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Preparation of $n\text{-}Bu_3SnCH_2CH{=}CH(CH_3)$ and $n\text{-}Bu_2(Cl)SnCH_2CH{=}CH(CH_3)$ by Elimination Reaction of Alkoxides of the Type $n\text{-}Bu_2(X)Sn{-}O{-}C(CH_3)(i\text{-}C_3H_7)CH(CH_3)CH{=}CH_2$ (X = n-Bu and Cl)

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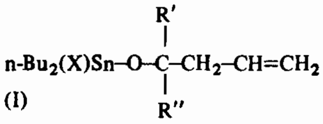
Recently it has been shown that di-n-butylallyltin chloride allows facile allylstannation of carbonyl compounds [1–3]. In addition it has been pointed out that organotin alkoxides of the type:

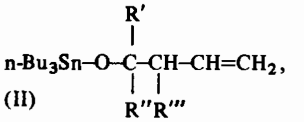


$$n\text{-}Bu_2(X)Sn{-}O{-}\overset{R'}{\underset{R''}{C}}{-}CH_2{-}CH{=}CH_2 \qquad (X = n\text{-}Bu, Cl)$$

(I)

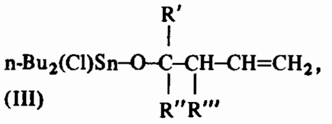
which are the products of the addition reaction, can reversibly form $n\text{-}Bu_2(X)SnCH_2CH{=}CH_2$ by elimination of the unsaturated organic compound R′COR″ [2, 3].

As a consequence of these findings we should expect that organotin alkoxides II and III,



$$n\text{-}Bu_3Sn{-}O{-}\overset{R'}{\underset{R''}{C}}{-}\underset{R'''}{CH}{-}CH{=}CH_2,$$

(II)



$$n\text{-}Bu_2(Cl)Sn{-}O{-}\overset{R'}{\underset{R''}{C}}{-}\underset{R'''}{CH}{-}CH{=}CH_2,$$

(III)

having an α-substituted allyl group joined to the tertiary carbon atom, could undergo an elmination reaction to give the corresponding ketone R′COR″ and the mixed 2-butenyl-butyltins, $n\text{-}Bu_3SnCH_2CH{=}CHR'''$ and $n\text{-}Bu_2(Cl)SnCH_2CH{=}CHR'''$, respectively. Thus we have prepared by transalkoxilation reaction between 2,3,4-trimethyl-5-hexen-3-ol and tri-n-butyltin- and di-n-butylchlorotin-methoxide the two alkoxides II and III having $R'' = (CH_3)_2CH$ and $R' = R''' = CH_3$. These, on heating, furnish the two mixed 2-butenyl-butyltins, $n\text{-}Bu_3SnCH_2CH{=}CHCH_3$ (IV) and $n\text{-}Bu_2(Cl)SnCH_2CH{=}CHCH_3$ (V) as *cis* and *trans*-isomer mixtures.

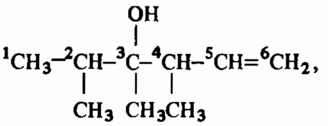
It is to be pointed out that this work deals with a simple route to new mixed substituted allyl-tins and shows the organometallic synthetic rôle of the found 'reversible allylstannation'.

Experimental

Preparation of 2,3,4-Trimethyl-5-hexen-3-ol

This compound was prepared by reacting crotyl bromide (100 g, 0.75 mol) and magnesium turnings (27.3 g, 1.12 mol) under reflux of diethyl ether as previously described [4]. The obtained crude liquid distilled twice under reduced pressure gave a final sample of 20.6 g (26% yield) of the title compound, b.p. 69–70 °C/16 mm (Lit., 63 °C/15 mm [4]).

The IR spectrum registered as a thin film (KBr optics) shows the following relevant bands: ν_{OH} at 3480 cm^{-1} and $\nu_{C=C}$ at 1635 cm^{-1}. The ^1H NMR spectrum of the carbinol,



$${}^1CH_3{-}{}^2\underset{CH_3}{CH}{-}{}^3\overset{OH}{\underset{CH_3}{C}}{-}{}^4\underset{CH_3}{CH}{-}{}^5CH{=}{}^6CH_2,$$

has been registered by using a Bruker WH 90 operating in FT mode using TMS as internal standard. It clearly shows an ABC pattern in the range 6.02–4.91 ppm typical of the terminal ${}^5CH{=}{}^6CH_2$ group, a multiplet centered at 2.39 ppm of the proton in the position 4, and another multiplet in the range 1.92–1.65 ppm for the i-propyl proton 2. The singlet of the OH proton is centered at 1.25 ppm, while all CH_3 protons resonate in the interval 1.14–0.84 ppm.

Preparation of 2-Butenyl-tri-n-butyltin from Tri-n-butyltin Methoxide and 2,3,4-Trimethyl-5-hexen-3-ol

In a three necked flask (50 ml) equipped with condenser, thermometer and separating funnel, 9.49 g (29.5 mmol) of $n\text{-}Bu_3SnOMe$ were mixed with 4.2 g (29.5 mmol) of the carbinol under stirring. The temperature was raised to 190–200 °C. Over 22 hours a mixture of methanol and 2-methyl-buten-3-one (2.2 g) was condensed and collected. The residue in the reaction flask was distilled under reduced pressure to give 6.5 g (63% yield) of $n\text{-}Bu_3SnCH_2CH{=}CH(CH_3)$ boiling at 98 °C/0.1 mm.

The IR spectrum registered on a thin film (KBr optics) shows two medium bands centered at 1655 and 1640 cm^{-1} attribuable to two C=C stretching vibrations dealing with a *cis*- and *trans*-isomeric mixture. The presence of *cis*-2-butenyltributyltin together with *trans*-2-butenyltributyltin has been confirmed by both ^1H and ^{13}C NMR spectra registered in $CDCl_2$ using TMS as internal standard.

^1H NMR spectrum: a complex multiplet in the range 4.88–5.76 ppm for the CH=CH protons is observed. This is centered in the same interval found for the *cis*- and *trans*-2-butenyl-trimethyltin [5].

^{13}C NMR spectrum (CH_3–(2)CH=(3)CH–CH_2–$SnBu_3$): the 2 and 3 olefinic carbons have four resonance peaks, two of which at 129.1 (152) and 130.0 (150) ppm are attribuable to the carbon 3, the others at 117.9 (155) and 119.9 (150) ppm to the carbon 2 (then coupling constants $^1J_{^{13}C-^1H}$ (Hz) are in brackets).

Preparation of 2-Butenyl-di-n-butylchlorotin from Di-n-butylchlorotin Methoxide and 2,3,4-Trimethyl-5-hexen-3-ol

Following the above procedure, 4.51 g (14.9 mmol) of n-Bu_2SnCl_2 were added to 4.38 g (14.9 mmol) of n-$Bu_2Sn(OMe)_2$ under stirring at room temperature. 29.8 mmol of n-$Bu_2Sn(OMe)Cl$ were assumed to be formed [6]. Then the carbinol (4.24 g, 29.8 mmol) was added dropwise and the temperature was raised to 165–170 °C. Over 4 hours a liquid sample (2.7 g), consisting of a mixture of methanol and 2-methyl-buten-3-one, was condensed and collected.

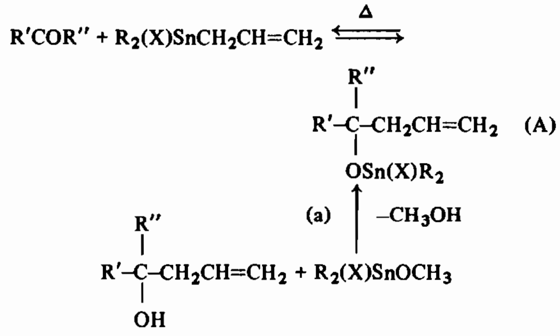
The residue was distilled under reduced pressure to give 5.7 g (59% yield) of a mixture of *cis*-2-butenyl-dibutylchlorotin and *trans*-2-butenyl-dibutylchlorotin, b.p. 102 °C/0.2 mm.

The IR spectrum shows two bands at 1655 and 1642 cm^{-1} dealing with two C=C stretching vibrations.

The ^{13}C NMR spectrum (CH_3–(2)CH=(3)CH–CH_2–$SnBu_2Cl$) shows four resonance peaks attribuable to the olefinic carbon 2 and 3. They are centered at 125.1 (155) and 126.0 (152) ppm for carbon 3 and at 122.1 (156) and 124.1 (152) ppm for carbon 2 (the coupling constants $^1J_{^{13}C-^1H}$ (Hz) are in brackets).

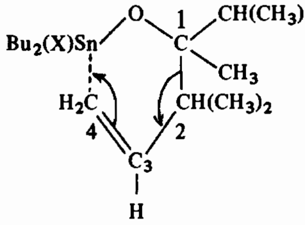
Discussion

The 2-butenyltin synthesis is based on the previously found 'allylstannation reversibility' [2, 3], which can be described by the following reactions:



Alkoxides of the type (A) may be formed through a *trans*-alkoxilation reaction described by step (a). These, on heating, give the allyltin derivatives by elimination of ketone. Thus alkoxides having a methylallyl group joined to the tertiary carbon atom, prepared from 2,3,4-trimethyl-5-hexen-3-ol and n-$Bu_3Sn(OCH_3)$ and n-$Bu_2(Cl)Sn(OCH_3)$, furnish an isomer mixture of *cis*- and *trans*-2-butenyltributyltin and *cis*- and *trans*-2-butenyl-dibutylchlorotin respectively.

These findings confirm that the elimination reaction should go through a cyclic transition state as previously suggested [3],



in which nucleophilic attack of the carbon 4 to the tin atom takes place together with the breaking of the Sn–O and C(1)–C(2) bonds. In this way *cis*- and *trans*-isomers of 2-butenyltins are produced as is revealed on following the reaction by scanning the IR spectra in the range of the $\nu_{C=C}$ absorption (1640–1655 cm^{-1}) [5].

Both ^1H and ^{13}C spectroscopy give a better description of these new compounds. The proton resonance of compound IV displays a complex pattern for the olefinic protons in the line of that found for the butenyltrimethyltin isomers [5]. More useful information comes from the proton decoupled ^{13}C NMR spectra studied in the resonance range of the olefinic carbon atoms (*cf.* Fig. 1). For both compounds each 2 and 3 carbon atom shows two well resolved resonance lines relative to the *cis*- and *trans*-isomers. The two peaks at higher fields for both compounds may be assigned to the carbon 2, those at lower fields to the carbon 3, since these carbons bear a relative negative and positive charge respectively, as is known for allylic moieties bound to the tin atom [7]. This assignment as well as that of the *trans*-isomer resonance lines at lower fields is in agreement with the ^{13}C NMR pattern of some linear 2-alkenes [8–10]. As a result the *trans/cis* ratio is about 65/35 and 50/50 for compound IV and V respectively.

It is to be pointed out (*cf.* Fig. 1) that on passing from compound IV to V the splitting between each couple of lines remains constant (0.9 ppm for carbon 3 and 2.0 ppm for carbon 2), while there is a noticeable change in the chemical shift for both carbons (4.0 ppm upfield and 4.2 ppm downfield for the 3 and 2 carbons respectively) which becomes nearly similar in the 2-butenyldibutylchlorotin. This

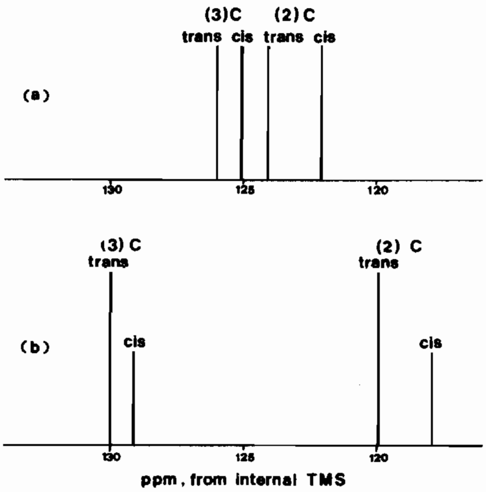


Fig. 1. Schematic diagram of the proton decoupled ^{13}C NMR spectra of CH_3–(2)CH=(3)CH–CH_2SnBu_2X (a, X = Cl; b, X = Bu) in the range of the olefinic carbon resonance.

behaviour may be ascribed to the electron withdrawing ability of the chlorine substituent which can modify the charge distribution of the double bond without affecting the geometrical arrangement of the olefinic moiety. The constant separation of the couple peaks of the *cis*- and *trans*-isomer in both compounds supports this view.

These results are promising for future development to new allyl-substituted tin compounds and work is now in progress in this laboratory.

Acknowledgments

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