Journal of Organometallic Chemistry, 212 (1981) C31—C34
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

Preliminary communication

NEW ORGANOTIN SYNTHONS PROVIDING α-ALKOXYORGANOLITHIUM REAGENTS

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(Received March 9th, 1981)

Summary

Diethoxymethyltributyltin was obtained in high yield from the reaction of tributylstannylmagnesium chloride with diethylphenylorthoformate. It reacted readily with acetyl chloride to give chloroethoxymethyltributyltin, which was easily transformed to ethoxymethyltributyltin by reduction with tributyltin hydride. Diethoxymethyltributyltin, a masked aldehyde anionic equivalent, was metallated with butyllithium, and the resulting new organolithium reagent was trapped with benzyl bromide, benzaldehyde, and cyclohexenone.

From recently published results it seems that α-heterosubstituted organotins may be of considerable value in synthesis. Besides their own intrinsic reactivity, they can lead to useful heterosubstituted carbanions through transmetallation with organolithium reagents [1—3]. In this context *gem*-dialkoxy-substituted derivatives would be especially interesting as masked carbonyl group reagents to complement the thio or seleno analogs which have been developed [4—6]. We report now our preliminary results on the synthesis and the reactivity of such organotin precursors.

Organotin synthons

Knowledge of the general behaviour of stannyl anions [7] led us to expect a reaction with orthoformates to give organotin reagents bearing a masked aldehyde group, and we did indeed obtain diethoxymethyltributyltin (Ia) and dimethoxymethyltributyltin (Ib) by treating tributylstannylmagnesium chloride [8] with appropriate orthoformates:

$$Bu_3SnH \xrightarrow[-C_3H_8]{i\text{-}PrMgCl} Bu_3SnMgCl \xrightarrow{HC(OR)_3} \underset{(I)}{Bu_3SnCH(OR)_2} + ROMgCl$$

Unfortunately we could not achieve yields of better than 25%. Introduction of a better leaving group should improve the yields [9], and when diethylphenylorthoformate was used it was possible to obtain Ia in 77% yield (distilled product) based on the tributyltin hydride taken:

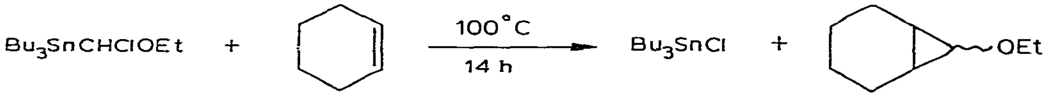
$$Bu_3SnH \xrightarrow[-C_3H_8]{i\text{-}PrMgCl} Bu_3SnMgCl \xrightarrow{(EtO)_2CHOPh} \underset{(Ia)}{Bu_3SnCH(OEt)_2} + PhOMgCl$$

This new organotin synthon reacts readily with acetyl chloride without cleavage of the organotin moiety to give a quantitative yield of chloroethoxymethyltributyltin (IIa) (Ib reacted similarly):

$$Bu_3SnCH(OEt)_2 + MeCOCl \xrightarrow[3\ h]{20°C} \underset{(IIa)}{Bu_3SnCHClOEt} + MeCO_2Et$$

These reactions can be compared with those recently reported for sulfur analogs [10].

Reagent IIa shows a number of promising possibilities but it is only moderately stable, partly decomposing to tributyltin chloride on standing. Decomposition in the presence of an excess of cyclohexene gave ethoxynorcaranes in reasonable yield (32%):



(exo/endo : 78/22)

However, freshly prepared II was quantitatively transformed to alkoxymethyltributyltin (III) by reduction with tributyltin hydride (exothermic reaction):

$$Bu_3SnCHClOR + Bu_3SnH \rightarrow Bu_3SnCl + \underset{(III)}{Bu_3SnCH_2OR}$$

Some NMR data for compounds I—III are listed in Table 1.

Transmetallations

Some α-alkoxy organotin derivatives have previously been transmetallated with lithium reagents: for instance, the organotin synthon III acts as a precursor for alkoxymethyl carbanions [1]. Similarly we have found that the dialkoxymethyltributyltin reagents I also readily exchange with butyllithium in THF at −78°C. New lithium intermediates are obtained and these have been treated below −50°C with a few reagents.

TABLE 1

NMR CHARACTERISTICS (δ, ppm; J, Hz) OF THE ORGANOTIN SYNTHONS

	Organotin synthons	δ(H$_A$)	δ(H$_B$)	δ(H$_C$)	J(3C)	^2J(Sn—H$_A$)
Ia[a]	$Bu_3Sn\overset{A}{C}H(O\overset{B}{C}H_2\overset{C}{C}H_3)_2$	5.10	3.44	1.14	6.5	33.3
Ib	$Bu_3Sn\overset{A}{C}H(O\overset{B}{C}H_3)_2$	4.93	3.22			34.9
IIa	$Bu_3Sn\underset{Cl}{\overset{A}{C}}HO\overset{B\text{-}B'}{C}H_2\overset{C}{C}H_3$	5.82	3.45 and 4.02 (J(BB') 8.8)	1.16	6.7	30.7
IIb	$Bu_3Sn\underset{Cl}{\overset{A}{C}}HO\overset{B}{C}H_3$	5.79	3.42			30.7
IIIa	$Bu_3Sn\overset{A}{C}H_2O\overset{B}{C}H_2\overset{C}{C}H_3$	3.63	3.30	1.10	7	15.5
IIIb	$Bu_3Sn\overset{A}{C}H_2O\overset{B}{C}H_3$	3.60	3.24			15.3

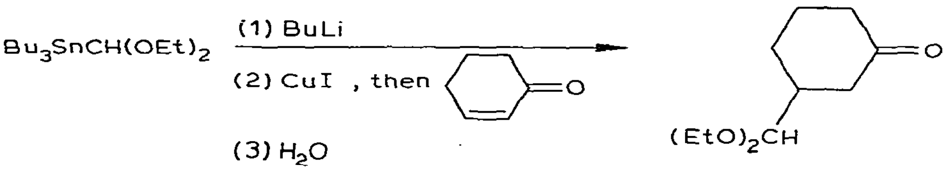
[a] ^{119}Sn NMR at 33.54 MHz in C_6D_6 showed a signal at −57.8 ppm (from Me_4Sn) and indicated over 98% purity.

Thus benzyl bromide gave 78% (isolated) yield of the acetal, and this gave phenylacetaldehyde upon mild hydrolysis:

$$Bu_3SnCH(OEt)_2 \xrightarrow[(2)\ PhCH_2Br]{(1)\ BuLi} PhCH_2CH(OEt)_2 \xrightarrow[H^+]{H_2O} PhCH_2CHO$$

When benzaldehyde was used as the trap, phenylacetic acid methyl ester was isolated (60% yield) following hydrolysis, probably because of further transformations during the work up.

Finally, in the presence of cuprous iodide, 1,4 addition of the new lithium reagent to cyclohexenone was observed (43% yield of isolated product):



The yields have not yet been optimized and only a few of the possible uses of the new organotin synthons have so far been explored. It is clear that they may become very valuable reagents, and we are currently exploring their potential.

Acknowledgments. Generous gifts of chemicals from Schering-France are warmly acknowledged.

References

1 D.J. Peterson, Organometal. Chem. Rev. A, 7 (1972) 295.
2 W.C. Still, J. Amer. Chem. Soc., 100 (1978) 1481.
3 N. Meyer and S. Seebach, Chem. Ber., 113 (1980) 1290.
4 D. Seebach, Synthesis, 1 (1969) 17.
5 D. Seebach and E.J. Corey, J. Org. Chem., 40 (1975) 231.
6 A. Krief, Tetrahedron, 36 (1980) 2531.
7 J.P. Quintard and M. Pereyre, Reviews on Si, Ge, Sn, Pb Compounds, 4 (1980) 151.
8 J.C. Lahournere and J. Valade, J. Organometal. Chem., 22 (1970) C3.
9 R.P. Houghton and A.D. Morgan, J. Chem. Soc., Perkin Trans I, (1980) 756.
10 P. Jutzi and O. Lorey, Phosphorus and Sulfur, 7 (1979) 203.