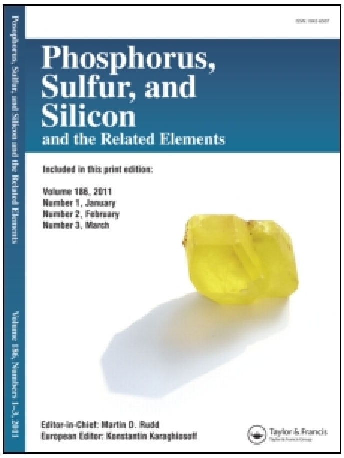


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Synthetic Applications of Coordinated TIN Enolates and TIN Hydrides

Akio Baba; Ikuya Shibata; Makoto Yasuda

To cite this Article Baba, Akio , Shibata, Ikuya and Yasuda, Makoto(1999) 'Synthetic Applications of Coordinated TIN Enolates and TIN Hydrides', Phosphorus, Sulfur, and Silicon and the Related Elements, 150: 1, 293 — 298

To link to this Article: DOI: 10.1080/10426509908546396
URL: http://dx.doi.org/10.1080/10426509908546396

Phosphorus, Sulfur and Silicon, 1999, Vol. 150-151, pp. 293-298
Reprints available directly from the publisher
Photocopying permitted by license only

Published by license under the
Gordon and Breach Science Publishers imprint.
Printed in Malaysia

Synthetic Applications of Coordinated TIN Enolates and TIN Hydrides

AKIO BABA, IKUYA SHIBATA and MAKOTO YASUDA

Department of Applied Chemistry, Faculty of Engineering, Osaka University, Yamadaoka, Suita, Osaka 565–0871, Japan

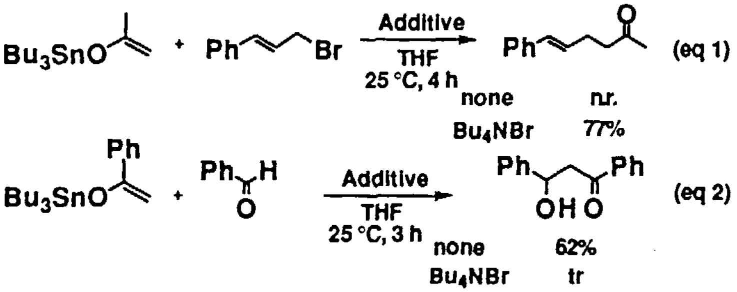
Bromo anion-coordinated tin enolates readily coupled with organic halides, while the inherent reactivity of non-coordinated enolates toward aldehydes was dramatically depressed by the coordination. HMPA-Coordinated dibutyl-iodotin hydride chemoselectively reduced oxirane rings, where such reducible groups as halides, esters, and ketones were tolerated.

Keywords: high-coordination; tin enolate; tin hydride; ^{119}Sn NMR; coupling; reduction

The variety of organotin compounds are utilized in organic synthesis, in which coupling reactions with organic halides and the additions to carbonyl moieties have been extensively studied. In general, as the reactivity of tin reagents is considerably low, a variety of activators are required. Because almost of them are Lewis acids or transition metal catalysts which generally interact with the partner reagents of organotin compounds, the development of novel activators of tin compounds is an important subject. In this paper, we wish to report on the activation of organotin enolates and hydrides by coordination of halide anions or weak Lewis bases. The coordination could dramatically depress the addition reaction to carbonyl moieties, promoting other nucleophilic substitutions.

Non-coordinated tin enolates readily react with aldehydes to give the corresponding aldols after hydrolysis, while no coupling reactions with organic halides take place[1]. Although some couplings with active halides have been applicated to the synthesis of natural compounds, all the enolates are generated *in situ* where many reagents like alkali metal halides, lewis acids or bases exist together[2]. Because distillated pure enolates proved to be unreactive toward halides, the reported coupling should receive some assistance.

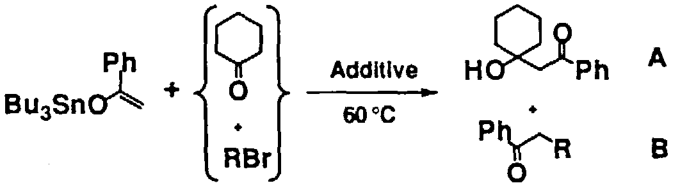
A non-coordinated tin enolate gave the adduct with benzaldehyde, and no adduct with cinnamyl bromide (eqs 1 and 2). In contrast, the use of Bu_4NBr almost completely depressed the addition to benzaldehyde, whereas the coupling with cinnamyl bromide facily took place, furnishing γ, δ-unsaturated ketone.



This change of reactivity was further demonstrated by intermolecularly competitive reactions as shown in Table 1[3]. The typical reaction was carried out as follows. A mixture of a tin enolate (1.2 mmol) and Bu_4NBr in acetonitrile (1 mL) was stirred for 10 min. Then to this solution was added a mixture of a halide (1.0 mmol) and cyclohexanone (1,0 mmol), and the resulting mixture was stirred for 3 hrs at 60°C. After workup, the yields of products were determined by ^1H NMR. In the presence of

Bu_4NBr, no formation of hydroxy ketones **B** was observed, furnishing adduct **A** exclusively. Using the equimolar of tributyltin enolate derived from cyclohexanone and Bu_4NBr in C_6D_6, the coordination of the bromide was confirmed by upfield shift of ^{119}Sn NMR from 90 ppm to 63 ppm.

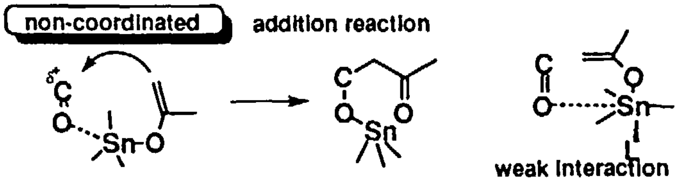
Table 1



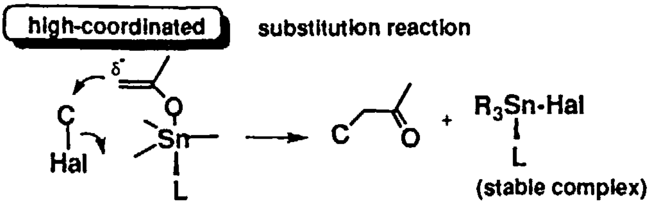
R	Additive	Time	Solv	Yield/% A	Yield/% B
$PhCH_2$	none	6 h	THF	24	tr
	Bu_4NBr	3	CH_3CN	0	56
$PhCH{=}CHCH_2$	none	6	THF	40	0
	Bu_4NBr	3	CH_3CN	0	99

The reason why the change of chemoselectivity was promoted by the coordination is assumed as follows (Scheme 1). In the case of addition to carbonyl moieties (an addition reaction), because the interaction between non-coordinated tin center and carbonyl oxygen is followed by nucleophilic addition of the enolate to the carbonyl carbon, the coordina-tion interrupts the interaction. In the coupling with organic halides (a substitution reaction), a nucleophilic addition of enolate starts the reaction. The coordination of bromide anion must increase the nucleophilicity of the enolate, and moreover the complexation of tributyltin halide promotes the substitution reaction because of its stabilization effect.

Scheme 1

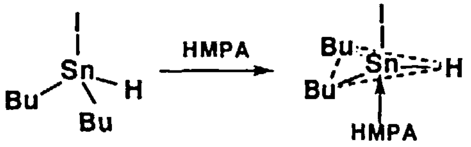


(scheme 1 continued)



HIGH-COORDINATED DIBUTYLIODOTIN HYDRIDE

Organotin hydrides have been widely utilized in dehalogenation *via* a radical mannner[4], and a few applications in ionical reductions of functional groups such as carbonyls have been reported[5]. The increasing the nucleophilicity of enolates by high-coordination prompted us to develop a new type of coordinated tin hydride, Bu_2SnIH - HMPA. Bu_2SnIH readily prepared by redistribution between Bu_2SnH_2 and Bu_2SnI_2 was coordinated by HMPA[6]. The structure and spectral data are shown in eq 3.

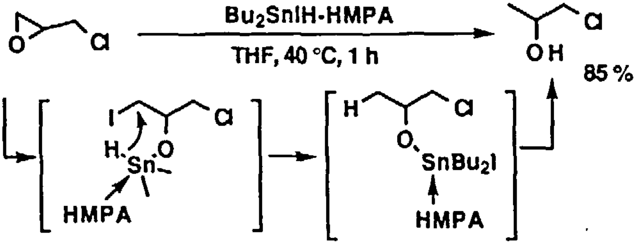


(eq 3)

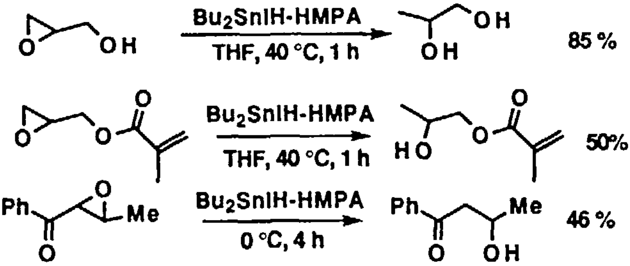
$\delta(^{119}Sn)$	- 76 ppm	-170 ppm
$^1J(Sn\text{-}C)$	399 Hz	513 Hz
$^1J(Sn\text{-}H)$	2060 Hz	2349 Hz

The large upfield shift from - 76 ppm to - 170 ppm apparently shows the generation of five coordinated complex. The increase of values of coupling constants, ^1J Sn-C and ^1J Sn-H, indicates that both the butyl and hydrogen group occupy the equatorial positions[7]. The nucleophilicity of the iodide in apical position is expected to be strengthened by the coordination of HMPA. Using this complex, chemoselective reductions of oxirane rings were achieved as shown in Scheme 2, in which the oxirane-cleavage by iodide is assumed to be the first step.

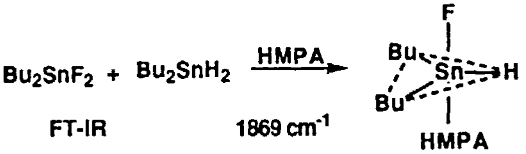
Scheme 2



The oxirane ring-selectivity was demonstrated in the following examples. Such groups as hydroxy, ester, carbon-carbon double bond and carbonyl tolerated the reduction with the tin hydride complex.



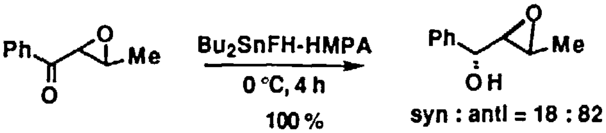
Instead of the iodide, the introduction of fluoride which has little nucleophilicity was attempted. The fluoride complex was also synthesized by redistribution between Bu_2SnF_2 and Bu_2SnH_2. This redistribution took place only in the presence of HMPA (eq 4), and so non-coordinated Bu_2SnFH could not be obtained.



(eq 4)

FT-IR	1869 cm^{-1}
^{119}Sn NMR	- 123 ppm
^{19}F NMR	- 164 ppm
$^{1}J\,(^{119}Sn\text{-}H)$	2428 Hz
$^{1}J(^{119}Sn\text{-}C)$	547 Hz

This fluoride complex reduced the keto oxirane into an α-hydroxy oxirane quantitatively, where the carbonyl group was selectively reduced in contrast to the reaction by the corresponding iodide complex[8].



References

[1] Y. Odic, M. Pereyre, J. Organomet. Chem., **11**, 21 (1968).

[2] H. Nishiyama, K. Sakuta, K. Itoh, Tetrahedron Lett., **25**, 2487 (1984). M. Suzuki, A. Yanagisawa, R. Noyori, J. Am. Chem. Soc., **107**, 3348 (1985).

[3] M. Yasuda, K. Hayashi, K. Katoh, I. Shibata, A. Baba, J. Am. Chem. Soc., **120**, 715 (1998).

[4] W. P. Neumann, Synthesis, 665 (1987).

[5] M. D. Castaing, A, Rahm, J. Org. Chem., **51**, 3653 (1970). N. Y. M. Fung, P. Mayo, J. H. Schauble, A. C. Weedon, J. Org. Chem, **43**, 3977 (1978).

[6] T. Kawakami, I. Shibata, A. Baba, J. Org. Chem., **61**, 81 (1996).

[7] J. Holecek, M. Nadvornik, K. Handlir, A. Lycka, J. Organomet. Chem., **241**, 177 (1983). M. Nadvornik, J. Holecek, K. Handlir, A. Lycka, J. Organomet. Chem., **275**, 43 (1984).

[8] Recently we reviewed on the reaction with tinhydride. I. Shibata, A. Baba, Reviews on Heteroatom Chemistry, **18**, 247 (1998).