SYNTHESIS OF KETOALKYLTIN CHLORIDES VIA IN-SITU CONDENSATION AND HYDROSTANNATION OF KETONIC SUBSTRATES

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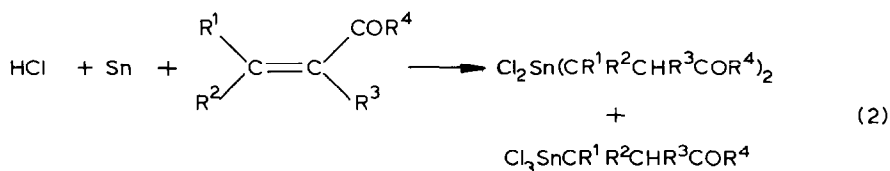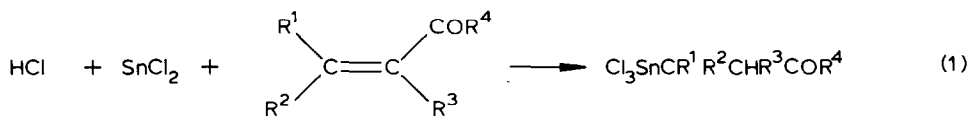
Summary

Reactions between hydrogen chloride, stannous chloride and aliphatic ketones yield 3-ketoalkyltin trichlorides via the in-situ generation of α,β-unsaturated ketones. The analogous reactions between hydrogen chloride, tin and aliphatic ketones give rise to mixtures of 3-ketoalkyltin trichlorides and the corresponding bis(3-keto-alkyl)tin dichlorides. β-Hydroxyketones, which are intermediates in the acid-catalysed synthesis of α,β-unsaturated ketones, can also be employed in conjunction with hydrogen chloride/stannous chloride and hydrogen chloride/tin to generate the 3-ketoalkyltin chlorides.
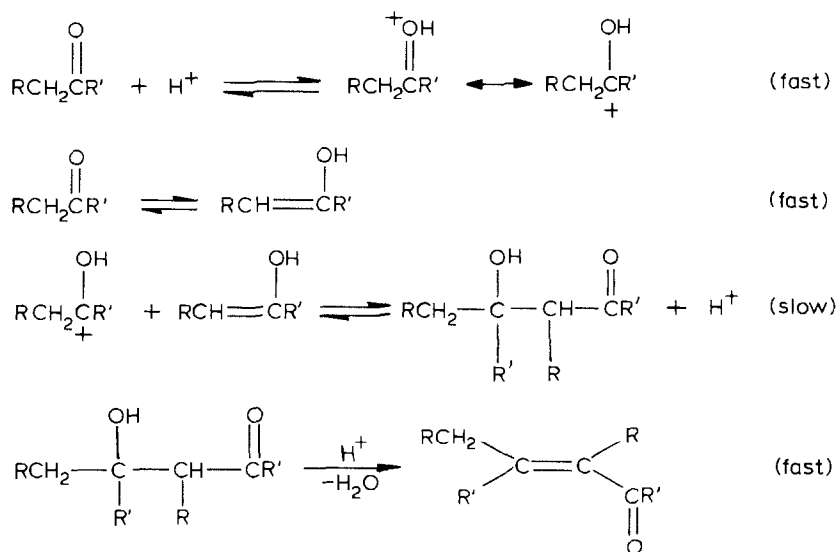
Introduction

Previous reports on the hydrostannation of carbonyl activated olefines with halogenostannane intermediates have largely focussed upon acrylic esters. However, relatively high yields of 3-ketobutyltin compounds are produced from α,β-unsaturated ketones such as methyl vinyl ketone and mesityl oxide and only the limited availability of these monomers has restricted a wider study of this type of compound. [1,2]. Equations 1 and 2 represent these reactions:

$$HCl + SnCl_2 + \underset{R^2}{\overset{R^1}{\diagdown}}C=C\underset{R^3}{\overset{COR^4}{\diagup}} \longrightarrow Cl_3SnCR^1R^2CHR^3COR^4 \qquad (1)$$

$$HCl + Sn + \underset{R^2}{\overset{R^1}{\diagdown}}C=C\underset{R^3}{\overset{COR^4}{\diagup}} \longrightarrow Cl_2Sn(CR^1R^2CHR^3COR^4)_2$$
$$+ \qquad (2)$$
$$Cl_3SnCR^1R^2CHR^3COR^4$$

Preparation of the α,β-unsaturated ketones in which R^1, R^2, R^3 and R^4 are all alkyl groups is accomplished by the acid-catalysed condensation of the appropriate ketones [3–5], whereas synthesis of the compounds with $R^1 = H$ and R^2, R^3 and $R^4 = $ alkyl is achieved by an exactly similar process with aldehyde/ketone mixtures [6]. The chemistry of these condensation reactions is well documented [7]: β-ketols are intermediates, and the immediate precursors to the α,β-unsaturated ketones (see Scheme 1).

SCHEME 1

$$\underset{\substack{\| \\ O}}{RCH_2CR'} + H^+ \rightleftharpoons \underset{\substack{\| \\ {}^+OH}}{RCH_2CR'} \longleftrightarrow \underset{\substack{| \\ OH}}{RCH_2\overset{+}{C}R'} \qquad \text{(fast)}$$

$$\underset{\substack{\| \\ O}}{RCH_2CR'} \rightleftharpoons \underset{\substack{| \\ OH}}{RCH=CR'} \qquad \text{(fast)}$$

$$\underset{\substack{| \\ OH \\ +}}{RCH_2CR'} + \underset{\substack{| \\ OH}}{RCH=CR'} \rightleftharpoons \underset{\substack{| \\ OH}}{RCH_2}-\underset{\substack{| \\ R'}}{C}-\underset{\substack{| \\ R}}{CH}-\underset{\substack{\| \\ O}}{CR'} + H^+ \qquad \text{(slow)}$$

$$\underset{\substack{| \\ OH}}{RCH_2}-\underset{\substack{| \\ R'}}{C}-\underset{\substack{| \\ R}}{CH}-\underset{\substack{\| \\ O}}{CR'} \xrightarrow[-H_2O]{H^+} \underset{R'}{\overset{RCH_2}{>}}C=C\underset{\underset{\substack{\| \\ O}}{CR'}}{\overset{R}{<}} \qquad \text{(fast)}$$

With aldehyde/ketone mixtures the aldehyde always acts as the carbonyl component and the ketone as the enol component.

Potentially, a wide range of ketoalkyltin chlorides might be produced by the one step in-situ acid-catalysed condensation of simple ketones and hydrostannation of the resultant α,β-unsaturated ketones since trichlorostannane is known to be very strong acid [8].

Results and discussion

Self condensation of symmetrical ketones

A mixture of HCl, SnCl$_2$, and an ethereal solution of acetone (SnCl$_2$/acetone = 1/2) reacts exothermically to give a reasonable yield (see Table 1) of $Cl_3SnCMe_2CH_2COMe$ (eq. 3). A similar reaction between HCl, Sn and acetone (Sn/acetone = 1/4) produced a mixture of $Cl_2Sn(CMe_2CH_2COMe)_2$ and $Cl_3SnCMe_2CH_2COMe$ (eq. 4). Characterisation of this and other reaction mixtures was aided by the development of a purification process by which the pure bis(ketoalkyl)tin dichlorides could be efficiently isolated from the mixed ketoalkyltin compounds.

$$HCl + SnCl_2 + 2Me_2CO \rightarrow Cl_3SnCMe_2CH_2COMe \tag{3}$$

$$HCl + Sn + 4Me_2CO \rightarrow Cl_2Sn(CMe_2CH_2COMe)_2 \tag{4}$$
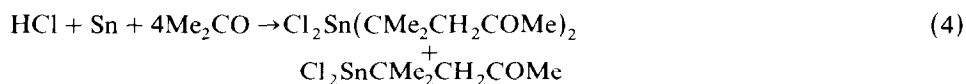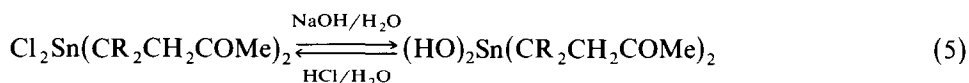$$\overset{+}{Cl_2SnCMe_2CH_2COMe}$$

TABLE 1

THE REACTION OF DIALKYL KETONES RCOR' WITH TIN AND HYDROGEN CHLORIDE
(AT 35 °C) (MOLAR RATIO KETONE/Sn/HCl = 4/1/2)

Ketone		Solvent	Reaction time (h)	Number of organotin products (TLC)	Yield (%)	Monoketo-alkyltin (%)
R	R'					
Me	Me	Me_2CO	4	2	64	30
Et	Et	Et_2O	168	2	29	a
Pr	Pr	Et_2O	144	2	32	a
Me	Et	–	12	5	22	48
Me	Pr	Hexane	168	1	85	100
Me	Bu	Et_2O	312	2	71	a

a Largely ketoalkyltin trichloride.

Hydrolysis of bis(3-ketobutyl)tin dichlorides with a dilute (4%) aqueous sodium hydroxide solution gives rise to water soluble organotin compounds. This is unusual since hydrolysis of dialkyltin dichlorides in aqueous media gives water insoluble organotin oxides [9]. However, it is clear from the NMR spectra of the solutions produced from reactions between the bis(3-ketobutyl)tin dichlorides and NaOH in D_2O that the Sn–C bond is intact in the hydrolysed compounds (see Table 2). The water solubility of these products can conceivably be explained if they exist as dihydroxides.

$$Cl_2Sn(CR_2CH_2COMe)_2 \underset{HCl/H_2O}{\overset{NaOH/H_2O}{\rightleftharpoons}} (HO)_2Sn(CR_2CH_2COMe)_2 \qquad (5)$$

(R = H, Me)

Furthermore, several workers have reported the formation of dialkyltin dihydroxides ($R_2Sn(OH_2)$) upon hydrolysis of sterically hindered dialkyltin dichlorides (R = o-PhOC$_6$H$_4$ [10]; R = t-Bu [11,12]). Carbonyl coordination to tin in Cl_2Sn-$(CR_2CH_2COMe)_2$ (R = H, Me) is almost certainly a source of steric hindrance at the tin centre with respect to attack by OH⁻.

Reacidification of these aqueous solutions with hydrochloric acid regenerated the bis(3-ketobutyl)tin dichlorides. $Cl_2Sn(CMe_2CH_2COMe)_2$ was recovered in 99% yield and $Cl_2Sn(CH_2CH_2COMe)_2$ in 96% yield after the hydrolysis and acidification cycle. Aged solutions (a few hours) of the hydrolysed products were, however, unstable and reacidification resulted in lower yields of the corresponding chlorides.

When mixtures of $Cl_2Sn(CMe_2CH_2COMe)_2$ and $Cl_3SnCMe_2CH_2COMe$ were hydrolysed and reacidified in the above fashion only $Cl_2Sn(CMe_2CH_2COMe)_2$ was recovered (NMR and TLC evidence). The most plausible explanation for this observation is that the mono ketoalkyltin compound remains water soluble in both alkaline and acidic media as do the simple alkyltin analogues [13]. The hydrolysis/acidification cycle is, therefore, useful for the isolation of pure bis(ketoalkyl)tin dichlorides, from mixtures of mono- and di-(ketoalkyl)tin chlorides.

Extension of the hydrostannation reaction to other symmetrical ketones was attempted. With 3-pentanone, or 4-heptanone reaction with HCl and Sn gave a mixture of two organotin compounds (eq. 6). In both cases the proton NMR spectra

TABLE 2

60 MHz NMR DATA FOR KETOALKYLTIN CHLORIDES

Compound	Chemical shifts (τ)[a]				Coupling constants[b] (Hz)	
	CH (α)	CH (β)	CH (γ)	COMe	J(Sn–H(α))	J(Sn–H(β))
Cl₃SnCH₂CH₂COMe	8.12	6.84		7.52	85	177
Cl₃SnCH.Me.CH₂COMe	7.52	6.83[c] (CH₂) 8.49 (Me)		7.51	[d]	[e]
Cl₃SnCMe₂CH₂COMe	–	6.85 (CH₂) 8.77 (Me)		7.43	–	204 (Me) 210 (CH₂) 204 (Me)
Cl₂Sn(CH₂CH₂COMe)₂	8.44	6.79		7.67	86	145
Cl₂Sn(CHMe.CH₂COMe)₂	~7.87	6.84[c] (CH₂) 8.50 (Me)		7.67	[d]	[e]
Cl₂Sn(CMe₂CH₂COMe)₂	–	7.01 (CH₂) 8.57 (Me)		7.68	–	144 (Me) 138 (CH₂) 129 (Me)
Cl₂Sn(CH₂CHMe.COMe)₂	8.30[c]	6.83	8.53	7.74	[e]	[e]
Cl₂Sn(CMe₂CH₂COMe)₂/2NaOH[f]	–	7.06 (CH₂) 8.67 (Me)		7.63	–	125 (CH₂) 114 (Me)

[a] Spectra recorded in CDCl₃, solution-internal TMS, τ = 10.0. [b] The reported values are the mean of the ¹¹⁷Sn–H and ¹¹⁹Sn–H coupling constants. [c] Centre of the doublet of doublets. [d] The Sn–H satellite peaks are masked by other signals. [e] The Sn–H satellite peaks are too weak to be observed. [f] Spectrum recorded in D₂O; internal reference 3-(trimethylsilyl) propionic acid sodium salt, τ = 10.0

of the product mixtures were very complex and it was impossible to assess the relative quantities of the mono- and bis-ketoalkyltin chlorides. TLC evidence did, however, suggest that in each case the monoalkyltin trichloride was the major product.
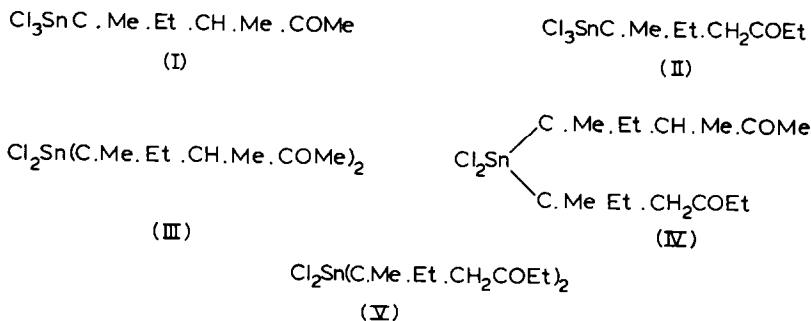
$$HCl + Sn + (RCH_2)_2CO \rightarrow Cl_2Sn(C(CH_2R)_2CHRCOCH_2R)_2 \quad (6)$$

$$+$$

$$Cl_3SnC(CH_2R)_2CHRCOCH_2R$$
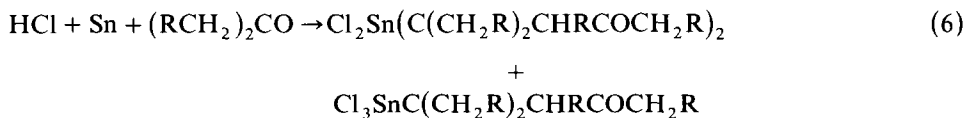
(R = H, Me, Et)

Formation of largely the monoketoalkyltin trihalides in these reactions is consistent with the effect of increasing alkyl chain length upon the rate of the ketone condensation reaction. A slow rate of α,β-unsaturated ketone generation will result in a low monomer concentration and in the case of methyl acrylate these reaction conditions favour a product mixture with a high monoalkyltin trichloride content [2].

Self condensation of unsymmetrical ketones

A reaction between HCl, Sn and 2-butanone resulted in the formation of a complex mixture of organotin compounds (see Table 1). TLC suggested that five (2 mono- and 3 dialkyl-) different organotin compounds were produced. IR spectroscopy revealed the presence of three carbonyl stretching frequencies at 1650, 1670 and 1680 cm^{-1} indicating that carbonyl to Sn coordination is present in the organotin compounds [14]. The 60 MHz proton NMR spectrum of the product mixture was complicated but exhibited singlets at 6.96τ (broad), 7.48 and 7.65 τ. By comparison with the spectra of $Cl_2Sn(CMe_2CH_2COMe)_2$ and Cl_3SnCMe_2-CH_2COMe (Table 2) the lowest field signal is consistent with the presence of a CH_2CO group (in $Cl_2Sn(\overset{|}{C}CH_2COR)_2$) and the higher field signals are consistent with the presence of COMe groups (in Cl_3Sn-$\overset{|}{C}.\overset{|}{C}$-COMe and $Cl_2Sn(\overset{|}{C}.\overset{|}{C}$-COMe)$_2$ at 7.48 and 7.65τ respectively).

Acid-catalysed condensation of 2-butanone is reported to give, in most instances, 3,4-dimethyl-3-hexane-2-one [3], although, in a limited number of cases a small amount of 3-condensation may also result in the formation of 5-methyl-4-heptene-3-one [5].

The multiplicity of organotin products generated in the HCl/Sn/2-butanone reaction can, therefore, be explained by the formation of both the α,β-unsaturated ketones. In accord with the available information the probable organotin products are I–V.

Cl$_3$SnC . Me . Et . CH . Me . COMe

(I)

Cl$_3$SnC . Me . Et . CH$_2$COEt

(II)

Cl$_2$Sn(C.Me.Et .CH.Me.COMe)$_2$

(III)

$$Cl_2Sn \overset{\diagup C . Me . Et . CH . Me . COMe}{\diagdown C. Me Et . CH_2COEt}$$

(IV)

Cl$_2$Sn(C.Me .Et .CH$_2$COEt)$_2$

(V)

A mixture of only the 3 dialkyltin chlorides (III–V) (NMR and TLC evidence) was obtained by the hydrolysis/acidification cycle.
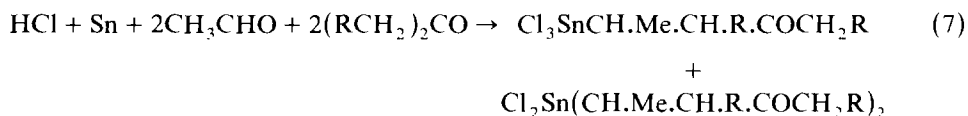
2-Pentanone and 2-hexanone also reacted with the HCl/Sn couple but only monoketoalkyltin trichlorides were formed (TLC evidence).

Aldehyde / ketone condensation

An equimolar mixture of acetone and acetaldehyde reacted with Sn and HCl in Et_2O to give a mixture of two organotin compounds (TLC). NMR spectroscopy and comparative TLC with $Cl_3SnCH.Me.CH_2COMe$ and $Cl_2Sn(CH.Me.CH_2COMe)_2$ verified that these were the products from the HCl/Sn/acetone/acetaldehyde reaction. Details of these reactions are presented in Table 3. 60 MHz proton NMR data for these compounds is recorded in Table 2 and 270 MHz data is reported in Table 4. 67.88 MHz ^{13}C NMR spectra for these two organotin compounds are presented in Table 5.

From the reaction between HCl/Sn and acetone/acetaldehyde (mol ratio 2/1/2/2) (eq. 7, R = H) a mixture of $Cl_3Sn.CH.Me.CH_2COMe$ and $Cl_2Sn(CH.Me.CH_2COMe)_2$ was obtained with a relatively high monoketoalkyltin trichloride content (Table 3) whereas the mixture of these compounds produced directly from HCl/Sn and 3-pentene-2-one (mol ratio 2/1/2) contained much less of the monoketoalkyltin compound. Under the conditions of in-situ generation the concentration of 3-pentene-2-one will remain relatively low throughout the experiment. Consistent with the mechanism previously proposed for the generation of mono-/di-mixtures of β-carboalkoxyethyltin halides (from HCl/Sn and acrylic monomers [2]) a low monomer concentration will result in the formation of a high level of mono-ketoalkyltin trichloride.

A mixture of acetaldehyde and 3-pentanone reacted with HCl and Sn to give a mixture of organotin compounds in which the mono-ketoalkyltin trichloride was the major product but the complexity of the 60 MHz NMR spectrum prohibited any further characterisation of the products.
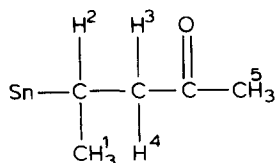
$$HCl + Sn + 2CH_3CHO + 2(RCH_2)_2CO \rightarrow Cl_3SnCH.Me.CH.R.COCH_2R \qquad (7)$$

$$+$$

$$Cl_2Sn(CH.Me.CH.R.COCH_2R)_2$$

(R = H, Me)

TABLE 3

THE SYNTHESIS OF 3-KETO-1-METHYL, BUTYLTIN CHLORIDES

Reagents	Reaction time (h)	Products	Monoketo-alkyltin (%)	Yield (%)
HCl, $SnCl_2$, $CH_3 \cdot CH=CH \cdot COMe$	10	$Cl_3SnCHMeCH_2COMe$	100	79
HCl, Sn, $CH_3 \cdot CH=CH \cdot COMe$	8	$Cl_3SnCHMeCH_2COMe$ $Cl_2Sn(CHMeCH_2COMe)_2$	18	55
HCl, Sn, $(CH_3)_2CO$, CH_3CHO	5	$Cl_3SnCHMeCH_2COMe$ $Cl_2Sn(CHMeCH_2COMe)_2$	67	34

TABLE 4

270 MHz ^{1}H NMR DATA FOR 3-KETO-1-METHYL, BUTYLTIN CHLORIDES

Compound	Chemical shifts (τ) [a]			
	H^1	H^2	H^3/H^4	H^5
Cl$_3$SnCHMeCH$_2$COMe	8.51	7.62	6.69/7.07	7.53
Cl$_2$Sn(CHMeCH$_2$COMe)$_2$	8.48	7.86	6.62/7.10	7.68

Compound	Coupling constants (Hz)				
	J(H^1–H^2)	J(H^2–H$^{3/4}$)	J(H^3–H^4)	J(^{117}Sn–H^1)	J(^{119}Sn–H^1)
Cl$_3$SnCHMeCH$_2$COMe	8	6/8	20	200	212
Cl$_2$Sn(CHMeCH$_2$COMe)$_2$	8	6/9	20	138	152

[a] Spectra recorded in CDCl$_3$ solution-internal TMS, $\tau = 10.0$.

Ketol dehydration

The acid-catalysed dehydration of ketols (β-hydroxy ketones) to give α,β-unsaturated ketones is well known [15–18] and another potential source of α,β-unsaturated ketones for ketoalkyltin synthesis. 4-Hydroxy-4-methyl-2-pentanone (diacetone alcohol) reacted with the HCl/SnCl$_2$ couple in Et$_2$O at 35°C to give Cl$_3$SnCMe$_2$CH$_2$COMe and under the same conditions the HCl/Sn couple gave a mixture of Cl$_3$SnCMe$_2$CH$_2$COMe and Cl$_2$Sn(CMe$_2$CH$_2$COMe)$_2$ (Table 6). 4-Hydroxy-2-butanone gave a mixture of Cl$_3$SnCH$_2$CH$_2$COMe and Cl$_2$Sn-(CH$_2$CH$_2$COMe)$_2$ with the HCl/Sn couple and 4-hydroxy-3-methyl-2-butanone gave a mixture of Cl$_3$SnCH$_2$CH.Me.COMe and Cl$_2$Sn(CH$_2$CH.Me.COMe)$_2$. A pure sample of Cl$_2$Sn(CH$_2$CH.Me.COMe) for spectroscopic purposes was obtained by application of the NaOH/HCl cycle to the crude reaction mixture. An attempt to

TABLE 5

67.88 MHz ^{13}C NMR DATA FOR 3-KETO-1-METHYL, BUTYLTIN CHLORIDES

| Compound	Chemical shifts (δ) [a]				
	C^1	C^2	C^3	C^4	C^5
Cl$_3$SnCHMeCH$_2$COMe	16.5(q) [b]	32.0(d)	46.7(t)	215.1(s)	28.9(q)
Cl$_2$Sn(CHMeCH$_2$COMe)$_2$	16.5(d.q)	30.4(d)	53.1(d.t)	217.3(s)	29.3(d.q)

[a] Spectra recorded in CDCl$_3$ solution-chemical shifts relative to internal TMS. $\delta = 0$. [b] Multiplet obtained with residual C–H coupling.

TABLE 6

THE SYNTHESIS OF KETOALKYLTIN CHLORIDES FROM β-HYDROXY KETONES

Reagents	Reaction time [a] (h)	Products	Monoketo-alkyltin (%)	Yield (%)
$HCl/SnCl_2/CH_3COCH_2CMe_2OH$	3	$Cl_3SnCMe_2CH_2COMe$	100	76
$HCl/Sn/CH_3COCH_2CMe_2OH$	9	$Cl_3SnCMe_2CH_2COMe$ + $Cl_2Sn(CMe_2CH_2COMe)_2$	35	44
$HCl/Sn/CH_3COCH_2CH_2OH$	7	$Cl_3SnCH_2CH_2COMe$ + $Cl_2Sn(CH_2CH_2COMe)_2$	25	79
$HCl/Sn/CH_3COCH \cdot Me \cdot CH_2OH$	7	$Cl_3SnCH_2CH \; Me \cdot COMe$ + $Cl_2Sn(CH_2CH \cdot Me \cdot COMe)_2$	39	60

[a] Solvent Et_2O; temperature 35 °C.

react the α-OH ketone, 3-hydroxy-3-methyl-2-butanone, with the HCl/Sn couple did not produce any organotin products.

$$HCl + Sn + 2MeCO.CHR.CR'_2OH \rightarrow Cl_3SnCR'_2CH.R.COMe \qquad (8)$$
$$+$$
$$Cl_2Sn(CR'_2CH.R.COMe)_2$$
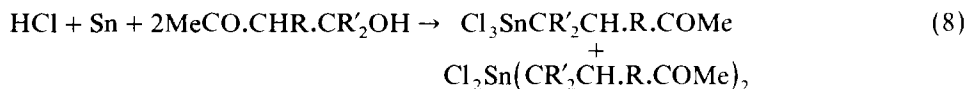
(R = H; R' = H or Me)
(R = Me; R' = H)

Experimental

Spectroscopy. IR spectra were recorded on a Perkin–Elmer 577 grating spectrophotometer. 60 MHz NMR spectra were recorded on a Perkin–Elmer R12B instrument. 270 MHz proton NMR and 67.88 MHz ^{13}C NMR were recorded on a Bruker WH270 instrument. All NMR spectra were recorded as $CDCl_3$ solutions.

Chromatography. Thin layer chromatographic separation of the organotin chlorides was effected on silica plates. The eluting solvent was chloroform (100)/formic acid (10)/acetyl acetone (4) (by volume) and detection was by catechol violet.

Reagents. Ketones, α,β-unsaturated ketones and β-hydroxy ketones were obtained from commercial sources and utilised without purification.

Syntheses

(i) The reaction between HCl, $SnCl_2$ and acetone. Hydrogen chloride (0.52 mol) was passed into a stirred suspension of $SnCl_2$ (0.51 mol) in acetone (0.99 mol) and diethyl ether (100 ml) over a period of 2 h. Over this period the temperature rose from ambient to 35 °C. After this time unreacted $SnCl_2$ was removed by filtration, the filtrate was concentrated, and the residue was extracted with chloroform. The extract gave 42.0 g (56%) of $Cl_3SnCMe_2CH_2COMe$. Identification was by IR and NMR spectroscopies by comparison with an authentic sample prepared from HCl, $SnCl_2$ and mesityl oxide.

(ii) The reaction between HCl, Sn and acetone. Hydrogen chloride (1.08 mol) was passed into a stirred suspension of powdered Sn (0.49 mol) in acetone (5.17 mol)

over a period of 4 h. An exothermic reaction occurred, after which the whole reaction mixture was concentrated by removal of unreacted acetone. The residue was extracted with chloroform and this extract concentrated to leave 255.3 g of an off-white solid which was shown to be a mixture of $Cl_3SnCMe_2CH_2COMe$ (29%) and $Cl_2Sn(CMe_2CH_2COMe)_2$ (71%) by NMR spectroscopy (relative intensities of the COMe signals) and the overall yield was 65%. TLC (thin layer chromatography) analysis of the product mixture on silica gave an efficient separation of the two organotin compounds with the bis(ketoalkyl)tin dichloride having the higher R_f value and showing up as a light blue spot and the monoketoalkyltin trichloride showing up as a deep blue spot.

Other reactions involving symmetrical or unsymmetrical ketones listed in Table 1 were performed in a similar fashion. In some cases the product mixture was obtained as a viscous oil.

(iii) Isolation of $Cl_2Sn(CMe_2CH_2COMe)_2$ from a mixture of $Cl_2Sn(CMe_2-CH_2COMe)_2$ and $Cl_3SnCMe_2CH_2COMe$. 25 g of the mixture of $Cl_2Sn(CMe_2-CH_2COMe)_2$ and $Cl_3SnCMe_2CH_2COMe$ obtained in (ii) was added in portions at 20 °C to a stirred solution of 4% aqueous sodium hydroxide solution (155 g). After 15 min stirring the reaction mixture was filtered and the filtrate acidified with hydrochloric acid (36%) until no more precipitation occurred. The precipitate was isolated by extraction with chloroform. Evaporation of this solution gave 18.45 g of $Cl_2Sn(CMe_2CH_2COMe)_2$ (99%).

(iv) The reaction between HCl, $SnCl_2$ and 3-pentene-2-one. To a stirred suspension of $SnCl_2$ (0.22 mol) in 3-pentene-2-one (0.21 mol) and Et_2O (150 ml) was added HCl (0.27 mol) over a period of 10 h. During this period an exothermic reaction occurred which was controlled by the use of a cold water bath. The reaction mixture was then concentrated on a rotary evaporator and the residue extracted with cold chloroform (2 × 100 ml). Evaporation of this solution gave 49 g of a brown oil which crystallised on standing and was shown to be $Cl_3SnCHMeCH_2COMe$ by NMR spectroscopy and elemental analysis (yield 79%).

(v) The reaction between HCl, Sn and 3-pentene-2-one. HCl (0.27 mol) was passed into a stirred suspension of tin powder (0.097 mol) in 3-pentene-2-one (0.22 mol) and Et_2O (150 ml) over an 8 h period. Solvent was removed from the reaction mixture on a rotary evaporator and the residue extracted with 2 × 100 ml portions of cold chloroform. Evaporation of this solution left a dark brown solid (19.3 g) which was shown by NMR spectroscopy to be a mixture of $Cl_2Sn(CH.Me.CH_2COMe)_2$ (82%) and $Cl_3SnCH.Me.CH_2COMe$ (18%). The overall yield of organotin products was, therefore, 55%.

(vi) The reaction between HCl, Sn, acetaldehyde and acetone. Over a 5 h period hydrogen chloride (1.09 mol) was passed into a stirred suspension of powdered tin (0.51 mol) in acetone (1.03 mol), acetaldehyde (1.02 mol) and Et_2O (100 ml). Unreacted tin was removed by filtration and the filtrate concentrated to leave a dark brown oil. This was extracted with cold chloroform and the extract concentrated to leave 56.6 g of a mixture of $Cl_2Sn(CHMeCH_2COMe)_2$ (33%) and Cl_3-$SnCH.Me.CH_2COMe$ (67%). The overall yield of organotins was 34%.

(vii) The reaction between HCl, Sn and 4-hydroxy-4-methyl-2-pentanone (diacetone alcohol). To a stirred suspension of powdered tin (0.49 mol) in a solution of diacetone alcohol (1.01 mol) in Et_2O (100 ml) was added HCl (1.04 mol) over a period of 9 h. At this·stage the reaction mixture was filtered to give a pale grey solid

and a dark brown solution. Extraction of the solid with hot chloroform (2×50 ml) gave 32 g of an off-white solid which was shown to be $Cl_2Sn(CMe_2CH_2COMe)_2$ (17%). Evaporation of the above filtrate, and extraction with chloroform yielded 48.6 g of a mixture of $Cl_2Sn(CMe_2CH_2COMe)_2$ (65%) and $Cl_3SnCMe_2CH_2COMe$ (35%). The overall yield of organotin compounds was 44%.

References

1 R.E. Hutton, J.W. Burley and V. Oakes, J. Organomet. Chem., 156 (1978) 369.
2 J.W. Burley, P. Hope, R.E. Hutton and C.J. Groenenboom, J. Organomet. Chem., 170 (1979) 21.
3 V. Grignard and J. Cologne, Compt. Rend., 190 (1930) 1349.
4 A.E. Abbott, G.A.R. Kon and R.D Satchell, Chem. Soc., (1928) 2514.
5 J. Cologne, Bull. Soc. Chim. France, 49,4 (1931) 426.
6 H. Hoeussler and J. Dijkema, Ber., 77 (1944) 601.
7 A.T. Nielson and W.J. Houlihan in R. Adams, A.H Blatt, V. Boekelheide, T.L. Cairns, A C. Cope, D.J. Cram and H.O. House (Eds.), Organic Reactions, Vol. 16, John Wiley and Sons, Inc , New York, (1968), p. 1.
8 E.J. Bulten and J.W.G. van den Hurk, J. Organomet. Chem., 162 (1978) 161.
9 A.J. Bloodworth and A.G. Davies, in A.K. Sawyer (Ed), Organotin Compounds, Vol. 1, Marcel Dekker Inc., New York, (1971), p. 209.
10 R.C. Poller, J. Chem. Soc., (1963) 706.
11 G.A. Baum and W.J. Considine, J. Polymer Sci. B, Polymer Letters, 1 (1963) 517.
12 C.K. Chu and J.D. Murray, J. Chem. Soc. (A), (1971) 360.
13 W.P. Neumann, The Organic Chemistry of Tin, Interscience, J. Wiley and Sons, (1970), p. 163
14 I. Omae, Rev. Silicon, Germanium, Tin and Lead Compounds, 1 (1972) 59.
15 D.S. Noyce and L.R. Snyder, J. Amer. Chem. Soc., 81 (1959) 620.
16 D.S. Noyce and W.L. Reed, J. Amer. Chem. Soc., 80 (1958) 5539.
17 M. Stiles and A. Longroy, Tetrahedron Lett., (1961) 337
18 S. Cabani and N. Ceccanti, J. Chem. Soc. Phys. Org., (1966) 77.