

THE REACTION OF TRIMETHYLSTANNYLMETHYLLITHIUM WITH ELECTROPHILES

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Trimethylstannylmethyllithium was found to be a versatile reagent for the preparation of 1-alkenes from carbonyl compounds, allyl alcohols from α -chloro ketones, and cyclopropanes from oxiranes.

The methylenation of carbonyl compounds is one of the most important reactions in organic synthesis, and Wittig or Horner-Emmons reaction using phosphorus ylides or Peterson reaction using α -silyl carbanions are the most-widely known reactions. However, these reactions are not always satisfactory particularly with enolizable ketones, which produce only low yields of the desired products or induce the extensive epimerization (vide infra). Kauffmann and his coworkers reported an alternative method of methylenation of ketones using triaryl or trialkylstannylmethyllithium as key reagents.¹⁾ Since carbonyl compounds examined in their papers have been limited to a few fundamental ketones and aldehydes, we extended the variety of the carbonyl compounds to those which give poorer results with conventional methods. We now found that trialkylstannylmethyllithium is a versatile reagent not only for the methylenation of the carbonyl compounds but for the preparation of allyl alcohols and cyclopropanes from some electrophiles.

Trimethylstannylmethyllithium (2) has been prepared from trimethylstannyl chloride through the reaction with Simmons-Smith reagent ($\text{CH}_2\text{I}_2 + \text{Zn-Cu}$) followed by the lithiation with *n*-butyllithium.¹⁾ In order to avoid the use of expensive trimethylstannyl chloride, we elaborated on the preparation of 2 from bis(trimethylstannyl)methane 1. The compound 1 could be prepared from diiodomethane, tin(II) bromide, and methylmagnesium iodide according to the reported method,²⁾ but we found

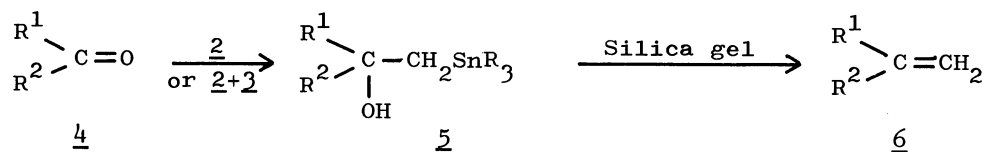
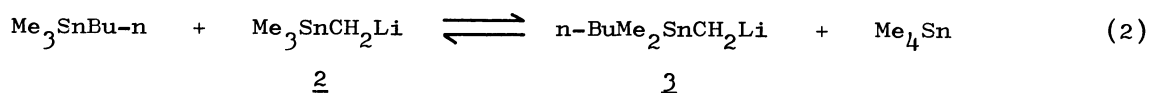
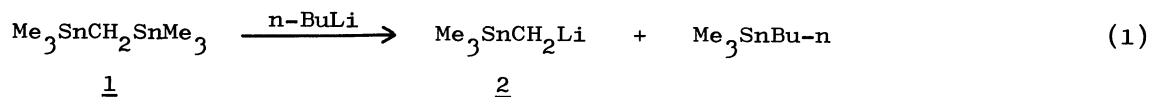


Table 1. Methylenation of Carbonyl Compounds 4

<u>4</u>	Carbonyl compounds R^1	R^2	Yields of olefins/% <u>6</u>
a	Ph	Ph	88
b	Ph	Et	78
c	PhCH_2CH_2	Me	81
d	1-Tetralone		91
e	Cycloheptanone		84
f	Cyclooctanone		64
g	$n\text{-C}_9\text{H}_{19}$	H	80
h	$p\text{-MeOC}_6\text{H}_4$	H	94
i	$\text{PhCH}=\text{CH}$	H	87
j	cis-1-Decalone		91
k	trans-1-Decalone		96

that the use of octane as a solvent, instead of the no-solvent procedure in the original report, was advisable for a larger scale preparation. The treatment of 1 with methyllithium produced 2, which was directly used for further reaction. When n-butyllithium was used instead of methyllithium, the product was contaminated by a butyl derivative 3, formed probably by the reaction (2). For the present study, however, the contamination does not make any trouble because the stannyl groups are removed during the reaction. When 2 or 2 + 3 was added to carbonyl compounds 4, 2-hydroxyalkylstannanes 5 were obtained. Upon treatment with silica gel at room temperature, they produced olefins 6 in good yields. The results are shown in Table 1.

The present reaction is characteristic in that propiophenone,³⁾

1-tetralone,^{4, 5)} or cycloheptanone,⁶⁾ which give the methylene compounds only in poor yields (5 - 20%) by the conventional Wittig reaction, gave the desired products in good yields, and that the reaction with cis-1-decalone⁵⁾ proceeded without any epimerization, when the reaction was carried out in the presence of HMPA.⁵⁾ Without HMPA, the epimerization occurred, and a mixture of cis and trans isomers (60 : 40) was produced in a yield of 66%. Under the conditions of Wittig reaction, the same mixture of the isomers was produced in 32% yield. Although two-step reaction via thiirane⁷⁾ and three-step reaction via phenylthiomethylation⁸⁾ have been reported for the satisfactory and epimerization-free methylenation of 1-tetralone and cis-1-decalone, respectively, the present reaction is far better in view of the better yield and simple operation.

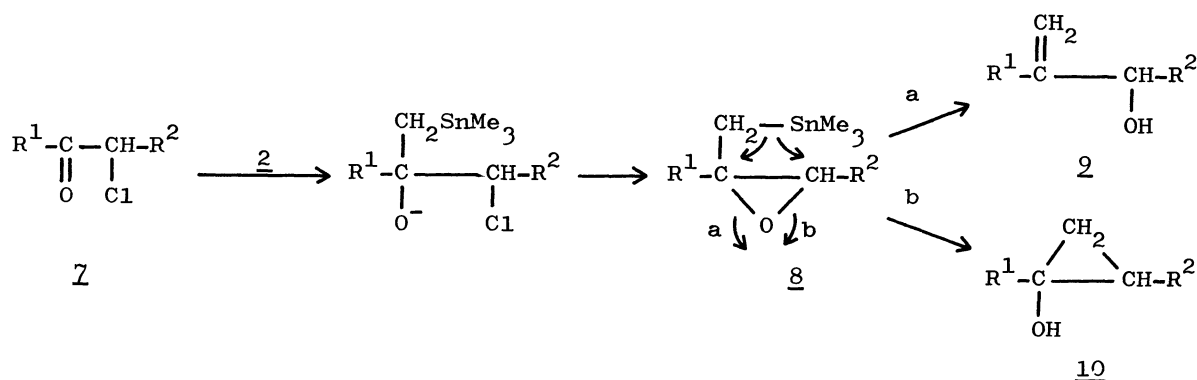


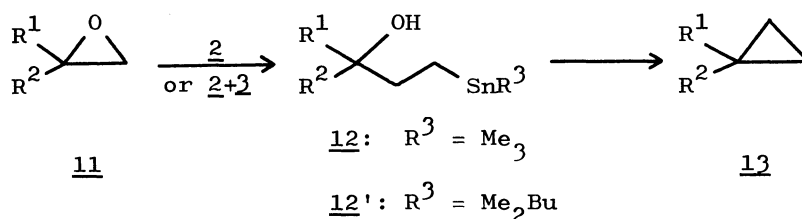
Table 2. Reaction of 2 with α -Chloro Ketones 7

<u>7</u>	α -Chloro ketones		Yields of allyl alcohols <u>2</u> /%
	R ¹	R ²	
a	Ph	H	67
b	Me	n-C ₅ H ₁₁	65
c	Ph	Me	70

Although it has been known that the presence of chlorine atom at the α -position of the carbonyl compounds makes the reaction by Wittig reagents very complicated,⁹⁾ the stannyl carbanion 2 reacted with α -chloro ketones 7 smoothly, and produced allyl alcohols 2 as shown in the Table 2. It is assumed that the reaction was initiated by the attack of the reagent to the carbonyl carbon, followed by

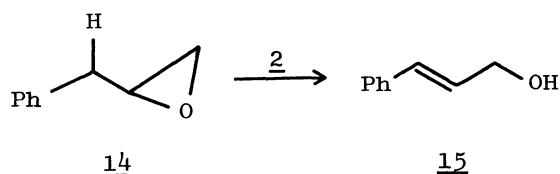
the formation of oxirane 8 and 1,2-elimination (path a) to afford 2. Notably, no cyclopropanols 10 through 1,3-elimination (path b) of 8 were detected.

It appeared that the nucleophilicity of the carbanion 2 was not strong enough to attack the oxiranes 11, since the oxirane 11a was recovered unchanged under the same conditions as above. The nucleophilicity of 2 was enhanced, however, upon the addition of HMPA to the reaction medium, and 3-hydroxyalkylstannanes 12 were obtained as shown in the Table 3. As mentioned above, the butyl derivative 12' was present in the product when n-butyllithium was used as a reagent. When the mixture of the stannanes (12 + 12') was treated with one of (A) trifluoroborane-etherate, (B) methanesulfonyl chloride-pyridine, or (C) triphenylphosphine, smooth reaction proceeded to afford cyclopropanes 13 in good yields. The cyclopropane 13a was also obtained when the reaction mixture from 11 and 2 was directly treated

Table 3. Reaction of 2 with Oxiranes 11

<u>11</u>	Oxiranes		Reagents	Yields of hydroxy stannanes /%		Cyclization methods ^{a)}	Yields of ^{b)} cyclopropanes /%
	R ¹	R ²		<u>12</u>	<u>12'</u>		<u>13</u>
a	Ph	Me	<u>1</u> -BuLi	50	20	A	98
			<u>1</u> -MeLi	78	-	D	66 ^{c)}
b	Ph	Ph	<u>1</u> -MeLi	75	-	A	97
						B	87
c	C ₆ H ₁₃	H	<u>1</u> -BuLi	45	13		
d	C ₁₀ H ₂₁	H	<u>1</u> -BuLi	42	12	C	82

a) See text. b) Yield from (12 + 12'). c) Overall yield from 11.



with trifluoroborane-etherate (Method D). Since oxiranes could be synthesized from olefins or carbonyl compounds through oxidation or reaction with sulfur ylides, respectively, the present reaction accomplish the preparation of cyclopropane from olefin or carbonyl compound. Although the preparation of cyclopropane from olefin could be achieved by using carbenoids as in Simmons-Smith reaction, the cyclopropanation of α -methylstyrene³⁾ or 1,1-diphenylethylene¹⁰⁾ proceeds with low yields (20 - 50%). With oxiranes having acidic hydrogen, such as 14, however, the carbanion 2 did not undergo the nucleophilic attack on the oxirane ring, but reacted as a base abstracting proton, thus producing an allyl alcohol 15.

It should be noted that only a reaction type observed with 3-hydroxyalkylstannanes 12 and 12' was cyclization, in contrast to the competing cyclization and 1,2-hydride shift in case of the corresponding silyl compounds.¹¹⁾

References

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