Journal of Organometallic Chemistry, 382 (1990) 361–373
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands
JOM 20446

Regiochemical and mechanistic studies of the addition of tin hydride and oxide to substituted ketenes

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(Received August 7th, 1989)

Abstract

The reactions of aryl-substituted ketenes with tri-n-butyltin hydride give rise to *O*-bound tin enolates. With unsymmetrically-substituted methyl phenyl ketene this process exhibits little or no stereoselectivity. The kinetic mixture consists of virtually equal proportions of *E* and *Z* enolate isomers, which then equilibrates to a 71/29 *Z/E* mixture under thermodynamic control. Mechanistic studies are not consistent with either radical or polar mechanisms, and a concerted pathway with differential rates of bond formation is proposed. With dimethyl ketene a similar reaction gives a vinyl ester enolate, which presumably results from an initially-formed aldehyde enolate. Finally, the reaction of diphenyl ketene with tri-n-butyltin oxide results in a tin carboxylate which adopts a polymeric structure in the solid state.

Introduction

Ketenes are highly unsaturated molecules which serve as reactive substrates toward a variety of nucleophiles and ketenophiles [1]. These reactions can proceed with high levels of stereoselectivity, and result in carbonyl and/or cycloaddition products. Further, ketenes are currently thought to be intermediates in the Fischer–Tropsch synthesis of hydrocarbons from synthesis gas (CO/H_2) mixtures [2]. Their formation is believed to involve the coupling of surface-bound methylene and carbon monoxide moieties [3], a process which has been amply modeled in homogeneous systems. Less is known, however, about the ultimate fate of the intermediate ketenes. Studies of their possible reduction pathways are thus important, bearing on both synthetic and catalytic processes.

One obvious means by which ketenes could be reduced is via insertion into a metal–hydride linkage. This process could exhibit a regiochemical preference for the

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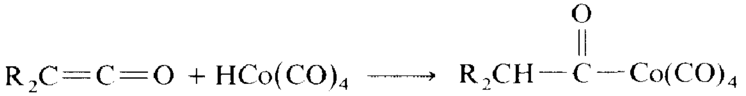
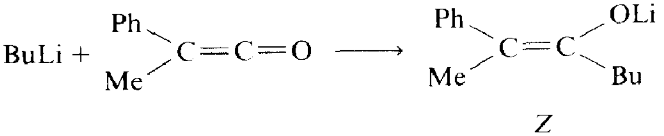
formation of metal acyls or metal enolates, and the latter could be either *C*- or *O*-bound. In spite of the importance of such a process, there have been very few studies of the reactions of ketenes with metal hydrides. Ungvary has shown that $HCo(CO)_4$ reacts with substituted ketenes to give acylcobalt species (eq. 1) [4], and Lutsenko has reported a similar result for the reaction of tri-n-propyltin hydride and the parent ketene [5]. Conversely, Musco et al. [6] and Herberich [7] have shown that addition of diphenyl ketene to either *trans*-$Pt(PR_3)_2(H)_2$ (eq. 2) or $Cp_2Nb(H)(CO)$, respectively, results in the formation of enolates. In addition, Tidwell [8] and Seebach [9] have shown that alkyllithiums and lithium aluminum hydride react with



$$R_2C{=}C{=}O + HCo(CO)_4 \longrightarrow R_2CH{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}Co(CO)_4 \qquad (1)$$

$$Ph_2C{=}C{=}O + t\text{-}Pt(PPh_3)_2(H)_2 \longrightarrow t\text{-}(PPh_3)_2(H)Pt{-}O{-}CH{=}CPh_2 \qquad (2)$$

ketenes to give enolates, and that with unsymmetrically-substituted ketenes the



(3)

addition is highly stereoselective; for the reaction shown in eq. 3 the *Z/E* ratio is ca. 99 [8]. Both $HCo(CO)_4$ [10] and R_3SnH [11] are susceptible to radical addition processes, so it is conveivable that acyl products could result from radical chain reactions with metal-centered radicals as the chain carrying species. Since tin hydrides are well known to effect hydrostannations via radical mechanisms [11], we set out to study the regiochemistry and mechanism of their addition to substituted ketenes; the results of these studies, which are not indicative of radical mechanisms, are reported here.

Results and discussion

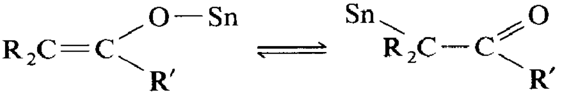
Regiochemistry of addition with aryl ketenes. The reactions of ketenes and Bu_3SnH were carried out at room temperature in benzene solution at 25 °C. They were complete in less than 3 min, as judged by the disappearance of the tin-hydride stretch at 1801 cm^{-1} and the bleaching of the yellow color of the free ketene (λ_{max} 401 nm). The products were colorless liquids which were best isolated and purified by distillation. For diphenyl ketene the product was identified as the *O*-bound aldehyde enolate **1** (eq. 4), based on its spectral characteristics. It exhibited an IR stretch at 1606 cm^{-1} for the C=C double bond in conjugation with two phenyl rings. The NMR spectrum showed the resonances for the butyltin groups and the

$$Ph_2C{=}C{=}O + Bu_3SnH \xrightarrow[C_6H_6]{} Bu_3SnOCH{=}CPh_2 \qquad (4)$$

(1)

phenyl rings, but no obvious resonance for the vinylic proton. Tin aldehyde enolates are not common, but in $Pr_3SnOC\underline{H}{=}CH_2$ the indicated proton resonates at 6.7 ppm [12]. As such, we suspect that the analogous proton in **1** is shifted slightly downfield and masked by the aromatic resonances. Further evidence for the formulation of **1** is gained by treating it with HCl; this resulted in free diphenyl acetaldehyde, as judged by comparison of its NMR and IR spectra with those of an authentic sample.

The spectral data for **1** were incompatible with either an acyl or *C*-bound enolate formulation. The acyl would have exhibited a C=O stretch [5,13] at ca. 1660 cm^{-1} and a $C\underline{H}Ph_2$ resonance at ca. 5 ppm, while the *C*-bound enolate would have exhibited a C=O stretch [12,14,15] at $\geq 1700\ \mathrm{cm}^{-1}$ and a downfield resonance for the aldehydic proton. Tin enolates undergo a tautomerization involving *O*-metal and *C*-metal forms (eq. 5) [14,15]. In the majority of cases studied thus far, the tin center (being a soft Lewis acid) prefers the carbon center and the depicted equilibrium lies well to the right. However, with substituted enolates (R ≠ H), steric crowding forces the equilibrium to the left and the *O*-bound enolate tautomer dominates. In **1** the two phenyl groups should exert steric and electronic influences favoring the *O*-bound enolate.



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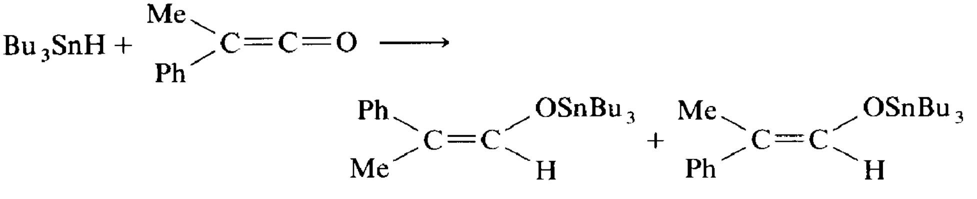
The reaction of methyl phenyl ketene proceeded similarly and resulted in *O*-bound tin enolate **2** with the same key spectral features discussed above for **1**. However, in the case of **2** the *O*-bound enolate can exhibit *E*/*Z* isomerism, and a mixture of isomers was formed with a combined yield of 81% (eq. 6). The NMR spectrum indicated the presence of two isomers, since the ketene-derived methyl groups resonated at 2.14 and 2.41 ppm for the *Z* and *E* enolate isomers, respectively. However, most of the remaining resonances overlapped and could not be assigned definitively. To verify these product assignments the tin enolates were converted to silyl enol ethers [8a], whose *E*/*Z* ratios could be determined by gas chromatography (the *Z* isomer elutes before the *E* under the conditions used, see Experimental Section). In several control experiments involving different *E*/*Z* ratios (vide infra) these ratios were found to match those assigned by NMR, indicating that the silylation step did not alter the enolate ratio. Accordingly, the enolates were routinely converted to the silyl enol ethers for determination of the product ratios.



(6)

(*Z*-**2**) (*E*-**2**)

The *E*/*Z* ratio for **2** was found to vary with temperature, so this was studied using three procedures. In one procedure (the "kinetic" case) the enolate was formed at −22°C and quenched with Me_3SiCl as soon as the reaction was complete. In another, the reaction was run at −22°C, allowed to warm to 25°C for 5 minutes, then quenched with Me_3SiCl. In the third procedure, the reaction and quench were run at 25 °C; aliquots were quenched and tested until the system had reached an equilibrium *E*/*Z* ratio. We attempted to run reactions at temperatures lower than −22 °C, but these were too slow to be practical. Using these three sets of conditions, we found that the kinetic ratio was *Z*/*E* 56/44 while the thermodynamic ratio was *Z*/*E* 71/29 (estimated error limits are ±5%). When the reaction was run at −22 °C and allowed to warm briefly to 25 °C before quenching, intermediate ratios were observed; this indicates that the approach to equilibrium was underway but not complete. The equilibrium ratio is roughly similar to those seen for the related ketones PhMeCHC(O)Bu and PhEtCHC(O)Bu, which exhibited equilibrium *Z*/*E* ratios of 60/40 and 85/15 for the potassium enolates [8]. However, the lack of selectivity in the low temperature addition reactions was unexpected. We saw no spectral evidence for the presence of a *C*-bound enolate, but we cannot discount the possibility that this isomer mediates the thermodynamic *E*/*Z* isomerization reaction.

Mechanistic studies. The regiochemical preference for enolate formation and the lack of *Z*-enolate specificity prompted us to undertake mechanistic studies. Initially we considered four likely mechanistic types. Hydrostannation reactions are typically free radical chain processes [11]. While an initiator like azobisisobutyronitrile (AIBN) is often required to break the Sn–H bond (estimated at 74 kcal/mol) [16], this is not necessary when the initial hydrogen atom abstraction generates a stabilized radical. If the addition process involves a highly electrophilic carbonyl compound [17,18] or a Lewis acid-complexed carbonyl [19], ionic addition mechanisms are possible. A third mechanism has been observed in the reactions of tin hydrides with electron-deficient olefins such as TCNE; Kochi and coworkers have presented convincing evidence for an electron-transfer mechanism involving the intermediate ion pair R_3SnH^+ $TCNE^-$ [20]. Finally, we considered non-chain radical addition and concerted addition processes as viable alternatives. To differentiate the polar and non-polar processes, we studied the kinetics of the addition processes as a function of solvent dielectric constant. These reactions involved diphenyl ketene and Bu_3SnH, and were studied by monitoring the disappearance of the UV-vis absorption of the free ketene (401 nm). Initial experiments indicated that the process was overall second order, first order in each of ketene and tin hydride. As a result, we studied the process using either pseudo-first order conditions or the initial rate method.

Kinetics experiments were carried out in hexane, diethyl ether, and THF solutions; in more polar solvents such as acetonitrile we observed that the reactions were not clean, but we were unable to identify the new products. Each determination was the average of three separate kinetic runs, and the reproducibility was quite good. The second order rate constants, for the reactions are given in Table 1. In the reactions with Bu_3SnH, the data indicate that the reaction exhibits a five-fold rate increase on going from hexane to THF. We may contrast this with data on the ionic addition of ethyl iodide to triethylamine, where the ratio of the rate constants in diphenyl ether and hexane is > 300 [21]. Indeed, the polar addition of Et_3SnH to $PhC(O)CF_3$ also exhibits a substantial solvent polarity effect [17]; here the rate constants for addition in cyclohexane and butyronitrile solvents differ by a factor of > 1200. A similar trend was seen in the electron-transfer process studied by Kochi ($k(Et_2O)/k(C_6H_{12}) > 20$) [20]. Although there may be some slight charge separation in the transition state, the relative insensitivity of the ketene addition

Table 1

Second order rate constants for the reaction of $Ph_2C{=}C{=}O$ with tin hydrides. Number in parentheses indicates the uncertainty in the last digit.

Tin hydride	Solvent	k (l/mol·s)
Bu_3SnH	hexane	1.0(1)
	ether	4.1(1)
	THF	5.0(4)
Ph_3SnH	THF	0.38(1)

reactions to solvent polarity suggests that the process is not ionic in nature; it is also consistent with the notion that the mechanism is similar in these solvents.

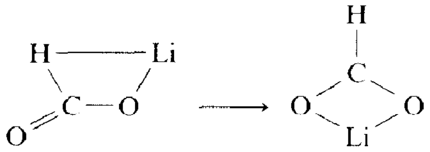
We next sought to gather information regarding the possibility of radical mechanisms. First, the reactions were run in the presence of the radical traps galvinoxyl and quinol; these inhibit the rate of radical chain hydrostannation reactions [11]. Kinetic studies carried out in the presence of these trapping agents showed no difference relative to the cases in which they were absent. Additionally, the reaction was carried out in the probe of the NMR spectrometer. Under these conditions, no CIDNP effects were observed. Finally, the additions were carried out in benzene solution in the presence of added AIBN; again, no effect was noted. We believe that the addition process does not involve a radical chain mechanism. The failure of AIBN to alter or speed up the course of the reaction may indicate that the substrates were consumed before an alternate reaction could be initiated.

The data cited above argue against a radical-chain process, but do not discount a non-chain radical pair mechanism. Regiochemical considerations are not useful in addressing this question either. First, there are relatively few examples of radical additions to ketenes (particularly in condensed phase), and second, there is no clear-cut regiochemical distinction evident from the cases which are known. Lillford and Satchell invoked a radical mechanism in the addition of thiols to dimethyl ketene [22]; here the $RS^{\cdot}$ radical was seen to add to the ketene central carbon to give an α-carbonyl radical center which ultimately resulted in a thioester. Conversely, 77 K matrix isolation studies of the addition of hydrogen atoms to ketene showed evidence for addition at both ketene carbons, depending on the matrix material [23]. Finally, gas phase studies of hydrogen atom addition have not given definitive information regarding the regiochemistry of addition, although addition at the terminal carbon appears more likely [24]. Indeed, a radical process might be difficult to differentiate from a semi-concerted addition. However, Sn–H bonds are known to be sensitive to the remaining tin substituents. Ingold has measured the rates of radical processes which involve the abstraction of the tin hydride in cyclohexane solution (eq. 7) [25]. For Ph_3SnH and Bu_3SnH the rate constants for these

$$R_3Sn{-}H + Me_3C^{\cdot} \longrightarrow Me_3CH + R_3Sn^{\cdot} \tag{7}$$

radical-molecule reactions were found to be 3.1×10^6 and 7.4×10^5; this four-fold enhancement parallels the experimental observation that Ph_3SnH is more reactive than Bu_3SnH in free radical chain reductions of halides, carbonyls, and alkenes [11]. In comparing the rates of ketene reactions, however, the data in Table 1 indicate that the rate constant for Bu_3SnH addition to $Ph_2C{=}C{=}O$ is nearly 15 times greater than that for Ph_3SnH addition. This argues against the involvement of radicals in the addition processes studied here.

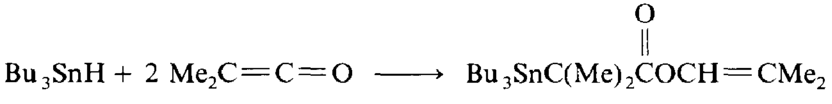
The remaining mechanism to be considered is a concerted addition of the Sn–H bond to the ketene, and this constitutes our preferred alternative. Schleyer has carried out theoretical studies of the addition of lithium hydride and methyllithium to carbon dioxide [26a]. These studies have indicated that the nucleophilic species RLi (R = hydride, alkyl) induces the addition by functioning first as an electrophile, such that the initial interaction is between lithium and the carbonyl oxygen. The hydride then swings around to form a 4-membered ring, which constitutes the transition state (shown below); Ashby had proposed a similar transition state for the bimolecular addition of aluminum alkyls to ketones [26b,c]. After addition, the lithium rotates about the C–O vector to give the ultimate formate. Schleyer et al. characterize this process as one involving substantial ionic character, but this is more likely for the lithium reagent than for the tin reagent used in our work. Indeed, recent calculations by Morokuma [26d] on the additions of methyllithium or methylcopper to acrolein indicate that the former adds via a charge-controlled process while the reactions of the latter are controlled by orbital symmetry effects. We tentatively propose an analogous 4-center process in the addition to ketenes. It should be noted that for ketenes a non-ionic suprafacial addition like that depicted above would violate orbital symmetry rules, but an antarafacial addition derived by crossing the Sn–H and C=O vectors is allowed and has been invoked to explain the facility with which ketenes undergo cycloaddition reactions at the C=C bond [27]. The other attractive feature of this mechanism is that it offers an explanation for the failure of these addition processes to exhibit facial selectivity; if the initial approach is dictated by an antarafacial interaction of Sn–H and C=O bonds, the steric properties of the ketene substitutents may be unable to affect the reaction appreciably. Finally, we note that a 4-center non-ionic mechanism is wholly consistent with the solvent polarity data. Marks has reported similar data for the hydrogenolysis of $(C_5Me_5)_2Th(O^tBu)(CH_2CMe_3)$ (eq. 8) [28], a reaction which has been widely agreed to proceed via a 4-center transition state [29]. The rate constants for this process in THF and toluene exhibit a ratio $k(\text{THF})/k(\text{tol}) = 2.9(4)$, which compares well with the modest 5-fold difference seen for THF and hexane in the ketene hydrostannations.



$$(C_5Me_5)_2Th\begin{matrix}\diagup OR\\ \diagdown CH_2R\end{matrix} + H_2 \longrightarrow (C_5Me_5)_2Th\begin{matrix}\diagup OR\\ \diagdown H\end{matrix} + RCH_3 \qquad (8)$$

Tin enolates have been utilized in synthetic organic applications, particularly when a relatively non-basic enolate is required [30]. Additionally, *O*-bound enolates have been found to react faster than *C*-bound enolates in Aldol condensations [30a–c]. We found that the enolates **1** and **2** are relatively inert to all but the strongest electrophiles (e.g. HCl), and suspected that the aryl substituents stabilized the enolate carbon via a combination of steric and electronic effects (predominantly the latter). As such, we attempted to prepare an analogue without aryl groups.

Reaction of dimethyl ketene with tin hydride. Initial studies of this reaction made it clear that the reaction stoichiometry was 2/1, in spite of various addition procedures. For this reason the reaction was subsequently carried out with two equivalents of ketene per equivalent of tin hydride. Under these conditions, we isolated a colorless liquid which decomposed upon attempted distillation. The product exhibited an IR band at 1706 cm^{-1} and NMR singlets at 7.46 ppm (1H), 1.80 (3H), 1.54 (3H), and 1.64 (6H); signals for the Sn-butyl groups were also apparent. We formulate this compound **3** as the *C*-bound enolate of a vinyl ester (eq. 9). Additional support for this comes from a protonolysis study with HCl, which generates the parent vinyl ester. It appears that the initial reactant generates an *O*-bound enolate, $Bu_3SnOCH{=}CMe_2$; without the stabilizing influence of aryl substituents this is considerably more reactive toward electrophilic reactants. Some substrates functionalize enolates at the oxygen terminus, and ketenes are among the most reactive of these [31]. Moreover, *O*-bound aldehyde enolates commonly give vinyl esters as the kinetic product of reactions with acyl halides [31]. Hence, the ultimate product **3** most likely derives from a secondary reaction between free ketene and an enolate intermediate. Consistent with this, we note that dimethyl ketene is known to undergo anionic polymerization catalyzed by Grignard reagents [32]. The initial products of this process (i.e., those identified at low conversions) are ketene oligomers, at least one of which is a vinyl ester. It is unlikely that **3** could derive from an acyltin precursor.



$$Bu_3SnH + 2\ Me_2C{=}C{=}O \longrightarrow Bu_3SnC(Me)_2\overset{\overset{\displaystyle O}{\|}}{C}OCH{=}CMe_2 \qquad (9)$$

(3)

Reaction of diphenyl ketene and a tin oxide. The results described above are consistent with Sn–H addition across the ketene C=O bond, and they indicate that the aryl-substituted carbon is unable to accomodate a trialkyltin center (no *C*-bound enolates were evident). Tin oxides are also known to effect addition across unsaturated centers [33], so we studied the reaction of $(Bu_3Sn)_2O$ with diphenyl ketene to see if a *C*-bound tin moiety would result. Such a process might be envisioned to give a carboxylate dianion equivalent [33a], which would be susceptible to electrophilic attack at the α-carbon. Indeed, even under rigorously anhydrous conditions we were unable to observed formation of the expected addition product. Instead, we observed colorless crystals of a compound which exhibited an infrared stretch at 1655 cm^{-1}. A crystallographic study revealed that this compound was the tin carboxylate $[Bu_3SnOC(O)CHPh_2]_x$ (**4**), and that it adopted a polymeric structure in the solid state. We have not established the source of the proton in this compound.

Figure 1 shows the monomer unit of **4** with a view which is approximately along the Sn–O(2) axis, and Fig. 2 contains a representation of the polymeric structure derived from the interaction of O(4) with an adjacent tin center; key bond lengths are contained in Table 2. The bridging by the carboxylate oxygen gives rise to a trigonal bipyramidal tin geometry with axial oxygens and three equatorial butyl groups. The two Sn–O bond lengths are 2.390(6) and 2.222(6) Å; the difference

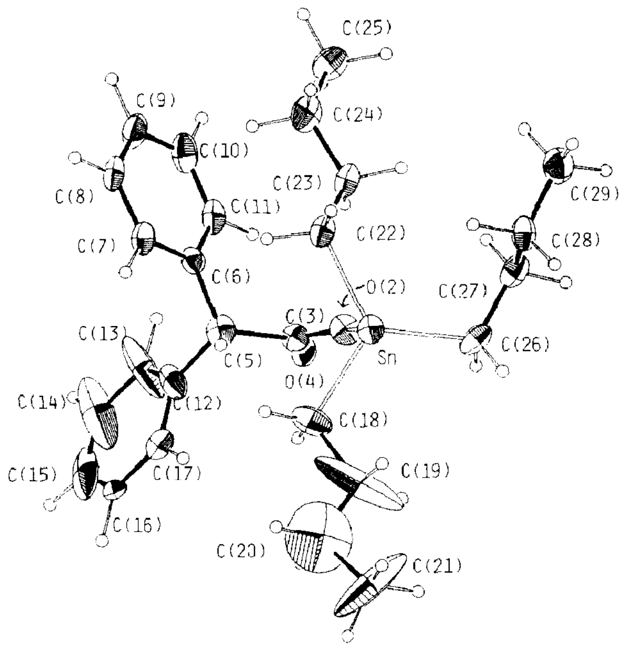


Fig. 1. ORTEP drawing of the monomeric unit in **4** with a view approximately along the Sn–O(2) vector.

(0.168 Å) is quite significant and corresponds to 28 standard deviations in the experimental determination. However, the carboxylate C–O bond lengths are indistinguishable, with values of 1.266(11) and 1.26(1) Å. The Sn–C bond lengths are

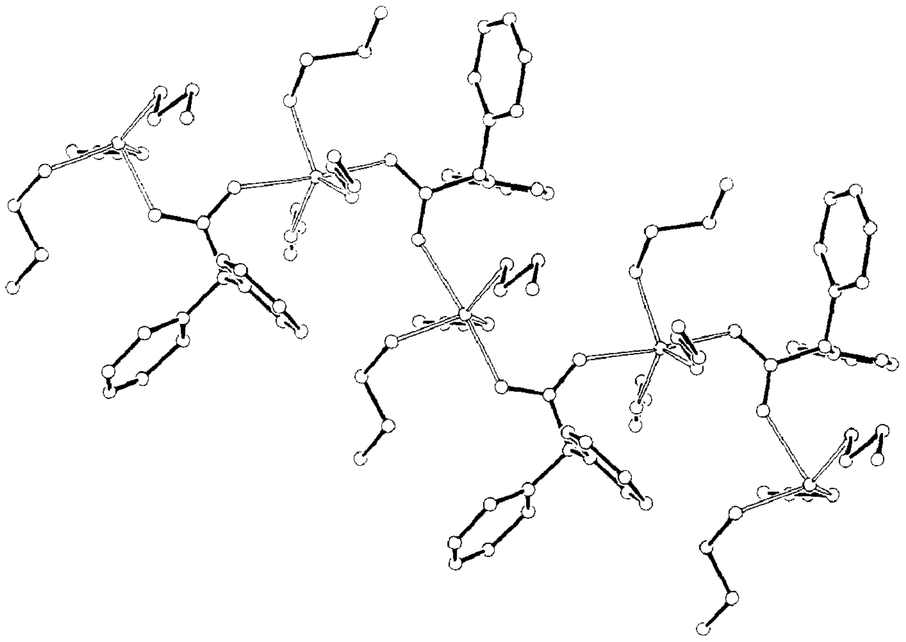


Fig. 2. ORTEP drawing of the polymer chain in **4**.

Table 2

Key bond lengths and angles for **4**

Bond lengths (Å)			
Sn-O(2)	2.390(6)	Sn-O(4)	2.222(6)
Sn-C(18)	2.14(1)	Sn-C(22)	2.15(1)
Sn-C(26)	2.14(1)	C(3)-O(2)	1.26(1)
C(3)-O(4)	1.26(1)	C(3)-C(5)	1.53(1)
C(5)-C(6)	1.50(1)	C(5)-C(12)	1.52(1)
Bond angles (deg.)			
O(2)-Sn-O(4)	175.0(2)	O(2)-Sn-C(18)	87.0(3)
O(2)-Sn-C(22)	87.1(3)	O(2)-Sn-C(26)	85.3(3)
O(4)-Sn-C(18)	95.5(3)	O(4)-Sn-C(22)	95.2(3)
O(4)-Sn-C(26)	89.7(3)	C(18)-Sn-C(22)	121.6(4)
C(18)-Sn-C(26)	117.1(4)	C(22)-Sn-C(26)	120.2(4)
Sn-O(2)-C(3)	141.0(6)	Sn-O(4)-C(3)	119.8(6)
O(2)-C(3)-O(4)	122.6(8)	O(2)-C(3)-C(5)	120.4(8)
O(4)-C(3)-C(5)	117.0(9)	C(3)-C(5)-C(6)	113.5(8)
C(3)-C(5)-C(12)	111.8(8)		

2.14(1), 2.15(1), and 2.14(1) Å, also identical to within experimental uncertainty. Even though the Sn-O bond lengths differ appreciably, the bond angles are quite close to those expected for a perfect trigonal bipyramid. The O-Sn-O angle is 175.0(2)°, while the O-Sn-C angles average 86.5° for O(2) and 93.5° for O(4). Likewise, the equatorial C-Sn-C angles are 121.6(4)°, 117.1(4)°, and 120.2(4)°. The majority of crystallographically-characterized trialkyltin carboxylates show a polymeric structure similar to that seen here [34]. Similar reactions with other ketenes were not clean, and we were unable to isolate or characterize the products.

Summary. The reactions of trialkyltin hydrides with aryl-substituted ketenes results in tin enolates. This contrasts with a similar reaction on ketene itself [5], from which a tin acyl results. The addition reaction exhibits clean, reproducible second order kinetics. The mechanism does not appear to involve radical or ionic intermediates, based on the relative intensitivity of reaction rates to changes in solvent polarity, the failure of radical traps to affect the rate, and substrate substituent effects; a semi-concerted addition to the ketene C=O is most consistent with the available data. With dimethyl ketene and tributyltin hydride the initially-formed product is presumed to be an aldehyde enolate, but this subsequently adds to another equivalent of ketene to give a vinyl ester enolate. Finally, bis(tributyltin)oxide adds to diphenyl ketene to give (ultimately) a tin carboxylate, which adopts a polymeric structure in the solid state. Further studies on these clean, high yielding reactions are in progress.

Experimental

General methods. Proton NMR spectra were obtained on a Varian XL-400 FT-NMR instrument. Solution infrared spectra were obtained in 0.05 mm path length liquid cells on a Perkin Elmer M1500 FT-IR spectrophotometer. Ultraviolet-visible spectra and solution kinetics were determined on a Hewlett-Packard 8451A diode array spectrophotometer. GC-MS studies were done on a Hewlett-Packard

5890A/5988A system, using a 50 ft. capillary column (methyl silicone liquid phase) operated with helium carrier gas at 140 °C. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN.

All manipulations were carried out under an atmosphere of either nitrogen or argon. Both gases were dried and deoxygenated by passage through columns of Linde 4A molecular sieves and activated BTS catalyst. Solutions were handled using Schlenk techniques, while solids were transferred in a Vacuum Atmospheres Corporation glove box under nitrogen. Benzene, tetrahydrofuran, hexanes, and diethyl ether were purchased from J.T. Baker, predried over activated molecular sieves, and distilled under nitrogen from sodium benzophenone ketyl. The NMR solvents C_6D_6 and THF-d_8 were freeze-thaw degassed and vacuum distilled from sodium-potassium alloy. Tri-n-butyltin hydride and bis(tri-n-butyltin)oxide were purchased from Aldrich Chemical Company and used as received. Diphenyl ketene and methyl phenyl ketene were prepared via deprotonation of the acyl halides with triethylamine. Dimethyl ketene was prepared in ether from 2-bromo-2-methylpropanoyl bromide and $[K][(C_5H_5)Fe(CO)_2]$ via a slight modification of the literature synthesis [35]; a solution of the dibromide was added via syringe to a frozen ether suspension of the iron salt at 77 K and the flask closed and degassed. The frozen suspension was allowed to thaw, stirred at 0 °C for several seconds, and then the volatiles were vacuum transferred into a flask containing the tin hydride.

Kinetics experiments. Stock solutions of diphenyl ketene and tributyltin hydride were prepared in the appropriate solvent. The desired amount of ketene solution was loaded into a square cuvette in the glove box and the cuvette was capped with a rubber serum cap. An initial spectrum was obtained, then the tin hydride solution was injected through the serum cap. The reaction was monitored by taking absorbance readings at 401 nm every second. In some cases it was possible to run the reaction in the presence of a ten-fold excess of tin hydride (pseudo-first order conditions), while in others the initial rate method was used. In these latter cases, only the first 5–10% of the rate data were used to calculate rate constants.

Synthesis of $Bu_3Sn(OCH=CPh_2)$ (1). Bu_3SnH (1.0 g, 3.44 mmol) was dissolved in 60 ml benzene, and a benzene solution containing 0.67 g (3.44 mmol) diphenyl ketene was added via syringe under a nitrogen purge at 25 °C. Within three minutes the yellow color faded, and solution IR indicated the loss of the ketene stretch at 2100 cm^{-1} and the Sn–H stretch at 1801 cm^{-1}. The solvent was removed in vacuo to give a pale yellow liquid which was distilled (0.15 mmHg); the fraction boiling at 205–208 °C was collected as a colorless liquid, yield 0.92 g (88%). IR (C_6H_6): 1606(s), 1593(vs), 1219(vs), 1070(s), 762(s) cm^{-1}. ^1H NMR (C_6D_6): 7.82–7.1 (mults., Ph–H), as well as multiplets for the Sn–Bu at 1.6–0.8 ppm. Anal. Found: C, 64.67; H, 7.88. $C_{26}H_{38}SnO$ calcd.: C, 64.35; H, 7.84%. A similar procedure was used in the synthesis of **2**, $Bu_3Sn(OCH=CMePh)$. The crude liquid was distilled (0.15 mmHg) and the fraction boiling at 165 °C was collected as a colorless liquid (yield 82%). IR (C_6H_6): 1626(s), 1598(s), 1190(s), 1173(vs), 1062(s), 756(m) cm^{-1}. ^1H NMR (C_6D_6): 7.6–7.1 (mults., Ph–H), 2.41, 2.14 (triplets, J 7 Hz, enolate methyls), 1.8–1.2 (mults., Sn–Bu). Anal. Found: C, 60.35; H, 8.53. $C_{21}H_{36}SnO$ calcd.: C, 59.60; H, 8.57%.

Synthesis of $Bu_3SnCMe_2CO_2CH=CMe_2$ (3). Dimethyl ketene (0.25 g, 3.44 mmol, assuming a 95% yield) [35] was generated as described above and vacuum transferred into a flask containing 0.5 g Bu_3SnH (1.72 mmol) in 60 ml diethyl ether. The solution was allowed to warm to room temperature for ca. 30 min. with stirring. After this time, the solvent was removed in vacuo to give a colorless oil (67%). This compound decomposed upon attempted vacuum distillation, but the crude product was spectroscopically pure. IR (THF): 1706(vs), 1378(s), 1261(s), 1242(vs), 1013(s) cm^{-1}. ^1H NMR (C_6D_6): 7.46 (s, 1H, vinylic =C–H), 1.8 (s, 3H, *trans*-CH=CCH_3), 1.64 (s, 6 H, Sn–CMe_2), 1.64 (s, 3H, *cis*-CH=CCH_3), 1.8–1.2 (mults., Sn–Bu).

Synthesis of $[Bu_3Sn(O_2CCHPh_2)]_x$ *(4).* Liquid $(Bu_3Sn)_2O$ (0.31 g, 0.52 mmol) was dissolved in 15 ml benzene. To this was added 2 ml of a benzene solution of diphenyl ketene (0.1 g, 0.68 mmol). The resulting solution was stirred for 20 min at 25 °C. The solvent was removed in vacuo and the resulting colorless solid was crystallized as colorless plates from a concentrated hexane solution at −20 °C. IR (C_6H_6): 1655(vs), 1602(m), 1458(s), 1379(m), 1262(m), 1217(m), 1071(s), 759(s) cm^{-1}. ^1H NMR (C_6D_6): 7.55 (d, 4H), 7.15 (mult., 4H), 7.03 (mult., 2H), 5.28 (s, 1H, $CHPh_2$), 1.6–0.8 (mults., Sn–Bu).

X-ray crystallography. Compound **4** was synthesized as described above and isolated from cold hexane as large plates. A crystal was transferred to the goniostat using standard air-sensitive manipulations. A systematic search of a limited hemisphere of reciprocal space revealed a set of diffraction maxima with symmetry and systematic absences corresponding to the unique monoclinic space group $P2_1/n$. Data were collected at −155 °C using a continuous θ–2θ scan with fixed backgrounds. The structure was solved using a combination of direct methods (MULTAN78) and Fourier techniques. An absorption correction was made and many of the hydrogen atom positions were visible in a difference Fourier phased on

Table 3

Crystal data for **4**

Empirical formula				$C_{26}H_{38}O_2Sn$
Color of crystal				colorless
Crystal dimensions:				
Face	−1	0	0	0.400 mm
Face	1	0	0	0.0400
Face	0	0	1	0.0600
Face	0	0	−1	0.0600
Face	0	1	0	0.0800
Face	0	−1	0	0.0800
Space group				$P2_1/n$
Cell dimensions (−155 °C; 24 reflections)				
			a =	15.618(6) Å
			b =	10.026(3)
			c =	15.987(6)
			β =	94.18(3)°
Z (molecules/cell)				4
Volume				2496.72 $Å^3$
Calculated density				1.334
Wavelength				0.71069
Molecular weight				501.28
Linear absorption coefficient				10.425
Max. absorption =				0.8850
Min. absorption =				0.9140

the non-hydrogen atoms. Hydrogen atoms were input at the idealized positions (d(C–H) 0.95 Å) for final refinement cycles. The final difference Fourier map was essentially featureless, with the largest peak being 0.52 e/Å^3. Crystal data are collected in Table 3 and key bond lengths and angles are in Table 2.

Supplementary material. Crystal data for **4**, including fractional coordinates, thermal parameters, tables of bond lengths and angles, and observed and calculated structure factors, are available (from JWB) upon request.

Acknowledgements

We thank Research Corporation for financial support of this work.

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