Journal of Organometallic Chemistry, 377 (1989) 205–210
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands
JOM 20189

Tin(II)-mediated allylation. Asymmetric induction with a chiral tin(II) alkoxide

Jacques Augé and Guy Bourleaux

Institut de Chimie Moléculaire d'Orsay, Laboratoire de Chimie Organique Multifonctionnelle, URA 462, Université Paris-Sud, F91405 Orsay Cédex (France)

(Received June 13th, 1989)

Abstract

In a study of tin-mediated allylation some tin(II) species including tin(II) halides, amides, acetonates, and alkoxides, have been shown to undergo oxidative addition of allyl halide in the presence of benzaldehyde to give the corresponding homoallyl alcohol. The first preparation of a chiral tin(II) alkoxide, tin(II) diethyltartrate is described; its ^{119}Sn NMR spectrum exhibits two signals at high field, consistent with a *trans* dimer structure. This new reagent undergoes oxidative addition of 1,3-chloroiodopropene in the presence of benzaldehyde to give an optically active phenylvinyloxirane; this represents the first enantioselective preparation of *cis*- and *trans*-vinyloxiranes from aldehydes.

Introduction

In recent years tin(II)-mediated allylation has been used to make homoallyl alcohols [1], vinyl epoxides [2], dienes [3], butyrolactones [4] or cycloadducts [5]. It is generally assumed that the initial step, which is identical for all the reactions, is the oxidative addition of tin(II) to generate an allylstannane, but such an intermediate has never been observed. We describe here the reactions of allylstannane species such as those which may be involved in the reaction. We also describe the first preparation of a chiral tin(II) alkoxide, which can bring about asymmetric induction during allylstannation.

Results and discussion

The first step in the tin(II)-mediated allylation of aldehydes may be represented as shown in eq. 1.

* Reference number with asterisk indicates a note in the list of references.

0022-328X/89/$03.50

$$CH_2{=}CHCH_2Br + \underset{(\mathbf{2}:\ X = (acac))}{SnX_2} \longrightarrow \underset{\substack{(\mathbf{1}:\ X = Cl;\\ \mathbf{3}:\ X = (acac))}}{CH_2{=}CHCH_2SnX_2Br} \qquad (1)$$

The oxidative addition of alkyl halides to divalent tin is well documented [6]. Allyl(bromo)(dichloro)tin was obtained [7] from allyl bromide and tin chloride. This reaction required refluxing in THF, whereas the reaction between this allylstannane and benzaldehyde rapidly gave allylphenyl carbinol at $-20\,^{\circ}C$. It is noteworthy that tin(II) chloride did not insert into the carbon–bromine bond of allyl bromide at room temperature in DMF, whereas a mixture of $SnCl_2$, allyl bromide and benzaldehyde, gave homoallyl alcohol in good yield in 16 h. It seemed that the benzaldehyde induced oxidative addition of allyl bromide to $SnCl_2$ to give allyl(bromo)(dichloro)tin, a very reactive species. A more convenient material is allyltin bis(acetylacetonate)bromide. This crystalline compound was prepared [8] from allyl bromide and tin(II) bis(acetylacetonate), $Sn(acac)_2$. The ^{119}Sn NMR spectrum of $Sn(acac)_2$ displayed a signal at high field (δ 704.7 ppm), as expected [9*] for a two-coordinate species, whereas the ^{119}Sn chemical shift in compound **3** (δ −596.1) provided evidence for an hexacoordinate tin(IV). The diastereotopic non equivalence of methylene protons ($^2J(^1H{-}^{119}Sn)$ 61 and 104 Hz) provided evidence for a *cis*-configuration in chloroform at room temperature. Allyltin bis(acetylacetonate)bromide reacted rapidly at room temperature with benzaldehyde to give the corresponding alcohol. Allylstannanes **1** and **3** were both reactive, whereas their preparation required more activation energy. These results show that the limiting step is still the insertion of divalent tin into allyl halide. Allyl iodide is a better substrate than allyl bromide for this reason.

At this stage, two extreme cases were examined, as follows.

With the tin(II) amide $Sn[N(SiMe_3)_2]_2$, the completion time for oxidative addition to alkyl iodides averaged 15 min at room temperature [10]. This tin(II) amide, a monomer in cyclohexane solution, was prepared from the parent amide and tin(II) chloride [11]. When the tin(II) amide in hexane was added to commercial crotyl bromide (*E*/*Z* 2/1) there was a rapid (5 min) disappearance of the orange colour, indicating that oxidation of the tin had provided a new allylstannane. This species was not isolated, but allowed to react with benzaldehyde. After 15 min, a mixture of diastereoisomers (*syn*/*anti* 40/60) was obtained in 66% yield (eq. 2).

$$CH_3CH{=}CHCH_2Br + SnX_2 \longrightarrow CH_3CH{=}CHCH_2SnX_2Br$$

$$\xrightarrow[2.\ H_2O]{1.\ PhCHO} Ph{-}\underset{\displaystyle OH}{\underset{|}{CH}}{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}{-}CH{=}CH_2 \qquad (2)$$

(X = Cl or $N(SiMe_3)$)

When the same reaction was carried out with tin(II) chloride in DMF instead of the tin(II) amide in hexane, homoallyl alcohols (*syn*/*anti* 35/65) were obtained [2] in 62% yield after 16 h.

The second extreme case involved tin(II) alkoxides, which are thought to be unreactive towards alkyl halides [12]. There are numerous examples of tin(II)

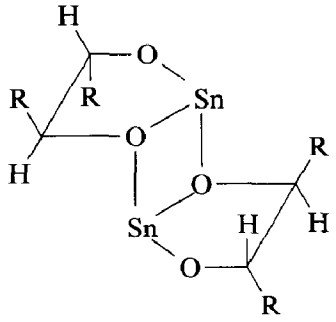
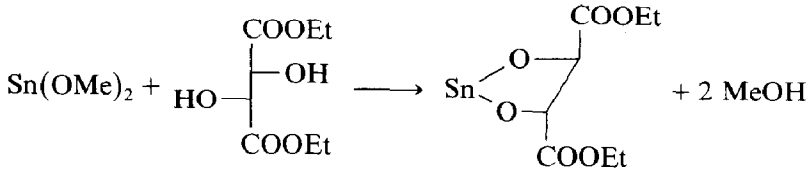


Fig. 1. *trans*-Dimer structure of tin(II) diethyltartrate (R = COOEt).

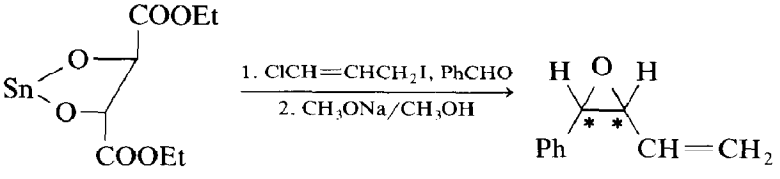
alkoxides which demonstrate the high aggregation tendency of this type of compounds [13]. Curiously no chiral tin(II) alkoxide has been yet isolated, but the use of $SnCl_2$ and diethyltartrate in an enantioselective synthesis of homoallyl alcohols was reported recently [14]. We have now prepared and isolated tin(II) diethyltartrate (85% yield) by a procedure [15] previously described for other tin(II) alkoxides.



(4)

The tartrate was obtained as an infusible white powder which was slightly soluble in chloroform. The ^{119}Sn NMR spectrum exhibited two signals at δ −439 and δ −552 ppm. The structure of **4** in the solid was not determined, but its ^{119}Sn NMR spectrum was compatible with the *trans* dimer structure which was recently demonstrated [16] for tin(II) t-butoxide. In such a structure (Fig. 1), the chirality of the tartrate ligand provides two different environments around tin, giving rise to two signals in ^{119}Sn NMR spectrum.

In an attempt to prepare optically active vinyloxiranes, we tried our methodology [2] with tin(II) tartrate instead of tin(II) chloride.



Two methods were investigated. In the first tin(II) diethyltartrate was prepared from $Sn[N(SiMe_3)_2]_2$ and used in situ; in the second one, tin(II) diethyltartrate, prepared from $SnCl_2$, was isolated before use. The first method yielded the best enantioselectivity we obtained for vinyloxiranes. The major isomer (*cis*) was produced with 28% enantiomeric excess, whereas the minor one (*trans*) was produced with 40% enantiomeric excess. The enantiomeric purities were determined with the aid of a chiral chemical shift reagent. The purities could not be compared with those

derived from optical data because optically pure vinyloxiranes are unknown. They would be excellent chiral synthons if they could be obtained optically pure. Owing to their fundamental interest in organic synthesis, we are now studying the possibility of improving the optical purity.

Experimental

^{119}Sn NMR spectra were recorded on a Bruker AM 250 spectrometer operating at 93.27 MHz in pulse mode with Fourier transform. Deuterated chloroform was used as internal lock. The chemical shifts were measured relative to internal Me_4Sn. Negative values of the shifts are to upfield. Concentrations of compounds **2**, **3** and **4** in $CDCl_3$ are respectively 0.4, 0.16 and 0.18 *M*.

Allylation with allyl(bromo)(dichloro)tin

To a solution of allyl(bromo)(dichloro)tin [7] (279 mg, 0.9 mmol) in toluene (2 ml) at −20 °C was added benzaldehyde (150 mg, 1.4 mmol). After 1 h at −20 °C, the mixture was diluted with hexane and filtered. The precipitate was washed with hexane, and the filtrate evaporated. The residue was purified by chromatography on silica gel (hexane, ethyl acetate 93/7) to afford 72 mg (54%) of phenylvinyl carbinol.

Allylation with allyltin bis(acetylacetonate) bromide

To a solution of allyltin bis(acetylacetonate)bromide [8] (510 mg, 1.16 mmol) in dichloromethane (2 ml) was added benzaldehyde (251 mg, 2.36 mmol). After 1 h at room temperature, and evaporation of the solvent, the residue was purified by chromatography on silica gel (hexane, ethylacetate 90/10) to afford 142 mg (82%) of phenylvinyl carbinol.

Tin(II) bis(trimethylsilyl)amide in hexane solution

Tin(II) bis(trimethylsilyl)amide was prepared by Lappert's method [11], except that it was not isolated. The hexane solution of tin(II) amide was titrated by iodometry with potassium iodate, and the crude solution used without purification.

Tin(II) amide-mediated allylation

To the yellow-orange hexane solution of tin(II) amide (5 ml, 1 mmol) was added crotyl bromide (135 mg, 1 mmol). The colour had disappeared within 5 min. Benzaldehyde (74 mg, 0.7 mmol) was then added. After 15 min, the mixture was evaporated and the residue chromatographed on silica gel, to give α-methylallylphenyl carbinol (74 mg, 66%) as a mixture of *syn* and *anti* isomers. The ratio *syn*/*anti* (40/60) was determined by ^{1}H NMR spectroscopy [2].

Tin(II) diethyltartrate

Tin(II) chloride (7.58 g, 40 mmol) was dissolved in methanol (150 ml), triethylamine (11.2 ml, 80 mmol) was added, and the mixture stirred for 30 min. L-Diethyltartrate (8.25 g, 40 mmol) was then added and the mixture stirred for 1.5 h. The precipitate was filtered off and washed with methanol (20 ml), followed by diethyl ether (60 ml). The yield of tin(II) diethyltartrate (nc) was 85%. Anal. Found: Sn, 35.95. $C_8H_{12}O_6Sn$ calcd.: Sn, 36.76%. IR 1740(s) cm^{-1}. ^{119}Sn NMR: δ −439 and −552 ppm.

Tin(II) diethyltartrate-mediated enantioselective synthesis of vinyloxiranes

First method. To (+)-diethyltartrate (1.92 g, 9.32 mmol) was added tin(II) bis(trimethylsilyl)amide (6.24 mmol) in hexane. After removal of hexane and hexamethyldisilazane, the residue was taken up in THF. After successive addition of 1,3-chloroiodopropene (1.4 g, 6.94 mmol) and benzaldehyde (0.38 g, 3.58 mmol), the mixture was stirred overnight at room temperature. The precipitate was filtered off and washed with diethyl ether. After evaporation of the bulk of the solvent, methanolic sodium methoxide was added. After extraction with diethyl ether and washings, the residue was purified by HPLC to give two isomers (*cis* and *trans*, 114 and 58 mg, respectively). The enantiomeric excesses of the *cis* and *trans* isomers determined by ^{1}H NMR (90 MHz) spectroscopy in the presence of Eu(hfc)$_3$ (37 mg of the shift reagent was added to 114 mg of this *cis* isomer, 49 mg of the shift reagent were added to 33 mg of the *trans* isomer). The relative intensities of protons attached to the chiral center at 4.16 ppm (*cis* isomer) and 3.71 ppm (*trans* isomer) were used for ee determination (28 and 40% for *cis* and *trans* isomers, respectively). The specific rotations were +47° (*c* 2, CH_2Cl_2) and +52° (*c* 1, CH_2Cl_2), respectively.

Second method. To a suspension of tin(II) diethyltartrate (5.78 g, 17.9 mmol) in DMF (14 ml) were added successively 1,3-chloroiodopropene (3.38 g, 16.69 mmol) and benzaldehyde (1.53 g, 14.43 mmol). The mixture was stirred overnight and treated with methanolic sodium methoxide. Work-up as above afforded the *cis* (880 mg) and *trans* (133 mg) isomers. Their specific rotations were +21° (*c* 2, CH_2Cl_2) and +16° (*c* 1, CH_2Cl_2), respectively. All the products gave satisfactory ^{1}H NMR spectra.

Acknowledgements

We are grateful to Claude Mérienne for assistance with the ^{119}Sn NMR spectroscopy. We thank CNRS and Université de Paris-Sud for financial support.

References

1 T. Mukaiyama, T. Harada and S. Shoda, Chem. Lett., (1980) 1507; T. Harada, T. Mukaiyama, Chem. Lett., (1981) 1109; T. Mukaiyama, K. Suzuki, T. Yamada, ibid., (1982) 929; Y. Masuyama, J.P. Takahara and Y. Kurusu, J. Am. Chem. Soc., 110 (1988) 4473.
2 J. Augé and S. David, Tetrahedron Lett., 24 (1983) 4009.
3 J. Augé, Tetrahedron Lett., 26 (1985) 753.
4 K. Uneyama, K. Ueda, S. Torii, Chem. Lett., (1986) 1201.
5 G.A. Molander and D.C. Shubert, J. Am. Chem. Soc., 108 (1986) 4683; G.A. Molander and D.C. Shubert, ibid., 109 (1987) 576; G.A. Molander and D.C. Shubert, J. Am. Chem. Soc., 109 (1987) 6877.
6 E.J. Bulten, J. Organomet. Chem., 97 (1975) 167; P.F.R. Ewings and P.G. Harrison, Inorg. Chim. Acta, 18 (1976) 165.
7 A. Gambaro, V. Peruzzo, G. Plazzogna and G. Tagliavini, J. Organomet. Chem., 197 (1980) 45.
8 K.D. Bos, E.J. Bulten and J.G. Noltes, J. Organomet. Chem., 99 (1975) 397.
9 For a review about ^{119}Sn NMR parameters, see B. Wrackmeyer, Ann. Rep. NMR Spect., 16 (1985) 73.
10 M.F. Lappert, M.C. Misra, M. Onyszchuk, R.S. Rowe, P.P. Power and M.J. Slade, J. Organomet. Chem., 330 (1987) 31.
11 M.J.S. Gynane, D.H. Harris, P. Rivière and M. Rivière-Baudet, J. Chem. Soc., Dalton, (1977) 2004.
12 I. Wakeshima and I. Kijima, J. Organomet. Chem., 76 (1974) 37.

13 G.T. Cocks and J.J. Zuckerman, Inorg. Chem., 4 (1965) 592; P.F.R. Ewings and P.G. Harrison, J. Chem. Soc. Dalton, (1975) 2015; W.T. Hall and J.J. Zuckerman, Inorg. Chem., 16 (1977) 1239.
14 G.P. Boldrini, E. Tagliavini, C. Trombini and A. Umani-Ronchi, J. Chem. Soc., Chem. Comm., (1986) 685.
15 W.D. Honnick and J.J. Zuckerman, Inorg. Chem., 17 (1978) 501.
16 T. Fjeldberg, P.B. Hitchcock, M.F. Lappert, S.J. Smith and A.J. Thorne, J. Chem. Soc., Chem. Comm., (1985) 939.