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Some further studies on acyltrimethylstannanes

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Abstract

The scope and limitations of the palladium-catalysed preparation of acyltins from ditins and acyl chlorides are discussed in detail. Preliminary studies on the chemistry of acyltrimethylstannanes are described.

Introduction

Although acylsilanes have been intensively studied from both the spectroscopic [1] and the synthetic [1,2] points of view, remarkably little is known about the corresponding acyltins [3–17]. As acylstannanes appear to be more promising as acyl anion synthons than are the acylsilanes, we have begun to study their chemistry in more detail.

A close look at the literature [3–17] revealed that the few methods available for the preparation of acylstannanes are limited to small scale syntheses (0.5–3 mmol) or to a small range of acyl groups (usually alkyl and alkenyl groups).

The reaction between acyl chlorides and triorganostannyllithiums generally proceeds in only low yields because of the much more rapid reaction of the latter with the product [3], though it can be used in selected cases for the preparation of triphenylacyltins (eq. 1):

$$RCOCl + Ph_3SnLi \rightarrow RCOSnPh_3 + LiCl \quad (1)$$

R = Me (88%), ^{t}Bu (63%), Ph (33%)

The yield was found to be improved by replacing the acyl chlorides by thioesters or ethylcarboxylates in the presence of an excess of $BF_3 \cdot Et_2O$ [4]. In this case the maximum scale reported was 0.68 mmol. The preparation of acyltributylstannanes introduced by Quintard [5] (eq. 2) is still the best route to alkanoyltributylstannanes on a preparative scale (up to 100 mmol).

$$Bu_3SnMgCl + 2\ RCHO \rightarrow R\text{–}CO\text{–}SnBu_3 + RCH_2OMgCl \quad (2)$$

R = Me, Et, ^{n}Pr, ^{i}Pr, ^{t}Bu, Ph: yield 60–66% (isolated or estimated)

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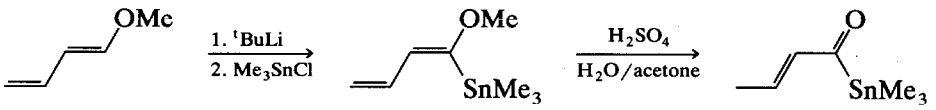
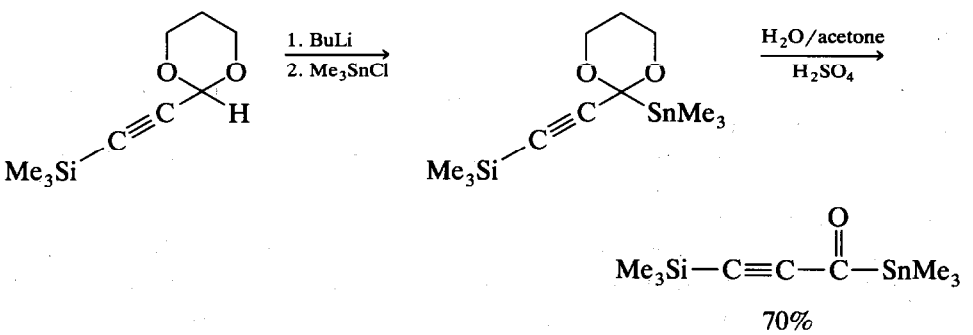
This method was improved by Marshall *et al.* [6], who used tributylstannyllithium and employed ADD (azodicarbonyldipiperidide) for the oxidation in the second step of the reaction. A variety of alkanoyl and alkenoyl stannanes have been synthesized either by Quintard's [7,8] or by Marshall's method [9,10], both of which appear to be inappropriate for the synthesis of aroylstannanes (only one example has been reported: $PhCOSnBu_3$, max. 64% crude product [5,8]).

The acidolysis of stannylated alkyl vinyl ethers developed by Soderquist *et al.* [11] (Scheme 1) was reported with unspecified yields. This procedure was later extended to include stannylated allenic alkyl ethers [12,13] on a 3 mmol scale, and is limited to the synthesis of alkenoylstannanes.



Scheme 1.

By analogy with the classic 1,3-dithiane route to acylsilanes [14,15], Klumpp and colleagues [16,17] used the hydrolysis of a 1,3-dioxane derivative to prepare (trimethylsilylethynyl)trimethylstannylketone in 250 mg yield (Scheme 2).



Scheme 2.

Results and discussion

1. Palladium-catalysed synthesis of acyltrimethylstannanes

In an earlier paper [18] we reported the palladium-catalysed cross-coupling of acyl chlorides with hexamethylditin as an alternative synthesis for acyltrimethyltins (eqs. 3 and 4).

$$RCOCl + Me_6Sn_2 \xrightarrow{[Pd]} RCOSnMe_3 + Me_3SnCl \quad (3)$$

$$Me_3SnCl + KF_{aq.} \rightarrow Me_3SnF \quad (4)$$

Three methods have been found to be suitable for carrying out the reaction: method A uses tetrakis(triphenylphosphine)palladium(0) (*ca.* 5 mol%) and method B benzylchlorobis(triphenylphosphine)palladium(II) (*ca.* 5 mol%), in both cases in THF as solvent. Method C involves the use of dichlorobis(triphenylphosphine)palladium(II) (*ca.* 5 mol%) in toluene at 100°C.

Table 1

Acyltins prepared from acyl chlorides and hexamethylditin

Entry	R	Reaction conditions [a]		Ditin consumed (%)	Yield [b] (%)	B.p. (°C/mmHg)
		Cat.	Time			
1	Me	A,B	12 h	100	70	55/0.005
2	Et	B	18 h	100	70	76/0.001
3	$PhCH_2$	B	14 h	70	[c]	
4	(*E*)-PhCH=CH	A,B	12 h	100	80 [d]	
5	C_6H_5	A,B	12 h	100	80	80/0.5
6	4-MeC_6H_4	B	14 h	100	64	83/0.001
7	4-$^tBuC_6H_4$	B	45 h	80	50	107/0.05
8	2-furyl	B	15 h	100	80 [d]	
9	2-$PhOC_6H_4$	C	22 h	25	–	
10	^tBu	A,B	21 d	0	0	
11	^tBu	D	23 h	100	[e]	
12	^tBu	C	16 h	80	80 [d]	
13	c-Pr	B	21 h	0	0	
14	c-Pr	C	16 h	50	43	43/0.003
15	2-MeC_6H_4	C	16 h	90	75 [d]	
16	4-ClC_6H_4	C	15 h	100	75 [d]	
17	4-$MeOC_6H_4$	B	6 d	5	–	
18	4-$MeOC_6H_4$	E	3 d	100	[f]	
19	4-$MeOC_6H_4$	C	30 h	80	54	95/0.02
20	C_6F_5	C	23 h	100	[g]	
21	1-naphthyl	C	22 h	100	[h]	
22	4-$NO_2C_6H_4$	C	22 h	100	[g]	
23	adamantyl	C	20 h	100	80 [d]	
24	$Cl(CH_2)_4$	B	24 h	0	–	
25	$Cl(CH_2)_4$	C	24 h	30	–	
26	Ph–C≡C	B	16 h	100	[i]	
27	Cl_2CH	A	1 h	100	[j]	

[a] A: THF, reflux, $Pd(PPh_3)_4$; B: THF, reflux, $PhCH_2PdCl(PPh_3)_2$; C: toluene, 100°C, $PdCl_2(PPh_3)_2$; D: HMPT, 65°C, $PhCH_2PdCl(PPh_3)_2$; E: N-Methylpyrrolidone, 70°C, $Pd(dba)_2$ (*ca.* 5 mol%), $P(OEt)_3$ (*ca.* 10 mol%). [b] With respect to ditin. [c] 60% decarbonylated (according to ^1H NMR). [d] Product after workup, *ca.* 90% pure according to ^1H NMR. [e] 70% decomposition of the product (w.r.t. Me_3SnCl). [f] Me_4Sn and Me_3SnCl formed. [g] 100% decarbonylation. [h] 43% decarbonylation. [i] 100% decarbonylation, 1,4-diphenylbutadiyne is the main product. [j] 100% 1,3-elimination of Me_3SnCl (see ref. 18).

This method had been used earlier for the *in situ* preparation of acyltriethyl- [19] and acyltributyltins [20] in a palladium-catalysed α-diketone synthesis. In our hands the cross-coupling reaction between acyl chlorides and hexaethyl- or hexabutylditin could be forced to completion either by use of an excess of acyl chloride or by use of other catalysts and high pressure techniques. Table 1 gives details of the trimethylacyltins so far prepared by this method.

We were able to extend the range of substituents R considerably by using a more active catalyst and more vigorous reaction conditions (method C: $PdCl_2(PPh_3)_2$ in toluene at 100°C) for acyl chlorides with sterically demanding groups R. With this improvement pivaloyl chloride, which we had hitherto suspected to be unreactive for steric reasons [18], formed the corresponding acyltrimethylstannane with 80% conversion of the ditin. We obtained similar

results with other acyl chlorides with sterically demanding substituents (Table 1, entries 14,15,21,23).

Method C also proved to be the correct choice for electronically hindered acyl chlorides such as 4-$MeOC_6H_4COCl$, which did not react under the conditions of method B. When method C was used the palladium-catalysed cross-coupling proceeded with 80% conversion (Table 1, entries 17,19).

As there is still no general rule for choosing the best reaction conditions, we recommend starting with mild conditions (method A or B) and using catalyst system C if no reaction occurs. Cross-coupling experiments with reactive acyl chlorides such as PhCOCl or MeCOCl under the conditions of method C lead to polymerisation.

In the course of our search for a suitable catalyst system we employed pivaloyl chloride or 4-methoxybenzoyl chloride with hexamethylditin as test cases. While with pivaloyl chloride the use of the donor solvent HMPA led to quantitative conversion of the ditin, 70% of the product decomposed during the reaction (entry 11, method D). Other reaction conditions such as $Pd(dba)_2$ (dba = dibenzylidene acetone) in N-methylpyrrolidone with two equivalents $P(OEt)_3$ (entry 18, method E), $PhCH_2PdCl(PPh_3)_2$ in MeCN with CuI or $(MeCN)_2PdCl_2$ in THF (THF = tetrahydrofuran) resulted either in no reaction or in formation of tetramethylstannane.

Some acyl chlorides are decarbonylated to various degrees during the palladium-catalysed cross-coupling reaction (Table 1, entries 3,20,22). As high pressure (1.0–1.3 GPa) is known to have a considerable effect on palladium-catalysed reactions which appear to involve an increase in the volume of reaction [21] we applied the high-pressure technique to the synthesis of four different acyltins. As can be seen from Table 2, the application of high pressure did indeed suppress decarbonylation in two cases (R = benzyl, naphthyl), but unfortunately failed when highly electron demanding substituents R (C_6F_5, *p*-nitrophenyl) were used.

1.1 Limitations of the method. The palladium-catalysed synthesis of acyltins is limited to methyl-substituted tin compounds and monoacyl chlorides (diacyl chlo-

Table 2

Preparation of acyltrimethyltins under high pressure

R	Reaction conditions		Ditin		
	Cat.	Time	Pressure (MPa)	Consumed (%)	Decarbonylation (%)
$PhCH_2$	A [a]	1 d	950	45	0
$PhCH_2$	A	14 h	0.1	100	60
1-naphthyl	C [b]	3 d	1200	100	0
1-naphthyl	C	22 h	0.1	100	43
C_6F_5	C [c]	3 d	1200	destroyed	
C_6F_5	C [d]	3 d	1200	100	100
C_6F_5	C	23 h	0.1	100	100
4-$NO_2C_6H_4$	C [c]	3 d	1200	100	100
4-$NO_2C_6H_4$	C	22 h	0.1	100	100

Catalyst and solvent A,C as given in Table 1. [a] 50°C. [b] 70°C. [c] 75°C in benzene. [d] 80°C.

Table 3

Carbon-13 and tin-119 NMR data for acyltrimethyltins

Entry	R	$\delta(^{119}Sn)$	$\delta(CH_3Sn)$	$\delta(C^1)$	$\delta(C^2)$	$\delta(C^3)$
1	Me	−91.0	−9.6	250.5	41.1	
			(309.2)	(413.4)	(205.2)	
2	Et	−94.0	−9.5	251.7	47.4	8.0
			(308.0)	(407.2)	(197.0)	
3	$PhCH_2$	−83.4	−9.0	248.3	60.4	142.6
			(316.3)	(402.3)	(190.0)	(38.8)
4	(*E*)-PhCH=CH	−83.1	−8.3	243.6	133.5	150.2
			(308.0)	(419.0)	(202.6)	(61.0)
5	C_6H_5	−81.3	−8.3	241.8	141.5	132.6
			(312.8)	(427.2)	(192.0)	
6	4-MeC_6H_4	−81.3	−8.3	240.9	139.6	129.2
			(316.3)	(441.1)	(119.8)	
7	4-$^tBuC_6H_4$	−83.2	−8.3	240.8	139.5	129.0
			(316.3)	(446.7)	(202.5)	(108.3)
8	2-furyl	−70.0	−9.0	227.8	157.6	114.4
			(317.0)	(427.2)	(216.4)	
12	^{t}Bu	−91.3	−8.0	251.3	50.2	23.8
			(305.2)	(391.2)	(177.6)	(42.4)
14	^{c}Pr	−89.9	−9.2	248.6	30.9	29.1
			(313.5)	(435.6)	(243.4)	
15	2-MeC_6H_4	−83.3	−8.2	245.3	140.8	134.6
			(313.5)	(452.2)	(202.5)	(19.4)
16	4-ClC_6H_4	−78.9	−8.1	240.1	139.9	128.9
			(321.8)	(434.2)	(199.0)	
19	4-$MeOC_6H_4$	−82.7	−8.3	238.4	135.8	113.7
			(314.9)	(450.8)	(205.3)	(41.6)
21	1-naphthyl	−79.9	−7.7	246.0	138.2	127.8
			(313.5)	(452.2)	(199.8)	
23	adamantyl	−92.6	−7.9	252.0	52.7	37.9
			(301.2)	(394.0)	(174.8)	
27	Cl_2CH	−56.8	−7.7	228.8	76.2	
			(349.6)			

Chemical shifts in ppm w.r.t. Me_4Sn and TMS, coupling constants (in parentheses) in Hz. Numbering of carbon atoms as follows: $Sn-C^1O-C^2-C^3$.

rides show a lack of reaction or polymerisation; carbamoyl chlorides, carboxylic acid anhydrides and cyanuric chloride do not react). Acyl groups with chloride (and probably other halides) in 1- or 2-position relative to the carbonyl group are also not suitable because the intermediate acyltins undergo elimination of trimethyltin halide; in the case of $Cl_2CHCOCl$ (Table 1, entry 27) the acyltin was detected by NMR spectroscopy [18]. Finally, acyl chlorides with highly electron demanding substituents tend to decarbonylate during the cross-coupling reaction. At present we can provide no clear rule as to when a high degree of decarbonylation is to be expected.

1.2 NMR spectroscopy. All acyltrimethylstannanes obtained during our work showed the unusual spectroscopic features observed in previously reported acyltins and in the acylsilane series [1]. The carbon-13 and tin-119 NMR parameters are given in Table 3.

Table 4

Comparison between the carbonyl carbon NMR shifts of some ketones R–CO–CMe_3 and the corresponding acylsilanes [24] and -stannanes R–CO–MMe_3, M = Si, Sn

R	δ(C)	δ(Si)	δ(Sn)
^{t}Bu	215.1	249.0	251.3
Me	210.4	247.6	250.5
Ph	209.1	233.6	241.6
2-furyl	–	220.7	227.8

1.2.1 Carbon-13 NMR. Relative to those of the corresponding ketones (Table 4) the carbon-13 signals of the carbonyl groups in acyltins are markedly shifted downfield, their chemical shifts differing by 30 to 40 ppm from those of the corresponding ketones, but by only 2–8 ppm from those of the corresponding acylsilanes. In a carbon-13 study on acylsilanes [22] the downfield shift was interpreted as a consequence of the inverse effect of σ- and π-charges, *i.e.* a downfield shift caused by an *increase* in charge which is dominated by the σ-population.

The values of one-bond couplings, $^1J(^{13}C, ^{119}Sn)$, of the carbonyl carbons (394–450 Hz) are in the range typical for corresponding vinyltin compounds. $Ph(Me_3Sn)C{=}CH_2$ (Table 5) may serve as an illustrative example.

The $^2J(^{13}C, ^{119}Sn)$ values (175–245 Hz) are significantly larger than those of corresponding vinyltin compounds (Table 5). The increase by a factor of about three cannot be satisfactorily explained on the basis of the four main factors usually considered to determine the $^2J(^{13}C, ^{119}Sn)$ value of a geminal scalar coupling (Sn–Z–C) [23]: a) the nature of the atom Z; b) the nature of the substituents on Sn, Z, C; c) the bond angle Sn–Z–C; d) the stereochemistry of the molecule with regard to the Sn–Z–C group. There is no clear correlation between the geminal couplings and the substituent constants [24,25] for *para*-substituted aroyltrimethylstannanes or between the geminal couplings and steric hindrance at the carbonyl group [26].

1.2.2 Tin-119 NMR. The tin-119 resonances (relative to Me_4Sn) are shifted upfield from those for vinyltin compounds (*e.g.* $Me_3SnC(Ph){=}CH_2$, Table 5). There is no evidence for an increase in the coordination number of the tin atom. The tin-119 signals lie within discrete limits: $\delta(^{119}Sn) = -81.3 \pm 2.1$ ppm for acyltrimethyltins with a conjugated C=O group (exception: Table 3, entry 8); $\delta(^{119}Sn) = -92.0 \pm 2.1$ ppm for acyltrimethyltins with a non-conjugated C=O group (exception: Table 3, entry 27).

Table 5

Comparison between selected NMR data of benzoyltrimethylstannane $Ph(Me_3Sn)C{=}O$ and the corresponding vinyltin $Ph(Me_3Sn)C^1H{=}CH_2$ (δ in ppm w.r.t. Me_4Sn and TMS, J in Hz). C^2 is the α-carbon of the phenyl group

	$\delta(^{119}Sn)$	$\delta(C^1)$	$\delta(C^2)$	$^1J(Sn,C)$	$^2J(Sn,C)$
O	−83.1	241.8	141.5	427.2	192.0
CH_2	−28.4	154.5	145.3	431.0	39.4

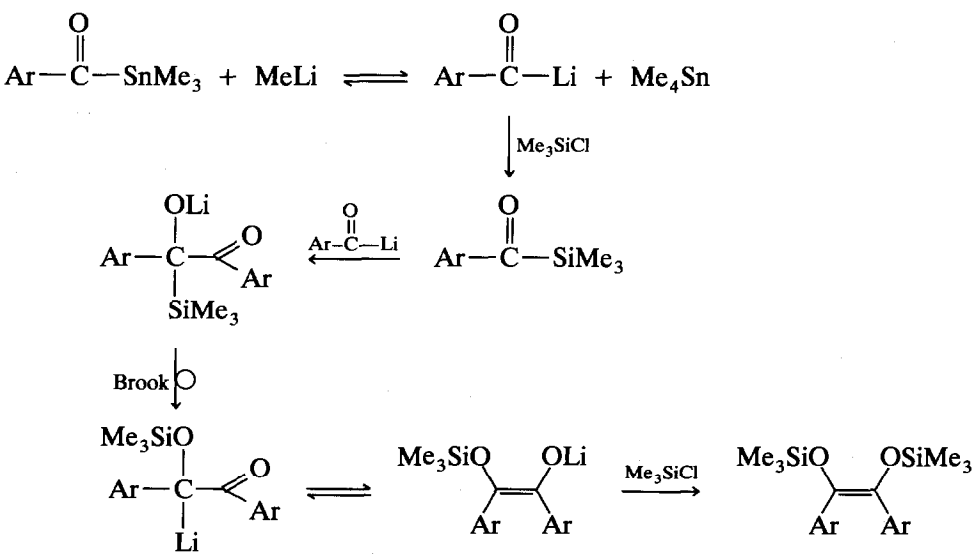
2. Reactions of acyltins

In recent years only three reactions of acyltins have been studied in detail: the palladium-catalysed cross-coupling mentioned above proceeds efficiently with acyl chlorides [18,20]. Verlhac *et al.* however turned their attention to masked acyltributylstannanes because of disappointing results obtained with other coupling partners [27,28].

The enantioselective reduction of acyltributylstannanes with derivatives of lithium aluminium hydride [6,7,10,29] has been efficiently employed to prepare chiral α-alkoxy stannanes in high enantiomeric excess. The reaction of acyltins with molecular oxygen is a ready, but normally unwanted, reaction known to all who work with acyltins; a possible mechanism has been proposed [8].

Because of our interest in acyl anion synthons we focused our attention on the lithiodestannylation of acyltrimethyltins. As aroyltrimethylstannanes proved to be the least sensitive acyltins (they can be stored for weeks under argon at ambient temperature and in daylight) we used *p*-toluoyltrimethylstannane for these experiments. Preliminary reactions with MeLi in THF at $-78°C$ gave mixtures of the following compounds in varying concentrations: p-tolyl methyl ketone, 4-methylbenzaldehyde and 4,4′-dimethylbenzil. In each case Me_4Sn was detected by means of ^1H NMR and GLC. By applying Seyferth's procedure [30,31], which involves *in situ* generation of the acyl anion in the presence of the trapping reagent (here Me_3SiCl) at -110 to $-135°C$, the selectivity of the reaction could be enhanced. The main product (63% according to GLC) was identified as 1,2-bis(trimethylsilyloxy)-1,2-ditolylethene, relevant spectroscopic data for which is given in the experimental section. The by-product has not yet been identified.

Assuming a slow reaction of Me_3SiCl with the acyl anion, the formation of 1,2-bis(trimethylsilyloxy)-1,2-ditolylethene can be accounted for in terms of a reaction sequence involving a Brook rearrangement [32], *i.e.* a 1,2-shift of the Me_3Si group from carbon to an alcoholate oxygen, and a subsequent keto-enol tautomerism, as shown in Scheme 3.



Scheme 3.

Table 6

Spectroscopic data of Lewis acid adducts of acyltrimethylstannanes and the corresponding free acyltrimethylstannanes

1: 4-MeC_6H_4–CO–$SnMe_3 \cdot BF_3$
2: 4-MeC_6H_4–CO–$SnMe_3$
3: 4-$MeOC_6H_4$–CO–$SnMe_3 \cdot BF_2$
4: 4-$MeOC_6H_4$–CO–$SnMe_3$

^{119}Sn-NMR: $CDCl_3$, r.t.
1: $\delta = -12.2$ ppm, broad
2: $= -81.3$ ppm
3: $= -16.3$ ppm, broad
4: $= -82.7$ ppm

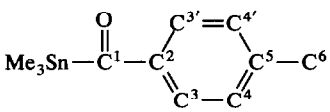
^{13}C-NMR: $CDCl_3$, r.t.

Cpd.	$\delta(CH_3Sn)$	$\delta(C^1)$	$\delta(C^2)$	$\delta(C^{3,3'})$	$\delta(C^{4,4'})$	$\delta(C^5)$	$\delta(C^6)$
1	0.2	265.4	139.2	131.4	130.1	151.2	21.4
	(400.8)	(180.3)	(66.3)				
2	−8.3	240.9	139.6	129.2	127.6	143.4	21.2
	(316.3)	(441.1)	(199.8)				
3	0.03	256.9	135.4	115.0	135.1	168.5	56.1
	(383.6)	(194.2)					
4	−8.3	238.4	135.8	113.7	129.8	163.1	55.0
	(314.9)	(450.8)	(205.3)	(41.6)			

IR: (in CH_2Cl_2, 50 ml)
3: ν(C=O) 1552 cm^{-1}
4: ν(C=O) = 1618 cm^{-1}

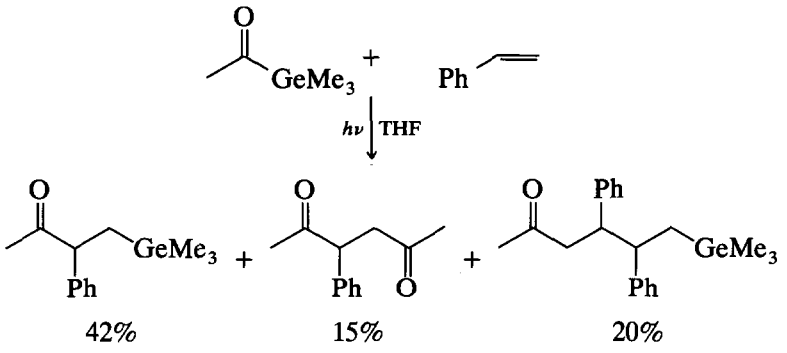
UV/VIS: λ_{max} (nm)
3: 423 nm
4: 517 nm

Numbering of carbon atoms as follows:



The synthetic value of the transmetallation of acyltins appears to have the same limitations as the *in situ* generation of acyl anions by carbonylation of alkyl or aryllithiums, *i.e.* the applicability is dictated by a combination of relative reaction rates. We used ^{t}BuLi to favour the sterically less demanding nucleophilic addition to the carbonyl carbon, but even in this case the sterically hindered intermediate of the transmetallation [33] was apparently formed, as shown by the presence of ^{t}BuSnMe_3.

In order to obtain a less reactive and thus more generally useful acyl anion equivalent we tried to activate the CO–Sn bond with a Lewis acid. No reaction occurred at −78°C, but on warming to near room temperature the bright yellow reaction mixture (ArCOSnMe_3, 2 $BF_3 \cdot OEt_2$ and Me_3SiCl in CH_2Cl_2) turned red. After the removal of all volatile compounds an amorphous brown-red powder, which could not be recrystallized, was obtained. The acyltrimethyltin was set free on addition of water, acetone or donor solvents such as DMF and DMSO to the powder. This powder, which is also obtained in the absence of Me_3SiCl, is thus apparently a Lewis acid adduct of the acyltrimethylstannane: in two cases it was possible to obtain a full set of spectroscopic data which corroborates this view (Table 6). Further investigations are under way to obtain more information about



Scheme 4.

the nature of the bonding and the position of the Lewis acid, as well as on how to use this activated functional group for synthetic purposes.

Our interest in the synthetic potential of acyltrimethylstannanes led us to check whether their photolytic reactions are comparable to those of acylgermanes, which have recently been studied in more detail [34–36]. The only preparatively useful application which has so far been described is the (non-selective) addition to olefins, *e.g.* styrene (Scheme 4).

An attempt to add $MeCOSnMe_3$ to styrene under photolytic conditions however failed; only decomposition products [Me_4Sn, Me_6Sn_2 and a little α-diketone] were detected. In the case of methyl propargyl ether there was again no reaction apart from decomposition. With dimethyl acetylenedicarboxylate a complex mixture of vinyltin products was obtained.

Since our attempts to carry out light-induced addition reaction of acyltins to alkenes and alkynes were disappointing we turned to radical reactions of acyltins with halides. Just like acylsilanes under certain conditions [37], benzoyltrimethylstannane reacts with CCl_4 in a free radical chain reaction according to eq. 5–8. Me_3SnCl and benzoyl chloride were identified by means of NMR spectroscopy.

$$PhCO\text{–}SnMe_3 \rightarrow PhCO\cdot + Me_3Sn\cdot \quad (5)$$

$$Me_3Sn\cdot + CCl_4 \rightarrow Me_3SnCl + \cdot CCl_3 \quad (6)$$

$$PhCO\cdot + CCl_4 \rightarrow PhCOCl + \cdot CCl_3 \quad (7)$$

$$2\cdot CCl_3 \rightarrow C_2Cl_6 \quad (8)$$

The reaction of toluoyltrimethylstannane with t-butyl iodide yielded t-butyl tolyl ketone, as shown by carbon-13 NMR [38] (eq. 9):

$$4\text{-}MeC_6H_4\text{–}CO\text{–}SnMe_3 + {}^tBuI \rightarrow 4\text{-}MeC_6H_4\text{–}CO{}^tBu + Me_3SnI \quad (9)$$

The ketone was not purified. An analogous reaction of toluoyltrimethylstannane with diphenylchlorophosphine led to the formation of the corresponding acyl phosphide, which was identified on the basis of its very characteristic phosphorus-31 and carbon-13 NMR data [39]. No attempt was made to isolate the product as a very efficient method for the preparation of acylphosphides is available [39]. Attempts to extend the procedure to antimony(III) and -(V) compounds unfortunately failed.

Our investigations on the chemistry of acyltins are continuing.

Experimental

All manipulations were carried out under argon. NMR spectra were recorded on Bruker AM 300 and AC 200 spectrometers (solutions in $CDCl_3$, standards TMS and Me_4Sn). GLC analyses were carried out with Carlo Erba HRGC-5300 and HRGC-4160 instruments fitted with either 25 m CP-SIL-5 CB or 30 m DB1-(5)-CB quartz columns (FID detector). Mass spectra were obtained with a Finnigan MAT 8230 instrument, IR spectra with Perkin-Elmer model 577 and Shimadzu model IR 470 spectrometers and UV/VIS spectra with Philips Unicam model SP 1800 and Hitachi model U 2000 spectrometers. Raman spectra were recorded using a Coderg model PHO with a Spectra Physics Kr laser, 514.5 nm, 300 mW.

Acyltrimethyltins, modified general procedure

A stirred mixture of hexamethylditin (10 mmol), the appropriate acyl chloride (10 mmol) and THF (20 mL) is refluxed in the presence of either tetrakis(triphenylphosphine)palladium(0) (*ca.* 5 mol%) (method A) or benzylchlorobis(triphenylphosphine)palladium(II) (*ca.* 5 mol%) (method B). In the case of unreactive acyl chlorides the mixture of hexamethylditin (10 mmol), acyl chloride (10 mmol) and toluene (20 mL) is stirred at 100°C in the presence of dichlorobis(triphenylphosphine)palladium(II) (*ca.* 5 mol%) (method C). The reaction can be monitored by ^{1}H-NMR spectroscopy. In all cases the formation of product is demonstrated by the development of a deep yellow coloration. Overlong reaction times or an ineffective catalyst are indicated by an intense red-brown coloration. Reactions with acetyl chloride and other alkanoyl chlorides with a CH_2 group next to the carbonyl function must be carried out in the dark.

Work-up. After removal of the solvents Me_3SnCl can be removed *in vacuo* (less effective) or by adding a saturated solution of KF in oxygen-free water (20 mL) and CCl_4 (25 mL). After thorough stirring (30 min) the Me_3SnF is filtered off, the organic layer separated and the aqueous layer extracted with CCl_4 (2×20 mL). The combined organic phases are dried over $CaCl_2$ or $MgSO_4$ and the solvent removed *in vacuo*. If all manipulations are to be carried out in a closed apparatus CCl_4 is the appropriate solvent. In other cases Et_2O is the solvent of choice [18]. Removal of the solvents in the first step facilitates the separation of organic and aqueous layers, particularly in the case of THF. Scaling up has been done in some cases up to 50 mmol (*e.g.* for $MeOC_6H_4COCl$, 100% conversion, aqueous workup, 64% isolated yield, > 98% pure according to ^{1}H NMR). The volume of solvent should be in the range of 15–20 mL/10 mmol, otherwise yields decrease because of product decomposition during the reaction.

Preparation of acyltrimethyltins under high pressure

High pressure experiments were performed at the Laboratoire de Chimie Organique et Organométallique, Université de Bordeaux I. The reactions were carried out in a piston cylinder apparatus designed for pressures up to 1.5 GPa [21,40]. The reaction mixtures (3 mmol) were pressurized at the chosen temperature in a Teflon cell which was filled under nitrogen. The reaction mixtures were analysed using NMR spectroscopy. $C_6F_5SnMe_3$ was identified using GLC-MS coupling and tin-119 NMR: *m/e* (% rel. intensity): 317 (100) M^+-CH_3, 287 (19), 169 (50), 139 (50); $\delta(^{119}Sn) = -9.8$ ppm (m).

Lithiodestannylation of toluoyltrimethylstannane

A 0.84 M solution of MeLi in Et_2O (11 mL) is added dropwise at −110°C to a stirred mixture containing the acyltin (10 mmol), Me_3SiCl (10 mmol) and THF (10 mL). After 30 min the reaction mixture is allowed to warm to room temperature. After an aqueous workup the volatile compounds are removed *in vacuo* and shown to include Me_4Sn. The residue consists of 1,2-bis-(trimethylsilyloxy)-1,2-ditoluylethene (70% yield). ^1H NMR, $CDCl_3$, r.t.: δ 0.13 (s, 18 H, $Si(CH_3)_3$, 2.33 (s, 6 H, $-C_6H_4-CH_3$), 6.99 (d, 8 Hz, 4 H, $H^{3,5}$), 7.12 (d, 8 Hz, 4 H, $H^{2,6}$). ^{29}Si-NMR, $CDCl_3$, r.t.: δ 19.3. ^{13}C NMR, $CDCl_3$, r.t.: δ 0.66 ($Si(CH_3)_3$), 21.10 (Ar-CH_3), 128.37, 128.15 ($CH_{ar.}$), 136.43, 135.42 C_q(arom.), 136.10 C_q(olef.) Raman spectrum (in Et_2O), strongest absorptions: 1641 cm^{-1} vs, ν(C=C); 1619 cm^{-1} s, $\nu(C=C_{ar.})$; 1189 cm^{-1} m, ν(as) Si–O–R. Mass spectrum *m/e* (% relative intensity): 384 (100) M^+, 368 (10), 341 (5), 296 (17), 206 (10), 191 (6), 177 (7), 147 (80), 91 (5).

Adducts of acyltrimethylstannanes with BF_3Et_2O

A solution of $BF_3 \cdot Et_2O$ (15 mmol) in CH_2Cl_2 (15 mL) is added dropwise to a stirred mixture containing the acyltin [p-$RC_6H_4COSnMe_3$ (R = Me, MeO) or $^cPrCOSnMe_3$] (7.5 mmol) and CH_2Cl_2 (15 mL) at −78°C. After 1 h no reaction is observed. The mixture turns red on warming to room temperature. All volatile compounds are removed *in vacuo*. In the first two cases an amorphous red-brown solid remains, which resists attempts to recrystallize it. While for R = Me the compound decomposes on heating, for R = MeO it melts (in a sealed capillary) at 62–64°C. Because of the extreme air-sensitivity elemental analysis of the compounds is not possible. The corresponding acyltin is set free on adding water, acetone, DMF or DMSO to the powder. Spectroscopic data are given in Table 6. In the case of cyclo-$PrCOSnMe_3$ a black intractable and insoluble tar is obtained.

Photolytic reactions of acyltrimethylstannanes

a) With styrene. The acyltin (10 mmol) and destabilised styrene (10 mmol) are mixed and irradiated for 2 h in a quartz Schlenk tube. A white precipitate (polystyrene) is present. An NMR analysis shows complete decomposition of the acyltin with formation of Me_4Sn and Me_6Sn_2 as the sole tin-containing products; the corresponding diketone is also present in small amounts.

b) With methyl propargyl ether. A mixture containing the acyltin (3 mmol), methyl propargyl ether (3 mmol) and n-hexane (3 mL) is irradiated in a quartz tube for 65 h. NMR analysis shows that again no reaction apart from decomposition of the acyltin has occurred.

c) With dimethyl acetylenedicarboxylate. The mixture as for b) above is irradiated for 20 h. NMR analysis shows that the acyltin is no longer present. The ^{119}Sn NMR spectrum shows the presence of 4 signals of similar magnitude in the region typical of vinyltins (−15.0, −15.2, −20.2, −38.1 ppm).

d) With halides. The acyltin (7–10 mmol) and the corresponding halide (7–10 mmol) in 3–5 mL hexane or benzene are irradiated in a quartz tube. After 16 h the solvent is removed and the residue analysed by NMR spectroscopy. a) CCl_4: products identified Me_3SnCl, 4-MeC_6H_4COCl; b) ^tBuI: products identified Me_3SnI, ^tBuCOPh [38]; c) Ph_2PCl: products identified Me_3SnCl, 4-$MeC_6H_4COPPh_2$ [NMR data [39], C_6D_6, r.t.: $\delta(^{13}C{=}O)$ 212.3 ppm, $^1J(^{31}P, ^{13}C)$ 37.5 Hz. $\delta(^{31}P)$ 11.7 ppm].

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References

1 P.C.B. Page, S.S. Klair and S. Rosenthal, Chem. Soc. Rev., (1990) 147.
2 A. Ricci and A. Degl'Innocenti, Synthesis, (1989) 647.
3 G.J.D. Peddle, J. Organomet. Chem., 14 (1968) 139.
4 A. Capperucci, A. Degl'Innocenti, C. Faggi, G. Reginato and A. Ricci, J. Org. Chem., 54 (1989) 2966.
5 J.-P. Quintard, B. Elissondo and D. Mouko-Mpegna, J. Organomet. Chem., 251 (1989) 1657.
6 J.A. Marshall and W.Y. Gung, Tetrahedron Lett., 29 (1989) 1657.
7 P.M.C. Chan and M.J. Chong, J. Org. Chem., 53 (1988) 5584.
8 M. Kosugi, H. Naka, H. Sano and T. Migita, Bull. Chem. Soc. Jpn., 60 (1987) 3462.
9 J.A. Marshall and W.Y. Gung, Tetrahedron Lett., 30 (1989) 2183, 7349.
10 J.A. Marshall, G.S. Welmaker and B.W. Gung, J. Am. Chem. Soc., 113 (1991) 647.
11 J.A. Soderquist and A. Hassner, J. Am. Chem. Soc., 102 (1980) 1577; J.A. Soderquist and G. Hsu, Organometallics, 1 (1982) 830.
12 A. Ricci, A. Degl'Innocenti, A. Capperucci, C. Faggi, G. Seconi and L. Favoretto, Synlett, (1990) 471.
13 A. Ricci, A. Degl'Innocenti, A. Capperucci, G. Reginato and A. Mordini, Tetrahedron Lett., 32 (1991) 1899.
14 E.J. Corey, D. Seebach and R. Freedman, J. Am. Chem. Soc., 89 (1967) 434.
15 A.G. Brook, J.M. Duff, P.F. Jones and N.R. Dudes, J. Am. Chem. Soc., 89 (1967) 431.
16 K.J.H. Kruithof, R.F. Schmitz and G.W. Klumpp, J. Chem. Soc., Chem. Commun., (1983) 239.
17 K.J.H. Kruithof, R.F. Schmitz and G.W. Klumpp, Tetrahedron, 39 (1983) 3073.
18 T.N. Mitchell and K. Kwetkat, Synthesis, (1990) 1001.
19 N.A. Bumagin, Y.V. Gulevich and I.P. Beletskaya, J. Organomet. Chem., 282 (1985) 421.
20 J.-B. Verlhac, E. Chanson, B. Jousseaume and J.-P. Quintard, Tetrahedron Lett., 26 (1985) 6075.
21 T.N. Mitchell, N.M. Dornseifer and A. Rahm, J. High Pressure Res., 7 (1991) 165.
22 F. Bernardi, L. Lunazzi, A. Ricci, G. Seconi and G. Tonachini, Tetrahedron., 42 (1986) 3607.
23 B. Wrackmeyer, Annu. Rep. NMR Spectrosc., 16 (1985) 73.
24 D.H. McDaniel and H.C. Brown, J. Org. Chem., 23 (1958) 420.
25 C. Hansch, A. Leo and R.W. Taft, Chem. Rev., 91 (1991) 165.
26 A.L. Baumstark, P. Balakrishnan, M. Dutrong, C.J. McCloskey, M.G. Oakley and D.W. Boykin, J. Am. Chem. Soc., 109 (1987) 1059.
27 J.-B. Verlhac, M. Pereyre and H.A. Shin, Organometallics, 10 (1991) 3007.
28 M. Kosugi, H. Naka, S. Harada, H. Sano and T. Migita, Chem. Lett., (1987) 1371.
29 J.M. Chong and E.K. Mar, Tetrahedron, 45 (1989) 7709.
30 D. Seyferth, R.M. Weinstein and W.-L. Wang, J. Org. Chem., 47 (1983) 1146.
31 D. Seyferth, R.M. Weinstein, W.-L. Wang and C.M. Archer, J. Org. Chem., 56 (1991) 5768.
32 A.G. Brook, Adv. Organomet. Chem., 76 (1968) 96.
33 H.J. Reich, D.P. Green and N.H. Phillips, J. Am. Chem. Soc., 108 (1986) 2102.
34 S. Kiyooka, E. Matsue and R. Fujiyama, Chem. Lett., (1989) 1385.
35 S. Kiyooka, Y. Kaneko, E. Matsue, M. Hamada and R. Fujiyama, J. Org. Chem., 55 (1990) 5563.
36 D.P. Curran and H. Liu, J. Org. Chem., 56 (1991) 3463.
37 A.G. Brook, J.B. Pierce and J.M. Duff, Can. J. Chem., 53 (1975) 2874.
38 P.E. Hansen, O.K. Paulsen and A. Berg, Org. Magn. Res., 9 (1977) 649.
39 E. Lindner and G. Vordermeier, Chem. Ber., 112 (1979) 1456.
40 A. Rahm, Main Group Met. Chem., 12 (1990) 277.