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ALLYLBUTYLTIN HALIDES ($(CH_2{=}CHCH_2)SnBu_{3-n}Cl_n$ (n = 0, 1, 2, 3). PREPARATION, CARBON-13 NMR CHARACTERIZATION AND ALLYLSTANNYLATION ABILITY TOWARDS KETONES AND ALDEHYDES

ALESSANDRO GAMBARO

Istituto di Chimica Fisica, Università di Padova, Via Loredan, 2-I-35100 Padova (Italia)

VALERIO PERUZZO, GUALTIERO PLAZZOGNA, and GUISEPPE TAGLIAVINI *

Istituto di Chimica Analitica, Università di Padova, Via Marzolo 1-I-35100 Padova (Italia)

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Summary

Mixed allylbutyltin halides $(CH_2{=}CHCH_2)SnBu_{3-n}Cl_n$ (n = 0—3) have been prepared, and characterized by carbon-13 NMR spectroscopy. Their ability to bring about allylstannylation of ketones and aldehydes, to form organostannoxy compounds, $Bu_{3-n}SnCl_nOC(R')(R'')CH_2CH{=}CH_2$, has been shown to increase on increasing the value of n, that is on increasing the acceptor ability of the tin centre.

Introduction

We recently showed that facile allylstannylation of carbonyl compounds takes place with n-$Bu_2(CH_2{=}CHCH_2)SnCl$ and $(CH_2{=}CHCH_2)_3SnCl$ [1,2]. Following those studies, we decided to evaluate the reactivities in the allylstannylations of triallyltin chloride and various allyltin derivatives $AllSnR_{3-n}Cl_n$ (All = allyl, R = n-Bu, n-Pr; n = 0—3) in which the acceptor properties of the tin centre as well as the electron distribution in the allyl group are changed by varying the value of n. Thus we have prepared this series of mixed allyltins and compared their abilities to add to benzaldehyde, dimethyl, methyl vinyl and t-butyl methyl ketones.

The effect of changing the number of halide substituents on the electron density of the allyl carbons has been studied by carbon-13 NMR spectroscopy.

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* To whom inquiries should be addressed.

Experimental

Materials

2,2,3-Trimethyl-5-hexen-3-ol and 2,3-dimethyl-5-hexen-3-ol were prepared from the appropriate ketones and allylmagnesium bromide by the Barbier—Grignard procedure [3].

Commercial samples of aldehydes and ketones were of reagent grade, and were freshly distilled and kept overnight over molecular sieves 4A before use.

IR spectra were recorded on a Perkin—Elmer model 599B spectrophotometer. Carbon-13 NMR spectra were recorded with a Bruker WH90 spectrometer operating in FT mode.

Preparation of allyltins

Di-n-propylallyltin chloride

This compound was prepared by elimination from 2,2,3-trimethyl-5-hexen-3-di-n-propylchlorostannoxy by a reported method [2,4].

Equimolecular amounts (28.5 mmol) of di-n-propyltin dimethoxide and di-n-propyltin were allowed to react with stirring at room temperature to form di-n-propylchlorotin methoxide [5]: and it was assumed that 57 mmol of this compound were formed. Subsequently 9.6 ml (about 56 mmol) of 2,2,3-trimethyl-5-hexen-3-ol were added and the temperature was raised to 160°C, and during 2 h a liquid (2 g) consisting of methanol and 2,2-dimethyl-3-butanone was condensed out. The residue was distilled under reduced pressure to give 10.5 g (66% yield) of $n\text{-}Pr_2(CH_2{=}CHCH_2)SnCl$, b.p. 81—81.5°C/0.1 mmHg.

The IR spectrum recorded as a thin film (KBr disc) shows the characteristic band centered at 1625 cm^{-1} due to the C=C stretching vibration of the allyl group linked to the tin atom [6,7].

n-Butylallyltin dichloride

Procedure A. This compound was prepared by elimination from 2,3-dimethyl-3-n-butyldichlorostannoxy-5-hexene by the route previously reported [3].

To 10 g of 2,3-dimethyl-5-hexen-3-ol and 10 ml of anhydrous benzene, 1.2 g of metallic sodium were added to form the corresponding alcoholate. Then 6.8 g (48.2 mmol) of $BuSnCl_3$ were added and the mixture left at 50—60°C for 2 h. After removal of the sodium chloride, the solution was heated and benzene and the excess of carbinol were pumped off. At this stage the formation of methyl isopropyl ketone was observed at 70—80°C, the complete evolution of ketone took less than one hour at 130°C. The residue was distilled under reduced pressure to give 10.4 g of n-butylallyltin dichloride (75% yield) at 91°C/0.25 mmHg.

The IR spectrum recorded as a thin film showed the $\nu(C{=}C)$ band centered at 1625 cm^{-1}.

Procedure B. This compound was also prepared by a redistribution reaction: $(CH_2{=}CHCH_2)_3SnBu + 2\ BuSnCl_3 \rightarrow 3\ Bu(CH_2{=}CHCH_2)SnCl_2$.

To 3.53 g (11.8 mmol) of All_3SnBu prepared as previously described [6] were slowly dropped (45 min) at 0°C with stirring 6.66 g (23.6 mmol) of $BuSnCl_3$. The mixture was set aside for 3 h at room temperature. The title compound

(7.5 g, 73% yield) was obtained by distillation under reduced pressure (b.p. 90°C/0.25 mmHg).

Allyltin bromodichloride

This compound was prepared following three different procedures.

Procedure C. To 11 g (58 mmol) of anhydrous tin(II) chloride, 21 g (176 mmol) of allyl bromide were added. The mixture was refluxed and stirred for 24 h. Then the solid residue was filtered off under dry nitrogen and the liquid distilled under reduced pressure to give 7.65 g (42% yield) of a pale yellow product, b.p. 75—78°C/0.1 mmHg.

The IR spectrum shows the characteristic band centered at 1625 cm^{-1} of an allyl group joined to tin and ν(Sn—C), ν(Sn—Cl) and ν(Sn—Br) at 485, 365 and 260 cm^{-1}, respectively [8,9].

Procedure D. The same reaction was carried out in the presence of a catalytic amount of diallyl sulphide, as in the preparation of alkyltin trihalides from $SnCl_2$ and alkyl halides [10].

To the same amounts of reagents as above were added a few drops of diallyl sulphide. The mixture was kept under reflux for ca. 30 min., and gave 14.6 g (80% yield) of pure product boiling at 75—78°C/0.1 mmHg.

Procedure E. Using the same amounts of the reagents, $(CH_2{=}CHCH_2)SnCl_2Br$ was prepared in solution of anhydrous THF by refluxing for about 2 h. The solvent was taken off under reduced pressure, and the residue was distilled under vacuum to give 8.73 g of product (48% yield).

Triallyltin chloride, allyl-di-n-butyltin chloride and tri-n-butylallyltin

The two organotin chlorides were prepared by redistribution as previously reported [3]. Tri-n-butylallyltin was prepared by interaction of allylmagnesium bromide and butyltin trichloride in ether [11].

Addition reactions of n-Pr_2AllSnCl and n-Bu_{3-n}AllSnCl_n (n = 1, 2)

All the experiments were performed on the neat reactants. Equimolar amounts (7—10 mmol, 30—50 for preparative purposes) of the examined mixed allyltin derivatives and the appropriate organic substrate were stirred together under the conditions specified in Table 1. The progress of the reaction was followed by infrared spectroscopy as described in ref. 2. In some cases the addition products were hydrolysed [1,2] in order to check the yield of carbinol.

Experiments with tributylallyltin gave no indication of easy addition to the carbonyl compounds.

Additions of AllSnCl_2Br to acetone and benzaldehyde

The reactions of AllSnCl_2Br with acetone or benzaldehyde using the neat reagents at 0 or 25°C gave no infrared evidence for the formation of the expected adducts. A heavy brown slush was obtained and not further analysed.

Addition reaction was found to occur in THF. Only the reaction of acetone was examined.

Following procedure E, anhydrous tin(II) chloride (22 g, 116 mmol) and allyl bromide (42 g, 348 mmol) were mixed in 50 ml of THF. After 2 h reflux acetone (6.7 g, 116 mmol) was added. The mixture was heated under reflux for

TABLE 1

ADDITION REACTIONS OF THE EXAMINED ALLYLTINS WITH SOME CARBONYL COMPOUNDS [a]

Carbonyl compound	Allyltins		
	$(CH_2{=}CHCH_2)Bu_2SnCl$ [b]	$(CH_2{=}CHCH_2)BuSnCl_2$	$(CH_2{=}CHCH_2)Pr_2SnCl$
PhCHO	exothermal reaction (25°C) few min 100% —	exothermal reaction (25°C) few min 100% allyl-phenyl-carbinol (65%)	exothermal reaction (25°C) few min 100% —
CH_3COCH_3	25°C 24 h 100% —	25°C 20 h 100% allyl-dimethyl-carbinol (70%)	25°C 10 h 100% —
$CH_3COCH{=}CH_2$	25°C 7 h 100% —	25°C 20 min 100% —	25°C 6 h 100% allylvinylmethyl carbinol (50%)
$CH_3COC(CH_3)_3$	80°C 70 h 50% allylmethylbutyl carbinol (20%)	80°C 42 h 50% —	— — — —

[a] For each system the following data are given from the top to the bottom: temperature, time, approximate % of the reaction progress as estimated by the IR pattern, isolated carbinol, yield between brackets. [b] See also ref. 2.

20 h, then most of the solvent was removed. After hydrolysis as in procedure A of ref. 2, 3.5 g (35 mmol) of dimethylallylcarbinol (30% yield) was isolated.

Addition reactions of $(CH_2{=}CHCH_2)_3SnCl$

Several experiments with different acetone/All_3SnCl ratios (1, 2 and 3) were performed on the neat reagents using 10 mmol of the organotin. The reagents were mixed at 0°C then allowed to reach room temperature. In all cases the addition reaction went nearly to completion. Depending on the ratio employed, $All_2Sn(OR)Cl$, $AllSn(OR)_2Cl$ and $Sn(OR)_3Cl$ ($OR = OC(CH_3)_2CH_2$-$CH{=}CH_2$) were formed as indicated by the IR spectra. The IR spectra, show that the reactions are complete after about 1 hour for reactant ratios of 1 and 2. For a ratio of 3, 90% of reaction takes place in two hours.

In a typical run, acetone (5.3 g, 91.2 mmol) was added to triallyltin chloride (8.4 g, 30.4 mmol). An exothermic reaction took place. The mixture was stirred for five hours then hydrolysed with aqueous HCl. After extraction with two samples of 25 ml of CH_2Cl_2 the organic layer was separated and distilled to give dimethylallylcarbinol (3.1 g, 31 mmol, 34% yield). These addition reactions also occur readily in CH_2Cl_2 and n-hexane.

Discussion

The carbon-13 shifts δ (cf. Table 2) of the three carbons of the allyl moiety, $Sn{-}\overset{1}{C}H_2{-}\overset{2}{C}H{=}\overset{3}{C}H_2$ are linearly related to the number n of the halide substitu-

TABLE 2

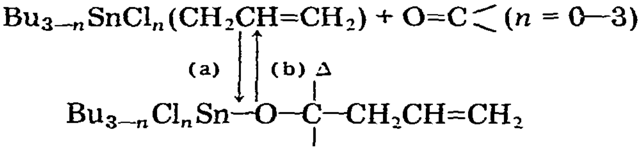
CARBON-13 CHEMICAL SHIFTS [a] OF THE EXAMINED ALLYLTINS

Compound	4′ CH_3	3′ CH_2	2′ CH_2	1′ CH_2	Sn	1 CH_2	2 CH	3 CH_2
$(CH_2{=}CHCH_2)Bu_3Sn$	13.7	27.4	29.2	9.2		16.2	138.1	109.3
$(CH_2{=}CHCH_2)Bu_2SnCl$	13.6	26.8	27.8	17.5		23.8	134.2	113.3
$(CH_2{=}CHCH_2)BuSnCl_2$	13.5	26.2	26.9	26.5		31.7	130.3	117.4
$(CH_2{=}CHCH_2)SnCl_2Br$	—	—	—	—		36.9	127.4	121.4

[a] ppm from internal TMS (305 K).

ents by the equation $\delta = \delta_0 + kn$, where δ_0 is the chemical shift of the relevant carbon in the Bu_3SnAll substrate. The k-values (ppm/Cl) are 7.7, —3.9 and 4.0 for carbon 1, 2 and 3, respectively, and reflect the downfield shift of carbon 1 and 3 and the upfield shift of carbon 2 on increasing the number n of the substituents. Similar trends were found for analogous silicon derivatives $Me_{3-n}Si(CH_2CH{=}CH_2)Cl_n$ (n = 0—3) [12] and for the proton shifts in the $(CH_2{=}CHCH_2)_{4-n}SnX_n$ series [13]. The variations in the electronic charge density of these carbon atoms can thus be ascribed to the inductive effect of the halide ligands. We also observe that the total electronic charge around the ethylenic carbons 2 and 3 is unaffected by the halide substituents, since the baricentre of the two chemical shifts remains fairly constant. Thus the most significant decreases of the charge density involve carbon 1 (k = 7.7 ppm/Cl downfield) and carbon 1′ (k = 8.6 ppm/Cl downfield), the carbon atoms directly joined to the tin atom. On the other hand, increasing the number of halide ligands raises the acceptor property of the tin centre, as indicated by the stability constants of complexes of the type $R_{4-n}SnCl_{n+1}^-$ (n = 1, 2, 3; R = Me, Bu, Ph) in acetonitrile [14]. The tin-119 NMR data for the compounds $R_{4-n}SnCl_n$ (n = 1—4) [15—17] can also be interpreted in terms of the enhanced ability of tin to accept charge from the ligands as the number of halide ligands is increased.

These effects of the halides seems also to be responsible for the behaviour in the reversible allylstannylation, for both the addition (a) and the elimination (b) paths.



$$\begin{array}{c}
Bu_{3-n}SnCl_n(CH_2CH{=}CH_2) + O{=}C\!<\;(n = 0\text{—}3)\\
(a)\ \downarrow\uparrow\ (b)\ \Delta\\
Bu_{3-n}Cl_nSn{-}O{-}\overset{|}{\underset{|}{C}}{-}CH_2CH{=}CH_2
\end{array}$$

The electron transfer in the cyclic transition state proposed [2] involves nucleophilic attack at the tin centre and this is clearly favoured by an increase in the number of halogens. Thus for the substrates considered the ability to add to the carbonyl compounds increases in the order, $Bu_3SnAll < ClBu_2SnAll < Cl_2BuSnAll$.

The same effects account for the order of ease of the preparation of the allyltins by elimination (path b) from the chlorobutylstannoxy compounds: $Bu_3SnOC < ClBu_2SnOC < Cl_2BuSnOC$.

Recent findings [18] have shown that tetraallyltin is a better allylating agent than tributylallyltin. This result is in agreement with the present observations provided replacement of the butyl by the allyl groups increases the acceptor property of the tin. It has, in fact, been observed that the allyl groups, through an hyperconjugation-like interaction between the Sn—C bond and the double bond, decrease the electron density at the tin atom [19,20]. As expected, the allylating ability of $\mathrm{All_3SnCl}$ seems to be between that of $\mathrm{BuAllSnCl_2}$ and $\mathrm{Bu_2AllSnCl}$.

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