Journal of Organometallic Chemistry, 204 (1981) 191—196
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

REVERSIBLE CROTYLSTANNATION OF CARBONYL COMPOUNDS. CROTYLSTANNATION ABILITY OF $Bu_{3-n}Cl_nSnCH_2CH{=}CHCH_3$ (n = 0, 1, 2) COMPOUNDS TOWARDS ACETONE AND BENZALDEHYDE AND ^{13}C NMR CHARACTERIZATION

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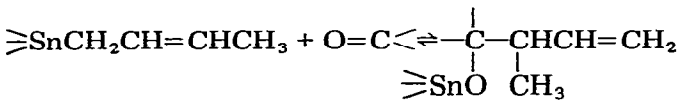
(Received June 30th, 1980)

Summary

The crotylstannation reaction:



has been found to be reversible. The compounds *trans/cis*-$Bu_{3-n}Cl_nSnCH_2CH{=}CHCH_3$ (n = 0, 1, 2) have been prepared by elimination reactions of organostannoxy compounds, $Bu_{3-n}Cl_nSn{-}O{-}C(Me)(i\text{-}Pr)CH(Me)CH{=}CH_2$, which were synthesized by means of transalkoxylation between $Bu_{3-n}Cl_nSn(OMe)$ compounds and *threo/erithro*-2,3,4-trimethyl-5-hexen-3-ol. Under the conditions used the elimination occurs stereospecifically and with complete allylic rearrangement. The ability of the organostannoxy compounds to yield crotylbutylchlorotins via elimination increases in the order, $Bu_3Sn{-}O{-}C{\equiv} < Bu_2ClSn{-}O{-}C{\equiv} < BuCl_2Sn{-}O{-}C{\equiv}$. In the addition reactions, the sequence of increasing reactivity is $Bu_3SnCrot < ClBu_2SnCrot < Cl_2BuSnCrot$ (Crot = crotyl). The ^{13}C NMR spectra of the compounds made reveal that the chemical shifts of the allylic carbon atoms are related to the inductive effects of the chloro-substituents.

Introduction

During our earlier studies on the reversible allylstannation [1—5] we examined the following reactions:

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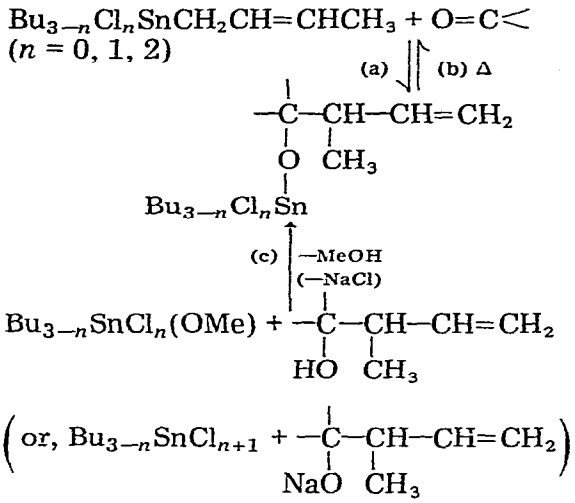


We prepared crotyltins of the type $Bu_{3-n}Cl_nSnCH_2CH{=}CHCH_3$ (n = 0, 1, 2) through reaction c followed by b. In addition we examined the stereochemistry of this elimination, which leads to a mixture of *trans*- and *cis*-crotyltin isomers starting from the 2,3,4-trimethyl-5-hexen-3-ol containing both *threo* and *erithro* isomers.

The crotylstannation abilities of these substrates towards acetone and benzaldehyde have now been compared, data being available previously only for the system $Bu_3SnCrot$/PhCHO [6,7]. The electron densities at the crotyl carbon atoms, which are expected to be modified by the halo-substitution, have been examined by ^{13}C NMR spectroscopy.

Experimental

Materials

2,3,4-trimethyl-5-hexen-3-ol was prepared as previously described [8]. Commercial samples of acetone and benzaldehyde were of reagent grade, freshly distilled before use. IR spectra were recorded on a Perkin-Elmer Model 599B spectrophotometer.

Carbon-13 NMR spectra were recorded at 305°K on a Burker WH 90 spectrometer operating in the FT mode.

Elimination reactions

2-Butenyl-n-butyldichlorotin. Sodium (1.4 g, 61 mmol) was added to a solution of 20 ml of 2,3,4-trimethyl-5-hexen-3-ol in 20 ml of benzene. The mixture was refluxed until complete disappearance of the sodium. The sodium alcoholate solution was added to $BuSnCl_3$ (16.9 g, 60 mmol). After 1 h the sodium chloride was separated by centrifugation and washed twice with 10 ml portions of CH_2Cl_2. All the liquid fractions were placed together in a three necked flask (50 ml) equipped with a condenser, thermometer and separating funnel. The solutions was heated for 1 h at 100—120°C, during which the solvent (benzene, dichloromethane and i-propylmethylketone) distilled out. The formation of the

ketone reveals that the elimination from 2,3,4-trimethyl-3-butyldichlorostannoxy-5-hepten takes about one hour at 100—120°C.

The residue was distilled under reduced pressure to give 13.4 g (74% yield) of n-$BuCl_2SnCH_2CH{=}CHCH_3$, b.p. 92°C/0.06 mm Hg.

2-Butenyl-di-n-butylchlorotin. To 7.4 g (25 mmol) of $Bu_2Sn(OMe)_2$ contained in a three necked flask (50 ml) equipped with a condenser, thermometer and separating funnel, 7.6 g (25 mmol) of Bu_2SnCl_2 were added at room temperature with stirring: 50 mmol of n-$Bu_2Sn(OMe)Cl$ were assumed to be formed [9]. 7.6 g (53.4 mmol) of 2,3,4-trimethyl-5-hexen-3-ol were then added dropwise and the temperature was raised to 170—180°C. A distillate (2.5 g) consisting of methanol and methyl-i-propylketone was collected during 4 h. The elimination occurs at 140—180°C in this case.

The liquid residue in the reaction flask was distilled under reduced pressure to give 12.5 g (38.6 mmol, 77% yield) of 2-butenyl-di-n-butylchlorotin, b.p. 102°C/0.15 mm Hg.

2-butenyl-tri-n-butyltin. Following the above procedure, a mixture of equimolar amounts (49.5 mmol) of Bu_3SnOMe (15.9 g) and carbinol (7 g) was kept at 190—200°C. During 20 h a mixture of methanol and ketone was collected. Distillation under vacuum of the liquid residue gave 6.5 g (38% yield) of n-$Bu_3SnCH_2CH{=}CHCH_3$, b.p. 100°C/0.04 mm Hg.

Addition reactions

Equimolecular amounts (5—10 mmol) of the organotin and carbonyl compounds (acetone or benzaldehyde) were mixed. The reaction was monitored by recording the IR spectrum of the mixture at appropriate times. The disappearance of the bands at 1720 (ν(C=O)), 1655 (ν(C=C) *trans*-crotyl group joined to a tin atom) and 1640 cm^{-1} (ν(C=C), *cis*-crotyl group joined to a carbon atom) indicate the extent of reaction.

The results together with the experimental conditions are given in Table 1. For comparison, data for the previously described crotyl-tributyltin/benzaldehyde system [6,7] are also given.

TABLE 1

RESULTS FOR THE ADDITION REACTION OF $Bu_{3-n}SnCl_nCH_2CH{=}CHCH_3$, PhCHO AND ACETONE

Crotyltin	Carbonyl compound	
	C_6H_5CHO	$(CH_3)_2CO$
$Bu_3SnCrot$	200°C, 3 h [a] (60% yield)	no reaction
$Bu_2ClSnCrot$	60°C, 24 h (complete reaction)	60°C, 26 h (40% yield) [b]
$BuCl_2SnCrot$	25°C, few min (exothermic complete reaction)	r.t., 10 h (60% yield) [b]

[a] See reference 6. [b] Approximate yield as determined from IR spectrum.

TABLE 2

CARBON-13 CHEMICAL SHIFTS OF THE CROTYLTIN COMPOUNDS [a]

Compound	4′ CH_3	3′ CH_2	2′ CH_2	1′ CH_2		1 CH_2	2 CH	3 CH	4 CH_3
$Bu_3SnCrot$	13.7	27.5	29.3	9.4	*trans*	14.2	130.2	120.0	17.8
	13.7	27.4	29.2	9.2	*cis*	10.2	129.3	117.9	12.4
	13.7	27.3	28.3	8.8					
$Bu_2ClSnCrot$	13.6	26.8	27.9	17.5	*trans*	22.2	126.2	124.2	17.8
					cis	18.2	125.3	122.2	12.7
$BuCl_2SnCrot$	13.5	26.3	27.0	26.5	*trans*	30.8	122.6	128.6	17.9
					cis	26.7	121.7	126.6	13.0

[a] ppm from internal TMS.

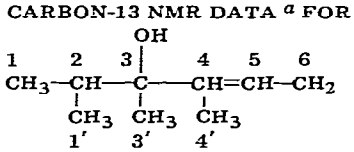
^{13}C *NMR data*

The ^{13}C NMR chemical shifts (ppm) of the prepared compounds in $CDCl_3$ solution (about 0.5 *M*) are listed in Table 2. The crotyl carbon resonances are split into doublets. The peaks at higher fields are assigned to the *cis*-isomer and those at lower fields to the *trans*-isomer, in agreement with the pattern for some linear 2-alkenes [10—12]. Thus, from the intensities of these peaks, the *trans/cis* ratio was found to be 2/1 for all three prepared compounds.

The carbon-13 NMR data for 2,3,4-trimethyl-5-hexen-3-ol are given in Table 3. Owing to the presence of the *threo* and *erythro* isomers the signals are split into doublets with an intensity ratio 2/1. The peak assignements (cf. Table 3) and consequently the allocation of a 2/1 *threo/erythro* isomer ratio, were made *a posteriori* following the preparation of the crotyltins from this carbinol. In this reaction the *trans* and *cis* isomers come from the *threo* and *erythro* forms, respectively (see discussion).

TABLE 3

CARBON-13 NMR DATA [a] FOR 2,3,4-DIMETHYL-5-HEXEN-3-OL

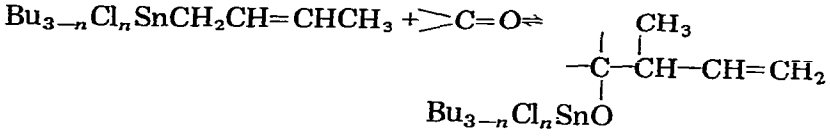


Isomer	Carbon atom								
	1	1′	2	3	3′	4	4′	5	6
threo	17.5 [b]	16.6	34.6	75.4	19.4	44.8	14.7	140.7	115.7
erythro	17.3 [b]	16.6	34.2	75.4	19.8	45.0	14.0	141.2	115.2

[a] ppm from internal TMS. [b] The values for carbon atom 1 may be exchanged with those for carbon atom 1′.

Discussion

The results can be interpreted in terms of "reversible crotylstannation" as follows:



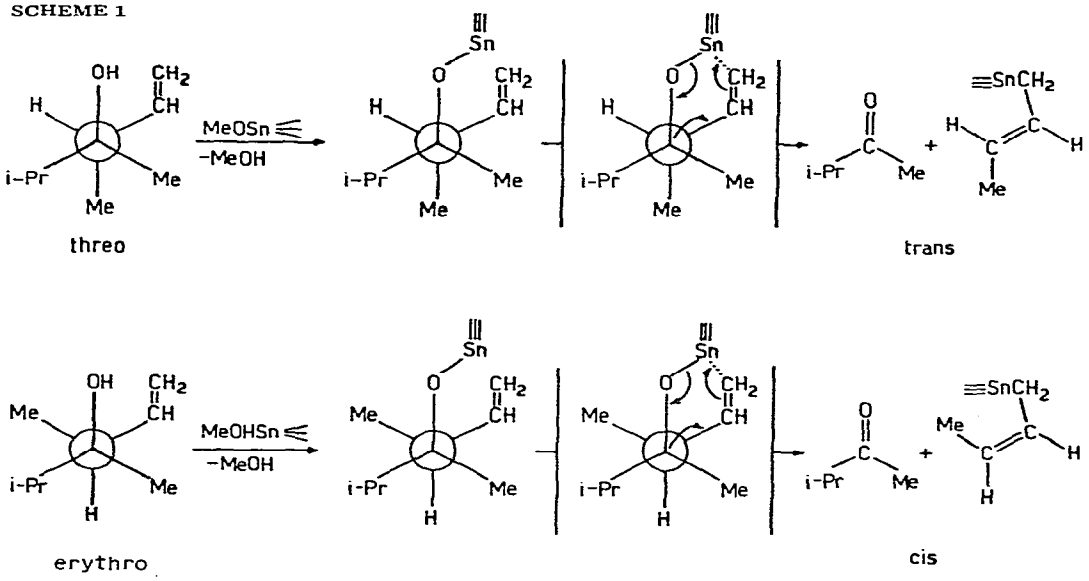
(n = 0, 1, 2)

This is similar to the process observed for mixed butylchloroallyltins [2—4].

The following features of the additions are of interest: (i) The reaction conditions (time, temperature, yield) which have to be used for each system (cf. Table 1) indicate that the addition ability of the examined crotyltins to acetone and benzaldehyde follows the order: $Bu_3SnCrot < Bu_2ClSnCrot < BuCl_2SnCrot$ (1). This behaviour is similar to that found in the case of butylchloroallyltins [4]. (ii) Addition occurs with complete allylic rearrangement; this is in line with many findings: e.g., the addition of aldehydes to crotyltributyltin [6,7] and the insertion of SO_2 [13] and $(SCN)_2$ [14] into crotyltrimethyltin. Allylic rearrangement also predominates in the protic cleavage of crotyltrimethyltin [15].

As for the elimination, it can be concluded that under the conditions used *, which bring about irreversible elimination of the yielded ketone, complete rearrangement of the allylic group also occurs. It may be inferred that the ability of the adducts to yield the initial products through the reverse reaction follows the order: $Bu_3Sn—O—C\equiv < Bu_2ClSn—O—C\equiv < BuCl_2Sn—O—C\equiv$ (2).

SCHEME 1



* It should be remembered that ketone is irreversible eliminated upon heating the organostannoxy adduct at the appropriate temperature.

As in the case of additions (see order (1)), eliminations depend upon the inductive effect of the substitutents. The trend of the ^{13}C NMR chemical shifts (cf. Table 2) which are linearly related to the number of chlorine substitutents, also depends on the same inductive effect.

The eliminations give rise to a mixture of *trans* and *cis*-isomers in the ratio 2/1 in all examined cases. Considering that the carbinol used is a mixture of two isomers, *threo* and *erythro*, the formation of the two geometrical organotin isomers can be explained by the following scheme, which emphasizes the stereospecificity of the eliminations.

The allylic rearrangement and the stereospecificity support the proposed pericyclic mechanism. It may be seen that the *threo*-carbinol leads to the *trans*-isomer whereas the *erythro* carbinol leads to the *cis*-isomer. Thus, since the ratio of the two configurational isomers is 2/1, it must be concluded that the carbinol mixture consist of about 66% and 33% of the *threo* and *erythro* isomer, respectively.

Acknowledgements

We thank the CNR (Rome) for financial support.

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