On the Mechanism of the Reaction of α-Substituted Ketones with Allyltributylstannane

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Received January 4, 1996[⊗]

The mechanisms for the reaction of allyltributylstannane with a number of fragmentation probes, α-substituted acetophenones, were studied. All reactions were shown to proceed through free radical chain sequences since they could be initiated by AIBN and inhibited by *m*-dinitrobenzene (DNB). α-Halo- and α-(benzoyloxy)acetophenones (**I** and **II**, $PhCOCR_1R_2X$; X = F, Cl, Br, OCOPh; R_1, R_2 = H, Me) yielded the allylation products, $PhCOCR_1R_2CH_2CH{=}CH_2$), through a chain sequence involving as the propagation step: an electron transfer from $Bu_3Sn^•$ to **I** and **II**, fragmentation of the ketyl anion $PhCOCR_1R_2X^{•-}$, and addition of $PhCOCR_1R_2^•$ to allyltributylstannane. The reactions of α-(arylsulfonyl)acetophenones (**IIIa**−**c**, $PhCOCR_1R_2Y$, Y = SO_2Tol-*p*), however, gave a nearly 1:1 mixture of allyl tosyl sulfone and the corresponding ketone, $PhCOCHR_1R_2$. The ^1H and ^{13}C NMR of the reaction mixture between allyltributylstannane and α-(*p*-methylbenzenesulfonyl)-isobutyrophenone substantiated the intermediacy of the tin enolate $PhC(OSnBu_3){=}CMe_2$. These results suggested that a radical addition elimination mechanism was involved in the reactions of **IIIa**−**c** with allylstannane. The reaction of α-phenylthioacetophenone (**IV**, $PhCOCH_2SPh$) gave both the electron transfer and the addition elimination products ($PhCOCH_2CH_2CH{=}CH_2$, $PhCOCH_3$), indicating that both pathways were involved in the formation of the products.

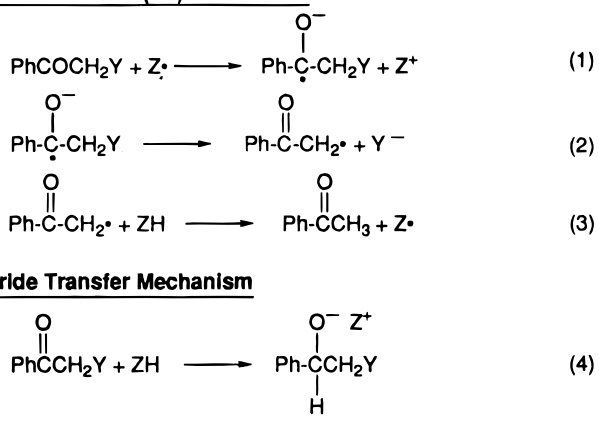
Introduction

A recent publication reported that a series of α-substituted acetophenones ($PhCOCH_2Y$, Y = Br, Cl, F, OPh, OCOPh, SO_2Ar, and SPh) can be used as ketone fragmentation probes to study the involvement of electron transfer (ET) steps in the reactions of these ketones.[3] Since these substituted acetophenone ketyls undergo very fast cleavage ($k_f > 10^6$ s^{-1}) to yield the enolyl radical $PhCOCH_2^•$, formation of the products derived from the enolyl radical can be used as a diagnostic tool for detecting the involvement of ET reactions. These probes have been used to distinguish between ET and hydride transfer mechanisms in the reductions by organotin hydrides,[4] organosilanes,[5] *N*-benzyl-1,4-dihydronicotinamide (BNAH),[6] and 1,3-dimethyl-2-phenylbenzimidazoline (DMBI).[7] Acetophenone is the diagnostic product of the ET pathway, see Scheme 1, while the alcohol ($PhCHOHCH_2Y$) is the product of hydride transfer.

The reaction of organotin hydrides with a variety of alkyl or aryl halides has been studied extensively.[8] The reactions of α-arylsulfonyl or α-phenylthioacetophenones with tin hydride have also been reported,[4c,9] The mechanistic details for these reactions are, however, still not conclusively established.

Scheme 1

Electron Transfer (ET) Mechanism



Hydride Transfer Mechanism

Y = Br, Cl, F, OCOR, OPh, SO_2Ar, SPh

ZH = R_3'SnH, R_3'SiH, BNAH, DMBI

The allylation of organic halides with allyltributylstannane provides a powerful and selective synthetic method for C−C bond formation with the introduction of an allyl group.[10−13] The reaction has been shown to proceed through a free radical chain mechanism (eqs 5 and 6). The chain-propagating steps involve displacement of halogen (X) by the tin radical (eq 5) and the addition of the alkyl radical to the allylstannane (eq 6).

⊗ Abstract published in *Advance ACS Abstracts,* June 1, 1996.

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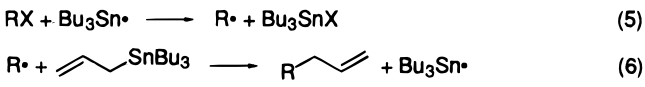


Since one of the radical chain transfer species in both the allylation reaction and the tin hydride reduction is the tin radical, it was of interest to investigate the mechanism of the reaction of the recently reported ketone fragmentation probes (α-substituted ketones)[3,4] with an allylstannane. This approach can provide additional mechanistic details for the tin hydride reduction of these ketones. In addition, it was anticipated that the synthetic utility of an allylstannane could be extended to other organic substrates.

Results and Discussion

The α-substituted acetophenones studied in this work were easily prepared using methods described previously.[3,4c] The reactions of **I**−**IV** with allyltributylstannane were carried out at 61 °C in dry benzene. Radical initiation (AIBN) and inhibition (*m*-dinitrobenzene, *m*-DNB) were used to establish whether a free radical chain mechanism was involved in these reactions. The results of the reactions are summarized in Tables 1−4.

$C_6H_5COCR_1R_2X$ **Ia-e**	$C_6H_5COCH_2X$ **IIa-b**
a, X=F, R_1=R_2=H	a, X=OCOPh
b, X=Cl, R_1=R_2=H	b, X=OPh
c, X=Br, R_1=R_2=H	
d, X=Br, R_1=Me, R_2=H	
e, X = Br, R_1=R_2=Me	
$C_6H_5COCR_1R_2SO_2Tol$-*p* **IIIa-c**	$C_6H_5COCR_1R_2SPh$ **IVa-b**
a, R_1=R_2=H	a, R_1=R_2=H
b, R_1=Me, R_2=H	b, R_1=R_2=Me
c, R_1=R_2=Me	

1. Reactions of α-Halo-, α-(Benzoyloxy)-, and α-Phenoxyacetophenone with Allyltributylstannane. The reaction of the α-haloacetophenones (**Ia**−**c**) with allyltributylstannane gives 4-pentenophenone as the only product in 0−39% yields in the absence of AIBN (Table 1, entries 1, 3, and 6). Qualitatively, the reactivity of these compounds follows the order $PhCOCH_2Br$ > $PhCOCH_2Cl$ > $PhCOCH_2F$, the same as that obtained previously for the reductions by organotin hydrides,[4a] dihydropyridines,[6] and 1,3-dimethyl-2-phenylbenzimidazoline.[7] The addition of small amounts of AIBN initiates the reactions to yield near quantitative amounts of allylation products (Table 1, entries 2, 4, and 7). When there is an uninitiated reaction product, formation is completely inhibited by the addition of *m*-DNB (Table 1, entries 5 and 8).

Similarly, the reaction of α-(benzoyloxy)acetophenone (**IIa**) with allyltributylstannane is initiated by the addition of AIBN (5%) to give 4-pentenophenone in 83% yield (Table 2, entry 14), while the mixture of **IIa** and allyltributylstannane yields only 14% of the allylation product at 61 °C without the presence of AIBN (Table 2, entry 13). The reaction of α-phenoxyacetophenone (**IIb**) with allyltributylstannane, however, seems to be much slower

Table 1. Reaction of α-Substituted Ketones with Allyltributylstannane[a,b]

reaction	compound $PhCOCR_1R_2X$	additive (%)	products (%) $PhCOCR_1R_2$-$CH_2CH{=}CH_2$	unreacted ketone (%)
1	**Ia**	−	0	99.6 ± 0.1
2	**Ia**	AIBN (5)	94.7 ± 0.1	6.1 ± 1.0
3	**Ib**	−	29.6 ± 5.6	62.4 ± 6.2
4	**Ib**	AIBN (5)	95.0 ± 0.5	0
5	**Ib**	*m*-DNB (5)	0	98.2 ± 0.0
6	**Ic**	−	38.9 ± 13.2	47.1 ± 10.0
7	**Ic**	AIBN (5)	95.4 ± 0.4	0.9 ± 0.9
8	**Ic**	*m*-DNB (5)	0	102 ± 0.0
9	**Id**	−	0	93.6 ± 1.1
10	**Id**	AIBN (5)	99.5 ± 6.3	0
11	**Ie**	−	0	90.3 ± 0.9
12	**Ie**	AIBN (5)	trace	80.2 ± 2.1

[a] All reactions were carried out at 61 °C in benzene for 53 h with a mole ratio of 1:2 of ketone to allyltributylstannane. [b] Yields determined by GC.

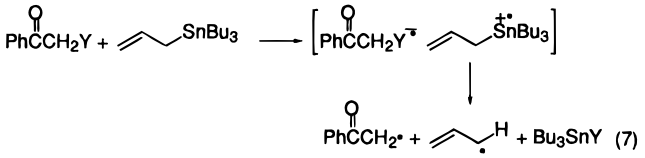
Table 2. Reaction of α-Substituted Ketones with Allyltributylstannane[a,b]

reaction	compound $PhCOCH_2X$	additives (%)	products (%) $PhCOCH_2CH_2$-$CH{=}CH_2$	unreacted ketone (%)
13	**IIa**	−	14.2 ± 0.5	80.9 ± 1.0
14	**IIa**	AIBN (4)	82.8 ± 1.1	0
15	**IIb**	−	0	>95.0
16	**IIb**	AIBN (4)	tr	>95.0

[a] All reactions were carried out at 61 °C in benzene for 53 h with a mole ratio of 1:2 of ketone to allyltributylstannane. [b] Yields determined by GC.

than the reaction of **IIa**, since it gives only a trace amount of 4-pentenophenone even in the presence of AIBN (Table 2, entry 16).

Initiation and inhibition of the reaction of these α-substituted acetophenones with allyltributylstannane clearly establishes that the reaction proceeds via a free radical chain mechanism. The initiation step in the absence of AIBN presumably occurs by an electron



transfer from allyltributylstannane to these ketones (eq 7). Photoinduced electron transfer reaction from allylstannanes to electron acceptors such as quinones,[13] aromatic ketones,[14] α,*β*-diketones,[15] and α-epoxy ketones[16] have recently been reported. On the basis of results obtained from studies of the reduction of α-halo ketones and α-(benzoyloxy)acetophenone with tin hydrides,[4] an electron transfer promoted chain mechanism is proposed to account for the formation of addition product, see Scheme 2. The chain propagation sequence (eqs 8−10), proceeds by enolyl radical, $PhCOCH_2^{\bullet}$, addition to allyltributylstannane to give 4-pentenophenone with the regeneration of a tributyltin radical (eq 10).

An apparent steric effect is observed for the allylation reactions of the series of α-bromo ketones. In the absence

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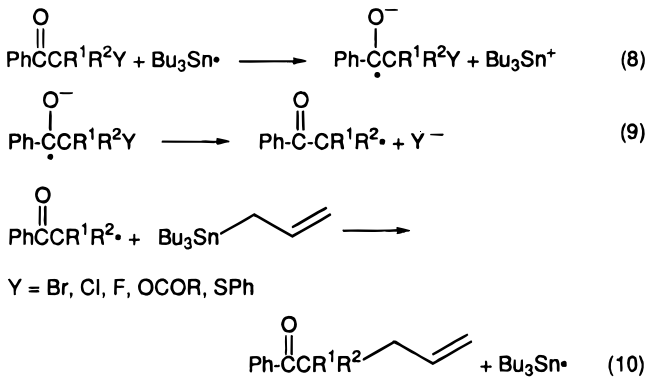
Scheme 2



of AIBN, the reaction of α-bromoacetophenone (**Ic**) with allyltributylstannane gave 4-pentenophenone in a 39% yield (Table 1, entry 6) whereas the reaction of α-bromopropiophenone (**Id**) does not occur without AIBN initiation. In the presence of 5% AIBN, **Id** gave 2-methyl-4-pentenophenone in a 99% yield (Table 1, entry 10). None of the expected allylation product, 2,2-dimethyl-4-pentenophenone, was produced from the reaction of α-bromoisobutyrophenone (**Ie**) (Table 1, entries 11, 12). These results are consistent with the proposed electron transfer free radical chain mechanism. For the secondary bromide **Id**, slower addition of the enolyl radical to allylstannane (eq 10) will result in a shorter chain and for the tertiary bromide, the addition is too slow to carry the chain.

Consistent with the chain mechanism is the observation that the reaction of **Ic** with allyltributylstannane is inhibited by the addition of 1 equiv of the unreactive tertiary bromoacetophenone, **Ie**. For example, **Ic** reacts with allyltributylstannane to give a 24% yield of 4-pentenophenone in 1 h, but only 0.45% of 4-pentenophenone is formed when 1 equiv of nonreactive **Ie** is added. A similar observation has been made for the reduction of α-halo ketones by 1,3-dimethyl-2-phenylbenzimidazoline (DMBI).[7a]

ET from the tin radical to **Ie** is not expected to be more favorable than that to **Ic**, and the radical addition to the allylstannane should be faster for the primary radical than for the tertiary radical (eq 10). As a result, the addition of the tertiary radical to the allylstannane (eq 10) is so slow that no tin radical is regenerated to carry the chain. The α-bromoacetophenone consequently appears to be unreactive.

The poor reactivity of α-phenoxyacetophenone (**IIb**) is no doubt due to the slow cleavage of its ketyl anion, since it has been shown that the ketyl anion of **IIb** cleaves approximately 1000 times more slowly than that of **IIa**[3] and that the addition of a simple alkyl radical to allylstannane is also relatively slow (10^{4-5} M^{-1} s^{-1} at 50−80 °C).[17] Combination of slower ketyl cleavage (eq 9) and enolyl radical addition (eq 10) results in inefficient chain propagation.

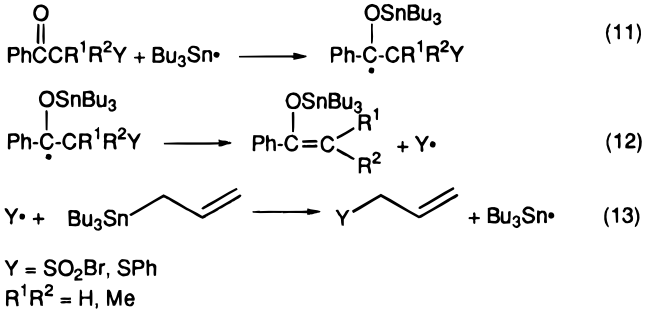
2. Reaction of α-Arylsulfonyl and α-Phenylthio Ketones with Allyltributylstannane. The reactions of α-arylsulfonyl ketones (**IIIa**−**c**, $PhCOCR_1R_2SO_2Tol$-*p*) with allylstannane were carried out under the same conditions as for the reactions of **I** and **II**. The initiation-inhibition studies showed that the reactions also proceed via a free radical chain mechanism. It was originally

Table 3. Reaction of α-Substituted Ketones with Allyltributylstannane[a]

reaction	compound $PhCOCR_1R_2$-SO_2Tol-*p*	additive (%)	products (%)[c,d] $PhCOCHR_1R_2$	products (%)[c,d] *p*-$TolSO_2CH_2$-$CH{=}CH_2$
19	**IIIa**	−	32.3 ± 10.4	31.4 ± 8.5
20	**IIIa**	AIBN (5)	89.4 ± 3.2	89.1 ± 1.9
21	**IIIa**	*m*-DNB (5)	0	0
22[b]	**IIIa**	−	1.3 ± 0.7	2.5 ± 1.3
23[b]	**IIIa**	AIBN (5)	77.9 ± 2.5	77.8 ± 1.3
24	**IIIb**	−	3.7 ± 3.7	3.0 ± 3.0
25	**IIIb**	AIBN (5)	79.1 ± 1.0	86.9 ± 0.2
26	**IIIc**	−	4.4 ± 4.0	7.9 ± 7.9
27	**IIIc**	AIBN (5)	95.5 ± 3.5[e]	91.5 ± 1.0

[a] All reactions were carried out at 61 °C in benzene for 48 h with a mole ratio of 1:2 of ketone to allyltributylstannane except noted. [b] With a mole ratio of 1:1 ketone to allyltributylstannane. [c] Yields determined by GC. [d] Recovered ketone accounts for the material balance. [e] The yields given were obtained when the reaction was carried out in the presence of added H_2O (10 equiv). The yield obtained without added H_2O was 36.8 ± 2.7 due to the formation of the unhydrolyzed tin enolate.

Scheme 3



expected that these reactions would afford the same products as the reactions of **I** and **II**. The enolyl radical trapping product, $PhCOCR_1R_2CH_2CH{=}CH_2$, however, was not formed. A nearly 1:1 mixture of allyl tosyl sulfone and $PhCOCHR_1R_2$, was obtained, instead (see Table 3).

The reactions of the compounds **I** and **II** with allyltributylstannane give free radical trapping products, whereas the reactions of the structurally similar compounds **IIIa**−**c** with allyltributylstannane gives quite different products. Since the enolyl radical trapping products are not formed in the chain reaction of **IIIa**−**c**, a different mechanistic sequence that does not involve the enolyl radical, $PhCOCR_1R_2^{\bullet}$, appears to be operative. A reaction pathway involving the attack by the tin radical at either the oxygen[18] or sulfur atom[9] of the sulfonyl or thio group can be ruled out, since one of the chain propagating species in all these free radical chain reactions would then be the enolyl radical, $PhCOCR_1R_2^{\bullet}$. Alternatively, a radical addition−elimination process can be envisioned to account for the formation of the products formed in the reaction of **IIIa**−**c** with allyltributylstannane (Scheme 3).

The addition of a tin radical to **IIIa**−**c** generates a stannylketyl radical[9b] (eq 11, Scheme 3) which undergoes fragmentation to give the tin enolate upon elimination of the arylsulfonyl radical (Y = $ArSO_2^{\bullet}$, eq 12). The arylsulfonyl radical adds to the allylstannane leading to allyl tosylsulfone and $Bu_3Sn^{\bullet}$ (eq 13).[19] The initially

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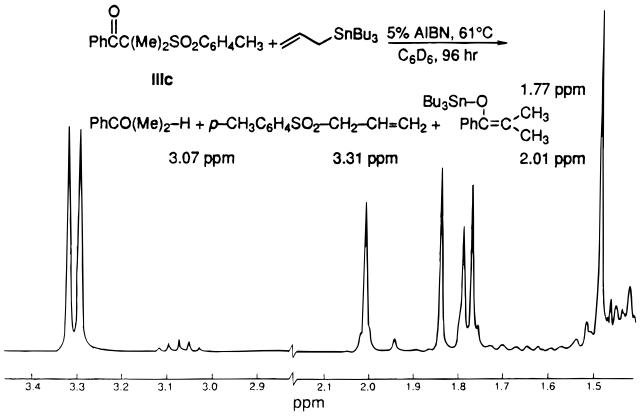

Figure 1. ^{1}H NMR (200 MHz, $CDCl_3$) spectra of the reaction mixture of **IIIc** with allyltributylstannane.

formed tin enolate is presumably hydrolyzed by adventitious water to afford the corresponding ketone.

In accordance with the proposed addition elimination mechanism, no steric effect is observed for the reaction of **IIIa**−**c** (Table 3, entries 20, 25, and 27) since it is expected that the rate for the addition of tributyltin radical to the carbonyl oxygen of **IIIa**−**c** would not be significantly affected by the bulkiness of the groups R_1 or R_2.

When **IIIc** reacts with allyltributylstannane, 92% of the allyl tosylsulfone is formed. However, only 37% of isobutyrophenone is produced (Table 3, entry 27). Presumably the intermediate, the tin enolate from **IIIc**, is not very susceptible to hydrolysis by adventitious water. In order to substantiate this proposal, the reaction of **IIIc** with allyltributylstannane was carried out with added water. When 0.02 mL of water is added to the reaction mixture of **IIIc** before the reaction tube is degassed, both isobutyrophenone and allyl tosyl sulfone are formed in a 96% yield. These results demonstrate that the tin enolate formed as an intermediate can be completely hydrolyzed to isobutyrophenone with sufficient water.

More conclusive evidence for the formation of the tin enolate is obtained from the NMR of the reaction mixture resulting from the reaction of **IIIc** with allyltributylstannane. The ^{1}H NMR spectrum of the reaction mixture of **IIIc** with allyltributylstannane shows that allyl tolyl sulfone is formed as a major product. However, only a trace of isobutyrophenone ($COCMe_2H$, δ = 3.07 ppm) is detected. Instead, two new single peaks (δ = 1.77 ppm and δ = 2.01 ppm) are observed. The signal at δ 1.77 can be assigned to the methyl protons of the tin enolate *trans* to the phenyl group, while the deshielded signal at δ 2.01 can be assigned to the methyl protons *cis* to the phenyl group (see Figure 1). The integrations of the methyl protons are in the same mole ratio as that of the methyl protons assigned to the allyl tolyl sulfone ($SO_2C_6H_4$-CH_3). A ^{13}C APT spectrum is also in agreement with the intermediacy of the tin enolate since it shows that carbons 1, 2, and 3 have no attached protons, (δ = 107.18 ppm, C1; δ = 142.55 ppm, C2; δ = 150.40 ppm, C3). When the same reaction was carried out in another NMR tube with added D_2O (0.02 mL), the ^{1}H spectrum showed that the methyl protons assigned to the tin enolate had disappeared. The absorption of the methyl groups of the isobutyrophenone increased at the expense of the methyl groups of the tin enolate.

Previous efforts to isolate or intercept the tin enolate in the tin hydride reductions of α-arylsulfonyl ketones have been unsuccessful.[3,4b,8,20] We now have been able to observe the formation of this intermediate in the reaction of **IIIc** with allylstannane. Since the tin enolate from **IIIc** is a tetrasubstituted alkene, it is more resistant to hydrolysis than the unhindered tin enolate from **IIIa**.

The reaction of α-phenylthioacetophenone (**IVa**) with allylstannane appears to be slower than that of α-arylsulfonyl acetophenone. Even in the presence of AIBN only a 41% yield of acetophenone and a 39% yield of allyl phenyl sulfide is achieved. In addition, 6% of 4-pentenophenone is also formed (Table 4, entry 29). In contrast to the reaction of **IIIc**, the tertiary sulfide, **IVb**, does not react with allylstannane even in the presence of 5% AIBN.

These results from the reactions of **IVa,b** cannot be explained by the addition elimination mechanism alone (Scheme 3, Y = SPh). According to Scheme 3, 4-pentenophenone should not be formed and **IVb** should be as reactive as **IVa**. Two competing radical chain sequences, *i.e.* electron transfer (Scheme 2, Y = SPh) and addition elimination (Scheme 3, Y = SPh) can explain our experimental observations.

For the reaction of **IVa**, both ET and addition of the tin radical are competitive. The slow cleavage of the ketyl radical anion (eq 9, Scheme 2) results in a short and inefficient chain, decreasing the concentration of tin radical available for the addition step (eq 11, Scheme 3). The overall result is a low yield of reaction products. For the tertiary sulfide **IVb**, the slow ketyl cleavage combined with very slow addition of the enolyl radical (eqs 9 and 10, Scheme 2) leads to the absence of the ET chain sequence, and no tin radical available for the addition−elimination sequence. Consequently, **IVb** appears to be unreactive toward allylstannane.

3. Mechanisms for the Reaction of α-Substituted Acetophenones with Allylstannane. The results of the present study demonstrate that the reactions of α-bromo, -chloro-, -fluoro-, and -(benzoyloxy)acetophenones (Ia−c, IIa) with allylstannane yield 4-pentenophenone as the only product. The reaction of α-(arylsulfonyl)acetophenone (IIIa−c) gives only acetophenone and aryl allyl sulfone; no enolyl radical addition product is produced. α-(Phenylthio)acetophenone gives both acetophenone and 4-pentenophenone. These results suggest that the reaction mechanism changes when the nature of the α-substituent is varied. For Ia−c and IIa an ET chain sequence is operative whereas an addition−elimination sequence appears involved for the reactions of IIIa−c. An alternative chain sequence can also be suggested to explain the products formed from the α-arylsulfonyl ketones, IIIa−c (see, Scheme 3). The ketyl anion intermediates may proceed by fragmentation to enolate anions and $ArSO_2^{\bullet}$ radicals. The strongly electron-withdrawing $ArSO_2$ group might favor this pathway and would be consistent with the destabilization of the formation of the enolate anion by methyl substitution.

Both an ET and addition−elimination sequence are in competition for the reaction of **IVa**.

For **Ia**−**c** and **IIa** ketyl cleavage is extremely fast,[1] so that the ET pathway is preferred. Cleavage of the ketyl radical is slow for **IIIa**−**c** so that the addition−elimination pathway or the enolate fragmentation (Scheme 3) predominates. Although the ketyl cleavage for **IVa** is slower than those of **IIIa**−**c**, the β-elimination (eq 12, Scheme 3) and radical ($Y^{\bullet}$) addition (eq 13, Scheme 3)

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Table 4. Reaction of α-Substituted Ketones with Allyltributylstannane[a,b]

reaction	compound $PhCOCR_1R_2SPh$	additive (%)	products (%)[c] $PhCOCR_1R_2CH_2CH{=}CH_2$	$PhCOCHR_1R_2$	$PhSCH_2CH{=}CH_2$
28	**IVa**	–	0	2.4 ± 0.7	3.6 ± 1.5
29	**IVa**	AIBN (5)	6.2 ± 1.0	41.0 ± 1.8	38.7 ± 0.4
30	**IVb**	–	–	–	–
31	**IVb**	AIBN (5)	–	trace	trace

[a] All reactions were carried out at 61 °C in benzene for 48 h with a mole ratio of 1:2 of ketone to allyltributylstannane. [b] Yields determined by GC. [c] Recovered ketones accounts for the material balance.

are also slower than those in **IIIa**–**c**. Therefore, both ET and addition–elimination pathways are competitive. For α-phenoxyacetophenone (**IIb**) the ketyl cleavage and *β*-elimination of the stannylketyl (eqs 9 and 12) are even slower than that of **IVa**, and therefore the phenoxide appears to be inert toward allylstannane.

Since the enolyl radical is the reactive intermediate in the reaction of allylstannanes with α-bromo- and chloroacetophenones and with α-(benzoyloxy)acetophenone it is expected that synthetically other α-acyloxy carbonyl compounds would be excellent substrates for allylation using allylstannanes. Examples of these reactions have recently been reported.[21]

Experimental Section

Materials. Commercial benzene (Fisher Scientific) was shaken with concentrated sulfuric acid (10% V/V) several times, washed with water, 10% sodium carbonate solution, and water, and then dried over anhydrous calcium chloride. Benzene was fractionally distilled from CaH_2, and the middle fraction was collected and stored over molecular sieves (3 Å).

The preparation or purification of acetophenone, α-fluoroacetophenone (**Ia**), α-chloroacetophenone (**Ib**), α-bromoacetophenone (**Ic**), α-bromopropiophenone (**Id**), α-(benzoyloxy)-acetophenone (**IIa**), α-phenoxyacetophenone (**IIb**), α-(*p*-methylbenzenesulfonyl) acetophenone (**IIIa**), α-(*p*-methylbenzenesulfonyl)propiophenone (**IIIb**), α-(*p*-methylbenzenesulfonyl)-isobutyrophenone (**IIIc**), α-(phenylthio)acetophenone (**IVa**), *p*-di-*tert*-butylbenzene, α,α-azobisisobutyronitrile (AIBN) and *m*-dinitrobenzene [*m*-(DNB)] have been described previously.[3,6,7]

α-Bromoisobutyrophenone (**Ie**) (Aldrich, 98%), propiophenone (Aldrich, 99%), and isobutyrophenone (Aldrich, 97%) were redistilled and their purity was found to be >99% by GC.

Allyltributylstannane (Aldrich, 97%) was used as supplied.

α-(Phenylthio)isobutyrophenone (**IVb**) was prepared according to the literature procedure,[21] bp 160–170 °C (3.5 mmHg) [lit.[21] 141 °C (0.45 mmHg)]; ^{1}H NMR ($CDCl_3$) δ 1.6 (s, 6H), 7.25–7.6 (m, 8H), 8.2–8.32 (m, 2H).

4-Pentenophenone was isolated from the reaction mixture (Table 1, reaction 7) by flash chromatography as a colorless oil (ether/petroleum ether = 1/4),[22] ^{1}H NMR ($CDCl_3$) δ 2.53 (m, 2H), 3.08 (t, 2H), 5.05 (m, 2H), 5.75 (m, 1H), 7.40–7.96 (m, 5H).

2-Methyl-4-pentenophenone was isolated from the reaction mixture (Table 1, reaction 10) by flash chromatography as a colorless oil (ether/petroleum ether = 1/4);[23] ^{1}H NMR ($CDCl_3$) δ 1.13 (d, 3H), 2.13 (m, 1H), 2.48 (m, 1H), 3.47 (m, 1H), 4.96 (m, 2H), 5.71 (m, 1H), 7.32–7.90 (m, 5H).

Allyl tosyl sulfone was prepared according to the literature procedure[24] and recrystallized from ether and petroleum ether, mp 50.5 °C (lit.[25] 50.5–51 °C); ^{1}H NMR ($CDCl_3$) δ 2.44 (s, 3H), 3.78 (d, 2H), 5.12 (m, 2H), 5.78 (m, 1H), 7.24–7.76 (m, 4H).

Allyl phenyl sulfide was prepared according to the literature procedure,[25] bp 102–105 °C (25 mmHg) [lit.[26] 104–106 °C (25 mmHg)]; ^{1}H NMR ($CDCl_3$) δ 3.59 (d, 2H), 5.15 (m, 2H), 5.93 (m, 1H), 7.22–7.44 (m, 5H).

Instrumentation. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker-200 or Bruker-300 spectrometer (200 or 300 MHz) with deuteriochloroform as solvent and residual chloroform (δ 7.26) as the standard. Gas chromatography–mass spectra (GC/MS) were recorded on a VG-70 E mass spectrometer fitted with a 1125 data system. The products were analyzed using a Varian Vista 6000 glass chromatograph fitted with a gas capillary column (DB-5, 30 m × 0.25 mm i.d. × 0.25 μm, J & W Scientific). Gas chromatography–infrared spectra (GC/IR) were obtained using a HP 5965A IRD spectrometer interfaced to a HP 5890 gas chromatograph (Hewlett-Packard) fitted with a glass capillary column (Ultra 2, 25 m × 0.32 mm i.d. × 0.52 μm, Hewlett-Packard).

GC analyses with packed columns were carried out using a Hewlett-Packard 5840A gas chromatograph equipped with a flame ionization detector. The detector was coupled to a Hewlett-Packard 5840A terminal integrator. Several analyses of each solution were carried out to obtain the average relative area ratios. Reaction ampules were Pyrex tubes joined to 10/30 joints. The ampules were cleaned with chromic acid solution, water, concentrated ammonium hydroxide, and distilled water and oven dried at 120 °C.

General Procedure for the Reactions of α-Substituted Ketones with Allyltributylstannane. An aliquot of the ketones (0.05 M), allyltributylstannane (0.10 M), and the internal standard (*p*-di-*tert*-butylbenzene, 0.02 M) was placed in a Pyrex ampule with or without additives. The initiator, AIBN, or inhibitor, *m*-DNB, was added before the reaction mixture was degassed. The ampule was degassed, sealed under vacuum, and thermostated at 60 °C for the specified time. After the required reaction time, the ampule was opened and analyzed by GC using a 20 ft × 1/8 in glass column packed with 10% QF-1 on chromosorb WAW DMCS 80–100 mesh. For each reaction the products were identified by a comparison of their GC retention times, GC-IR spectra, and GC-MS spectra with those of authentic samples.

Observation of the Tin Enolate from the Reaction of IIIc with Allyltributylstannane. An aliquot of the substrate (**IIIc**) (0.2 M), allyltributylstannane (0.2 M), and AIBN (0.001 M) in deuteriobenzene (1 mL) was placed in a Pyrex ampule with an attached NMR tube. The ampule was degassed, sealed under vacuum, and thermostated at 60 °C. After 96 h, the ^{1}H and ^{13}C NMR were taken. The peaks for the unreactive starting materials, allyl tolylsulfone and α-(*p*-methylbenzenesulfonyl)isobutyrophenone were assigned by a comparison of the spectra of the mixture with those of the pure compounds (see Figure 1).

JO960043R

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