

ALLYLIC REARRANGEMENT IN REDISTRIBUTION REACTIONS. THE SYSTEM *cis/trans*- n -Bu₃SnCH₂CH=CHCH₃/ n -Bu₂SnCl₂

ALESSANDRO GAMBARO

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

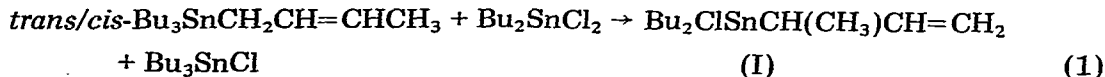
DANIELE MARTON and GIUSEPPE TAGLIAVINI

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

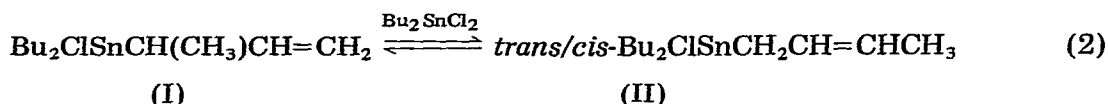
(Received November 4th, 1980)

Summary

Allylic rearrangement occurs in the solvent-free redistribution reaction between *trans/cis*-Bu₃SnCH₂CH=CHCH₃ and Bu₂SnCl₂:



Subsequent isomerization of I is catalyzed by Bu₂SnCl₂ (see eq. 2) to an equilibrium mixture of *cis*-II (72–74%) *trans*-II (12–14%) and I (14–16%) at 30°C as shown by ¹³C NMR spectroscopy:



¹³C NMR spectra also reveal that the terminal olefinic carbon in I is involved in an exchange process. The mechanisms of both reactions probably involve cyclic transition states.

Introduction

No study has been made hitherto of redistribution reactions involving substituted allyltins. Isomerization of allyltins has been previously reported: for example, Kuivila et al. [1] found that in a chromatograph Me₃SnCl catalyses the isomerization of 1-buten-3-yltrimethyltin to a *trans/cis* (25/75) mixture of Me₃SnCH₂CH=CHCH₃. In addition, it has been generally found that α-methylallyltin species readily isomerise to *trans/cis*-crotyl mixtures in kinetically con-

trolled processes [1–3]. We now report a study of the reaction between $\text{Bu}_3\text{SnCH}_2\text{CH}=\text{CHCH}_3$, and Bu_2SnCl_2 , in which both redistribution and allylic rearrangement are operating.

Experimental

Butenyltributyltins

Mixtures of *trans*- and *cis*-2-butenyltributyltin were prepared by two different procedures.

Procedure A. 2-butenyltributyltin (*trans/cis* = 9/11) was prepared from tributyltin chloride and crotylmagnesium bromide in diethyl ether. The Grignard compound was made from commercially available crotyl bromide (from Ega Chemie, Germany) which consisted of a mixture of 3-bromo-1-butene (15%) and 1-bromo-2-butene (85%).

Procedure B. 2-butenyltributyltin (*trans/cis* = 2/1) was synthesized via an elimination reaction from 2,3,4-trimethyl-3-tributylstannoxy-5-heptene as previously reported [4,5].

In both cases, the *trans/cis* ratio was determined by ^{13}C NMR spectroscopy from the integration of the olefinic crotyl carbon atoms [6].

Commercially available dibutyltin dichloride was purified by re-crystalliza-

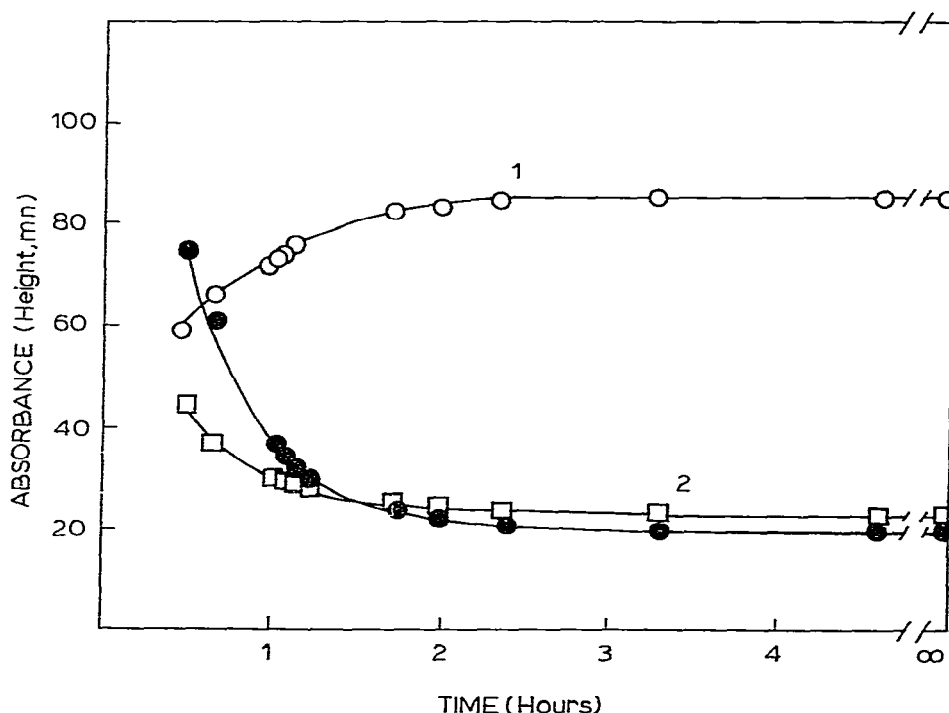


Fig. 1. Plots of intensities of $\nu(\text{C}=\text{C})$ with time for the reaction between $\text{Bu}_3\text{SnCH}_2\text{CH}=\text{CHCH}_3$ (13.5 mmol: *trans/cis* = 9/11) and Bu_2SnCl_2 (29.7 mmol). 1. $\nu(\text{C}=\text{C})$ of a *cis*-crotyl group in both 2-butenyltributyltin and 2-butenyldibutylchlorotin. 2. $\nu(\text{C}=\text{C})$ of an α -methylallyl group joined to a tin atom in methylallyldibutylchlorotin. 3. $\nu(\text{C}=\text{C})$ of a *trans*-crotyl group in both 2-butenyltributyltin and 2-butenyldibutylchlorotin.

tion from petroleum ether (b.p. 40–60°C).

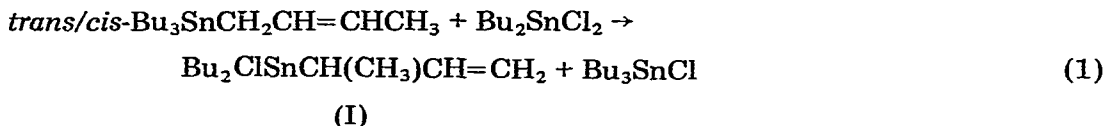
IR spectra were recorded on a Perkin-Elmer Model 599B spectrophotometer using KBr optics. ^{13}C NMR spectra were recorded at a fixed temperature (303 K) on a Bruker WH 90 spectrometer operating in the FT mode.

Redistribution reactions

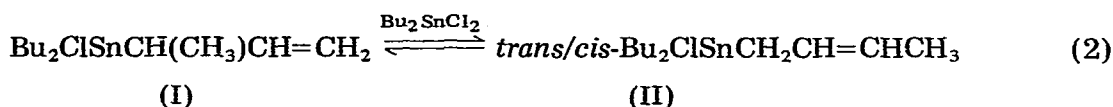
Five reactions involving different ratios of dibutyltin dichloride (III) and 2-butenyltributyltin (IV), were performed (III/IV ratios, 2.2 and 1.4 for a 9/11 *trans/cis* mixture and 1.5, 1.1 and 0.24 for a 2/1 *trans/cis* mixture; amount of IV (mmol) = 29.7, 29.9, 13.1, 5.8 and 2.3, respectively). Stirring for 20–30 min at room temperature gave homogeneous system. The progress of the reaction was then followed by infrared spectroscopy using liquid cells (0.2 mm thickness). The intensities of the double bond stretching frequencies were noted as a function of time. The frequencies used were 1625 cm^{-1} , $\nu(\text{C}=\text{C})$ of an α -methylallyltin compound [2,3], 1645 cm^{-1} , $\nu(\text{C}=\text{C})$ of a *cis*-crotyl group and 1655 cm^{-1} , $\nu(\text{C}=\text{C})$ of a *trans*-crotyl group in 2-butenyltin species [5]. Data for a typical reaction are shown in Fig. 1. For all reactions, equilibrium was achieved after 3–7 hours, and the composition then established by ^{13}C NMR spectroscopy.

Results and discussion

Our observations indicate that a redistribution reaction initially, takes place, leading to 1-butenyl-3-ylidibutylchlorotin (I) and tributyltin chloride:



With an excess of Bu_2SnCl_2 isomerization of I occurs and an equilibrium between three isomers is reached:



Analysis by ^{13}C NMR spectroscopy shows that the equilibrium (see eq. 2) composition at 30°C in all cases consists of 72–74% *cis*-II, 12–14% *trans*-II and 14–16% (I). In Fig. 2 is shown the ^{13}C NMR spectrum in the olefinic carbon region of a typical equilibrium mixture. The peak assignments (cf. Table 1) were made on the basis of the proton-coupled spectra and of our previous data on crotyl- [4,5] and analogous allyl-tin derivatives [6]. The carbon-3 resonance of the α -methylallyl derivative (cf. Fig. 2) is very broad and indicates the existence of the exchange process (eq. 2) involving this carbon.

Only I, is formed along with Bu_3SnCl when an excess of $\text{Bu}_3\text{SnCH}_2\text{CH}=\text{CHCH}_3$ is used. The recovered $\text{Bu}_3\text{SnCH}_2\text{CH}=\text{CHCH}_3$ has the same *trans/cis* isomer ratio as the starting material.

The isomerization of I is a pseudo-first order process (Fig. 3) and the rate depends upon the excess of Bu_2SnCl_2 , which acts as a catalyst. Without an

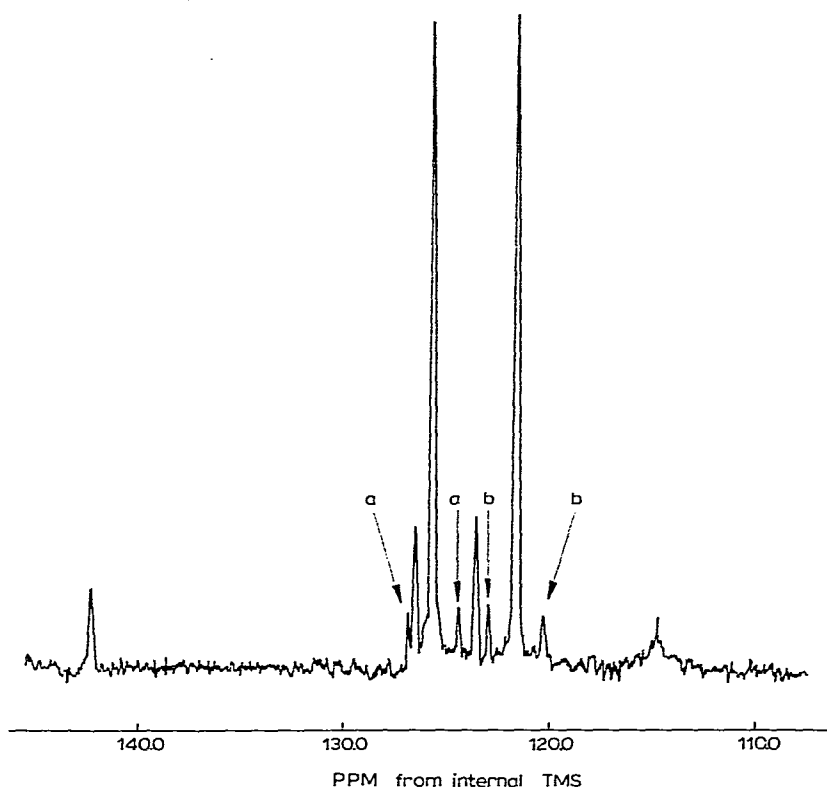


Fig. 2. ^{13}C NMR spectrum of the olefinic carbon region of the product mixture from the reaction of $\text{Bu}_3\text{SnCH}_2\text{CH}=\text{CHCH}_3$ (21.3 mmol: *trans/cis* = 9/11) and Bu_2SnCl_2 (29.9 mmol). (For peak assignments, see Table 1). a, b: doublets due to the coupling with the tin atom in the *cis* isomer (a: 2J 56 Hz; b: 3J 62 Hz).

excess of Bu_2SnCl_2 , no isomerization of I occurs. Reactions 1 and 2 can be regarded as exchange processes, such processes are usually assumed to be bimolecular and to proceed through cyclic transition states [7]. In the present case, the dependence of the rates on the Bu_2SnCl_2 concentration, the allylic rearrangements, and the broad signal for carbon-3 in the ^{13}C NMR spectrum of I also point to cyclic transition states.

TABLE 1
CARBON-13 CHEMICAL SHIFTS OF THE C=C GROUPS OF THE EQUILIBRATED MIXTURES ^a

Isomer	Chemical shift (ppm)	
	C(2)	C(3)
<i>trans</i> - $\text{Bu}_2\text{ClSn}-\overset{1}{\text{CH}_2}-\overset{2}{\text{CH}}=\overset{3}{\text{CH}}-\text{CH}_3$	126.7	123.7
<i>cis</i> - $\text{Bu}_2\text{ClSn}-\overset{1}{\text{CH}_2}-\overset{2}{\text{CH}}=\overset{3}{\text{CH}}-\text{CH}_3$	125.8	121.7
$\text{Bu}_2\text{ClSnCH}(\text{CH}_3)-\overset{2}{\text{CH}}=\overset{3}{\text{CH}}_2$	142.4	115.1

^a ppm from TMS as internal standard.

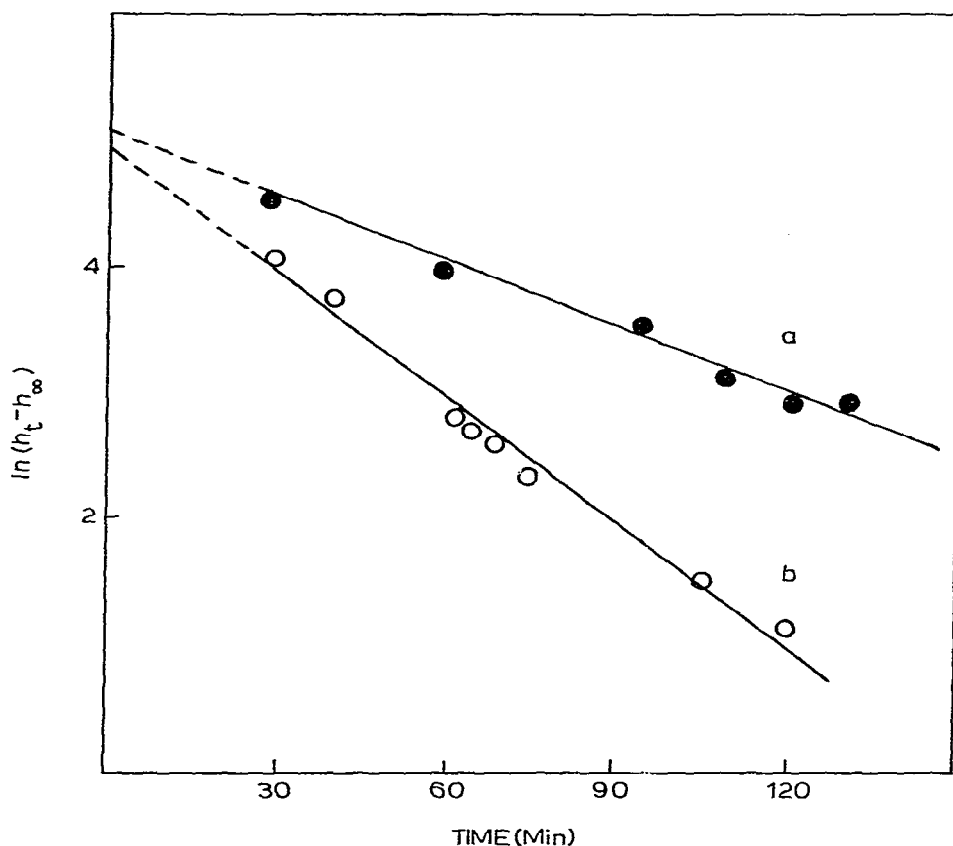
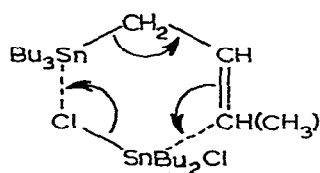
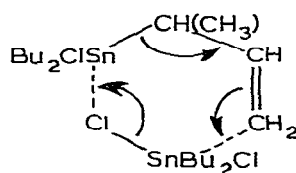


Fig. 3. Plots of $\ln(h_t - h_\infty)$ vs time. Rates of isomerization as a function of the Bu_2SnCl_2 concentration. (a) $[\text{Bu}_3\text{SnCH}_2\text{CH}=\text{CHCH}_3]$, 21.3 mmol; $[\text{Bu}_2\text{SnCl}_2]$, 29.9 mmol; (b) $[\text{Bu}_3\text{SnCH}_2\text{CH}=\text{CHCH}_3]$; 13.5 mmol; $[\text{Bu}_2\text{SnCl}_2]$, 29.7 mmol.



redistribution



isomerization

This is in line with our previous findings on allylic rearrangements in the reversible allylstannations [4–6,8]. Exchange between Me_3SnCl and Me_3SnSR is also thought to occur through cyclic mechanism [9].

Acknowledgements

We thank Dr. James Wardell (University of Aberdeen, Scotland) for useful discussions. We thank also CNR (Rome) for financial support.

References

- 1 J.A. Verdone, J.A. Mangravite, N.M. Scarpa and H.G. Kuivila, *J. Amer. Chem. Soc.*, **97** (1975) 843.
- 2 E. Matarazzo-Tchiroukhine and P. Cadot, *Comp. Rend. Acad. Sci. Paris Ser. C.*, **274** (1972) 2118.
- 3 E. Matarazzo-Tchiroukhine and P. Cadot, *J. Organometal. Chem.*, **121** (1976) 169.
- 4 V. Peruzzo, G. Tagliavini and A. Gambaro, *Inorg. Chim. Acta*, **34** (1979) L 263.
- 5 A. Gambaro, D. Marton, V. Peruzzo and G. Tagliavini, *J. Organometal. Chem.*, **204** (1981) 191.
- 6 A. Gambaro, V. Peruzzo, G. Plazzogna and G. Tagliavini, *J. Organometal. Chem.*, **197** (1980) 45.
- 7 K. Moedritzer, *Advan. Organometal. Chem.*, **6** (1968) 171, and references therein.
- 8 V. Peruzzo and G. Tagliavini, *J. Organometal. Chem.*, **162** (1978) 37.
- 9 E.D. Korniets, E.M. Rokhlina, L.A. Federov, D.N. Kravtsov and E.I. Fedin, *Bull. Acad. Sci. USSR. Div. Chem. Ser.*, **28** (1979) 297.