Journal of Organometallic Chemistry, 391 (1990) 283–288
Elsevier Sequoia S.A., Lausanne

JOM 20840

3-Methoxy-1-(tributylstannyl)-1-propene, a versatile vinyltin synthon

Jean-Baptiste Verlhac * and Michel Pereyre

Laboratoire de Chimie Organique et Organométallique, URA 35 CNRS, Université Bordeaux I, 351 cours de la Libération, 33405-Talence (France)

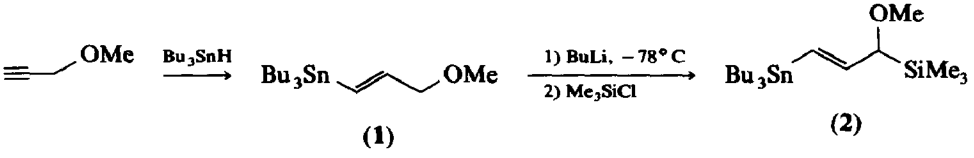
(Received February 12th, 1990)

Abstract

3-Methoxy-1-(tributylstannyl)-1-propene (1) can be readily transformed into the silylated analogue (2), which can react both as a vinyltin and as an allylsilane. Thus, transmetallation of 2 with n-butyllithium, followed by quenching with various electrophiles, gives functionalized allylsilanes. Although reagent 2 can react with benzaldehyde as an allylsilane, the diastereoisomeric mixture of monoprotected 1,2-diols (14) can be best obtained from 1 by direct lithiation and quenching with benzaldehyde. The use of Lewis acids allows the control of the stereochemistry of the condensations.

Introduction

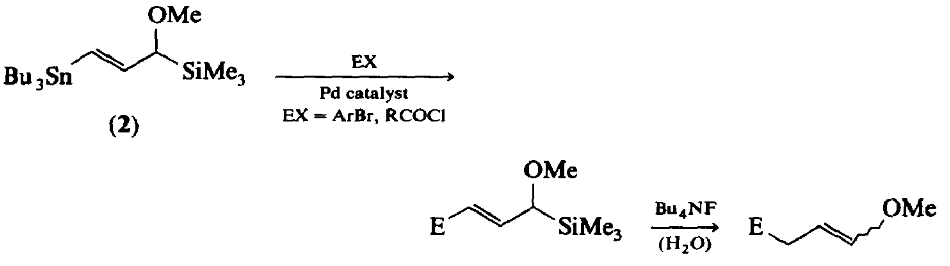
Alongside the large number of methods available for the homologation of organic molecules by a three carbon unit [1,2], we have recently proposed the use of a new umpolung reagent which reacts smoothly in the presence of a palladium catalyst with acyl or aryl halides [3]. This reagent, 3-methoxy-1-(tributylstannyl)-3-(trimethylsilyl)-1-propene (2), is easily obtained by hydrostannation of methyl propargyl ether [4] and subsequent silylation of 1 at the allylic position (eq. 1).



(1) (2)

(1)

In the presence of a palladium catalyst, **2** reacted as a vinyltin with the electrophiles aryl bromides and acyl chlorides to give products **3** and **4** (eq. 2).



(**2**)

(**3**: E = Ar;
4: E = RCO)

(**5**: E = Ar;
6: E = RCO)

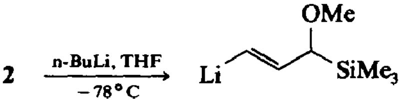
(2)

Desilylation of **3** and **4**, with Bu_4NF gave **5** and **6**, respectively in good yields.

The bimetallic reagent **2** obviously has a number of other synthetic possibilities and some of them have been already explored [5*].

Results and discussion

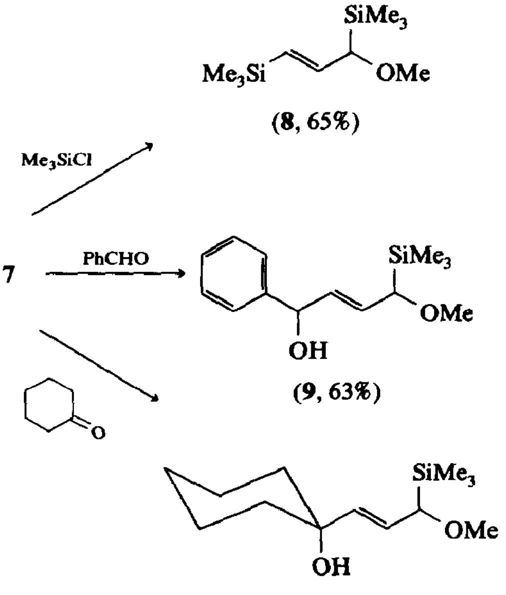
We first treated reagent **2** with n-butyllithium; under these conditions, it reacts as a vinyltin to give the corresponding vinyllithium derivative (eq. 3):



(**7**)

(3)

Compound **7** could be readily trapped by various electrophiles (eq. 4):



(**8**, 65%)

(**9**, 63%)

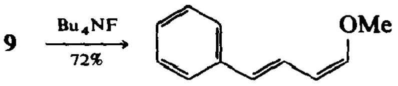
(**10**, 51%)

(4)

---

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

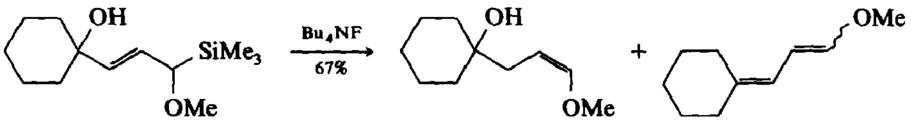
The allylsilanes obtained in that way have a high synthetic potential; for example, we carried out desilylation of **9** and **10** with Bu_4NF. In the case of **9**, a dienol ether was obtained as a result of 1,4-dehydroxysilylation (eq. 5).



(5)

(11)

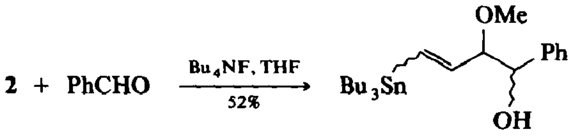
In the case of **10** the desilylation gave a mixture of the 1,4-dehydroxysilylation product and simple desilylation products (eq. 6).



(6)

(12) **(13)**

We also showed that in the presence of fluoride anion, compound **2** reacts as an allylsilane, as shown in equation 7:

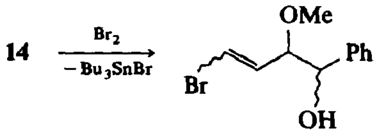


(7)

(14)

The product **14** is a diastereoisomeric mixture of monoprotected 1,2-diols, which still contains the tributyltin moiety. It is noteworthy that they are vinyltins, indicating that the cleavage of the silicon–carbon bond has occurred without allylic rearrangement. The reaction of allylsilanes with fluoride anion generally proceeds via an allylic anion [6]. In the case of **2** the γ site (relative to the methoxy group) is more hindered (tributyltin substituent), and it is known that quenching with carbonyl compounds of the anions derived from allylic ethers, generally leads to monoprotected 1,2-diols (involving attack of the electrophile at the other end) [7,8].

The vinyltin compounds **14** can undergo a variety of other reactions: for instance, with bromine, only cleavage of the tin–vinyl bond occurred (eq. 8).



(8)

(15)

However, we have found that the organometallic compounds **14** can be more conveniently obtained directly from the γ-methoxyvinyltin **1** by deprotonation followed by regioselective addition of benzaldehyde (eq. 9):

$$\mathbf{1} \xrightarrow[\text{2) PhCHO}]{\text{1) s-BuLi, }-78^\circ\text{C}} \mathbf{14} \qquad (9)$$

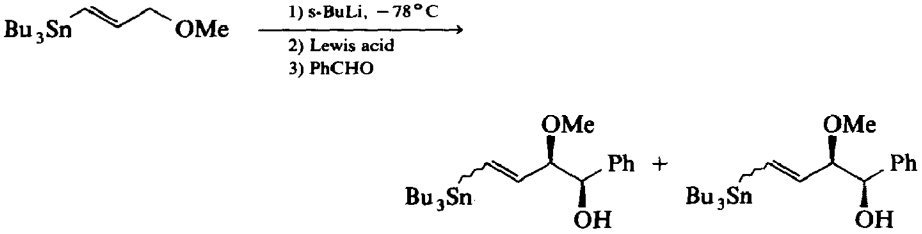
Table 1

The influence of Lewis acid on the composition of **14**

Lewis acid (equiv.)	Yield	*syn*-(*Z*)	*syn*-(*E*)	*anti*-(*E*)	*anti*-(*Z*)
None	63%	3	50	47	0
$ClTi(OiPr)_3$ (1) [a]	78%	0	45	55	0
$Ti(OiPr)_4$ (1)	74%	0	15	85	0
$ZnCl_2$ (0.5)	68%	35	54	11	0
$ZnCl_2$ (1)	71%	43	43	14	0
$ZnCl_2$ (2)	67%	50	29	21	0
[b]	52%	0	56	44	0

[a] Equimolar quantity of Lewis acid added. [b] Composition of the product shown in eq. 7.

A few preliminary results have shown that it is possible to control to some extent the relative stereochemistries of the chiral centers by the use of Lewis acids before the addition of benzaldehyde (Table 1). Thus the addition of isopropyl titanate yielded mainly the *anti*-(*E*)-isomer, whereas addition of zinc chloride gave mainly the *syn*-isomer as an (*E*)/(*Z*) mixture (eq. 10):



(*syn*-**14**) (*anti*-**14**) (10)

In the case of isopropyl titanate, the reaction probably proceeds via a six-membered transition state which leads mainly to the *anti*-isomer.

Although all the presently available stereochemical results are not easy to rationalize, the fact that the very reactive vinyltin moiety is retained and the prospect that it may be possible to control the *syn/anti* stereochemistry, clearly suggest the potential for new stereoselective synthesis of complex polyoxygenated molecules [9].

Experimental

All compounds were characterized by ^1H NMR spectroscopy by use of a Hitachi R 24B instrument (60 MHz). In some specified cases a Bruker AC 200 (^1H: 200 MHz; ^{119}Sn: 74.63 MHz) instrument was used. The spectra were usually recorded for solutions in carbon tetrachloride with tetramethylsilane as internal standard. The products were purified by distillation or column chromatography on silica gel.

Preparation of reagent 2

To a solution of 21.7 g of compound **1** (prepared essentially as the *E*-isomer by hydrostannation of propargyl ether [4]) in 150 ml of THF under nitrogen at −78 °C was added 43.5 ml of 1.4 *M* s-BuLi solution in cyclohexane. Chlorotrimethylsilane

(6.5 g) was then added dropwise and the mixture was kept for 1 h at $-78\,^{\circ}$C then treated at $-10\,^{\circ}$C with saturated aqueous NH_4Cl. Evaporation of the organic phase and subsequent distillation (b.p. 120–125°C/0.05 mmHg) gave 14.5 g of the organotin reagent **2**: ^1H NMR: δ, 0.12 (s,9H); 0.7–1.6 (m,27H); 3.25 (s,3H); 3.44 (m,1H); 5.89 (m,2H). ^{119}Sn NMR (74.63 MHz, C_6D_6): δ, -45.52 ppm (Me_4Sn as internal standard).

Preparation of reagent 7 and subsequent derivatization

Transmetallation of **2** was performed in a Schlenk tube in THF (0.5 *M* solution) at $-78\,^{\circ}$C with n-BuLi (1.8 *M* in hexane).

8: b.p. 90°C/760 mmHg; ^1H NMR: δ, 0.02 (s,9H); 0.10 (s,9H); 3.27 (s,3H); 3.40 (d, J 5 Hz, 1H); 5.56 (d, J 18 Hz, 1H); 5.96 (m,1H).

9: Isolated by column chromatography in 63% yield (eluent: 30% Et_2O–70% petroleum ether). ^1H NMR: δ, 0.12 (s,9H); 3.26 (s,3H); 3.30 (m,2H); 5.10 (m,1H); 5.67 (m,2H); 7.29 (apparent s,5H).

10: Isolated by column chromatography in 51% yield (eluent: 30% Et_2O–70% petroleum ether). ^1H NMR: δ, 0.10 (s,9H); 1.63 (m,10H); 1.90 (s,1H, exchangeable with D_2O); 3.31 (s,3H); 3.40 (m,1H); 5.67 (m,2H).

Desilylation of compounds 9 and 10

Compound **9** was treated with an equimolar quantity of Bu_4NF (1 *M* solution in THF) at 0°C during 5 min. The mixture was chromatographed on Florisil (Aldrich) (eluent: 10% Et_2O–90% petroleum ether) to give **11** in 72% yield. ^1H NMR: δ, 3.65 (s,3H); 5.73 (dd, J 10 Hz, J 6 Hz, 1H); 5.88 (d, J 6 Hz, 1H); 6.30 (d, J 16 Hz, 1H); 7.06 (dd, J 10 Hz, J 16 Hz, 1H); 7.25 (m,5H). IR (cm^{-1}): 1645, 1600, 1495, 1400.

The same treatment as above, from **10**, gave a 50/50 mixture of **12** and **13** (chromatography on Florisil, eluent: 10% Et_2O–90% petroleum ether).

12: ^1H NMR: δ, 1.51 (m,10H); 1.89 (s,1H, exchangeable with D_2O); 2.12 (d, J 7.7 Hz, 2H); 3.58 (s,3H); 4.44 (dt, J 7.7 Hz, J 6 Hz, 1H); 5.93 (d, J 6 Hz, 1H).

13: ^1H NMR: δ, 1.46 (m,6H); 2.07 (m,4H); 3.48 (s,3H); 4.46 (dd, J 12.5 Hz, J 6 Hz, 1H); 5.63 (d, J 6 Hz, 1H); 5.89 (d, J 12.5 Hz, 1H).

Preparation of 14 from reagent 2

To an equimolar mixture of **2** and benzaldehyde (1 *M* solution in THF) an equimolar quantity of Bu_4NF (1 *M* solution in THF was added at 0°C via a syringe pump. The mixture was treated with water and worked up as usual. Physical data for **14** are given below.

Preparation of 14 from reagent 1

Lithiation of **1** was performed as described for the preparation of reagent **2**. The Lewis acid was added at $-78\,^{\circ}$C and the solution was quenched with benzaldehyde. Hydrolysis and subsequent purification by column chromatography on silica gel yielded **14**. The product mixtures were also treated with bromine in CCl_4 for further analysis by capillary column chromatography (CPWAX 42 CP (Chrompack), 25 m length).

syn-(*E*)-**14**: ^1H NMR (200 MHz, C_6D_6): δ, 0.8–1.5 (m,27H); 3.20 (s,3H); 3.50 (apparent t, J 6.7 Hz, J 8 Hz, 1H); 3.61 (s,1H, exchangeable with D_2O); 4.51 (d, J

8 Hz, 1H); 5.65 (dd, *J* 6.7 Hz, *J* 19 Hz, 1H); 5.93 (d, *J* 19 Hz; 1H); 7.14 (m,3H); 7.30 (m,2H).

anti-(*E*)-**14**: ^{1}H NMR (200 MHz, C_6D_6): δ, 0.8–1.5 (m,27H); 3.06 (s,1H, exchangeable with D_2O); 3.16 (s,3H); 3.65 (dd, *J* 5.8 Hz, *J* 4 Hz,1H); 4.89 (d, *J* 4 Hz,1H); 5.94 (dd, *J* 5.8 Hz, *J* 19 Hz,1H); 6.08 (d, *J* 19 Hz,1H); 7.20 (m,3H); 7.40 (m,2H).

syn-(*E*)-**14**: ^{1}H NMR (200 MHz, C_6D_6): δ, 0.8–1.5 (m,27H); 3.19 (s,3H); 3.38 (s,1H, exchangeable with D_2O); 3.49 (apparent t, *J* 7.2 Hz, *J* 6Hz, 1H); 4.63 (d, *J* 7.2 Hz, 1H); 6.11 (d, *J* 13.5 Hz, 1H); 6.34 (dd, *J* 6 Hz, *J* 13.5 Hz, 1H); 7.15 (m,3H); 7.39 (m,2H).

Bromodestannylation of compound 14

A 1 *M* carbon tetrachloride solution of bromine was added dropwise to compound **14** (from reaction catalyzed with $Ti(OiPr)_4$) until the red color persisted. After evaporation of the solvent and treatment of the residue with aqueous KF (to remove tributyltin bromide), the *anti*-(*E*) isomer was isolated in 51% yield by column chromatography on silica gel (eluent: 10% Et_2O–90% petroleum ether):

anti-(*E*)-**15**: ^{1}H NMR: δ, 3.08 (d, *J* 5 Hz, 1H, exchangeable with D_2O); 3.18 (s,3H); 3.53 (m, *J* 4 Hz, *J* 5 Hz, 1H); 4.64 (d, *J* 4 Hz,1H); 6.01 (apparent d,2H); 7.23 (s,5H). MS: *m/z*, 151(7.2), 149(7.6), 107(100), 79(73), 77(38), 71(63).

Acknowledgements

We are indebted to Schering for a generous gift of tributyltin oxide and to the CNRS and the "Conseil Régional d'Aquitaine" for financial support.

References

1 J.C. Stowell, Chem. Rev., 84 (1984) 409.
2 D. Hoppe, Angew. Chem., Int. Ed. Engl., 23 (1984) 932.
3 J.B. Verlhac, J.P. Quintard and M. Pereyre, J. Chem. Soc., Chem. Commun., (1988) 503.
4 J.W. Labadie and J.K. Stille, J. Am. Chem. Soc., 105 (1983) 6129.
5 Some of the results described in this paper were presented as a poster at the VIth International Conference on the Organometallic and Coordination Chemistry of Germanium, Tin and Lead, Brussels, July 1989.
6 E.J. Corey and B.B. Snider, J. Amer. Chem. Soc., 94 (1972) 2549.
7 W.C. Still and T.L. McDonald, J. Org. Chem., 41 (1976) 3620.
8 D.A. Evans, G.C. Andrews and B. Bruckwalter, J. Am. Chem. Soc., 96 (1974) 5560.
9 M. Pereyre, J.P. Quintard and A. Rahm, Tin in Organic Synthesis, Butterworths, London, 1987.