Tetrahedron Letters, Vol.27, No.7, pp 857-860, 1986 0040-4039/86 $3.00 + .00
Printed in Great Britain

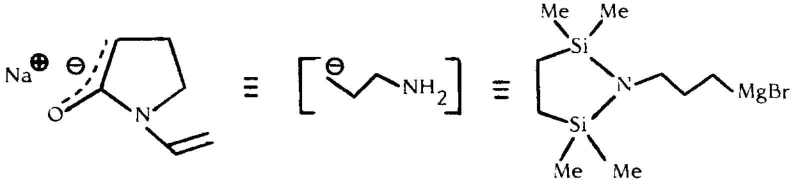
CHELATION ASSISTED TRANSMETALLATION OF TETRAALKYL TIN DERIVATIVES : C-METALLATED LITHIOCARBAMATES AS d^3 REAGENTS FOR THE SYNTHESIS OF δ-HYDROXYCARBAMATES.

Ahmed ZIDANI and Michel VAULTIER *

Groupe de Recherches de Physicochimie Structurale, U.A. n° 704, Campus de Beaulieu,
Avenue du Général Leclerc, 35042 RENNES CEDEX (FRANCE).

Abstract - The γ-stannylcarbamates **4** and **5** were subjected to metallation with two equivalents of BuLi to give the dianions **6** and **7** acting as d^3 reagents. The C-metallation involves a chelation assisted transmetallation.

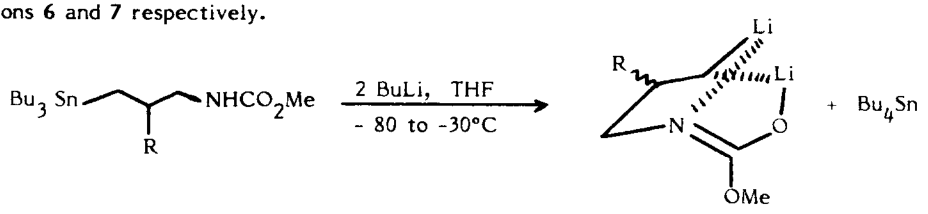
Primary amino protected Grignard or lithio reagents that can be easily formed are scarce(1). Recently, the sodium enolate of N-vinylpyrrolidone (2) **1** and the Grignard reagent (3) **3** were used as synthetic equivalents of the synthon **2**.



1 **2** **3**

We wish to report herein on the formation of a new synthetic equivalent of the synthon **2** and its reactions with some electrophiles.

The γ-stannylcarbamates **4** and **5** (4) were subjected to metallation with two equivalents of BuLi (2,0 M in hexane) in THF at low temperature to give rapidly (1 hour) and quantitatively the dianions **6** and **7** respectively.



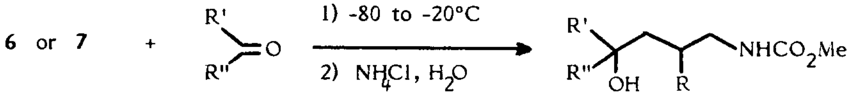
4 : R = H

5 : R = Me

6 : R = H

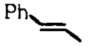
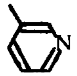
7 : R = Me

The hydrolysis of solutions of **6** and **7** with saturated NH_4Cl gave quantitatively (G.C. Yields ≚ 99 %) the N-methoxycarbonyl propylamine and N-methoxycarbonylisobutylamine respectively and the tetrabutyltin. The dianion **6** was C-methylated with dimethylsulfate leading to the N-methoxycarbonylbutylamine in an 71 % isolated yield. No alkylation could be achieved with alkylhalides (ICH_3, Br). The dianions **6** and **7** react with carbonyl derivatives to give the protected aminoalcools **8** with good yields.



8

Table - Synthesis of the δ-hydroxycarbamates **8** (5)

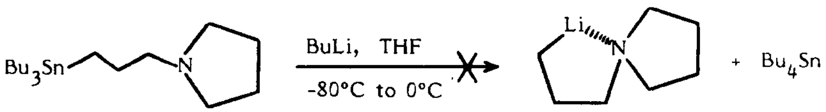
N°	R	R'	R''	$Eb_{mm/Hg}$ °C or m.p. °C	Yield % (a)
8 a	H	Ph	H	80-81	72
8 b	H	Et	H	100-105/0,01	72
8 c	H		H	58-59	61
8 d	H	Ph	Ph	105-106	80
8 e	H	Me	Me	100-103/0,01	68
8 f	H	$-(CH_2)_5-$		74-75	71
8 g	H	$-(CH_2)_4-\underset{CH_3}{\underset{\mid}{CH}}-$		67-68	74 (b)
8 h	H		H	(c)	70
8 i	Me	Ph	H	120-122/0,01	80 (d)
8 j	Me	Ph	Ph	108-109	80

(a) Yields are of isolated pure products after column chromatography and distillation or recristallization. (b) A single diastereoisomer (^{13}C NMR) of unknown stereochemistry was obtained. (c) oil, TLC : Rf = 0,45 (ether/methanol 8/2). (d) 1/1 mixture of two diastereoisomers.

The very easy transmetallation of the tetraalkyltin derivatives **4** and **5** is intriguing. It has been shown that transmetallation of tetraalkyltin compounds with alkyllithiums would give complex equilibrium mixtures (6) except in special cases (7).

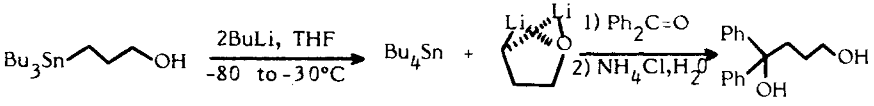
Recently, B.K. Carpenter and R.H. Newman-Evans (8) have published a stereoselective synthesis of bicyclo [2-1-1] hexenes-5-d using a transmetallation of a tetraalkyltin assisted by chelation with an OLi group. These authors suggest the possibility of having a tin "ate" complex instead of a dianion. In order to get some insight into this problem, we have recorded the ^{119}Sn NMR spectrum (9) of the solution obtained by treatment of 4 with 2 BuLi at -20°C. A single sharp singlet was observed at -11.3 ppm. This spectrum was not modified by the addition of one equivalent of pure Bu_4Sn. Therefore, we believe that, in our case, there is only the formation of the dianion **6** and Bu_4Sn. The presence of an anion in δ position to the tin atom seems to be necessary to shift the transmetallation equilibrium towards the formation of the dianions **6** and **7** (10). This stems from the following experiments.

The addition of one equivalent of BuLi to the tetraalkyltin **9** did not produce any anion **10** nor Bu_4Sn as it could be seen from the GC analysis of the hydrolyzed crude reaction mixture. **9** was quantitatively recovered.



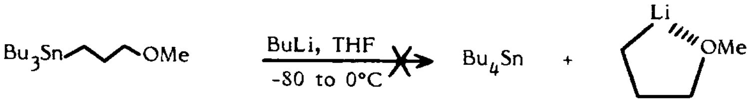
9 **10**

Furthermore, the treatment of **11** with two equivalents of BuLi (2,0 M in hexane) gave the dianion **12** which was added to benzophenone leading to the diol **13**.



11 **12** **13** (80 %)

The anion **15** could not be generated from **14** in the indicated conditions.



14 **15**

Finally, we believe in agreement with B.K. Carpenter and R.H. Newman-Evans (8) and in a more general way that it could be possible to use a suitably disposed negatively charged atom to direct a tetraalkyltin transmetallation and thus to obtain a variety of new useful nucleophilic reagents.

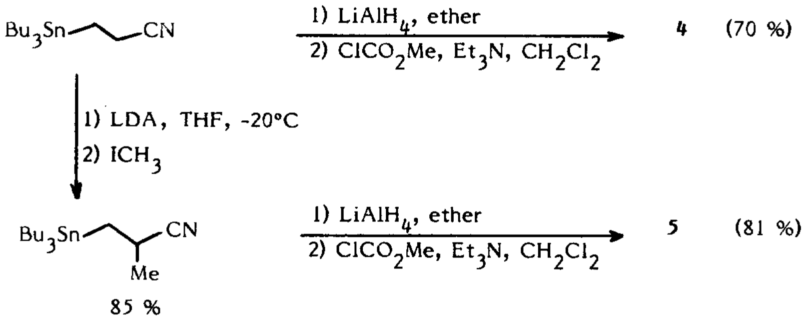
References and Notes

1 - J.C. STOWELL, Chem. Rev., 1984, 84, 409.

2 - P. JACOB III, J. Org. Chem., 1982, 47, 4165.

3 - F.Z. BASHA and J.F. DEBERNARDIS, Tetrahedron Letters, 1984, 25, 5271.

4 - The tetralkyltin reagents **4** and **5** were prepared from β-tri-n-butylpropionitrile (A.J. Leusing and J.G. Noltes, Tetrahedron Letters, 1966, p. 335) according to the following scheme :



5 - All new compounds gave satisfactory analytical data for C and H and spectra (^1H, ^{13}C, IR and mass) in accord with the proposed structures.

6 - D. SEYFERTH and M.A. WEINER, J. Am. Chem. Soc., 1962, 84, 361.

7 - D.J. PETERSON, J. Am. Chem. Soc., 1971, 93, 4027. D.J. PETERSON and J.F. WARD, J. Organomet. Chem., 1974, 66, 209.
W.C. STILL, J. Am. Chem. Soc., 1978, 100, 1481.
E.J. COREY and T.M. ECKRICH, Tetrahedron Letters, 1984, 25, 2415.
R. GOSWAMI and D.E. CORCORAN, Tetrahedron Letters, 1982, 23, 1463.

8 - R.H. NEWMAN-EVANS and B.K. CARPENTER, Tetrahedron Letters, 1985, 26, 1141.

9 - ^{119}Sn NMR spectra (proton decoupled) were recorded at 111,9 MHz. Me_4Sn was used as the reference (capillary tube).

10 - The treatment of the aminostannanes $Bu_3Sn\text{-}(CH_2)_3\text{-}NH_2$ and $Bu_3Sn\text{-}(CH_2)_3\text{-}NHSi(Me)_3$ respectively with three and two equivalents of BuLi in the aforementionned conditions leads to the quantitative formation of Bu_4Sn and therefore indicating that the transmetallation is also possible for these substrates. The chemistry of the corresponding anions has not yet been studied.

(Received in France 11 December 1985)