A FACILE ROUTE TO (β-ALKOXYCARBONYL)VINYLSTANNANES

KONRAD VON WERNER *, HERMANN BLANK,

Hoechst AG, 6230 Frankfurt-Main 80, Werk Gendorf (F.R.G.)

and KATSUTOSHI YASUFUKU

The Institute of Physical and Chemical Research, Wako-Shi, Saitama 351 (Japan)

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Summary

Substituted vinylchlorostannanes of the types $Cl_3SnC(R)=CHCO_2CH_3$ (R = H, CO_2CH_3, C_6H_5 or CH_3) and $Cl_3SnCH=C(CO_2CH_3)SnCl_2CH=CHCO_2CH_3$ have been prepared. On reaction with metal couples or tin the monovinyl compounds are transformed into the divinyl species $Cl_2Sn[C(R)=CHCO_2CH_3]_2$. Bonding in the products is discussed in terms of their IR, ^1H NMR and ^{13}C NMR spectra.

Introduction

A new type hydrostannation of carbonyl-activated olefins involving use of a combination of stannous halides with halogen acids has recently been employed to prepare alkyltin derivatives having β-substituents [1a,1b]. We have now investigated similar reactions of alkynes, the major objective being to find a practicable route to vinyltin halides containing the structural element $SnC=CC=O$, which are not accessible through the usual syntheses using magnesium or lithium reagents.

Results and discussion

Synthesis of (β-methoxycarbonyl)vinyltin trihalides

No reaction took place when acetylene, phenyl- or diphenyl-acetylene, or even the normally highly reactive 1,1,1-trifluoropropyne was added to a mixture of stannous chloride and an excess of hydrogen chloride in ether. In contrast, propiolic or acetylenedicarboxylic acid reacted rapidly, but very impure products were obtained. This was because of side reactions, mainly the addition of HCl to the triple bond. Surprisingly, when a variety of methyl acetylenecar-

boxylates were examined under the same conditions, high yields of the organo-tin chlorides I were obtained; the only reason for using methyl esters was to keep the NMR spectra as simple as possible.

$$SnCl_2 \ + \ HCl \ + \ RC\equiv CCO_2CH_3 \ \xrightarrow[\text{Et}_2\text{O}]{20°C} $$

(Ia), R = H
(Ib), R = CO$_2$CH$_3$
(Ic), R = C$_6$H$_5$
(Id), R = CH$_3$

The reaction rate decreased in the order R = H > CO$_2$CH$_3$ >> C$_6$H$_5$ > CH$_3$, implying that it is influenced by both steric and electronic factors.

The reaction was also performed at lower temperatures by passing a stream of hydrogen chloride very slowly into a mixture of SnCl$_2$ with the alkynyl ester. Under these conditions a by-product II was formed from the most reactive ester (R = H), and, to a lesser extent, also with R = CO$_2$CH$_3$. The formation of II could be completely suppressed by working at 35°C.

It can be assumed that trichlorostannane, reversibly formed in solution from stannous chloride and hydrogen chloride [2], adds to the conjugated system in a polar 1,4-addition, the initial step probably being the protonation of the ester carbonyl. The products isolated may then be formed as depicted in Scheme 1.

SCHEME 1

(II)   (a: R = H)

At room temperature, neither the signals expected for the ketene acetal type intermediate nor any signals due to a possible isomer of I having a *cis*-arrangement of tin and hydrogen at the (C=C) bond were detectable in the NMR spectrum. However, the life time of the allenic intermediate at low temperatures must be sufficient to allow a further reaction with I, which affords II by a subsequent migration of a vinyldichlorotin group from oxygen to the β-carbon. Apparently this step is inhibited by free hydrogen chloride since the reaction of preformed Cl_3SnH in the presence of an excess of HCl gave only I, even at $-40°C$ and with R = H. Exploratory experiments using stannous bromide together with hydrogen bromide indicated the formation of vinyltin tribromides analogous to I.

Synthesis of related divinyltin compounds.

When treated with various metallic halogen acceptors the monovinyltins I underwent a vinyl transfer reaction to yield divinyltins of type III. These reactions occurred under very mild conditions and with complete retention of configuration around the (C=C) bond (Scheme 2). The rate of formation of III is

SCHEME 2

$$2\,Cl_3Sn \overset{R}{\underset{O=C\diagdown OCH_3}{\underset{|}{C=C-H}}} + Sn \xrightarrow[Et_2O]{20°C} Cl_2Sn\left[\overset{R}{\underset{O=C\diagdown O-CH_3}{\underset{|}{C=C-H}}}\right]_2 + 2\,SnCl_2$$

(I) (III)
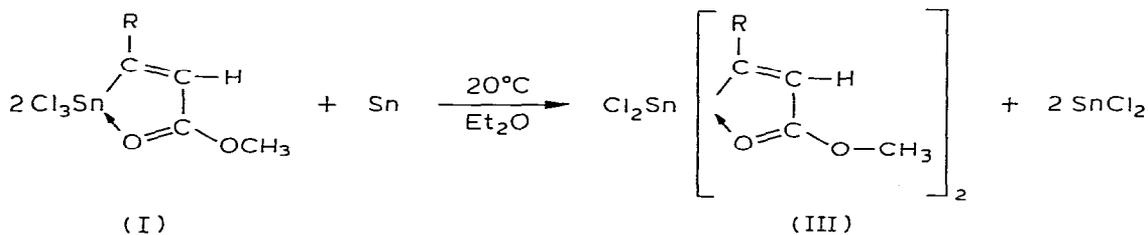
(a: R = H; b: R = CO_2CH_3; c: R = C_6H_5; d: R = CH_3)

very low in ether. It is greatly enhanced in boiling tetrahydrofuran, but the changed conditions give reduced yields and lower product purity. A more useful method of increasing the rate involves use of metal couples instead of tin. The reactivity of the metals examined decreased in the order of M = Zn(Cu) > Pb(Na) > Sn >> Mg. A further factor influencing the rate is the nature of the substituent R: electron-attracting groups (R = CO_2CH_3) accelerate the reaction, while donating groups (R = CH_3) clearly slow it down. Neither addition of a free-radical initiator (azobis(isobutyronitrile) or benzoyl peroxide) to a mixture of Ia and tin in THF, at 65°C, nor UV irradiation, changed the rate and so a radical process may be excluded.

The remarkable ease of vinyl transfer is probably related to the ability of the β-methoxycarbonyl group to coordinate to a neighbouring tin atom. A plausible mechanism accounting for the products observed, which involves an initial insertion of the halide acceptor M into a (Sn—Cl) bond, is depicted in Scheme 3.

Although it is difficult to define a route not involving a vinylstannylene intermediate, our efforts to trap this species have so far failed. Thus a reaction in the presence of twentyfold excess of butyl bromide failed to give any new products, while di-t-butyl disulfide proved to be an unsuitable scavenger because of its tendency to form donor adducts with the starting material. Fur-

SCHEME 3

$Cl_3SnC(R){=}CHCO_2CH_3$ $\xrightarrow{\text{+ M}}$ $\left[\begin{array}{c} Cl \\ | \\ ClMSnC(R){=}CHCO_2CH_3 \\ | \\ Cl \end{array}\right]$

$\Big\downarrow -MCl_2$

$\left[ClSnC(R){=}CHCO_2CH_3\right]$

$\Big\downarrow +\,I$

$Cl_2Sn\left[C(R){=}CHCO_2CH_3\right]_2$ $\xleftarrow{-SnCl_2}$ (complex structure)

(III)
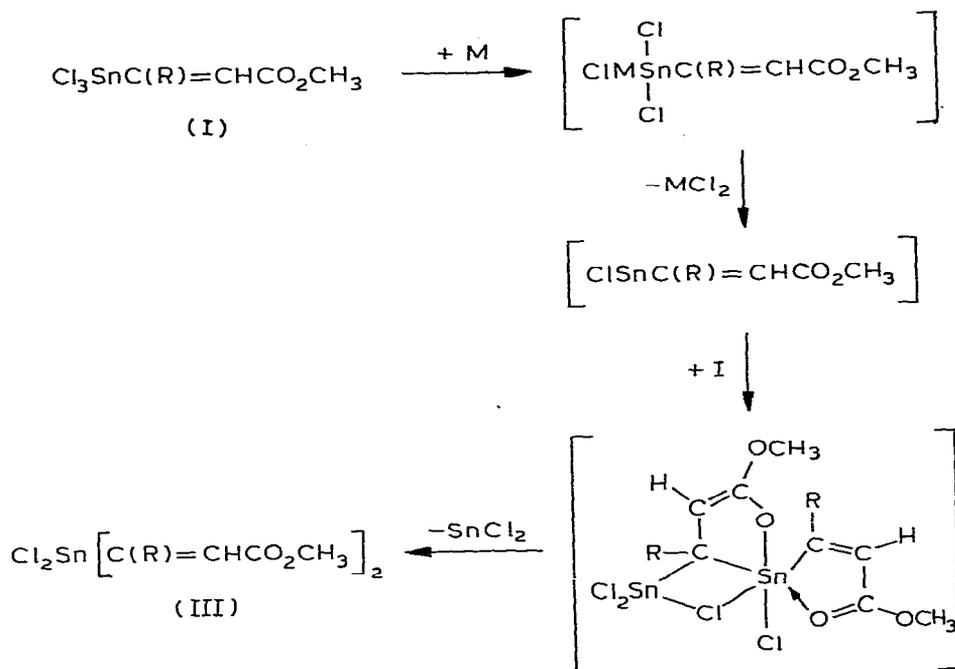
ther experiments are needed to check the validity of the proposed scheme.

Following the procedure described by Graham [3], the compounds I were treated in THF with 3 equivalents of sodium tetracarbonylcobaltate in order to investigate whether the polar substituent attached to the vinyl group of I would favour the formation of $(CO)_{12}Co_3[SnC(R){=}CHCO_2CH_3]$ or that of the metal—metal bonded complexes $(CO)_9Co_3[SnC(R){=}CHCO_2CH_3]$. Again, Ib (R = CO$_2$-CH$_3$) reacted much faster than Id (R = CH$_3$) but even at $-70°C$ a complicated mixture was obtained, from which octacarbonyldicobalt and cobalt(II) chloride but none of the desired products could be separated. We suggest that a vinyl transfer from tin to cobalt, leading to complexes which are too unstable for isolation, may be responsible for this failure.

Apart from vinyl transfer reactions, the new compounds offer some further interesting synthetic possibilities, mainly associated with the presence of a still activated (C=C) bond, e.g. addition of appropriate nucleophiles such as thiols.

Bonding features

Both the mono- and the di-vinyltins were proved by molecular weight determinations to be strictly monomeric. The IR spectra, presented in Table 2, show $\nu(C{=}O)$ of the β-methoxycarbonyl groups at frequencies which are characteristic for carbonyl coordination to tin. It can thus be concluded that compounds I possess a five-coordinate, possibly square pyramidal structure, while the compounds of type III are six-coordinate and octahedral.

The large coupling constants between the β-vinylproton and tin ($^3J(^{119}Sn-$ H) I : 357 — 440 Hz, III: 313 — 360 Hz) are indicative of a *trans*-vinylic geometry. Combined with the information form IR, a five-membered chelate ring

TABLE 1

(β-METHOXYCARBONYLVINYL)CHLOROSTANNANES

Compound	Mol. weight (found^a (calcd.))	Analysis (found (calcd.) (%))				M.p. (°C)	Yield (%)
		C	H	Cl	Sn		
Ia	$Cl_3SnCH=C(CO_2CH_3)H$	15.9 (15.49)	1.8 (1.63)	35.5 (34.29)	38.2 (38.27)	58—60	98
Ib	$Cl_3SnC(CO_2CH_3)=C(CO_2CH_3)H$	19.8 (19.57)	2.1 (1.92)	28.8 (28.89)	32.0 (32.24)	134	82
Ic	$Cl_3SnC(C_6H_5)=C(CO_2CH_3)H$	31.1 (31.10)	2.4 (2.35)	27.4 (27.54)	30.6 (30.73)	176	89
Id	$Cl_3SnC(CH_3)=C(CO_2CH_3)H$	18.5 (18.53)	2.2 (2.18)	33.0 (32.81)	36.9 (36.61)	119—122	81
IIa	Cl_2Sn $\Big\langle$ $CH=C(CO_2CH_3)H$ / $C(CO_2CH_3)=CHSnCl_3$; (583.8)	16.6 (16.46)	1.6 (1.55)	30.8 (30.36)	40.5 (40.66)	173	26
IIIa	$Cl_2Sn[CH=C(CO_2CH_3)H]_2$	26.2 (26.71)	3.0 (2.80)	20.3 (19.71)	32.0 (32.99)	159	90
IIIb	$Cl_2Sn[C(CO_2CH_3)=C(CO_2CH_3)H]_2$	30.4 (30.29)	3.0 (2.97)	15.1 (14.90)	24.9 (24.94)	151	80
IIIc	$Cl_2Sn[C(C_6H_5)=C(CO_2CH_3)H]_2$	46.8 (46.92)	3.6 (3.54)	14.0 (13.85)	23.7 (23.18)	197	97
IIId	$Cl_2Sn[C(CH_3)=C(CO_2CH_3)H]_2$	30.6 (30.97)	3.6 (3.64)	18.4 (18.28)	30.5 (30.60)	140—145	93

Mol. weight values: Ia 315 (310.1); Ib 358 (368.2); Ic — (386.2); Id — (324.2); IIa (583.8); IIIa 363 (359.8); IIIb — (457.8); IIIc 523 (512.0); IIId 389 (387.8).

^{a} Osmometrically in butan-2-one.

TABLE 2

^{1}H NUCLEAR MAGNETIC RESONANCE AND INFRARED DATA OF VINYLCHLOROSTANNANES

Compounds	^{1}H NMR ^{a}				Solvent	IR (cm^{-1}) ^{b}	
	SnC=CH	SnCH=C	OCH$_3$	Other res.		ν(C=O)	ν(C=C)
$\begin{array}{c} H \\ Cl_3Sn \end{array} C=C \begin{array}{c} H \\ CO_2CH_3 \end{array}$	7.22d $^3J(^{119}SnH)$ 440 $^3J(^{117}SnH)$ 419 $^3J(HH)$ 9.0	7.32d $^2J(^{119}SnH)$ 263 $^2J(^{117}SnH)$ 252	4.15s	—	CDCl$_3$	1654	1576
$\begin{array}{c} CH_3O_2C \\ Cl_3Sn \end{array} C=C \begin{array}{c} H \\ CO_2CH_3 \end{array}$	7.30s $^3J(^{119}SnH)$ 357 $^3J(^{117}SnH)$ 341	—	4.15s 3.89s	—	CDCl$_3$	1727 1658	1610
$\begin{array}{c} C_6H_5 \\ Cl_3Sn \end{array} C=C \begin{array}{c} H \\ CO_2CH_3 \end{array}$	6.89s $^3J(^{119}SnH)$ 396 $^3J(^{117}SnH)$ 380	—	4.12s	7.46m (C$_6$H$_5$)	CDCl$_3$	1638	1562
$\begin{array}{c} CH_3 \\ Cl_3Sn \end{array} C=C \begin{array}{c} H \\ CO_2CH_3 \end{array}$	6.81q $^3J(^{119}SnH)$ 426 $^3J(^{117}SnH)$ 408 $^4J(HH)$ 1.6	—	4.08s	2.49d (CH$_3$) $^3J(^{119}SnH)$ 148 $^3J(^{117}SnH)$ 140	CDCl$_3$	1648	1594
$\begin{array}{c} H \\ Cl_2Sn \end{array} C=C \begin{array}{c} H \\ CO_2CH_3 \end{array}$ $\begin{array}{c} \\ CH_3O_2C \end{array} C=C \begin{array}{c} H \\ SnCl_3 \end{array}$	7.26d $^3J(^{119}SnH)$ 357 $^3J(^{117}SnH)$ 339 $^3J(HH)$ 9.0 8.22s $^3J(^{119}SnH)$ 323 $^3J(^{117}SnH)$ 309	7.58d $^2J(^{119}SnH)$ 196 $^2J(^{117}SnH)$ 186 $^2J(^{119}SnH)$ 122 $^2J(^{117}SnH)$ 116	4.15s 4.02s	—	(CD$_3$)$_2$CO	1656	1582 1568w
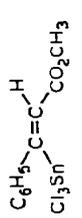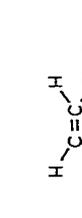
Compound						
$\left[Cl_2Sn \dfrac{H}{\;}C=C\dfrac{H}{CO_2CH_3} \right]_2$	6.83d $^3J(^{119}SnH)$ 360 $^3J(^{117}SnH)$ 343 $^3J(HH)$ 9.0	7.55d $^2J(^{119}SnH)$ 171 $^2J(^{117}SnH)$ 163	3.90s	—	CDCl$_3$	1663 1642w	1578
$\left[Cl_2Sn \dfrac{CH_3O_2C}{\;}C=C\dfrac{H}{CO_2CH_3} \right]_2$	7.06s $^3J(^{119}SnH)$ 313 $^3J(^{117}SnH)$ 298	—	3.99s 3.90s	—	CDCl$_3$	1722 1648	1599
$\left[Cl_2Sn \dfrac{C_6H_5}{\;}C=C\dfrac{H}{CO_2CH_3} \right]_2$	6.60s $^3J(^{119}SnH)$ 332 $^3J(^{117}SnH)$ 317	—	3.85s	7.42m (C$_6$H$_5$)	CDCl$_3$	1637	1561 1572(sh)
$\left[Cl_2Sn \dfrac{CH_3}{\;}C=C\dfrac{H}{CO_2CH_3} \right]_2$	6.50q $^3J(^{119}SnH)$ 344 $^3J(^{117}SnH)$ 329 $^4J(HH)$ 1.8	—	3.86s	2.48d (CH$_3$) $^3J(^{119}SnH)$ 120 $^3J(^{117}SnH)$ 115	CDCl$_3$	1649	1598

[a] δ (ppm), downfield from TMS; coupling constants (J) in Hz. [b] Measured with KBr pellets; spectra obtained from CHCl$_3$ solutions showed maximal deviations of ± 10 cm^{-1}.

formed by the vinyl ligand and tin can be derived for all compounds:
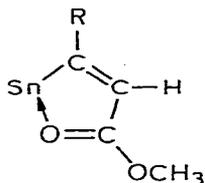
For Ia and IIIa with R = H, a *cis*-coupling constant of 9 Hz observed between the vinylic protons gives additional support for the above configuration. The most prominent feature in the NMR spectra of the present compounds, summarized in Tables 2 and 3, is the observation of very large values for the coupling between tin and the vinyl protons and, moreover, tin and the α-carbons. Unfortunately, $^1J(Sn-C)$ could be observed in only three cases because the carbon bonded to tin normally gave a low intensity signal because of unfavourable relaxation under standard conditions. The likeliest explanation of the unusual magnitude of these coupling constants may be the significant reduction of electron density at the central tin, and particularly its 5s orbital, caused by the chloride ligands.

The tin to β-hydrogen couplings observed for compounds I were rather solvent-dependent: the values of $^3J(Sn-H)$ found in acetone were larger than those for chloroform solutions by about ten percent, suggesting an interaction between the (C=O) group of acetone and the vacant, sixth coordination site in I.

A further point of interest is the arrangement of ligands in the divinyltins III. For the two vinyl groups, only one set of signals can be detected by proton and carbon NMR spectroscopy, at temperatures between +100 and −70°C. Hence, these groups occupy equivalent positions. In addition, with regard to the high values of $^1J(Sn-C)$ it seems unlikely that the two tin—carbon bonds would lie *trans* to each other. These restrictions leave only two possible isomers IIIA and IIIB. In order to distinguish between these isomers, the dipole moment of IIIc

(III A)

(III B)
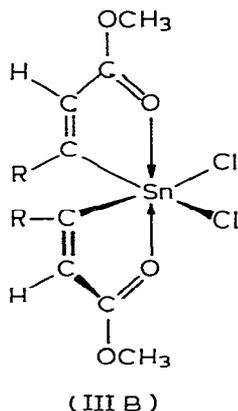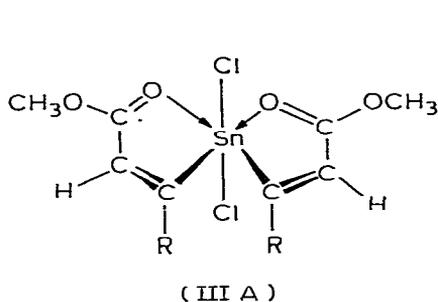
(R = C$_6$H$_5$), which is the most soluble in benzene, was determined by the method of Guggenheim [4], and gave μ(IIIc) 6.9 D. A calculation, based on the assumption of idealized bond angles and using literature data for organic group

TABLE 3

δ(¹³C)-VALUES AND COUPLING CONSTANTS OF VINYLCHLOROSTANNANES [a]

Compound	Sn—C=C	Sn—C=C	C=O	OCH₃	CCH₃	C₆H₅	Solvent
Cl₃Sn–C(H)=C(CO₂CH₃)	153.0 ¹J(SnC) 1073, 1123 ¹J(CH) 178.2	134.1 ²J(SnC) 16.0 ¹J(CH) 175.8	172.4	56.4 ¹J(CH) 150.1	—	—	CDCl₃
CH₃O₂C–C(Cl₃Sn)=C(H)(CO₂CH₃)	157.3	133.6 ¹J(CH) 177.0	172.1 165.2	56.9 ¹J(CH) 150.2 53.7 ¹J(CH) 148.9	—	—	CDCl₃
C₆H₅–C(Cl₃Sn)=C(H)(CO₂CH₃)	171.6	124.8 ²J(Snc) 54.9	174.3	56.6	—	135.5 ²J(SnC) 80.1 129.1, 129.4 131.3 ⁵J(SnC) 17.5	CDCl₃/CD₂Cl₂ (1/2)
CH₃–C(Cl₃Sn)=C(H)(CO₂CH₃)	169.3 ¹J(SnC) 1049, 1099 ²J(CH) 8.5	127.5 ²J(SnC) 47.6 ¹J(CH) 172.1	173.1	56.1 ¹J(CH) 150.1	22.2 ²J(SnC) 87.9 ¹J(CH) 130.6 ⁴J(CH) 6.2	—	CDCl₃
Cl₂Sn[–C(H)=C(CO₂CH₃)]₂	159.2 ¹J(SnC) 1112, 1163 ¹J(CH) 169.7	129.5 ²J(SnC) 25.0 ¹J(CH) 173.3	172.8	54.6 ¹J(CH) 148.9	—	—	CDCl₃
Cl₂Sn[–C(CH₃O₂C)=C(H)(CO₂CH₃)]₂	166.7	129.4	173.6 164.6	55.6	—	—	CDCl₃/CD₂Cl₂ (1/2)
Cl₂Sn[–C(C₆H₅)=C(H)(CO₂CH₃)]₂	177.3	122.7 ²J(SnC) 41.5 ¹J(CH) 170.4	174.9	55.1 ¹J(CH) 150.2	—	138.4 129.0, 129.8 130.3	CD₂Cl₂
Cl₂Sn[–C(CH₃)=C(H)(CO₂CH₃)]₂	176.4 ²J(CH) 5.4	123.3 ²J(SnC) 20.8 ¹J(CH) 167.2	173.1	56.1 ¹J(CH) 148.9	22.4 ²J(SnC) 67.1 ¹J(CH) 129.4 ⁴J(CH) 6.1	—	CDCl₃

[a] Chemical shifts (δ) are given in ppm, downfield from TMS, couplings (J) in Hz.

moments [5], μ(Sn—C) 0.6 D, μ(Sn—Cl) 4.2 D [6] and a roughly approximated value of μ(Sn←O) 0.5 D (taken as 1/4 μ of a full Sn—O bond), gave μ(IIIc, A) 2.76 D and μ(IIIc, B) 6.88 D. Thus, the experimental value is in precise agreement with structure IIIB. This assignment is further supported by the appearance of two intensive ν(Sn—Cl) vibrations in the IR spectra of IIIc (317 m cm^{-1}, 298 s cm^{-1}) and of IIIa (335 m cm^{-1}, 304 s cm^{-1}). The corresponding absorptions of $Cl_2Sn(CH_2CH_2CO_2CH_3)_2$, the saturated analogue of IIIa, appear at 302 and 290 cm^{-1}, with similar intensities.

Experimental

Methyl acetylenecarboxylates were prepared by literature procedures and were purified by fractional distillation. All solvents were carefully dried and saturated with nitrogen. The chloroform used for recrystallizations was freed from ethanol to avoid any ethoxide formation. Infrared spectra were recorded on a Perkin—Elmer 325 grating spectrometer and were calibrated with polystyrene bands. ^{1}H NMR spectra were recorded on a Jeol C60 instrument at 60 MHz, and the ^{13}C resonances on a Jeol JNM-FX-100 spectrometer, operating in the Fourier transform mode at 25.16 MHz; $CDCl_3$ was used as an internal lock.

All products resulting from the experiments described below were colourless crystals which proved indefinitely stable in the absence of moisture.

(a) Preparation of $Cl_3SnCH=CHCO_2CH_3$ (Ia)

Method A. In a 250 ml 5-neck flask equipped with mechanical stirrer, dry-ice condenser, dropping funnel, gas inlet tube and thermometer, a suspension of 47.4 g of stannous chloride (0.25 mol) in 150 ml of diethyl ether was heated until it refluxed gently. 24.3 g of gaseous hydrogen chloride (0.67 mol, dried by passing through $AlCl_3$) was bubbled into the vigorously stirred mixture within 30 min, while 21.0 g of $HC\equiv CCO_2CH_3$ (0.25 mol) were simultaneously added dropwise. Refluxing was continued for 2 h, then the mixture was stirred overnight at room temperature.

The ether was removed by means of a rotary evaporator, and the oily residue was heated at 50°C/0.2 Torr for 1 h and then redissolved in 300 ml of trichloromethane. The solution was stirred with 1 g of activated charcoal for 15 min at 60°C. Filtration and removal of solvent under vacuum gave a pale-yellow oil (69.6 g), which slowly solidified during 2 days. Recrystallization from ether afforded 67.1 g (92% yield) of pure product.

Method B. To 47.4 g of stannous chloride, suspended in ether (100 ml), hydrogen chloride (26.3 g, 0.72 mol) was added during 2 h at 20°C with vigorous stirring. After a further 4 h of stirring, all of the $SnCl_2$ had dissolved. The resulting emulsion, containing solvated Cl_3SnH, was cooled to —40°C, and 21.0 g of $HC\equiv CCO_2CH_3$ was gradually added during 3 h. Stirring was continued for 2 h at the same temperature, then the mixture was allowed to warm up to 20°C overnight. Purification was carried out as in method A. On evaporation of trichloromethane, 71.4 g of a colourless oil were obtained; this crystallised rapidly and proved to be pure Ia from its ^{1}H NMR (97.8% yield).

(b) Preparation of Cl₃SnC(CO₂CH₃)=CHCO₂CH₃ (Ib)

This compound was prepared as under (a), method A, from $SnCl_2$, HCl and dimethylacetylene dicarboxylate (35.5 g, 0.25 mol), with a reflux time of 3.5 h. When the purified trichloromethane solution was concentrated to 70 ml, the product started to precipitate. After cooling for 1 h at 0°C, the crystals (68.0 g) were filtered off and dried under vacuum. Another 7.4 g was recovered by adding ether to the mother liquor. Total yield: 82%.

(c) Preparation of Cl₃SnC(R)=CHCO₂CH₃ (Ic, R = C₆H₅ and Id, R = CH₃)

30.0 g hydrogen chloride gas (0.82 mol) was passed during 2 h into a stirred mixture of $SnCl_2$ (47.4 g), 0.25 mol $RC{\equiv}CCO_2CH_3$ (R = C_6H_5: 40.0 g or R = CH_3: 24.5 g), and ether (150 ml) maintained at 15—20°C by cooling. The mixture was stirred for 2 (Ic) or 4 days (Id) at room temperature. After evaporation of solvent and of excess HCl, the pale-yellow crude product was dissolved in hot trichloromethane (Ic: 800 ml, Id: 400 ml), and the solution was stirred for 2 h with 1.5 g of activated carbon, then filtered. The filtrate was reduced to 1/4 of its volume in a rotary evaporator and kept for 12 h at —10°C. The deposited crystals were separated by filtration and dried in vacuo. Yields: 86.2 g of Ic, 65.7 g of Id.

(d) Simultaneous preparation of Cl₂Sn(CH=CHCO₂CH₃)(C(CO₂CH₃)=CHSn-Cl₃) (IIa) and of Ia

A stirred mixture of $SnCl_2$ (37.92 g, 0.2 mol), $HC{\equiv}CCO_2CH_3$ (16.82 g, 0.2 mol) and of ether (140 ml) was cooled to —10°C and hydrogen chloride (7.3 g, 0.2 mol) was slowly introduced during 5 h at this temperature. Stirring was continued for 15 h at 20°C. The ether was then stripped off and the white, solid residue was dried at 40°C/0.1 Torr. It was dissolved in trichloromethane (50 ml); the solution was filtered and concentrated to half its volume. Ether (20 ml) was added and the solution was gradually cooled to 0°C. The solids were filtered off and recrystallised from chloroform to give 15.1 g of pure IIa; the filtrate was evaporated to dryness, and the residual brown oil was dissolved in ether and passed through a column of neutral alumina (10 × 1 cm). Concentration and cooling gave 27.5 g of compound Ia.

(e) Preparation of Cl₂Sn[C(R)=CHCO₂CH₃]₂ (IIIa: R = H, IIIb: R = CO₂CH₃, IIIc: R = C₆H₅, IIId: R = CH₃)

A mixture of 0.1 mol of a monovinyltin compound Ia, Ib, Ic or Id, respectively, tin powder (17.8 g, 0.15 mol) and carefully dried ether (1 l) was rapidly stirred at room temperature under nitrogen. The time required to complete the reactions was 13 d for Ia, 10 d for Ib, 17 d for Ic and 20 d for Id. The ether was removed under reduced pressure, the residue was stirred with hot trichloromethane, and the solids consisting of stannous chloride and unreacted tin were separated by filtration. The $CHCl_3$ solution was treated with charcoal and filtered. On concentration and cooling, crystals were obtained in the cases of IIIb (19.13 g) and IIIc (24.78 g). The other two compounds were isolated by evaporating the chloroform and recrystallizing the residue: IIIa (16.14 g) from ether, IIId (18.05 g) from $CHCl_3$/ether (1/10).

Treatment of Ia with an excess of metal couples instead of tin accelerated its

conversion into IIIa: the reaction was complete after 5 d with zinc—copper (100/1) and after 7 d with lead—sodium (9/1).

Acknowledgements

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