz), and 8.00—8.01 (2H, m). Found: C, 73.95; H, 5.38%. Calcd for $C_{14}H_{12}O_3$: C, 73.67; H, 5.30%.

1,4-Diphenyl-2-methyl-1,4-butanedione (25c):[31] Colorless oil; IR (neat) 1678, 1593, 1448, and 1213 cm^{-1}; ^1H NMR δ=1.27 (3H, d, J=7.0 Hz), 3.10 (1H, dd, J=17.9 and 4.9 Hz), 3.71 (1H, dd, J=17.9 and 8.5 Hz), 4.15—4.19 (1H, m), 7.42—7.49 (4H, m), 7.51—7.57 (2H, m), 7.96—7.98 (2H, m), and 8.03—8.04 (2H, m).

5-Methyl-1-phenyl-1,4-hexanedione (25d):[32] Colorless oil; IR (neat) 1711, 1685, 1450, and 1358 cm^{-1}; ^1H NMR δ=1.14 (6H, d, J=6.9 Hz), 2.71 (1H, quint, J=6.9 Hz), 2.89 (2H, t, J=6.4 Hz), 3.26 (2H, t, J=6.4 Hz), 7.42—7.45 (2H, m), 7.52—7.55 (1H, m), and 7.96—7.97 (2H, m).

2-Phenacylcyclopentanone (27):[2,4] Colorless oil; IR (neat) 1736, 1684, 1263, and 1215 cm^{-1}; ^1H NMR δ= 1.56—1.65 (1H, m), 1.79—1.89 (1H, m), 2.04—2.10 (1H, m),

2.22—2.30 (1H, m), 2.33—2.41 (2H, m), 2.63—2.66 (1H, m), 3.03 (1H, dd, J=18.0 and 8.1 Hz), 3.51 (1H, dd, J=18.0 and 3.3 Hz), 7.43—7.46 (2H, m), 7.53—7.56 (1H, m), and 7.93—7.95 (2H, m).

2-Phenacylcyclohexanone (29):[2,4] Colorless oil; IR (neat) 1706, 1685, 1448, and 1348 cm^{-1}; ^1H NMR δ= 1.41—1.88 (4H, m), 2.01—2.19 (2H, m), 2.29—2.42 (2H, m), 2.65 (1H, dd, J=17.6 and 5.7 Hz), 3.11—3.17 (1H, m), 3.57 (1H, dd, J=17.6 and 6.6 Hz), 7.41—7.44 (2H, m) 7.51—7.54 (1H, m), and 7.94—7.96 (2H, m).

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