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# (TRIMETHYLSILYLMETHYL)TRIBUTYLTIN: A CONVENIENT *IN SITU* PRECURSOR OF TRIMETHYLSILYLMETHYLLITHIUM

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*Abstract.* The transmetalation reaction between (trimethylsilylmethyl)tributyltin and *n*-butyllithium proceeds in quantitative yield at 0°C in a mixture of tetrahydrofuran and hexane to afford trimethylsilylmethyllithium and tetrabutyltin. The methylenation of aldehydes and ketones utilizing this *in situ* procedure is demonstrated.

Trimethylsilylmethyllithium (2) has enjoyed considerable popularity in recent years as a reagent for the methylenation of ketones and aldehydes (Peterson olefination),[2] the formation of α-trimethylsilyl ketones from esters,[3] and in organometallic synthesis.[4] Routine application of this versatile reagent in synthesis, however, is limited by the tedious preparation from chloromethyltrimethylsilane *via* lithium-halogen exchange[5] or from tetramethylsilane *via* direct lithiation.[6] Although a number of highly reactive α-neutral heterosubstituted carbanions are available *via* transmetalation of the corresponding organostannane with *n*-butyllithium,[7] Peterson has reported that a hexane solution of (trimethylsilylmethyl)tributyltin (1) is inert to *n*-butyllithium at room temperature and that only *ca*. 25% transmetalation could be realized over a reaction period of 24 hours upon addition of TMEDA.[8]

We have observed that the reaction of 1 with *n*-butyllithium is remarkably solvent dependent and that in a mixture of hexane and tetrahydrofuran a quantitative transmetalation occurs in 30 minutes at 0°C to yield 2 and tetrabutyltin (3). The utility of this *in situ* technique

$$\underset{1}{\mathrm{Me_3SiCH_2Sn}(\underline{n}\text{-}\mathrm{Bu})_3} + \underline{n}\text{-}\mathrm{BuLi} \xrightarrow[\substack{0^\circ\mathrm{C} \\ 30\ \mathrm{min}}]{\substack{\text{tetrahydrofuran} \\ \text{hexane}}} \underset{2}{\mathrm{Me_3SiCH_2Li}} + \underset{3}{\underline{n}\text{-}\mathrm{Bu_4Sn}}$$

for the generation of 2 is illustrated by methylenation of a series of representative aldehydes and ketones. Yields utilizing this method are comparable to or greater than reported procedures (Table). The by-product of the transmetalation, tetrabutyltin (3), is conveniently removed from the intermediate silyl alcohol adduct by rapid filtration through a short column of silica gel with hexane. Typically, 3 is isolated in >90% of the theoretical yield. The desired alkene may then be generated by standard procedures. Significantly, no alcohols corresponding to carbonyl addition by n-butyllithium have been observed.

The synthesis of 1 is accomplished in over 90% yield by reaction of chloromethyltrimethylsilane (4) with tributylstannyllithium (5)[9] in a mixture of tetrahydrofuran and hexane at 0°C for 30 minutes. The alternative approach using trimethylsilylsodium[10] or -potassium[11] (6), generated in situ from hexamethyldisilane[12] and sodium- or potassium methoxide, and chloromethyltributyltin (7)[13] gave a complex mixture of products.

$$\begin{array}{ccccc}
\text{Me}_3\text{SiCH}_2\text{Cl} & + & (\underline{\text{n}}\text{-Bu})_3\text{SnLi} & \xrightarrow[\text{0°C}]{\text{tetrahydrofuran} \atop \text{hexane}} & \text{Me}_3\text{SiCH}_2\text{Sn}(\underline{\text{n}}\text{-Bu})_3 \\
4 & & 5 & \text{30 min} & 1 \\
\text{Me}_3\text{SiNa(K)} & + & (\underline{\text{n}}\text{-Bu})_3\text{SnCH}_2\text{Cl} & \not\longrightarrow & 1 \\
6 & & 7 & &
\end{array}$$

The following procedure is representative of this method. To a flame-dried flask with septum-capped side arm under nitrogen was added a solution of 2.263 g (6.000 mmol) of (trimethylsilylmethyl)tributyltin (1) in 8 mL of dry tetrahydrofuran. The flask and contents were cooled to 0°C and 4.0 mL (6.0 mmol) of n-butyllithium in hexane was added dropwise with stirrin After 30 min the reaction mixture was cooled to -78°C and a solution of 998 mg (6.00 mmol) of veratraldehyde in 2 mL of dry tetrahydrofuran was added dropwise. The reaction was stirred at -78°C for 5 min, water was added and the mixture was extracted with three 10 mL portions of hexane. The combined organic extracts were washed with water, dried ($Na_2SO_4$) and concentrated under reduced pressure. Rapid filtration of the crude product over 15 g of silica gel with hexane afforded 2.083 g (100%) of tetrabutyltin (3). Elution with a mixture of ethyl acetate and hexane (1:1) gave 1.374 g of the silyl alcohol adduct which was stirred in a two phase mixture composed of 10 mL of hexane and 10 mL of 50% aqueous acetic acid for 30 min. The layers were separated and the organic phase was washed with 5% aqueous sodium bicarbonate, water, dried ($Na_2SO_4$) and concentrated under reduced pressure. Short column chromatography of the residue with a mixture of hexane and ethyl acetate (9:1) as eluant yielded 760 mg (77%) of 3,4-dimethoxystyrene. Spectral data were in accord with literature values.[14]

The ready availability of 1 and its facile transformation to the versatile reagent 2 augur well for the inclusion of this method into the standard repertoire of the synthetic organic chemist. We are currently exploring other facets of the chemistry of 1.

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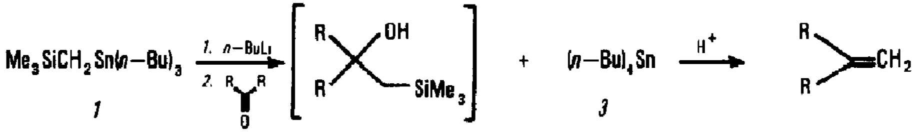
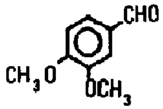
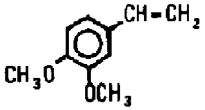
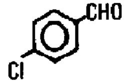
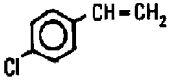
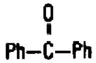
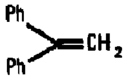
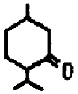
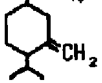
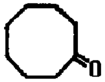
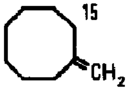
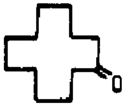
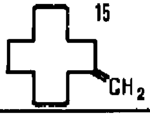
TABLE



| Substrate | Equivalents 1/Temp (°C)/Time | Acid[a]/Temp (°C)/Time | Product | Yield[b] |
|---|---|---|---|---|
| $CH_3(CH_2)_6CHO$ | 1/-78°15 min | $H_2SO_4$, THF/65°/2 hr. | $CH_3(CH_2)_6CH=CH_2$ | 61 |
|  | 1/-78°/5 min. | 25°/30 min |  | 77 |
|  | 1.2/-78°/5 min. | 25°/3 hr. |  | 72 |
|  $Ph-\overset{O}{\overset{\|}{C}}-Ph$ | 1/-78°/10 min. | 25°/10 min. |  | 78 |
|  | 1/-78°/1 hr. | 25°/24 hr. |  [15] | 80 |
|  | 1/-78°/30 min. | 25°/24 hr. |  [15] | 46[c] |
|  | 1/-78°/30 min. | 25°/48 hr. |  [15] | 90[c] |

*a. 50% aqueous acetic acid/hexane, unless otherwise specified.*

*b. all yields refer to isolated purified products.*

*c. yield based on recovered starting material.*

## References and Notes

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