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# PREPARATION OF SOME KETOORGANOSTANNANES AND KETOORGANOCHLOROSTANNANES. INTRAMOLECULAR COORDINATION IN KETOORGANOCHLOROSTANNANES*

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## Summary

Ketoorganostannanes of the structure $Me_3Sn(CH_2)_n$ COR with $n = 2,3$ and R = Me, Ph have been prepared by the oxidation of the corresponding alcohols, and by the reaction of the appropriate cyanoalkyltrimethylstannanes with methyl or phenyl Grignard reagents. The ketoorganostannanes have been converted to the chloro analogs $Me_2Sn(Cl)(CH_2)_nCOR$ by methyl—chlorine exchange with trimethyltin chloride. The reactions with these ketones are considerably faster than that with *n*-butyltrimethylstannane, suggesting that intramolecular nucleophilic catalysis of an electrophilic displacement reaction occurs. Evidence that the ketoorganochlorostannanes have a structure involving intramolecular coordination between the carbonyl oxygen and the tin is provided by studies of the infrared, ultraviolet, proton and carbon-13 magnetic resonance, and Mössbauer spectra. Pyridine is shown to compete with intramolecular carbonyl in coordination to the chlorotin function, the effect being more pronounced when $n = 3$ than when $n = 2$, reflecting the greater stability of the five-membered ring complex.

## Introduction

It is well known that an organotin compound in which at least one electronegative group (such as halogen or acyloxy) is attached to the tin atom is capable of coordinating with suitable ligands leading to an increase in the coordination

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[*] Taken in part from the doctoral dissertations of P.L. Maxfield, University of New Hampshire, 1964 and K-H. Tsai, State University of New York at Albany, 1970.

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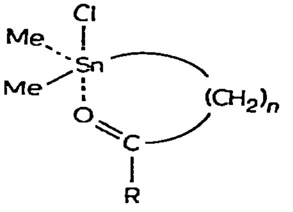
number of the tin atom from four to five or six [1]. On the other hand, if all of the four groups attached to the tin are alkyl and/or aryl, interactions with electron-donating ligands are so weak as to be undetectable by the usual physical measurements. It would be expected that a given ligand would be more effective in coordinating with the tin atom if it is suitably disposed within the same molecule than if it were a portion of another molecule. This type of intramolecular coordination has been observed when the ligand is the carbonyl group of an ester or of an amide, for example [2]. The only examples of the participation of the ketone carbonyl group have been reported by Matsuda in a series of compounds of the type $X_2Sn(CH_2CH_2COR)_2$ (X = Cl, Br, I; R = Ph, alkyl) [3]. These were distinguished by carbonyl stretching frequencies about 40 $cm^{-1}$ lower, and by electronic absorption maxima 10 nm shorter, than those of the unperturbed carbonyl groups. We wish to report similar studies involving compounds containing only one halogen atom on the tin atom, and two or three methylene groups intervening between this atom and the carbonyl carbon. The physical evidence comes from infrared and electronic spectra, proton and $^{13}C$ magnetic resonance spectra, and Mössbauer effect data. We conclude that rapidly reversible intramolecular coordination between the carbonyl oxygen and the tin atom in the chloroketones occurs. This probably results in approximately trigonal bipyramidal structures I as shown below. Our results will be discussed in this context.



(I, $n$ = 2,3)

## Results and discussion

### *Ketoorganostannanes*

Two synthetic routes to the ketoorganostannanes were used. The first involved the hydrostannation of the appropriate unsaturated nitrile, followed by reaction with a Grignard reagent, eqn. 1, ($m$ = 0, 1; R = Me, Ph) [4]. Yields

$$Me_3SnH + CH_2{=}CH(CH_2)_mCN \longrightarrow Me_3SnCH_2CH_2(CH_2)_mCN \longrightarrow$$

$$\xrightarrow[2.\ H^+,\ H_2O]{1.\ RMgX} Me_3SnCH_2CH_2(CH_2)_mC({=}O)R \qquad (1)$$

obtained in the facile hydrostannation of acrylonitrile, without a catalyst, were 70-75%. With allyl cyanide azobisisobutyronitrile was used as the catalyst and yields around 80% resulted. The conversions of the nitriles to the ketones were less satisfactory, yields ranging from 20 to 60%. A more satisfactory procedure for the methyl ketones was based on the observation that hydroxyorganostannanes can be oxidized by chromic acid without serious disruption of carbon—tin bonds, eqn. 2. The photochemically induced hydrostannation proceeded in yields around 90%, and the oxidation in yields around 65%. Although

$$Me_3SnH + CH_2{=}CH(CH_2)_mCHOHR \xrightarrow{h\nu} Me_3SnCH_2CH_2(CH_2)_mCHOHR \rightarrow$$
$$\xrightarrow{CrO_3,\ pyridine} Me_3SnCH_2CH_2(CH_2)_mC({=}O)R \qquad (2)$$

the phenyl ketones were not prepared by this method this same procedure should be useful because the 1-phenylprop-2-enols are readily available by reaction of the appropriate benzaldehydes with vinylmagnesium chloride [5].

*Ketoorganochlorostannanes*

We have examined the exchange reaction of Tagliavini et al., eqn. 3, as a means of preparation of the ketoorganochlorotins [6].

$$Me_3SnCH_2CH_2(CH_2)_mC({=}O)R + Me_3SnCl \rightleftharpoons Me_2Sn(Cl)CH_2CH_2(CH_2)_mC({=}O)R + Me_4Sn \qquad (3)$$

Under normal conditions one would expect that the distribution of products at equilibrium would be essentially statistical, as was observed previously [6], but this was not true with the compounds R = Me in eqn. 3, which we examined from this standpoint. Yields of the ketoorganochlorostannanes isolated were around 90% when $m$ = 0, and around 50% when $m$ = 1. The reason for the high yields obtained when $m$ = 1 was revealed by a rough study of the rates of the reactions. Equimolar amounts of the compounds with R = Me and trimethyltin chloride were mixed, and the course of the reactions were monitored by proton magnetic resonance (PMR). Trimethylbutylstannane was included in the study as a simple model compound. Results are shown graphically in Fig. 1, in which the extent of disappearance of $Me_3SnR$ is plotted as a function of time. Two facts become immediately obvious: first, the ketoorganostannanes react much

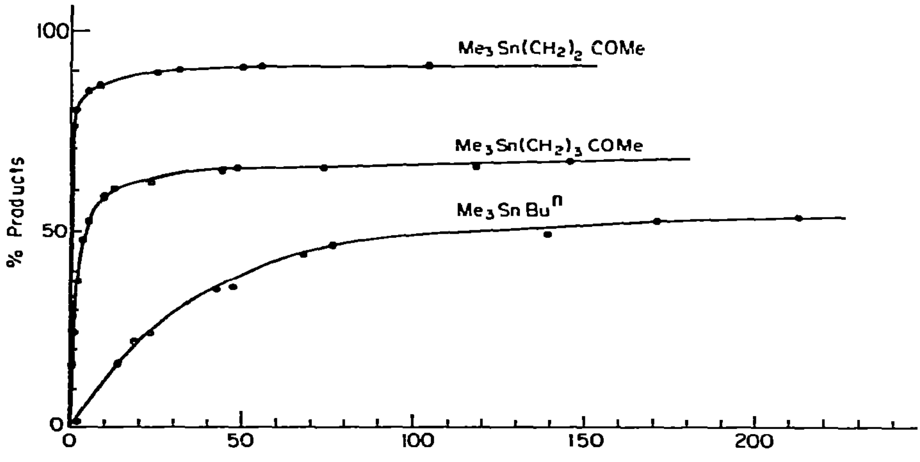


Fig. 1. Conversion—time profiles for reactions of $Me_3SnR$ with $Me_3SnCl$.

faster than the butyl analog; second, the extent of conversion to the ketoorganochlorostannanes is greater at equilibrium. The latter observation reflects stabilization of these compounds by intramolecular coordination (structure I) for which ample evidence will be provided below. The far greater rate of equilibration constitutes an example of *intramolecular nucleophilic catalysis of an electrophilic displacement reaction*. We are unaware of any other examples of this phenomenon. The magnitude can be placed on a quantitative basis. Because equimolar amounts of reactants were used, and the stoichiometry is shown by eqn. 3 the reaction can be expressed as eqn. 4, leading to the rate law of eqn. 5 if the reaction is assumed to be second order in each direction. Plots of the integrated rate equation (see Experimental) were linear over the initial 70% or more of conversion, and then became concave downward. This is not surprising in view of the fact that the medium changes as the reaction progresses from reactants to a mixture of reactants and products. The relative rate constants $k_f$ (in mol$^{-1}$ h$^{-1}$) for $Me_3SnR$ for variation in R at ambient temperature were: *n*-Bu, 1; $(CH_2)_2COMe$, 450; $(CH_2)_3COMe$, 21. Values of the equilibrium constants were 1.3, 120 and 4.3, respectively. From these values we obtain relative values for $k_r$: 0 78, 3.8 and 4.9, respectively. Thus the presence of the carbonyl group catalyzes the reaction in both directions, but the most pronounced effect is on the value of $k_f$ for $Me_3Sn(CH_2)_2COMe$. The enhancement in $k_r$ due to intramolecular coordination is puzzling because this should decrease the electrophilicity of the tin. Perhaps this is more than offset by the entropy decrease accompanying ring formation. The cyclic structure may provide a geometry which approximates that of the preferred transition state for reaction with tetramethyltin.

$$2A \rightleftharpoons 2B \tag{4}$$

$$-d[A]/dt = k_f[A]^2 - k_r[B]^2 \tag{5}$$

The molecular weights of the methyl ketoorganochlorostannanes in carbon tetrachloride indicated that they are substantially monomeric in this solvent, the values being 9.7% and 3.9% above those calculated for $n = 2$ and $n = 3$, respectively.

### *Infrared spectra*

Infrared data for the precursor ketones II and for the corresponding chloroketones III, along with appropriate controls, are gathered in Table 1. In order to elicit information concerning intermolecular interaction between the chlorotin group and the carbonyl group the IR spectra of mixtures of propiophenone and of 2-butanone with trimethyltin chloride were examined with the results shown in the bottom four entries in the table. No change is observed in the carbonyl stretching frequency at 1685 cm$^{-1}$ of propiophenone upon admixture with the chloride. However, there is a shift from 1716 to 1702 cm$^{-1}$ in the case of 2-butanone. The new band is distorted by a shoulder on the high frequency side suggesting the presence of the unresolved 1716 cm$^{-1}$ band also, implying that the ketone is not completely complexed with the chloride.

It is known that acetophenone is about one p*K* unit more basic than acetone [7]. This must be due primarily to delocalization of $\pi$ electron density

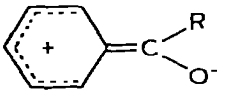
TABLE 1

CARBONYL STRETCHING FREQUENCIES OF KETOORGANOSTANNANES $RC(=O)-(CH_2)_n-Sn(R')Me_2$[a]

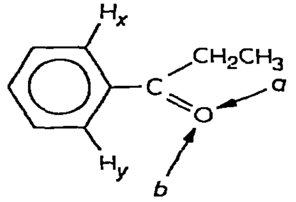
| Compound | | | Neat | | With pyridine | |
|---|---|---|---|---|---|---|
| R | *n* | R' | $\nu(C=O)$ | Δ | $\nu(C=O)$ | Δ |
| Me | 2 | Me | 1712 | 33 | $1712^c$ | |
| Me | 2 | Cl | 1679 | | $1712w^c$ | |
| | | | | | 1685s | 27 |
| Me | 3 | Me | 1710 | 26 | $1712^c$ | |
| Me | 3 | Cl | 1684 | | $1710s^c$ | |
| | | | | | 1685s | 25 |
| Ph | 2 | Me | 1680 | 39 | $1682^d$ | |
| Ph | 2 | Cl | $1641^b$ | | $1682w^d$ | |
| | | | | | 1650s | 32 |
| Ph | 3 | Me | 1680 | 31 | $1682^d$ | |
| Ph | 3 | Cl | $1649^b$ | | $1682s^d$ | |
| | | | | | 1655m | 27 |
| PhC(=O)Et | | | 1685 | 0 | $1685^c$ | |
| $PhC(=O)Et/Me_3SnCl^c$ | | | 1685 | | | |
| MeC(=O)Et | | | 1716 | 14 | $1714^c$ | |
| $MeC(=O)Et/Me_3SnCl^c$ | | | 1702 | | | |

[a] In $cm^{-1}$ (±2). [b] Nujol mull. [c] Equimolar. [d] Pyridine/ketone ≈ 16/1.

from the ring to the carbonyl oxygen as in II. This effect is sufficient to overcome the electron withdrawing effect expected from the σ bonding of the ring carbon to the carbonyl carbon through an $sp^2$ orbital as compared with an aliphatic carbon $sp^3$ orbital. However, it requires coplanarity of the ring and the carbonyl group. Examination of Dreiding models shows that, if the trimethyltin chloride coordinates from direction *a* in III, severe steric interactions between the methyl group on the tin atom and that of the ethyl group result. These can be relieved by rotation of the latter toward the ring, but this leads to new interactions with the *ortho* hydrogen $H_x$. If coordination occurs from direction *b*, then severe interactions arise between the tin methyls and the other *ortho* ring hydrogen, $H_y$. The most stable conformation of the complex becomes one in which the ring and the carbonyl group are not coplanar. In this situation ring-to-carbonyl electron delocation is lost, the inductive effect of the ring becomes predominant and the basicity falls below that of 2-butanone.



(II)

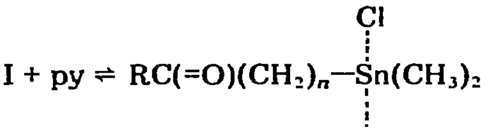


(III)

Data for the methylketostannanes and the methylketochlorostannanes, all neat, are shown in the first four entries of the table. In each case only a single carbonyl stretching frequency is observed. The band is shifted to lower frequency by 33 $\mathrm{cm^{-1}}$ when a methyl group on tin is replaced by chlorine when $n = 2$ and by 26 $\mathrm{cm^{-1}}$ when $n = 3$. Thus, only a single species is indicated in the chlorides; the interaction between tin and carbonyl oxygen is stronger than the intermolecular interaction observed between 2-butanone and trimethyltin chloride, suggesting that intramolecular interactions as in I are the cause of the frequency shifts.

The phenylketostannanes were liquids and their spectra were taken on neat films, whereas the chloro compounds were solids, and their spectra were taken on Nujol mulls. The results are similar to those obtained with the methyl ketones: single carbonyl bands were observed with each compound, and the chloroketones showed lower frequencies by 39 $\mathrm{cm^{-1}}$ when $n = 2$ and 31 $\mathrm{cm^{-1}}$ when $n = 3$. This suggests stronger coordination in the phenyl ketones as expected on the basis of carbonyl oxygen basicity. In the intramolecular coordination complex the steric effects discussed above in connection with intermolecular complexation disappear as can be seen by examination of models. In any event, it is apparent that the interaction is stronger when a five-membered ring is formed than when a six-membered ring is formed in both methyl and phenyl ketones.

The equilibrium constant for complex formation between trimethyltin chloride and pyridine is about twice as large as that for acetone [8]. It was, therefore, of interest to determine how the internal carbonyl and external pyridine compete as Lewis bases toward the chlorotin function. Control experiments were conducted by measuring the carbonyl stretching frequencies of propiophenone, 2-butanone and the simple ketoorganostannanes in the presence of pyridine. In each case only a single band was observed, and it appeared at the same frequency as in the absence of pyridine, as shown in Table 1. Thus there is no perceptible interaction between the pyridine and the carbonyl carbon. Each of the ketoorganochlorostannanes in pyridine, on the other hand, showed the free carbonyl absorption as well as another at a frequency 25 to 28 $\mathrm{cm^{-1}}$ lower. The free carbonyl bands are more intense in the ketones with $n = 3$ than with $n = 2$ as shown in Fig. 2. (The bands at 1580 and 1600 $\mathrm{cm^{-1}}$ are due to pyridine). These observations suggest that the following equilibrium (eqn. 6) is established and that it lies farther to the right when $n = 3$. Even though pyridine is a better Lewis base than the carbonyl group toward a trialkyltin chloride it



$$\mathrm{I} + \mathrm{py} \rightleftharpoons \mathrm{RC({=}O)(CH_2)}_n\mathrm{{-}}\overset{\mathrm{Cl}}{\underset{\mathrm{py}}{\mathrm{Sn}}}\mathrm{(CH_3)_2} \qquad (6)$$

(IV)

cannot compete effectively with the latter when intramolecular coordination leads to formation of a five-membered ring. The spectra of the methyl ketones shown in Fig. 2 were taken with equimolar pyridine. When a sixteen-fold excess of pyridine was used with these ketones the relative intensities of the free and

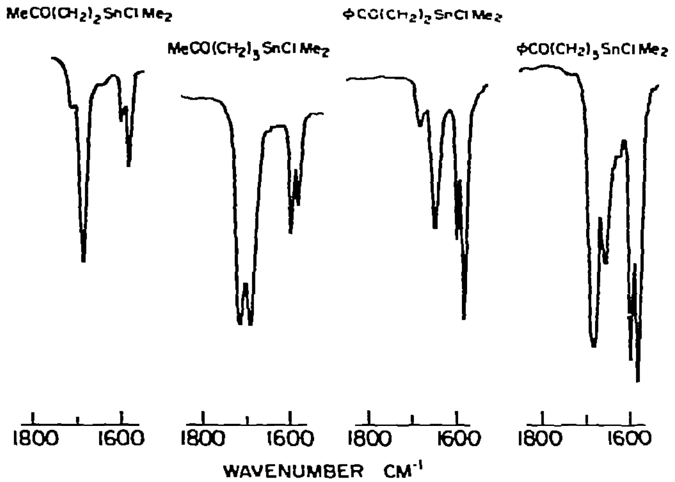


Fig. 2. Carbonyl region in infrared spectra of ketoorganochlorotins with pyridine. Pyridine/$Me_3SnR$ ratios: methyl ketones 1/1; phenyl ketones 16/1.

coordinated carbonyls changed to resemble those shown in the figure for the phenyl ketones, which were taken with sixteen-fold excess pyridine. Explicit measurements of the equilibrium constants for eqn. 4 were not attempted.

*Ultraviolet spectra*

Results obtained with the methyl ketones and relevant controls are displayed in Table 2. They reveal that 2-butanone alone or with equimolar trimethylbutyltin has the same absorption maximum and extinction coefficient both in cyclohexane solution and neat. Thus no intermolecular interaction between the organotin and carbonyl groups is indicated. However, when the trimethyltin group and carbonyl group are in the same molecule (first and third

TABLE 2

ULTRAVIOLET SPECTRAL DATA[a] ON $Me_2Sn(R)(CH_2)_nC(=O)R'$

| Compound | | | $\lambda_{max}$ | | |
|---|---|---|---|---|---|
| R | *n* | R' | nm | Δ | ε |
| Me | 2 | Me | 282.0 | −14 | 33 |
| Cl | 2 | Me | 268.0 | | 37 |
| Me | 3 | Me | 284.0 | −4 | 24 |
| Cl | 3 | Me | 280.0 | | 29 |
| $CH_3C(=O)CH_2CH_3$ | | | 278.0 | | 17 |
| $CH_3C(=O)CH_2CH_3/Me_3SnBu$[b] | | | 278.0 | | 17 |
| $CH_3C(=O)CH_2CH_3$[c] | | | 277.5 | | 17 |
| $CH_3C(=O)CH_2CH_3/Me_3SnCl$[b,c] | | | 275.0 | | 23 |
| $CH_3C(=O)CH_2CH_3/Me_3SnBu$[b,c] | | | 277.5 | | 17 |

[a] In cyclohexane. [b] Equimolar. [c] Neat.

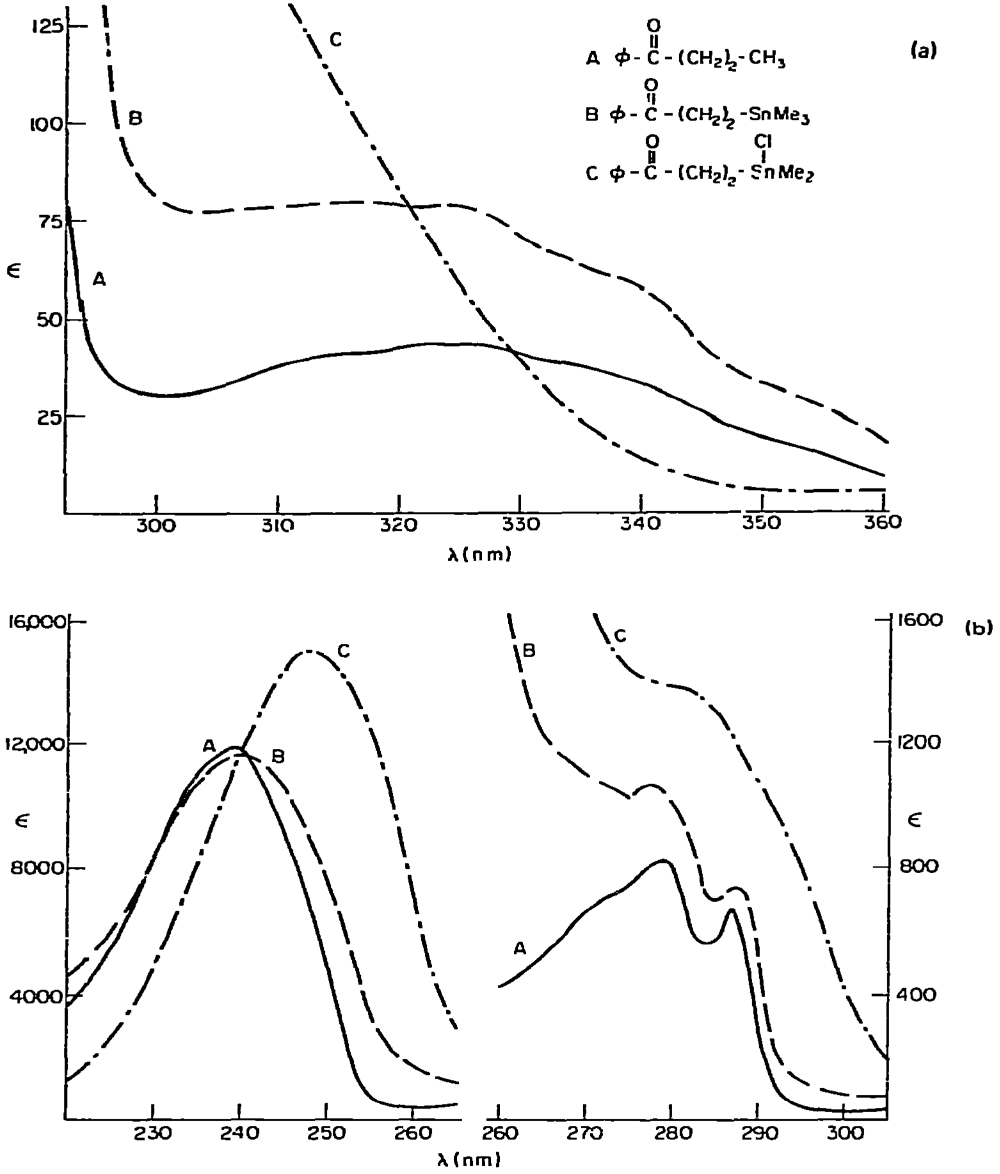


Fig. 3. Ultraviolet spectra in cyclohexane: (a) $n \rightarrow \pi^*$ region; (b) aromatic region.

entries) a shift to longer wavelength and more intense absorption are observed. These changes are probably not due to the inductive effect of the trimethyltin group because it is separated from the carbonyl carbon by two or three methylene groups. A non-bonding through-space interaction could distort the $n$ or $\pi^*$ orbital sufficiently to increase the transition probability such that the extinction coefficient increases from 17 to 24 or 33. However, it is not clear why the small red shift occurs in $\lambda_{max}$.

When trimethyltin chloride is added to 2-butanone a blue shift of 2.5 nm

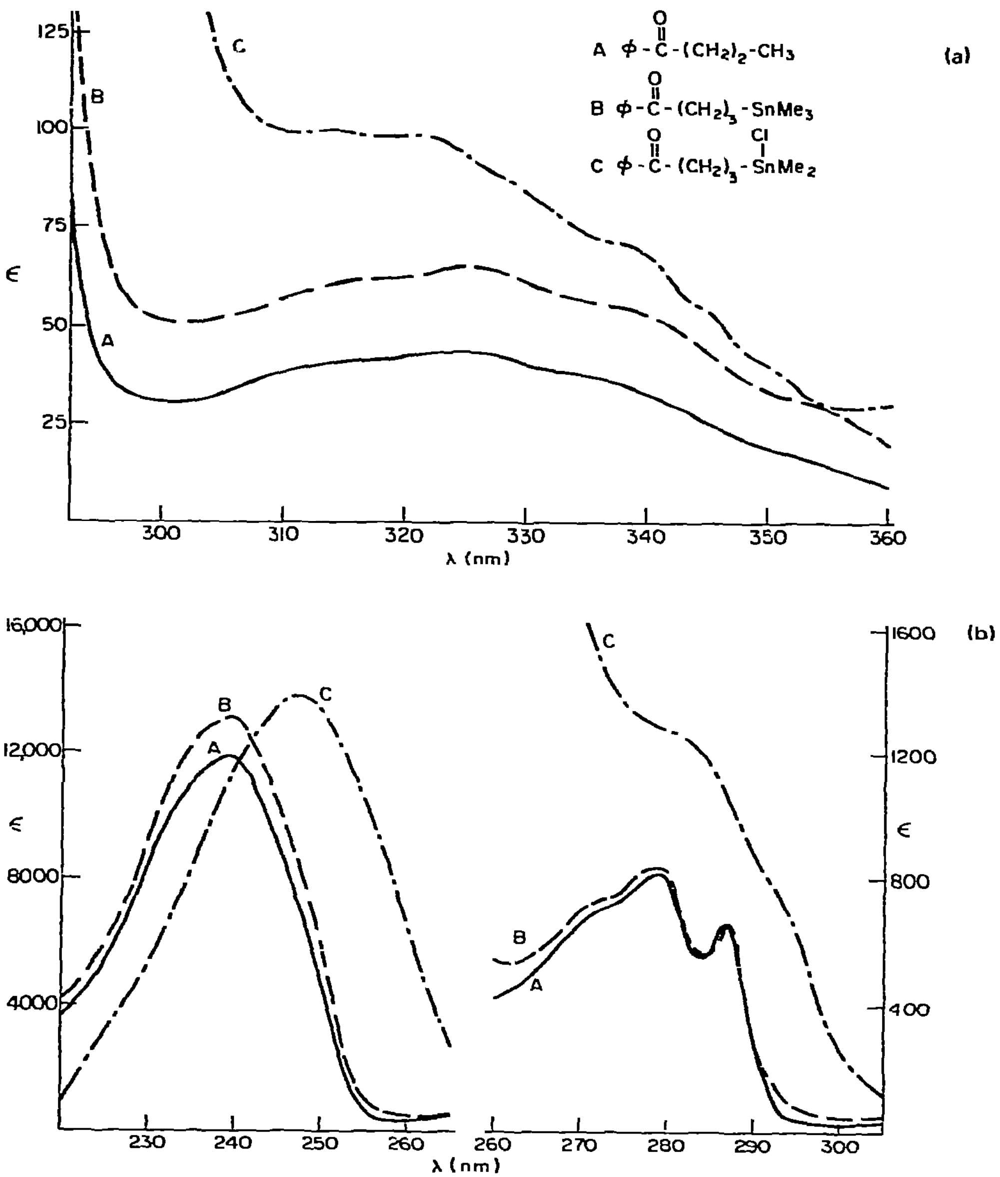


Fig. 4. Ultraviolet spectra in cyclohexane: (a) $n \rightarrow \pi^*$ region; (b) aromatic region.

is observed. This is consistent with weak complex formation between the two as suggested also by the increase in the carbonyl stretching frequency by 14 $cm^{-1}$ noted above. Replacement of a methyl group on tin in the ketoorganostannanes by chlorine results in blue shifts of 14 and 4 nm as expected if the non-bonding electrons of the carbonyl oxygen become involved in coordination with the tin atom.

The results obtained with the phenyl ketones in cyclohexane can be discussed with reference to Figs. 3 and 4. Introduction of a trimethyltin group increases the value of $\epsilon$ from 46 for propiophenone at 325 nm to 65 for $n = 3$ and to 79 for $n = 2$ in the $n \rightarrow \pi^*$ transition in the ketoorganostannanes. When chlorine replaces methyl on tin with $n = 3$ a blue shift of about 10 nm and an increase in $\epsilon$ to 100 are observed, Fig. 4a. When $n = 2$ the blue shift is so great that the maximum is masked by the long wavelength tail of the aromatic B-band, Fig. 3a. The B-band absorption is more intense in both of the chlorostannanes than in propiophenone or in the simple ketostannanes. Furthermore, they show maxima in this region corresponding to those at about 278 and 288 nm in the latter. In each of the chlorostannanes the K-band is shifted from 239 to 249 nm and is of slightly greater intensity than in propiophenone or simple ketostannanes which show fairly similar bands. This shift of 10 nm may be compared with the shift of 40 nm which is observed from unprotonated acetophenone to the completely protonated ketone in sulfuric acid solutions [9]. In this case complete localization of a non-bonded pair of the ketone has occurred in the formation of the fully covalent O—H bond with, presumably, the optimum geometry around the protonated carbonyl group. The absence of a band in the 239 nm region of the chloroketones indicates that all of the ketone in each case exists in a single form, the intramolecularly coordinated structure.

### *Proton magnetic resonance spectra*

The PMR spectra of the neat methyl ketones and the corresponding chlorine substituted analogs were obtained with the results displayed in Table 3. The chemical shifts may be compared with each other and with the value of 0.60 ppm observed for a 1/1 mixture of 2-butanone and trimethyltin chloride. In the spectra of the ketones replacement of a methyl group attached to tin by chlorine results in a downfield shift of *all* of the protons. The shift observed in the methyls

TABLE 3

PMR SPECTRAL PARAMETERS OF KETOORGANOSTANNANES AND KETOORGANOCHLOROSTANNANES[a]

| | a b c d<br>$CH_3C(=O)CH_2CH_2Sn(CH_3)_3$ | a b c d<br>$CH_3C(=O)CH_2CH_2SnCl(CH_3)_2$ | Δ |
|---|---|---|---|
| a | 2.02 | 2.18 | 0.16 |
| b | 2.62 | 2.97 | 0.35 |
| c | 0.82 | 1.12 | 0.30 |
| d | 0.03 | 0.53 | 0.50 |
| $^3J(^{119}SnCH_3)$ | 52.0 | 65.0 | 5.3[b] |
| | | | 2.5[c] |

| | a b c d e<br>$CH_3C(=O)CH_2CH_2CH_2Sn(CH_3)_3$ | a b c d e<br>$CH_3C(=O)CH_2CH_2CH_2SnCl(CH_3)_2$ | Δ |
|---|---|---|---|
| a | 1.96 | 2.13 | 0.17 |
| b | 2.30 | 2.58 | 0.28 |
| c | 1.70 | 1.92 | 0.22 |
| d | 0.78 | 1.20 | 0.42 |
| e | 0.05 | 0.55 | 0.50 |
| $^3J(^{119}SnCH_3)$ | 51.5 | 63.0 | 3.3[b] |
| | | | 0.5[c] |

[a] No solvent; chemical shifts in ppm downfield internal tetramethylsilane; coupling constants in Hz. [b] Relative to neat $Me_3SnCl$ (59.7 Hz). [c] Relative to 1/1 mixture of $Me_3SnCl$ and MeCOEt (62.5 Hz).

attached to tin is expected due to the greater electronegativity of chlorine relative to methyl. However, the shift to 0.53 ppm is less than that of trimethyltin chloride by 0.07 ppm. This is consistent with some replenishment of the electron deficiency in the chloroketone due to coordination by an unshared electron pair of the carbonyl oxygen to the tin atom. Such coordination enhances the electron deficiency at the carbonyl carbon, an effect which is transmitted to the protons on the attached carbons leading to downfield shifts of the $CH_3CO$-protons by 0.16 and 0.17 ppm; and for the $COCH_2$ protons by 0.35 and 0.28 ppm for the chloroketones relative to the simple ketones with $n = 2$ and $n = 3$, respectively.

The $^{119}$Sn-methyl proton coupling constants are also informative. Replacement of methyl by chlorine increases the coupling constants by 13.0 and 11.5 Hz for $n = 2$ and $n = 3$, respectively, as expected. More importantly, they are also larger than the value of 59.7 Hz for neat trimethyltin chloride [10] by 5.3 and 3.3 Hz. These results provide further support for intramolecular coordination as in I. In the $sp^3d$ hybridized trigonal bipyramid the chlorine and oxygen atoms would be more or less apical and the two methyl groups and the methylene group would be in the basal plane. According to the interpretation of Bolles and Drago [8] and of Matsubayashi et al. [11] if the oxygen is a strong donor, bonding to it and the chlorine from tin would be through a $p_z$ or $(p_z + d_{z^2})$ orbital, and to the three carbons through $sp^2$ orbitals. The increase in s character would then account for the increase in $^3J(^{119}Sn—H)$ [12].

Infrared data presented above showed a decrease by 14 $cm^{-1}$ in the carbonyl stretching frequency of 2-butanone when mixed with equimolar trimethyltin chloride. This interaction appears to be reflected also in the Sn—H coupling constants which are 62.5 Hz in the mixture, but 2.5 and 0.5 Hz larger in the ketochlorostannanes with $n = 2$ and $n = 3$, respectively. However, this is not reflected in the PMR parameters of 2-butanone. All three proton chemical shifts and the H—H coupling constant are identical within experimental error in the neat ketone, and in the mixture with trimethyltin chloride. Measured values of $\delta$ are 0.95, 2.04 and 2.41 ppm, and $^3J(H—H)$ is 7.2 Hz.

PMR data for the phenylketostannanes were taken on neat samples and in pyridine and carbon tetrachloride solutions; and the chlorostannanes in the two solvents only, because they are solids. Results are gathered in Table 4. The spectra of the latter indicated the presence of a single species. However, the infrared data indicated two types of carbonyl groups. This means that the rate of equilibration of I and IV in pyridine is rapid compared with the rate of proton spin inversion. Therefore, the parameters observed are weighted averages of the values for the two species. That IV is indeed present in pyridine can be seen particularly well by examining the chemical shifts of the methylene protons labeled b in the table. The downfield shift observed in going from the simple ketostannane to the chloro analog is 0.13 ppm in pyridine, while it is 0.32 in carbon tetrachloride when $n = 2$, and when $n = 3$ the values are 0.07 and 0.24 ppm, respectively. In pyridine the carbonyl groups are partly free as in IV, and less perturbation in the proton chemical shifts should be observed. In carbon tetrachloride only I is present and these effects are similar to those in the methyl ketones discussed above. The value of $^3J(^{119}Sn—CH_3)$ is smaller in pyridine for the ketochlorostannane than for trimethyltin chloride, which probably reflects tighter intermolecular coordination in the latter case. This may be due in part to the greater bulk of the carbonyl-

TABLE 4

PMR SPECTRAL PARAMETERS OF KETOORGANOSTANNANES AND KETOORGANOCHLOROSTANNANES[a,b]

| | a b c d<br>$C_6H_5C(=O)CH_2CH_2Sn(CH_3)_3$ | | | a b c d<br>$C_6H_5C(=O)CH_2CH_2SnCl(CH_3)_2$ | | | |
|---|---|---|---|---|---|---|---|
| | Neat | $C_5H_5N$ | $CCl_4$ | $C_5H_5N$ | $CCl_4$ | $\Delta(C_5H_5N)$ | $\Delta(CCl_4)$ |
| a | | | 7.88 | | 7.78 | | −0.10 |
| b | 3.20 | 3.29 | 3.19 | 3.42 | 3.51 | 0.13 | 0.32 |
| c | 1.00 | 1.09 | 0 99 | 1.30 | 1.32 | 0.21 | 0.33 |
| d | 0.77 | 0.15 | 0.07 | 0.65 | 0.63 | 0.50 | 0.56 |
| $^3J(^{119}SnCH_3)$ | 53.2 | 53.6 | 52.8 | 63.2 | 65.0 | 4.1[c] | 6.5[c] |
| | a b c d e<br>$C_6H_5C(=O)CH_2CH_2CH_2Sn(CH_3)_3$ | | | a b c d e<br>$C_6H_5C(=O)CH_2CH_2CH_2SnCl(CH_3)_2$ | | | |
| | Neat | $C_5H_5N$ | $CCl_4$ | $C_5H_5N$ | $CCl_4$ | $\Delta(C_5H_5N)$ | $\Delta(CCl_4)$ |
| a | | | 7.64 | | 7.70 | | 0.06 |
| b | 2.80 | 3.01 | 2.87 | 3.08 | 3.11 | 0.07 | 0.24 |
| c | 1.85 | 2.00 | 1.89 | 2.27 | 2.13 | 0.27 | 0.24 |
| d | 0.80 | 0.89 | 0.84 | 1.55 | 1.36 | 0.66 | 0.52 |
| e | 0.07 | 0.07 | 0.07 | 0.68 | 0.63 | 0.58 | 0.51 |
| $^3J(^{119}SnCH_3)$ | 52.0 | 52.8 | 52.8 | 64.0 | 63.1 | −3.3[c] | 4.6[c] |

[a] Chemical shifts in ppm downfield from internal tetramethylsilane; coupling constants in Hz. [b] Data for neat samples and (0.1 *M*) in pyridine ($C_5H_5N$) solution taken at 60 MHz; data in $CCl_4$ solution (ca. 0.07 *M*) taken at 100 MHz using Fourier transform. [c] Relative to $Me_3SnCl$ in py (67.3 Hz) or $CCl_4$ (58.5 Hz).

bearing chain and the competition with intramolecular coordination, which results in smaller coupling constants (65.0 and 63.1 Hz) in carbon tetrachloride.

### *Carbon-13 magnetic resonance spectra*

Because they were liquids it was possible to examine the natural abundance $^{13}C$ Fourier transform spectra of the methylketostannanes and the chlorides, both neat and mixed with equimolar pyridine. Results including chemical shifts and $^{119}Sn$—$^{13}C$ coupling constants are gathered in Table 5. The arguments used to assign the signals can be outlined with reference to the simple ketostannane with $n = 3$. The methyl carbons attached to tin are characterized by their appearance upfield from tetramethylsilane by 10-11 ppm, and by the large values of $^1J(^{119}Sn—^{13}C)$ (322 Hz). Other measurements of these parameters have been reported [13]. The methylene carbon attached to tin appears downfield of tetramethylsilane by 10.6 ppm, and displays a $^1J$ value of 359 Hz. A further downfield shift is reflected by the carbon $\beta$ to the tin; it appears at about 21 ppm, while its coupling constant is characteristically small (18 Hz) [14]. The $\gamma$-carbon shows up at 47 ppm, and has the significantly larger coupling constant of 57 Hz. This suggests that this carbon is in an *anti* relationship with respect to the tin atom in the most populous conformation. The $^3J(^{119}Sn—^{13}C)$ has been shown to obey a Karplus type of relationship with *anti* *J*'s about 60 ± 10 Hz [14]. As expected the carbonyl carbon signal appears at the lowest field (205.5 ppm) and is very weakly ($\approx$ 2.5 Hz) coupled to the tin. Finally, the signal of the methyl carbon attached to the carbonyl appears at about 47 ppm and shows no interaction with the tin atom.

TABLE 5

$^{13}$C MAGNETIC SPECTRAL PARAMETERS FOR KETOORGANOSTANNANES AND KETOORGANOCHLOROSTANNANES[a]

| δ | a b c d e<br>$(CH_3)_3SnCH_2CH_2C(=O)CH_3$ | | a b c d e<br>$(CH_3)_2SnClCH_2CH_2C(=O)CH_3$ | | a b c d e f<br>$(CH_3)_3SnCH_2CH_2CH_2C(=O)CH_3$ | | a b c d e f<br>$(CH_3)_2SnClCH_2CH_2CH_2C(=O)CH_3$ | |
|---|---|---|---|---|---|---|---|---|
| | Neat | 1/1 py | Neat | 1/1.5 py | Neat | 1/1 py | Neat | 1/1 py |
| a | −10.61 | −10.67 | 0.00 | 0.00 | −10.37 | −10.40 | 0.72 | 0.93 |
| b | 3.47 | 3.40 | 10.22 | 10.54 | 10.62 | 10.58 | 20.04 | 20.11 |
| c | 39.01 | 38.98 | 39.73 | 40.05 | 21.27 | 21.32 | 20.68 | 20.28 |
| d | 206.4 | 206.9 | 217.4 | 216.6 | 47.40 | 47.43 | 44.78 | 45.60 |
| e | 27.74 | 27.67 | 28.95 | 28.64 | 205.5 | 206.2 | 210.6 | 211.6 |
| f | | | | | 29.30 | 29.50 | 31.06 | 29.90 |
| $J(^{119}Sn-^{13}C)$ (Hz)[b] | | | | | | | | |
| a | 331.7[c] | 330.8[c] | 463.8[c] | 465.8[c] | 321.2[c] | 322.7[c] | 436.6[c] | 458.2[c] |
| b | 369.6[c] | 369.5[c] | 490.8[c] | 498.6[c] | 359.8[c] | 359.3[c] | 490.5[c] | 507.4[c] |
| c | 23.8 | 22.7 | 29.0 | 29.0 | 17.8 | 17.4 | 23.8 | 24.4 |
| d | 30.0 | 32[d] | 37.1 | 36.8 | 57.0[c] | 57.5 | 19.0 | 46[e] |
| e | [f] | [f] | $<5$ | [f] | $\approx 2.2$ | $\approx 2.5$ | $\leq 2.5$ | $\approx 2$ |

[a] Chemical shifts in ppm downfield from internal tetramethylsilane. [b] ± 0.9 Hz except where specified. [c] Satellites due to $^{119}$Sn and $^{117}$Sn resolved. Value given is for $^{119}$Sn obtained from measured average for $^{119}$Sn and $^{117}$Sn multiplied by $\gamma_{119}/\gamma_{117}$. [d] ± 2 Hz. [e] ± 2.5 Hz. [f] Not determined.

When one of the methyl groups is replaced by chlorine the remaining tin methyl carbon signals move downfield by 10 ppm as does that of the methylene carbon attached to tin. The carbonyl carbon moves downfield by 11 ppm (205.5 → 216.6) in the neat chloride, but the shift is only 5 ppm (206.2 → 211.6) in the presence of pyridine. This is consistent with rapid equilibration of I, with intramolecular coordination of the carbonyl to tin, and IV in which the carbonyl is free and pyridine is coordinated to tin. This equilibration is also reflected in the value of 19.0 Hz for $^3J(^{119}Sn—^{13}C)$ in the neat chlorostannane, and 45 Hz in the presence of pyridine. In the former case ring formation brings the γ-methylene carbon into an approximately gauche relationship to the tin atom, thus decreasing $^3J$ markedly. The larger value in the presence of pyridine represents the weighted average of the open and cyclic forms. A significant increase in the one-bond coupling of tin with the attached methyl and methylene carbons is observed upon addition of pyridine, the coupling to methyl increasing by 22 Hz and to methylene by 17 Hz. A much larger change in $^1J$ occurs in trimethyltin chloride (386 Hz) when it is dissolved in pyridine (472 Hz) [15]. No such change is observed with the simple ketostannane.

The behavior of the ketochlorostannane with $n = 2$ differs quantitatively from that with $n = 3$. For example, the one-bond couplings to tin change by only 2 ($CH_3$) and 8 Hz ($CH_2$) upon addition of pyridine, as would be expected if the structure I is still the predominant one. One puzzling feature is the small value of 30 Hz for $^3J(^{119}Sn—^{13}C)$ in the simple ketone. This is certainly smaller than would be expected for an *anti* disposition to the chlorotin, which contrasts with the decrease observed when $n = 3$.

*Mossbauer spectra*

The Mossbauer spectra of the ketones were taken at 77°K and are presented in Table 6. No resolvable quadrupole splitting is observed in the simple ketostannanes, indicating that in the solid state there is no significant interaction between the carbonyl oxygens and the tin atoms. However, in the chlorostannanes the expected splitting is observed due to coordination between the carbonyl oxygen and the tin atom which is now a stronger Lewis acid.

TABLE 6

THE $^{119}$Sn MÖSSBAUER SPECTRA$^a$ OF ORGANOSTANNANES $(CH_3)_2\overset{R}{Sn}(CH_2)_nC(=O)R'$

| Compound | | | *IS*$^b$ | *QS*$^c$ | $r_1$ | $r_2$ |
|---|---|---|---|---|---|---|
| R | *n* | R' | | | | |
| Me | 2 | Me | 1.41 | | 1.32 | |
| Me | 2 | Ph | 1.44 | | 1.21 | |
| Me | 3 | Me | 1.41 | | 1.30 | |
| Me | 3 | Ph | 1.42 | | 1.28 | |
| Cl | 2 | Me | 1.54 | 3.70 | 1.63 | 1.46 |
| Cl | 2 | Ph | 1.47 | 3.26 | 1.18 | 1.19 |
| Cl | 3 | Me | 1.51 | 3.66 | 1.44 | 1.33 |
| Cl | 3 | Ph | 1.52 | 3.48 | 1.06 | 1.06 |

[a] Run at 77°K vs. a Ba$^{119}$SnO$_3$ source (New England Nuclear) relative to β-tin 2.56 mm/sec. All data in mm/sec. [b] ± 0.06 mm/sec. [c] ± 0.12 mm/sec.

## Experimental

### *General*

Proton magnetic resonance spectra were recorded on Varian A-60 or HA-100 instruments. The $^{13}C$ magnetic resonance spectra were recorded on the HA-100 instrument interfaced with a Digilab NMR-FTS-3 pulse and data system. Infrared spectra were obtained with a Beckman IR-10 instrument and the electronic spectra with a Carey 14. Mössbauer spectra were recorded on a camdrive, constant acceleration spectrometer [16] using a $BaSnO_3$ source (New England Nuclear Corp.).

### *Materials*

*Trimethylstannane.* A flask containing a suspension of lithium aluminum hydride (8.0 g, 0.42 mol) in 100 ml of tetraethylene glycol dimethyl ether (tetraglyme) (Ansul) under argon was cooled in an ice-water bath. A solution of 83.7 g (0.42 mol) of chlorotrimethylstannane in 150 ml of tetraglyme was added with stirring, and stirring continued for an additional hour. The cooling bath was removed, and the trimethylstannane was distilled from the solvent at ambient temperature into a trap cooled by liquid nitrogen at 0.1 torr providing 67.0 g (96%) of trimethylstannane which was used without further purification.

*2-Cyanoethyltrimethylstannane.* A mixture of 30.0 g, (0.182 mol) of trimethyltin hydride, 1.91 g. (0.136 mol) of acrylonitrile and 1.0 g. (0.006 mol) of 2,2′-azobis(2-methylpropionitrile) was slowly warmed under argon in a water bath to 60° for 6 h. The reaction product mixture was filtered and the filtrate was distilled; b.p. 124-125°/20 torr, yield 70-75%, IR (film): 2980 s, 2930 m, 2260 m, 1425 m, 765 s, 713 m cm$^{-1}$; PMR: $\delta$ 2.22 t, 1.73 m, 0.80 t, 0.00 s ppm. (Found: C, 36.16; H, 6.42; N, 6.03. $C_6H_{13}NSn$ calcd.: C, 36.49; H, 6.31; N, 6.03%.)

*3-Cyanopropyltrimethylstannane.* Trimethyltin hydride, 30.0 g (0.182 mol) and 14.6 g (0.218 mol) of allyl cyanide were heated for 2 h with 1.02 g of AIBN. Distillation yielded 34.2 g (81%) of 3-cyanopropyltrimethylstannane, b.p. 61-63.5°/0.5 torr. (Found: C, 36.53; H, 6.57: N, 6.28. $C_7H_{15}NSn$ calcd.: C, 36.26: H, 6.52: N, 6.04%.) IR (film): 2980 s, 2910 s, 220 m, 1420 m, 1340 m, 760 s cm$^{-1}$; PMR: $\delta$ 2.29 t, 1.80 d, 0.87 t, 0.05 q ppm.

*3-Oxobutyltrimethylstannane.* To the Grignard reagent prepared from 2.0 g. (0.081 mol) of magnesium and methyl bromide in 150 ml of dry ether was slowly added 15.0 g (0.069 mol) of 2-cyanoethyltrimethylstannane in 100 ml of ether. The mixture was refluxed for 7 h. The complex was hydrolyzed by pouring onto 10 g of ammonium chloride with sufficient ice to cool the reaction. The ether layer was removed and concentrated. The ketimine was decomposed by heating for 2 h on a steam bath. The residue was extracted with ether, dried over anhydrous magnesium sulfate, and distilled; b.p. 55-57°/5 torr, yield 50-55%, IR (film): 2950 s, 2810 m, 1710 s, 1410 m, 1360 m, 1175 w, 770 s, and 715 w cm$^{-1}$; UV ($CH_3OH$) max.: 280 nm ($\epsilon$ 26) and 220 nm ($\epsilon$ 64); PMR ($CCl_4$): $\delta$ 2.78 t, 2.08 s, 0.85 t, 0.05 s ppm. (Found: C, 36.03; H, 6.60. $C_7H_{16}OSn$ calcd.: C, 35.71; H, 6.86%.)

*4-Oxopentyltrimethylstannane.* A solution of 19.0 g (0.082 mol) of 3-cyanopropyltrimethylstannane in 100 ml of ether was added dropwise to a solution of Grignard reagent prepared from 2.4 g (0.10 mol) of magnesium and methyl bromide in 150 ml of dry ether. The mixture was refluxed overnight. The product was worked up as in the preceding synthesis. Distillation through a spinning band column yielded 20-26% of colorless product at 60-66°/5-7 torr. IR (film): 2940 s, 2800 m, 1710 s, 1350 m, 1410 m, 1185 s, 1178 w, 770 s and 710 m cm$^{-1}$; UV ($CH_3OH$) max.: 280 nm ($\epsilon$ 35.2), 219 nm ($\epsilon$ 92.4); PMR ($CCl_4$): $\delta$ 2.31 t, 1.9 s, 1.65 m, 0.90 t, 0.45 d, 0.07 s ppm. (Found: C, 39.19; H, 7.23. $C_8H_{18}OSn$ calcd.: C, 38.56; H, 7.29%.)

*3-Phenyl-3-oxopropyltrimethylstannane.* This compound was prepared as in the preceding experiment from 1.34 g (0.055 mol) of magnesium, 8.4 g (0.055 mol) of bromobenzene, and 8.0 g (0.037 mol) of 2-cyanoethyltrimethylstannane. The ketone was obtained in 58% yield, b.p. 80°/0.09 torr; IR (film): 3060 w, 2790 s, 1600 m, 1585 w, 1452 m, 1353 m, 1224 s, 1280 m, 1180 w, 955 m, 810 m, 750 s, 685 m cm$^{-1}$; PMR ($CCl_4$): $\delta$ 2.94 m, 7.35 m, 3.13 t, 0.98 (3), 0.10 s ppm. (Found: C, 48.63; H, 6.31. $C_{12}H_{18}OSn$ calcd.: C, 48.42; H, 6.12%.)

*4-Phenyl-4-oxobutyltrimethylstannane.* This compound was prepared as in the preceding experiment from 1.5 g (0.060 mole) of magnesium, 9.4 g (0.06 mol) of bromobenzene and 10.0 g (0.043 mol) of 3-cyanopropyltrimethylstannane. The ketone was obtained in a 52% yield (7.1 g) b.p. 92°/0.09 torr; IR (film): 3060 w, 2970 s, 2920 m, 1680 m, 1598 m, 1580 w, 1450 m, 1355 m, 1210 s, 1180 w, 965 m, 755 s and 685 m cm$^{-1}$; PMR: $\delta$ 8.00 m, 7.40 q, 2.90 t, 1.90 m, 0.85 t, 0.50 d, 0.10 s ppm. (Found: C, 50.47; H, 6.68. $C_{13}H_{20}OSn$ calcd.: C, 50.18; H, 6.48%.)

*3-Oxobutyldimethylchlorostannane.* To 2.35 g (0.01 mol) of 3-oxobutyltrimethylstannane in a 5 ml round bottom flask was added 1.99 g (0.01 mol) of trimethyltin chloride. The resulting homogeneous liquid was stirred under nitrogen for 12 h. It was then distilled to afford 2.04 g (89%) of 3-oxobutyldimethylchlorostannane, b.p. 127°/0.01 torr; IR (film): 3000 w, 2920 m, 1679 s, 1400 w, 1370 m, 1340 m, 1190 s, 1130 w, 980 w, 770 s cm$^{-1}$; PMR (neat): $\delta$ 2.98 t, 2.18 s, 1.11 t, 0.54 s ppm. (Found: C, 28.23; H, 4.96. Mol. wt. ($CCl_4$), 281. $C_6H_{13}CClSn$ calcd.: C, 28.23; H, 5.13%. Mol. wt., 255.)

*4-Oxopentyldimethylchlorostannane.* A mixture of 1.0 g (0.005 mol) of trimethyltin chloride and 1.25 g (0.005 mol) of 4-oxopentyltrimethylstannane was stirred for 24 h in a 5 ml round bottom flask without solvent. 4-Oxopentyldimethylchlorostannane was distilled at 169°/0.4 torr, yield 1.13 g (84%); IR (film): 2980 w, 1370 s, 1230 w, 1180 s, 1130 w, 1060 w, 1010 w, 980 w, 913 w, 770 s cm$^{-1}$. PMR: $\delta$ 2.58 t, 2.14 s, 1.92 m, 1.27 t, 0.55 s ppm. (Found: C, 31.27; H, 5.51. Mol. wt. ($CCl_4$). 280. $C_7H_{15}OClSn$ calcd.: C, 31.21; H, 5.61%. Mol. wt., 269.)

*3-Phenyl-3-oxopropyldimethylchlorostannane.* To 2.6 g (0.013 mol) of trimethyltin chloride in a 10 ml flask was added 3.88 g (0.013 mol) of 3-phenyl-3-oxopropyltrimethylstannane. The mixture was flushed with nitrogen, and stirred for 48 h. The slurry was filtered, washed with 3 ml of carbon tetrachloride and the colorless solid dried under reduced pressure (0.009 torr) at room temperature; yield 2.05 g (50%); m.p. 124°. The infrared spectrum of the compound (KBr) has bands at 2990 w, 2890 m, 2310 w, 1641 s, 1580 s, 1560 s, 1470 m, 1430 m, 1380 s, 1330 s, 1210 s, 1160 m, 1140 s, 1110 m, 980 m, 940 s, 750 m, 670 s, 650 w cm$^{-1}$; PMR (pyridine): δ 3.42 t, 1.3 t, 0.65 s ppm. (Found: C, 41.30; H, 4.51. $C_{11}H_{15}OClSn$ calcd.: C, 41.63; H, 4.42%.)

*4-Phenyl-4-oxobutyldimethylchlorostannane.* This compound was prepared from a mixture of 1.79 g (0.009 mol) of trimethyltin chloride and 2.8 g (0.009 mole) of 4-phenyl-4-oxobutyltrimethylstannane in the manner described above. The product was white powder (1.7 g, 57%), m.p. 116-117°. IR (KBr): 300 w, 2920 m, 2880 m, 2860 m, 1649 s, 1597 s, 1580 w, 1450 s, 1397 m, 1365 s, 1345 s, 1305 s, 1270 s, 1240 s, 1220 s, 1180 m, 1080 w, 1060 w, 1000 s, 965 m, 920 w, 910 m, 860 w, 770 s, 690 s, 640 m cm$^{-1}$; PMR (pyridine): δ 3.08 t, 2.27 m, 1.55 t, 0.68 s ppm. (Found: C 43.28; H, 5.35. $C_{12}H_{17}OClSn$ calcd.: C, 43.49; H, 5.17%.)

*3-Hydroxybutyltrimethylstannane.* To 20 g (0.28 mol) of 3-buten-2-ol (Aldrich) in a 30 mm diameter tube was added 50 g (0.30 mol) of trimethylstannane under argon. The mixture was irradiated for 3.3 h in a Rayonet reactor (New England Scientific) using a battery of 3000 Å lamps. The product was filtered, stripped of volatile materials using a rotary evaporator and distilled, providing 3-hydroxybutyltrimethylstannane, bp. 45-48°/0.6 torr; 61.8 g (93%); IR (film): 3350 s, 2970 s, 2905 s, 1370 m, 1110 m, 1060 m, 1015 m, 930 m, 830 m, 760 s and 300 s cm$^{-1}$; PMR: δ 3.56 m, 1.54 m, 1.12 d, 0.77 t, 0.02 s ppm. The highest molecular weight peak in the mass 70 eV spectrum was at *m/e* 223 corresponding to the $(M - CH_3)^+$ species. (Found: C, 35.52, H, 7.81. $C_7H_{18}SnO$ calcd.: C, 35.49; H, 7.66%.)

*4-Hydroxypentyltrimethylstannane.* Under the same conditions as those described above 25 g (0.29 mol) of 4-penten-2-ol (Aldrich) and 50 g (0.30 mol) of trimethylstannane provided 65.0 g (89%) of 4-hydroxypentyltrimethylstannane; b.p. 60-62°/0.7 torr; IR (film): 3370 s, 2985 s, 2940 s, 2870 s, 1380 m, 1120 m, 770 s, 530 s and 315 s cm$^{-1}$; PMR: δ 3.60 m, 1.50 m, 1.12 d, 0.82 t, 0.03 s ppm. Mass spectrum (70 eV) *m/e* 237 $(M - CH_3)^+$. (Found: C, 37.93; H, 8.12. $C_8H_{20}SnO$ calcd.: C, 38.29; H, 8.03%.)

*3-Oxobutyltrimethylstannane from 3-hydroxybutyltrimethylstannane.* To 700 ml of pyridine (Fisher, ACS Grade) in a 2 l flask cooled in an ice-water bath was added 52 g (0.52 mol) of finely ground chromium trioxide (Baker, technical grade) over 3/4 h, with stirring [17]. Then 61.8 g (0.26 mol) of 3-hydroxybutyltrimethylstannane was added dropwise over one hour whereupon the bright yellow suspension gradually turned black. The ice bath was removed and stirring continued for 20 h. Then 700 ml of water was added, the resultant suspension filtered and the precipitate of chromium salts washed with five 400 ml portions of 1/1 benzene/ethyl ether. The organic fractions were combined, washed with two 200 ml portions of 5% aqueous hydrochloric acid, and concentrated to about 100 ml. Further washings with acid removed the remainder of the pyridine. The resultant solution was dried over sodium sulfate and distilled to give 40.8 g (66%) 3-oxobutyltrimethylstannane b.p. 53-56°/0.5 torr.

*4-Oxopentyltrimethylstannane.* Using the same procedure 65 g (0.26 mol) of 4-hydroxypentyltrimethylstannane was oxidized with 52 g (0.52 mol) of chromium trioxide to yield 42.9 g (65%) of 4-oxopentyltrimethylstannane, b.p. 60-63°/0.5 torr.

### *Kinetic and equilibrium studies*

PMR spectroscopy was used for the study of the rates and equilibria of the

TABLE 7

RATE AND EQUILIBRIUM DATA FOR REACTIONS OF TRIMETHYLTIN WITH KETOORGANOTINS AND n-BUTYLTRIMETHYLSTANNANE

| | n-BuMe$_3$Sn | CH$_3$CO(CH$_2$)$_3$SnMe$_3$ | CH$_3$CO(CH$_2$)$_2$SnMe$_3$ |
|---|---|---|---|
| $K$ | 1.3 | 4.3 | 120 |
| Initial conc. ($M$) | 3.18 | 3.18 | 3.18 |
| $k_f$ ($M$ h)$^{-1}$ | 0.0045 | 0.095 | 2.3 |
| $k_r = (k_f/K)$ | 0.0035 | 0.022 | 0.019 |

reaction of trimethyltin chloride with the ketoorganotins and *n*-butyltrimethylstannane. The reactants, and the relative areas of the methyl groups attached to carbonyl, which differed in chemical shift by 0.16 ppm, were used to determine the relative concentrations. In the case of *n*-butyltrimethylstannane, the areas of the methyl groups attached to tin were used because their chemical shifts differed by 0.09 ppm.

With equimolar reactants the reaction can be written as eqn. 4, and the rate law was assumed to be given by eqn. 5. These lead to expression 7 for the equilibrium constant from which the integrated expression for a reversible bi-

$$K = \frac{[\mathrm{B}]^2}{[\mathrm{A}]^2} = \frac{k_f}{k_r} \tag{7}$$

molecular reaction shown in eqn. 8 can be derived. Results are summarized in Table 7, and plotted in Fig. 1.

$$\frac{\sqrt{K}}{2\mathrm{A}_0} \ln \frac{(1 - K^{-1})\,\mathrm{B} - \mathrm{A}_0\,(1 + K^{-\frac{1}{2}})}{(1 - K^{-1})\,\mathrm{B} - \mathrm{A}_0\,(1 - K^{-\frac{1}{2}})} = k_f t \tag{8}$$

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