



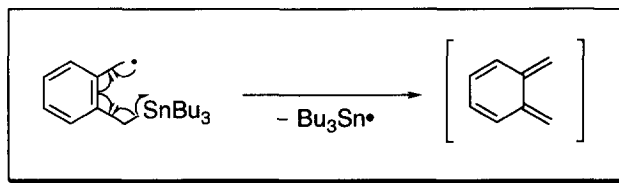
The Generation of α -Trimethylsiloxy-*o*-Quinodimethanes Induced by One-Electron Reduction to *o*-Acylbenzyltributylstannanes

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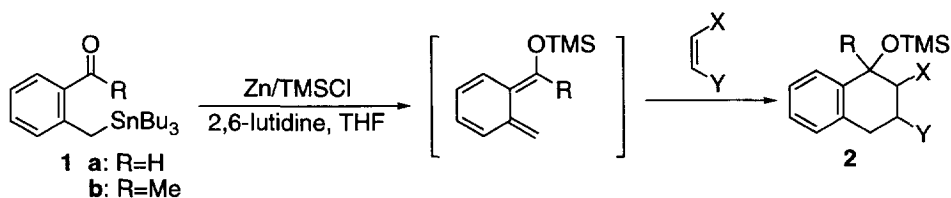
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Abstract: *o*-Tributylstannylmethyl benzaldehyde reacts with Zn in the presence of TMSCl and 2,6-lutidine at room temperature to give α -trimethylsiloxy-*o*-quinodimethane, which is trapped with dienophiles to afford cycloadducts in good to high yields. Copyright © 1996 Elsevier Science Ltd

Much attention has been focused on the synthesis of condensed cyclic compounds using *o*-quinodimethane intermediates, and numerous methods for the generation of the intermediates have been developed.¹ We previously reported new methods for the generation of *o*-quinodimethanes from tin precursors utilizing the high leaving ability of the tributylstannyl cation.² Our attention is now directed to the radical reactivity of tin compounds. Since cleavage of the carbon-tin bond takes place relatively easily under homolytic conditions,³ it can be expected that homolytic cleavage of the benzylic carbon-tin bond of the precursor would proceed to afford *o*-quinodimethane when a radical species is generated on the other benzylic position as illustrated below.



It is known that carbonyl groups are reduced by zinc in the presence of TMSCl to give α -trimethylsiloxy radicals, which are used for organic syntheses such as radical cyclizations.⁴ We would like to report here a new method for the generation of *o*-quinodimethanes involving the elimination of the tributylstannyl radical triggered by one-electron reduction of tin compounds **1**.



The precursor **1a** was prepared by the stannylation of *o*-methylbenzyl alcohol^{2a} followed by PDC oxidation in 55% overall yield, and **1b** was also successfully prepared in a similar manner.

The generation of *o*-quinodimethane intermediates followed by their intermolecular cycloadditions with electron-deficient olefins could be performed under mild conditions. Thus, the precursor **1a** reacted with zinc in the presence of TMSCl and 2,6-lutidine at room temperature to give α -trimethylsiloxy-*o*-quinodimethane which was efficiently trapped with various dienophiles. Table 1 shows the yield of the cycloadduct **2a** by the reaction of **1a** with dimethyl fumarate under various conditions, and that the conditions of entry 1 gave best result.

Table 1. Yield of **2a** by the treatment of **1a** with dimethyl fumarate under various conditions*

Entry	Zn(eq)	TMSCl(eq)	2,6-lutidine(eq)	Time(h)	GLC yield(%)
1	10	3	3	2	95
2	10	3	3	1	88
3	7	3	3	2	81
4	5	3	3	2	79
5	10	0	3	2	0
6	10	3	0	2	trace

* The reactions were carried out in THF at room temperature.

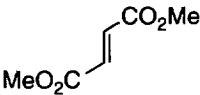
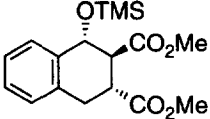
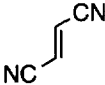
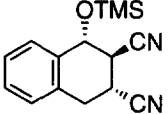
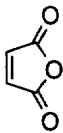
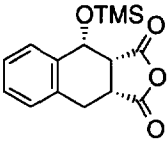
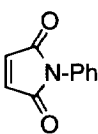
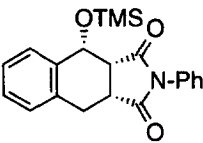
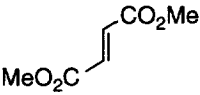
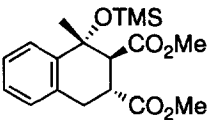
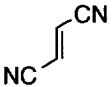
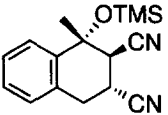
A typical experimental procedure is as follows. To a mixture of *o*-tributylstannylmethyl benzaldehyde **1a** (300 mg, 0.73 mmol), dimethyl fumarate (420 mg, 2.2 mmol), zinc (480 mg, 7.3 mmol), 2,6-lutidine (0.26 ml, 2.2 mmol), and THF (6 ml) was added TMSCl (0.28 ml, 2.2 mmol) with stirring at room temperature and the resulting mixture was stirred for 2 h. After filtration of the mixture, the solvent, excess TMSCl, and dimethyl fumarate were evaporated under reduced pressure, and the residue was chromatographed on silica-gel (hexane-ethyl acetate) to give pure cycloadduct **2a** in 79% yield as a mixture of two stereoisomers in a 62:38 ratio (Table 2, entry 1). ¹H-NMR indicated that the major stereoisomer was 1,2-trans exo adduct and the minor stereoisomer was 1,2-cis endo adduct.⁵ Similar selectivity was observed with fumaronitrile (entry 2). In the cases of maleic anhydride and *N*-phenyl maleimide, 1,2-cis endo stereoisomers were obtained with no detectable amount of 1,2-trans exo stereoisomers (entries 3 and 4). Stannyl ketone **1b** also afforded the corresponding cycloadducts in a similar manner, although somewhat higher temperature (40 °C) was necessary to obtain the cycloadducts in high yields (entries 5 and 6).

On the other hand, **1a** reacted with dimethyl maleate to give an unexpected adduct **6** in high yield (Scheme 1). The result indicates that the initially formed α -trimethylsiloxy radical **3** added to dimethyl maleate faster than the transformation of **3** to α -trimethylsiloxy-*o*-quinodimethane **4**.⁶ The fact that the reaction with dimethyl fumarate and dimethyl maleate gave different products, **5** and **6**, respectively excludes the possibility that the cycloadditions proceed via a stepwise mechanism such as an addition of radical **3** to dienophiles followed by intramolecular cyclizations of the resulting radical intermediates, because both radical intermediates formed by the addition of **3** to fumarate and maleate should be identical. Treatment of a germanium analog of the precursor **1a** with dimethyl fumarate in a similar reaction gave not the desired cycloadduct but an adduct **7** of radical **3** to dimethyl fumarate in high yield. It is conceivable that the elimination of the tributylgermyl radical from the intermediate **3** leading to *o*-quinodimethanes did not take place, presumably due to the larger bond energy of

carbon-germanium bond compared with that of the carbon-tin bond. It is obvious from these observations that the generation of α -trimethylsilyloxy-*o*-quinodimethane from tin precursors **1** proceeds via a radical process.

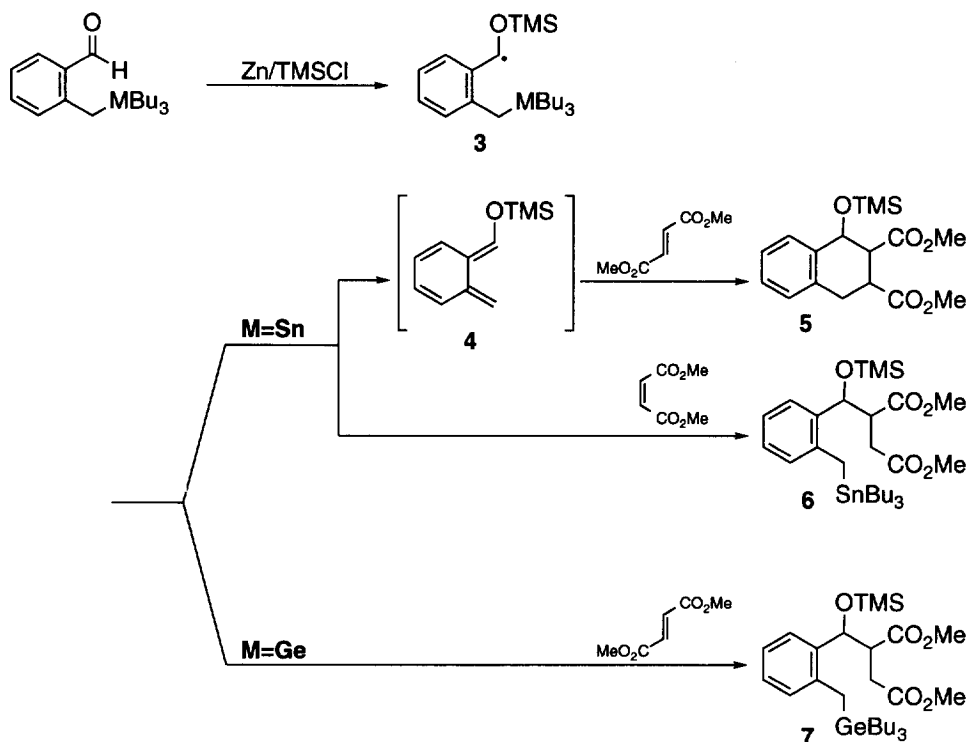
In summary, we have shown that the generation of α -trimethylsilyloxy-*o*-quinodimethanes was achieved utilizing the high leaving ability of a tributyltin radical, and one-electron transfer from zinc to the carbonyl moiety of the precursors in the presence of TMSCl was effective for the scission of the carbon-tin bond leading to the generation of *o*-quinodimethanes.

Table 2. Cycloadditions of α -Trimethylsilyloxy-*o*-quinodimethanes with Dienophiles^a

Entry	R	Dienophile ^b	Cycloadduct ^c	Yield(%) (isomer ratio)
1	H			79 (62:38)
2				70 (65:35)
3				28 (>99:1)
4				43 (>99:1)
5	Me			68 ^d (86:14)
6				65 ^d (79:21)

^a The reactions were carried out in THF at r.t. for 2h with Zn(10 equiv), TMSCl(3 equiv), and 2,6-lutidine(3 equiv) unless otherwise indicated. ^b 3 equiv of dienophiles were used. ^c The structures of the major isomer are represented. ^d The reactions were carried out at 40°C.

Scheme 1.



Acknowledgment: This work was partially supported by a Grant-in-aid for Scientific Research from the Ministry of Education, Science, and Culture, Japan.

References and Notes

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- 1,2-trans exo isomer: δ 0.10(s, 9H), 2.99-3.28(m, 4H), 3.70(s, 3H), 3.75(s, 3H), 5.08(d, J=8.5 Hz, 1H), 6.98-7.54(m, 4H).
1,2-cis endo isomer: δ 0.05(s, 9H), 2.83-3.28(m, 4H), 3.75(s, 6H), 5.19(d, J=3.2 Hz, 1H), 6.98-7.54(m, 4H).
- In a control experiment, it was observed that the α -trimethylsilyloxy radical derived from *o*-tolualdehyde reacted faster with dimethyl maleate than with dimethyl fumarate.

(Received in Japan 17 September 1996; accepted 21 October 1996)