Lithium Phenylthio(trimethylstannyl)cuprate, a New Reagent for Conjugate Addition of the Me_3Sn Group. The Synthesis of β-Trimethylstannyl-αβ-unsaturated Ketones

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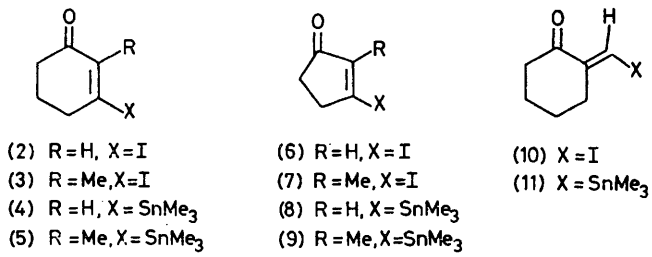
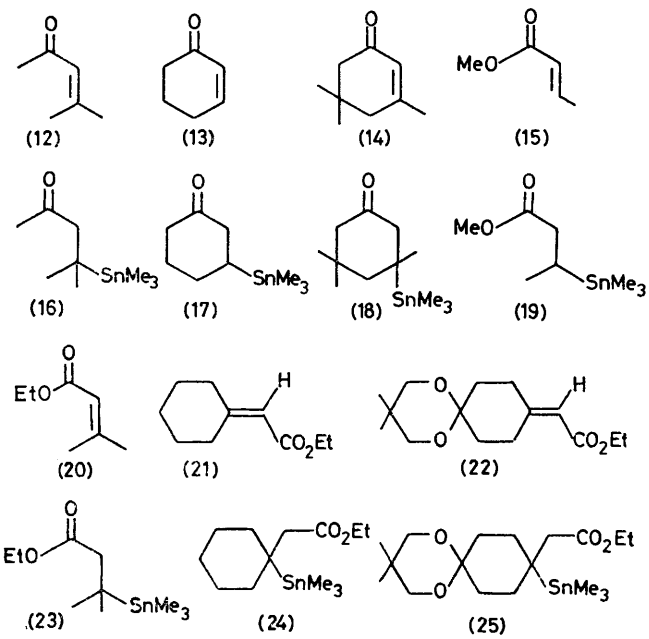
Summary Treatment of a solution of Me_3SnLi in tetrahydrofuran with 1 equiv. of PhSCu affords $PhS(Me_3Sn)CuLi$, a new reagent which efficiently transforms β-iodoenones into β-trimethylstannyl-αβ-unsaturated ketones, a new class of organotin derivatives.

RECENT reports clearly indicate that organotin compounds are highly versatile intermediates in organic synthesis.[1,2] Recently, we started to investigate the synthesis and chemical reactivity of β-trialkylstannyl-αβ-unsaturated ketones, a hitherto unknown class of organotin compounds. We report herein (a) the preparation of PhS(Me$_3$Sn)CuLi (**1**), a new reagent which efficiently transfers, in a conjugate sense, the Me$_3$Sn group to certain αβ-unsaturated carbonyl compounds, and (b) the use of (**1**) in effecting the smooth conversion of β-iodo-enones into the corresponding β-trimethylstannyl enones.





Although reaction of the iodo-enones (**2**), (**3**), and (**6**) with Me$_3$SnLi in tetrahydrofuran (THF)[2] resulted in the formation of moderate amounts of the corresponding substitution products (**4**), (**5**), and (**8**), respectively, these transformations were not very reproducible and gave, in addition to the desired products, varying amounts of starting material and/or diaddition products [ββ-bis(trimethylstannyl)cycloalkanones]. Therefore, the use of other reagents to effect this type of transformation was considered.

Addition of 1 equiv. of solid PhSCu[3] to a cold (−20 °C) solution of Me$_3$SnLi[2] in THF resulted in the immediate formation of a deep red solution of the cuprate reagent PhS(Me$_3$Sn)CuLi (**1**).† The latter reacted (−20 °C, 15 min; 25 °C, 30 min) smoothly and cleanly with 0·9 equiv. of the iodo-enone (**2**) to afford, in 86% yield, pure 3-trimethylstannylcyclohex-2-en-1-one (**4**): λ_{max}(MeOH) 236 nm (ε 12,100); ν_{max} (film) 1665 cm^{-1}; δ (CDCl$_3$) 0·17 (s, 9H), 1·82–2·12 (m, 2H), 2·28–2·56 (m, 4H), and 6·22 (t, 1H, *J* 2 Hz).‡ Similarly, a number of other β-iodo-enones (**3**), (**6**), (**7**), and (**10**) were converted efficiently into the corresponding β-trimethylstannyl enones (**5**), (**8**), (**9**), and (**11**), respectively (Table).

TABLE. Conjugate addition of Me$_3$Sn to β-iodo-enones and αβ-unsaturated carbonyl compounds

Substrate	Product	Yield (%)[a] Me$_3$SnLi	Reagent (**1**)
(**2**)[b]	(**4**)	—[d]	86
(**3**)[b]	(**5**)	—[d]	84
(**6**)[c]	(**8**)	—[d]	83
(**7**)[b]	(**9**)	—[e]	82
(**10**)[c]	(**11**)	—[e]	77
(**12**)	(**16**)	93[f]	76
(**13**)	(**17**)	96[f]	91
(**14**)	(**18**)	77[f]	69
(**15**)	(**19**)	71	67
(**20**)	(**23**)	74	—[g]
(**21**)	(**24**)	80[f]	—[g]
(**22**)	(**25**)	75	—[g]

[a] Yields from the present work refer to isolated, purified material. [b] E. Piers and I. Nagakura, *Synth. Comm.*, 1975, **5**, 193. [c] E. Piers, C. K. Lau, and I. Nagakura, *Tetrahedron Letters*, 1976, 3233. [d] See text. [e] Not attempted. [f] Taken from ref. 2. [g] Starting material recovered in high yield.

In terms of its ability to transfer conjugately the Me$_3$Sn group to αβ-unsaturated carbonyl systems, reagent (**1**) was found to be more selective than Me$_3$SnLi. Thus, the data in the Table show that although (**1**) readily transferred the Me$_3$Sn group to the unsaturated ketonic substrates (**12**)–(**14**) and to (*E*)-methyl crotonate (**15**), it failed to react with the ββ-disubstituted-αβ-unsaturated esters (**20**)–(**22**). On the other hand, Me$_3$SnLi smoothly converted all these substates [(**12**)–(**14**), (**15**), and (**20**)–(**22**)] into the corresponding trimethylstannyl derivatives.

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† The formation of (Me$_3$Sn)$_2$CuLi has been reported: J. Hudec, *J.C.S. Perkin I*, 1975, 1020. This reagent was used to effect conjugate addition of the Me$_3$Sn group to two cyclohexenone derivatives, although no yields were given. We have found that (Me$_3$Sn)$_2$CuLi will also convert β-iodo-enones into the corresponding trimethylstannyl derivatives. However, since 2 equiv. of Me$_3$SnLi are required to prepare 1 equiv. of (Me$_3$Sn)$_2$CuLi, it seems clear that PhS(Me$_3$Sn)CuLi is the preferred reagent.

‡ All new compounds reported herein exhibited expected spectral properties and gave satisfactory elemental analyses and/or molecular weight determinations (high-resolution mass spectrometry).

[1] Reports during 1977 include: R. Bürstinghaus and D. Seebach, *Chem. Ber.*, 1977, **110**, 841; B-T. Gröbel and D. Seebach, *ibid.*, p. 852, 867; R. T. Tayler, C. A. Degenhardt, W. P. Melega, and L. A. Paquette, *Tetrahedron Letters*, 1977, 159; J. Ficini, S. Falou, A-M. Touzin, and J. d'Angelo, *ibid.*, p. 3589; D. Seyferth, K. R. Wursthorn, and R. E. Mammarella, *J. Org. Chem.*, 1977, **42**, 3104; R. H. Wollenberg, K. F. Albizati, and R. Peries, *J. Amer. Chem. Soc.*, 1977, **99**, 7365; T. Kauffmann, R. Kriegesmann, and A. Woltermann, *Angew. Chem. Internat. Edn.*, 1977, **16**, 862.
[2] W. C. Still, *J. Amer. Chem. Soc.*, 1977, **99**, 4836.
[3] G. H. Posner, D. J. Brunelle, and L. Sinoway, *Synthesis*, 1974, 662.