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The Reaction of α-Tributylstannylthioacetals with Enol Trimethylsilyl Ethers. Preparation of β-Tributylstannyl-α, β-unsaturated Ketones

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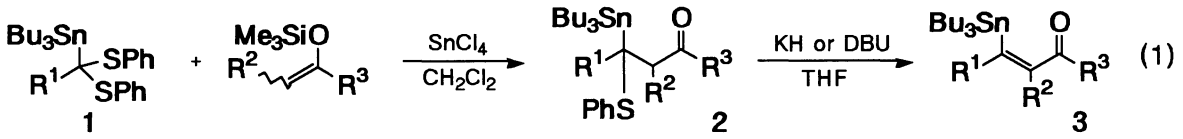
The tin(IV) chloride-promoted reaction of enol trimethylsilyl ethers with α-tributylstannylthioacetals gave β-phenylthio-β-tributylstannylketones, which were easily transformed to β-tributylstannyl-α, β-unsaturated ketones (3) by the treatment with potassium hydride or DBU. On the basis of the results obtained in the study of the reaction of 3 with copper(II) bromide, it was assumed that the present reaction gave Z-isomers predominantly.

Recently, the preparation and reactions of β-metaloketones and esters have been extensively studied because of their synthetic utility as homoenolates.[1] Concerning the preparation of β-stannyl carbonyl compounds, the following two main routes are known: the ring opening reaction of trimethylsiloxycyclopropanes with tin(VI) halides[2] and the reaction of α, β-unsaturated ketones with anionic complexes of organotin species[3] or trichlorotin hydride.[4] In this communication, we describe a convenient method for the preparation of β-phenylthio-β-tributylstannylketones (2) by the reaction of α-tributylstannylthioacetals (1) with enol trimethylsilyl ethers and the stereoselective transformation of 2 into (Z)-β-tributylstannyl-α, β-unsaturated ketones (3).

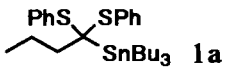
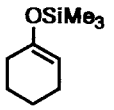
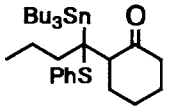
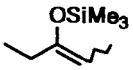
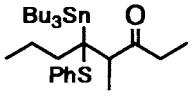
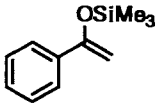
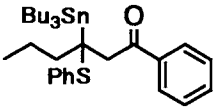
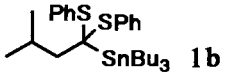
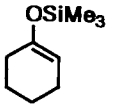
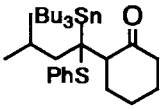
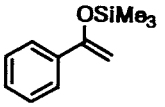
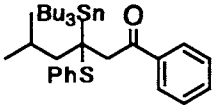
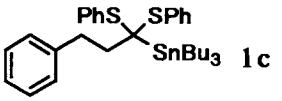
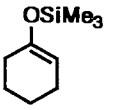
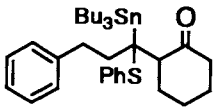
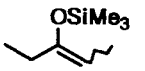
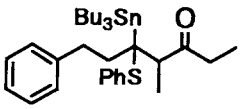
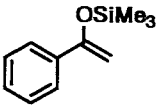
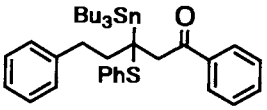


(1)

The starting materials, α-tributylstannylthioacetals (1), were easily synthesized by the treatment of the lithium salts of thioacetals (n-BuLi (1.0 equiv.), THF, -40 °C, 1 h) with tributyltin chloride (1.1 equiv., -40 °C, 1 h, **1a**; 93%, **1b**; 89%, **1c**; 97%). When the thioacetals (1) were treated with enol trimethylsilyl ethers in the presence of tin(IV) chloride, the coupling reaction proceeded to produce β-phenylthio-β-tributylstannylketones (2).[5] The coupling products (2) were stable under acidic reaction and work-up conditions and isolated by silica-gel chromatography as a mixtures of diastereomers in good to high yields (Table 1).

The typical reaction procedure is as follows: To a CH_2Cl_2 (15 ml) solution of 3-phenyl-1,1-bis(phenylthio)-1-tributylstannylpropane (**1c**) (3.08 g, 4.93 mmol) and 1-trimethylsiloxy-1-cyclohexene (1.26 g, 7.40 mmol) was added a CH_2Cl_2 (4.83 ml) solution of $SnCl_4$ (4.93 mmol) at -78 °C. After being stirred for 3 h, the reaction was quenched by addition of water and the organic materials were extracted with CH_2Cl_2, dried

Table 1. The reaction of α-tributylstannylthioacetals (1) with enol trimethylsilyl ethers [a]

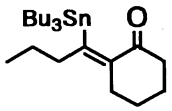
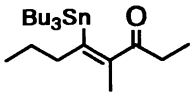
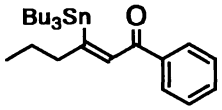
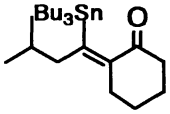
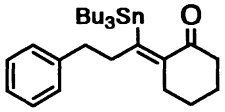
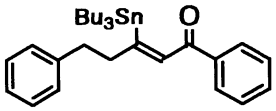
Run	1	Enol trimethylsilyl ether	Time h	2	Yield[b] %
1	 1a		5		2a 94
2			2.5		2b 71
3			5		2c 76
4	 1b		3		2d 89
5			5		2e 89
6	 1c		4		2f 90
7			3.5		2g 69
8			3.5		2h 92

a) All reactions were performed with a similar procedure as described in the text, unless otherwise noted. b) All products were identified by IR and NMR spectra.

(Na_2SO_4), and condensed under reduced pressure. The residue was purified by silica-gel chromatography (hexane : AcOEt = 98 : 2) to give 2-(3-phenyl-1-phenylthio-1-tributylstannyl)propylcyclohexanone (**2f**) (2.73 g, 90%).

Next the transformation of β-phenylthio-β-tributylstannylketones (**2**) to β-tributylstannyl-α, β-unsaturated ketones (**3**) by the base-promoted elimination of thiophenol was examined (Table 2). Among various bases examined, DBU was found to be effective for the transformation of acyclic ketones (runs 2, 3, and 6). On

Table 2. The preparation of β-tributylstannyl-α, β-unsaturated ketones (3)[a)]

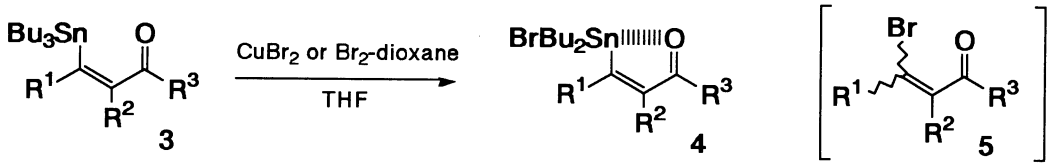
Run	2	Base (equiv.)	Temp ℃	Time h	3	Yield[b)] %
1[c)]	2a	KH(5)	0	3.5	 3a	77
2	2b	DBU(2)	reflux	17	 3b	65
3	2c	DBU(2)	0	3	 3c	89
4[c)]	2d	KH(5)	0	3	 3d	90
5[c)]	2f	KH(5)	0	3	 3f	85
6	2h	DBU(2)	0	3	 3h	88

a) The reaction was carried out using THF (3 ml / 1 mmol of 2). b) The structures of these compounds were supported by IR and NMR spectra. c) HMPA (1 ml / 1 mmol of 2) was used as a cosolvent.

the other hand, the cyclohexanone derivatives were obtained in good yields using potassium hydride in THF-HMPA (runs 1, 4, and 5).

The NMR spectra of 3 suggested that they consisted of single stereoisomers. Although it was difficult to determine their configuration and stereoisomeric ratio by spectral data, the configuration was assumed to be Z on the basis of the following experimental results. The reaction of 3 with copper(II) bromide (2.2 equiv.)[6)] or bromine-dioxane complex in THF (r.t., 3 h) gave the bromovinylstannanes (4), and the formation of the corresponding vinyl bromide (5) was not observed in all the reactions examined (Table 3). It is well known that vinyl group is more reactive than alkyl group in the electrophilic cleavage of organotin compounds.[7)] On the other hand, Jousseaume and Villeneuve reported that the intramolecular nucleophilic assistance dramatically change the reactivity of substituents on tin atom in halogenolysis; alkyl-tin bond is cleaved in preference to aryl-tin bond in the reaction of tributyl[2-(N,N-dimethylaminomethyl)phenyl]tin with iodine.[8)] Therefore, it is reasonable to assume that the observed unusual cleavage of alkyl-tin bond of 3 is due to the intramolecular nucleophilic assistance of carbonyl oxygen. Moreover, the fact that C=O stretching frequency of 4 is lowered by

about 30 cm^{-1} compared with the corresponding tributylstannyl derivative (3) (see Table 3) indicates the existence of intramolecular coordination of carbonyl group to tin atom,[2] which is only possible in Z-configuration. These results suggest that the present reaction gave Z-stereoisomers predominantly.



(2)

Table 3. The reaction of β-tributylstannyl-α, β-unsaturated ketones (3) with copper(II) bromide

Run	3	C=O stretching frequency of 3	Yield of 4[a]	C=O stretching frequency of 4
		cm^{-1}	%	cm^{-1}
1	**3a**	1669	74	1630
2	**3b**	1670	83	1639
3	**3c**	1649	77	1617
4	**3d**	1660	89 (92)[b]	1630
5	**3f**	1662	91	1630
6	**3h**	1646	88	1617

a) Isolated by TLC (AcOEt-AcOH then AcOEt-hexane). b) Bromine-dioxane complex was used.

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References

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