*Journal of Organometallic Chemistry*, 162 (1978) 37—44


# REVERSIBLE ALLYLSTANNATION OF CARBONYL COMPOUNDS; A NEW ROUTE TO MIXED ALLYLTINS VIA ALLYLCARBINOLS

VALERIO PERUZZO and GIUSEPPE TAGLIAVINI

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

(Received June 8th, 1978)

## Summary

Di-n-butylallyltin chloride readily adds to ketones and aldehydes to form organotin alkoxides of the type: n-$Bu_2ClSnOCR'R''(CH_2CH{=}CH_2)$. In some cases this reaction is reversible. Thus, under suitable conditions, alkoxides of the type: n-$Bu_2XSnOCMeR(CH_2CH{=}CH_2)$ (X = n-Bu, Cl; R = Me, i-Pr, i-Bu, t-Bu), obtained by transalkoxylation reactions, furnish ketones and mixed allyltins, n-$Bu_2YSn(CH_2CH{=}CH_2)$ (Y = n-Bu, $CH_2CH{=}CH_2$, Cl). In the light of these findings, allyldialkyl carbinols have been catalytically oxidized to ketones by organotin compounds such as n-$Bu_2XSn(CH_2CH{=}CH_2)$ (X = n-Bu, Cl) and n-$Bu_3SnOCOMe$.

## Introduction

The formation of carbon—carbon bonds using organotin compounds has received occasional attention: α-functionally substituted and β-unsaturated organotin derivatives have been successfully employed [1—5]. In particular allyl-triorganotin compounds are active towards organic substrates containing strongly electrophilic carbon centres such as perhalogenated ketones and aldehydes: when unactivated carbonyl compounds are used, the reactions are incomplete even at high temperature [2,4,5].

Recently, we reported the facile addition of dibutylallyltin chloride to methyl i-propyl ketone [6]. We also found that $(n\text{-}Bu_3Sn)_2O$ and $(n\text{-}Bu_2SnCl)_2O$ react with allyldialkylcarbinols with transfer of the allyl group from the organic substrate to the tin atom probably through an organotin alkoxide intermediate of the type n-$Bu_2XSnOCMeR(CH_2CH{=}CH_2)$ (X = n-Bu, Cl; R = Me, i-Pr, i-Bu) [7].

These observations taken together can be interpreted in terms of a reversible reaction (eq. 1), which is similar to those between ketones and allylic Grignard or zinc reagents [8—10].

$$\text{n-BuXSn}(CH_2CH{=}CH_2) + \begin{matrix} R \\ \diagdown \\ \quad C{=}O \\ \diagup \\ CH_3 \end{matrix} \rightleftharpoons \text{n-}Bu_2XSnOCMeR(CH_2CH{=}CH_2) \qquad (1)$$

In the present work allylstannation reactions have been carried out between dibutylallyltin chloride and several ketones and aldehydes. Conversely mixed allyltins, $n\text{-}Bu_2Sn(X)(CH_2CH{=}CH_2)$ (X = n-Bu, $CH_2CH{=}CH_2$, Cl) have been prepared from alkoxides of type I obtained through a transalkoxylation reaction [11] between allyldialkyl carbinols and organotin methoxides, $n\text{-}Bu_2Sn(OMe)X$ (X = n-Bu, OMe, Cl).

The effect of the R groups (R = Me, i-Pr, i-Bu, t-Bu) in the carbinols used as well as the influence of the electronegative substituent attached to the tin atom has been observed. In addition we show that allyldialkyl carbinols can be catalytically oxidized to ketones in the presence of organotin compounds such as dibutylallyltin chloride, tributylallyltin and tributyltin acetate.

## Experimental

Dibutyltin methoxide and tributyl- and dibutylchloro-tin methoxide were prepared from the appropriate chlorides and sodium methoxide as previously described [12,13].

2-Methyl-4-penten-2-ol, 2,3-dimethyl-5-hexen-3-ol, 2,4-dimethyl-6-hepten-4-ol and 2,2,3-trimethyl-5-hexen-3-ol were prepared from the appropriate ketones and allylmagnesium bromide following the Barbier—Grignard procedure [13].

Tributylallyltin and dibutylallyltin chloride were products of the reactions described in this work.

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 457 spectrophotometer.

### *Addition reactions*

Equimolar amounts of dibutylallyltin chloride and organic substrate were stirred together under the conditions indicated in Table 1.

The progress of the reaction was followed by means of infrared spectroscopy at intervals with thin films of the mixture. A progressive decrease in the stretching band of both C=O (about 1700 $cm^{-1}$) and C=C (1625 $cm^{-1}$) groups, and the appearance, with increasing intensity, of a new band (1640 $cm^{-1}$), attributable to the C=C stretch of a terminal alkenyl linkage removed from tin [4], were observed. In some cases the disappearance of the 1700 and 1625 $cm^{-1}$ bands indicated complete addition, whereas, in other cases, the presence of both 1625 and 1640 $cm^{-1}$ bands, having a constant intensity ratio during the time, revealed the coexistence of allyltin and allylcarbon moieties.

The reaction mixtures were then hydrolyzed by one of the following procedures:

*Procedure A.* The mixture was dissolved in a small volume of $CH_2Cl_2$ and treated with aqueous HCl. The volatile components of the organic layer were transferred in vacuum to a trap cooled at —78°C. The allyl carbinols were recovered by distillation on an Auto Anular Still Perkin—Elmer, Model 251.

*Procedure B.* This was used when high boiling alcohols were formed. The reaction mixture was hydrolyzed with oxalic acid in ethyl ether [2,3] and the dibutyltin oxalate was filtered off. The filtrate was washed with water, then dried, and evaporated to give the carbinol.

The results are listed in Table 1.

TABLE 1

ADDITION REACTIONS OF DIBUTYLALLYLTIN CHLORIDE WITH CARBONYL COMPOUNDS

| Substrate (g) | Reaction conditions (time (h)/temp.) | Yield (%) of add. product [a] | Alcohol obtained b.p. (°C) [b] (Lit. (°C)) [c] | Yield | |
|---|---|---|---|---|---|
| | | | | g | % |
| MeCOMe (0.95) | 24/r.t. | 100 | $Me_2C(OH)CH_2CH=CH_2$ 118–120 (119.5) | 1.24 | 75 |
| $Me_2CHCH_2COMe$ (1.94) | 16/r.t.; 5/55°C; 3½/80°C | 70 | $Me_2CHCH_2C(OH)Me(CH_2CH=CH_2)$ 180 (180–182) | 0.75 | 27 |
| $Me_3CCOMe$ (3.23) | 71/80°C | 50 | $Me_3CC(OH)Me(CH_2CH=CH_2)$ 165–167 (168.4) | 0.70 | 15 |
| $MeCOCH=CH_2$ (3.50) | 8/r.t. | 100 | $MeC(OH)(CH=CH_2)CH_2CH=CH_2$ 134–135 (137) [d] | 4.0 | 71 |
| $MeCOC\equiv CH$ (3.52) | 7/r.t. | 100 | $MeC(OH)(C\equiv CH)CH_2CH=CH_2$ 126–128 | 2.1 | 37 |
| $EtCOC_6H_5$ (1.34) | 33/r.t.; 12½/80°C | 90 | $EtC(OH)(C_6H_5)CH_2CH=CH_2$ 237–239 (238–242) | 0.71 | 40 |
| $Me_2CHCHO$ (4.66) | Exothermic at r.t. | 100 | $Me_2CHCH(OH)CH_2CH=CH_2$ 138–140 (139–141) | 4.23 | 56 |
| $C_6H_{11}CHO$ (3.0) | Exothermic at r.t. | 100 | $C_6H_{11}CH(OH)CH_2CH=CH_2$ 216–218 | 2.55 | 62 |
| $C_6H_5CH_2CHO$ (3.88) | Exothermic at r.t. | 100 | $C_6H_5CH_2CH(OH)CH_2CH=CH_2$ 239–240 | 2.8 | 54 |

[a] Approximate value from IR spectrum. [b] Uncorrected. [c] From Beilstein. [d] See ref. 21.

TABLE 2

REACTIONS BETWEEN n-$Bu_2Sn(OMe)Cl$ AND ALLYLDIALKYLCARBINOLS

| Carbinol | Collection time (h) | Liquid collected [a] (g) | Yield of n-$Bu_2(CH_2{=}CHCH_2)SnCl$ (g (%)) |
|---|---|---|---|
| $MeC(OH)Me(CH_2CH{=}CH_2$ | 12 | 3.8 | 9.5 (65) |
| $MeC(OH)$-i-$Pr(CH_2CH{=}CH_2)$ | 9 | 3.8 | 9.4 (64) |
| $MeC(OH)$-i-$Bu(CH_2CH{=}CH_2)$ | 6 | 4.1 | 10.1 (69) |
| $MeC(OH)$-t-$Bu(CH_2CH{=}CH_2)$ | 1.5 | 4.9 | 12.0 (82) |

[a] Condensed mixture of methanol and the corresponding ketone.

*Synthesis of n-$Bu_2XSn(CH_2CH{=}CH_2)$ compounds (X = Cl, n-Bu, $CH_2{=}CHCH_2$)*

*System di-n-butylchlorotin methoxide/2,2,3-trimethyl-5-hexen-3-ol.* In a three necked flask (50 ml), equipped with condenser, thermometer and separating funnel, 7.2 g (23.7 mmol) of n-$Bu_2SnCl_2$ were added to 7.0 g (23.7 mmol) of n-$Bu_2Sn(OMe)_2$ with stirring at room temperature; 47.4 mmol of n-$Bu_2Sn(OMe)Cl$ were assumed to be formed [12]. The carbinol (6.8 g, 48 mmol) was then added dropwise and the temperature was raised to 165—170°C using an oil bath. Reflux was soon observed and during 1.5 h a liquid sample (4.9 g) consisting of methanol and 2,2-dimethyl-3-butanone was condensed and collected. The residue in the reaction flask was distilled under reduced pressure to give 12 g (82% yield) of n-$Bu_2ClSn(CH_2{=}CHCH_2)$ (b.p. 102—103°C/0.3 mmHg).

The same molar amounts of reagents were used for the systems di-n-butylchlorotin methoxide/2,4-dimethyl-6-hepten-4-ol and 2,3-dimethyl-5-hexen-3-ol/2-methyl-4-hepten-2-ol.

The results, together with the experimental conditions, are shown in Table 2: "collection time" indicates the time during which the methanol/ketone mixture was collected.

*System-tri-n-butyltin methoxide/2,2,3-trimethyl-5-hexen-3-ol.* Following the procedure above, 5.5 g (38.9 mmol) of the carbinol was added to 12.5 g (38.9 mmol) of n-$Bu_3SnOMe$. The mixture was kept at 160—170°C. The transalkoxylation took 7 h and during this time only methanol was collected: the infrared spectrum of the mixture revealed the complete absence of the OH stretching band and the presence of the C=C stretching band at 1640 $cm^{-1}$, thus indicating

TABLE 3

REACTIONS BETWEEN n-$Bu_3Sn(OMe)$ AND ALLYLDIALKYLCARBINOLS

| Carbinol | Transalkoxilation reaction (a) time (h) | Transfer reaction time [b] (h) | Ketone collected (g) | Yield of n-$Bu_3Sn$-($CH_2CH{=}CH_2$) (g (%)) | Yield of n-$Bu_3SnOCMeR$-($CH_2CH{=}CH_2$) (g (%)) |
|---|---|---|---|---|---|
| $MeC(OH)$-i-$Pr(CH_2CH{=}CH_2)$ | 3 | 10 | 1.2 | 6.4 (50) | 4.4 (27) |
| $MeC(OH)$-i-$Bu(CH_2CH{=}CH_2)$ | 5 | 25 | 2.0 | 6.8 (55) | 3.0 (18) |
| $MeC(OH)$-t-$Bu(CH_2CH{=}CH_2)$ | 7 | 6 | 2.8 | 7.9 (62) | 1.5 (9) |

[a] At 160—170°C. [b] At 200—210°C.

TABLE 4

CATALYTIC OXIDATION OF ALLYLDIALKYLCARBINOLS BY $n\text{-}Bu_2XSn(CH_2CH{=}CH_2)$ (X = n-Bu, Cl) AND $n\text{-}Bu_3SnOOCCH_3$ COMPOUNDS

| Carbinol (mmol) | Organotin (mmol) | Time (h) | Ketone collected | | Organotin recovered (%) |
|---|---|---|---|---|---|
| | | | (mmol) | yield (%) | |
| $MeC(OH)\text{-}t\text{-}Bu(CH_2CH{=}CH_2)$ (49.2) | $n\text{-}Bu_3Sn(CH_2CH{=}CH_2)$ (9.6) | 25 | 18.2 | 37 | 95 |
| $MeC(OH)\text{-}i\text{-}Bu(CH_2CH{=}CH_2)$ (59.6) | $n\text{-}Bu_3Sn(CH_2CH{=}CH_2)$ (9.6) | 45 | 15.4 | 26 | 97 |
| $MeC(OH)t\text{-}Bu(CH_2CH{=}CH_2)$ (49.2) | $n\text{-}Bu_2ClSn(CH_2CH{=}CH_2)$ (9.7) | 5 | 37.8 | 77 | 90 |
| $MeC(OH)\text{-}i\text{-}Bu(CH_2CH{=}CH_2)$ (49.2) | $n\text{-}Bu_2ClSn(CH_2CH{=}CH_2)$ (9.7) | 8 | 26.5 | 54 | 85 |
| $MeC(OH)\text{-}i\text{-}Pr(CH_2CH{=}CH_2)$ (48.5) | $n\text{-}Bu_2ClSn(CH_2CH{=}CH_2)$ (9.7) | 11 | 22.3 | 46 | 85 |
| $MeC(OH)\text{-}t\text{-}Bu(CH_2CH{=}CH_2)$ (29.1) | $n\text{-}Bu_3SnOOCMe$ (29.1) | 22 | 22.0 | 75 | 100 |

the formation of the tri-n-butyltin alkoxide: $n\text{-}Bu_3SnOCMe\text{-}t\text{-}Bu(CH_2CH{=}CH_2)$.

The temperature was raised to 200—210°C, and during 7 h, 2.8 g of ketone were condensed. Distillation under reduced pressure gave 7.9 g (62% yield) of tri-n-butylallyltin (b.p. 77—81°C/0.1 mmHg; Lit. [15] 89°C/0.3 mmHg) and 1.5 g of the alkoxide (9% yield, b.p. 90—93°C/0.1 mmHg).

The same molar amounts of reagents were used for the reactions of tri-n-butyltin methoxide with 2,4-dimethyl-6-hepten-4-ol or 2,3-dimethyl-5-hexen-3-ol. Table 3 lists the results; "transfer reaction time" represents the time during which ketone was collected at an appreciable rate, the temperature being kept at 200—210°C.

*System di-n-butyltin dimethoxide/2,2,3-trimethyl-5-hexen-3-ol.* In a 100 ml three necked flask fitted as above described, 22.6 g (76.6 mmol) of dibutyltin dimethoxide were allowed to react with 19.6 g (153.2 mmol) of carbinol at 140°C for 1 h. The mixture was then kept at 170°C for 4 h, and during this time 7.6 g of a mixture of methanol and ketone were collected. Distillation of the reaction residue under reduced pressure gave 17 g (62% yield) of di-n-butyldiallyltin (b.p. 142—146°C/16 mmHg; Lit. [16] 145—146°C/17 mmHg).

*Catalytic oxidation of allyldialkyl carbinols to ketone and propene.* All the carbinols used are oxidized to ketone and propene, in the presence of dibutylallyltin chloride, tri-n-butylallyltin or tri-n-butyltin acetate, while the organotin remains unchanged. The results are given in Table 4.

The reactions were carried out in a three-necked flask equipped with separating funnel and condenser. Mixtures of carbinol and the organotin compounds in a molar ratio 5/1 were allowed to react at 150—180°C. The ketone was continuously condensed and collected, and the formation of propene was revealed by reaction with bromine in carbon tetrachloride (5%).

## Discussion

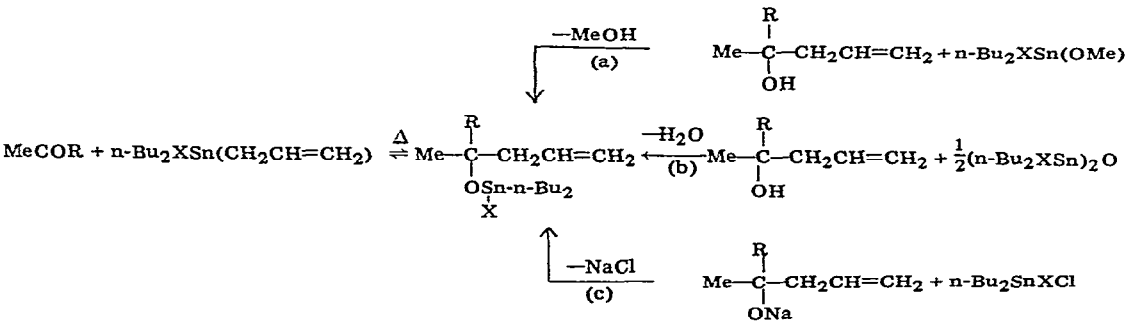
Dibutylallyltin chloride brings about allylstannation of unactivated carbonyl compounds under mild conditions. Such reactions can also be readily carried out in solution (e.g. in $CHCl_3$, $CCl_4$, MeCN) [17], and in this respect can be regarded as analogues to addition reactions of unsaturated organic compounds with lithium-, magnesium- and zinc-organic derivatives [18,19]. In our case the active reagent is the organotin substrate, which because of the presence of the chloride ligand, can coordinate the carbonyl group [14]: thus a coordination complex $\geqslant Sn \leftarrow O=C \lessdot$ [20] may facilitate the overall reaction. Dibutylallyltin chloride also adds to epoxides [17] in the presence of a Lewis acid such as $ZnCl_2$ in a way similar to the addition of Grignard reagents [18].

Aldehydes react exothermally very soon after mixing. The ketones take a much longer time, and the reaction seems to be hindered by the presence of bulky groups joined to the carbonyl carbon. An acceptable addition rate velocity was observed with the i-butyl and t-butyl methyl ketone at 80°C. But the formation of the alkoxide I is disfavoured by the increase of temperature, and the addition may be incomplete because an equilibrium is reached. Because of this equilibrium in many cases separation of alkoxide I by distillation fails, heating furnishing only the initial reagents.

The features of the preparation of mixed allyltins which are depicted in Scheme 1 are a consequence of the above findings. Routes (b) and (c) have been previously described [7], whereas route (a) was employed in the present work.

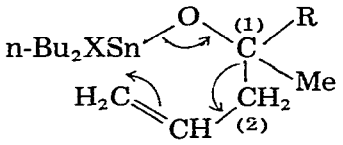
This route to $n\text{-}Bu_2SXSn(CH_2{=}CHCH_2)$ derivatives (X = n-Bu, $CH_2{=}CHCH_2$, Cl), takes place through a transalkoxylation followed by elimination. From the results it is clear that the velocity of both reactions is influenced by the R groups. The velocity of the transalkoxylation decreases in the order: R = Me > i-Pr > i-Bu > t-Bu. This may be accounted for by the acidity of the employed carbinols which decreases in the same order, as well as by steric hindrance between the bulky R group and the butyl groups around the tin atom. The velocity of the elimination reaction decreases in the reverse order. An explanation of such behaviour may be given in terms of a transition state such as that has been

SCHEME 1




(X = n-Bu, Cl; R = Me, i-Pr, i-Bu, t-Bu)

previously suggested for reversible Grignard reactions [8,9]:



Breaking of the C(1)—C(2) bond may be facilitated by the increase of the $+I$ inductive effect of the R group. It is relevant to note that alkoxides of this type, with strong electron-withdrawing perhalogenated groups attached to the C(1) carbon, can be distilled without any elimination [4]. Another factor may be found in the energy gain involved in rehybridizing C(1) from $sp^3$ to $sp^2$, which is greater when R is a bulky group. The proposed transition state, which represents an internal nucleophilic substitution, also accounts for the increase of the velocity on passing from X = n-Bu to Cl.

This procedure for preparing mixed allyltins is feasible provided that the formation of the alkoxide does not give rise to an acidic product which can cleave the tin—allyl bond (cf. Scheme 1). Because of the greater acidity of water than of methanol and the lower rate of production of the alkoxide, path (b) of Scheme 1 gives lower yields than path (a). This is clearly shown by the reaction of 2,2,3-trimethyl-5-hexen-3-ol and 2,3-dimethyl-5-hexen-3-ol and tri-n-butyltin acetate (see Table 4), in which the overall reaction furnishes only propene and ketone the organotin compound is completely recovered. Acetic acid must be the product responsable for cleavage of the tin—allyl bond, as follows:

$$n\text{-}Bu_3SnOOCMe + HOCMeR(CH_2CH{=}CH_2) \rightarrow n\text{-}Bu_3SnOCMeR(CH_2CH{=}CH_2) + MeCOOH$$

$$n\text{-}Bu_3SnOCMeR(CH_2CH{=}CH_2) \rightarrow n\text{-}Bu_3Sn(CH_2CH{=}CH_2) + MeRC{=}O$$

$$n\text{-}Bu_3Sn(CH_2CH{=}CH_2) + MeCOOH \rightarrow CH_2{=}CHCH_3 + n\text{-}Bu_3SnOOCMe$$

This represents a catalytic oxidation of allyldialkyl carbinols to ketones: it is best performed with $n\text{-}Bu_2XSn(CH_2CH{=}CH_2)$ compounds (cf. Table 4). The X and R groups again affect the reaction velocity in the order mentioned above.

It is noteworthy that organotin substrates having a strongly acidic character, which do not react with the acidic proton of the carbinol, do catalyse the usual formation of alkenes. This has been verified for the reaction of $n\text{-}BuSnCl_3$ with tertiary carbinols [17].

## Acknowledgement

We are most grateful to Mr. D. Marton for technical assistance and to CNR (Rome) for financial support.

## References

1 S.V. Ponomarev and I.F. Lutsenko. Zh. Obshch. Khim., 34 (1964) 3450; Chem. Abstr., 62 (1965) 2787f.

2 K. Konig and W.P. Newmann, Tetrahedron Lett., (1967) 495.

3 J.G. Noltes, F. Verbeek and H.M.J.C. Creemers, Organometal. Chem. Syn., 1 (1970/1972) 57.
4 E.W. Abel and R.J. Rowley, J. Organometal. Chem., 84 (1975) 199.
5 C. Servens and M. Pereyre, J. Organometal. Chem., 26 (1971) C4.
6 G. Tagliavini, V. Peruzzo, G. Plazzogna and D. Marton, Inorg. Chim. Acta, 24 (1977) L47.
7 G. Tagliavini, V. Peruzzo and D. Marton, Inorg. Chim. Acta, 26 (1978) L4.
8 R.A. Benkeser and W.E. Broxterman, J. Amer. Chem. Soc., 91 (1969) 5162.
9 P. Miginiac, Bull. Soc. Chim. France, (1970) 1077.
10 F. Barbot and P. Miginiac, J. Organometal. Chem., 132 (1977) 445.
11 A.J. Bloodworth and A.G. Davies, in A.K. Sawyer (Ed.), Organotin Compounds, Vol. I, Marcel Dekker, New York, 1971, p. 159.
12 A.G. Davies and P.G. Harrison, J. Chem. Soc. C, (1976) 298.
13 D.L. Alleston and A.G. Davies, J. Chem. Soc., (1962) 2050.
14 M.P. Dreyfuss, J. Org. Chem., 28 (1963) 3269.
15 W.T. Schwartz Jr. and H.W. Post, J. Organometal. Chem., 2 (1964) 357.
16 W.J. Jones, W.C. Davies, S.T. Bowden, C. Edwards, V.E. Davies and L.H. Thomas, J. Chem. Soc., (1947) 1446.
17 V. Peruzzo and G. Tagliavini, unpublished results.
18 G. Courtois and L. Miginiac, J. Organometal. Chem., 69 (1974) 1 and ref. therein.
19 T.A. Killinger, N.A. Boughton, T.A. Runge and J. Wolinsky, J. Organometal. Chem., 124 (1977) 131 and ref. therein.
20 T.F. Bolles and R.S. Drago, J. Amer. Chem. Soc., 88 (1966) 3121.
21 A. Viola, E.J. Iorio, K.K. Chen, G.M. Glover, U. Nayak and P.J. Kocienski, J. Amer. Chem. Soc., 89 (1967) 3462.