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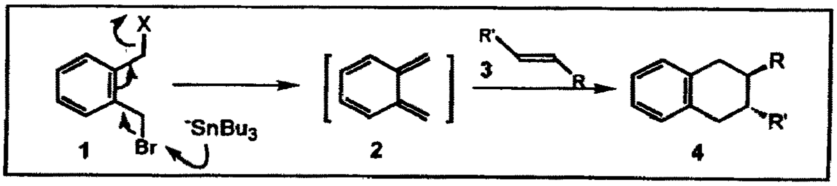
Utilization of $Me_3SiSnBu_3$ in Organic Synthesis. Generation of *o*-Quinodimethane from α,α'-Dibromo-*o*-xylene and $Me_3SiSnBu_3$-CsF

Hiroki Sato,[a] Naohiro Isono,[a] Kimio Okamura,[b] Tadamasa Date,[b] and Miwako Mori[a]*
[a] Faculty of Pharmaceutical Science, Hokkaido University, Sapporo 060, Japan
[b] Analytical Center, Tanabe Seiyaku Co., Toda, Saitama 335, Japan

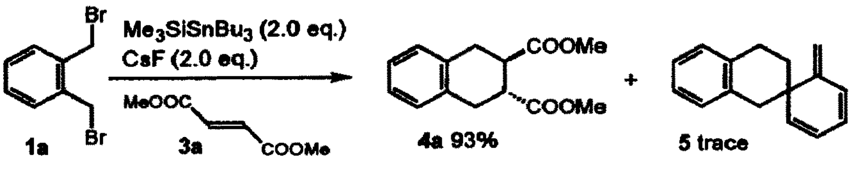
Summary: The reaction of α,α'-dibromo-*o*-xylene with stannyl anion generated from $Me_3SiSnBu_3$ and CsF or TASF $[(Et_2N)_3S^+SiMe_3F_2^-]$ in the presence of dienophiles afforded the [4+2] cyclization products in good to moderate yields.

The stannyl anion, generated from $Me_3SiSnBu_3$[1] and R_4NX, TASF[2] or CsF, is effective in producing an aryl or vinyl anion.[3] This result prompted us to produce the *o*-quinodimethane **2** from α,α'-dibromoxylene **1a**.[4a~4l] The [4+2] Cycloaddition of *o*-quinodimethane to an olefin is a convenient synthetic method for tetrahydronaphthalene.[4m~4x] We now want to report the generation of *o*-quinodimethane **2** from α,α'-dibromoxylene **1a** using $Me_3SiSnBu_3$ and CsF, and the [4+2] cycloaddition of the resulting *o*-quinodimethane **2** to olefins **3**.

$$Bu_3SnSiMe_3 + MF \longrightarrow [\overset{F}{\overset{|}{Bu_3SnSiMe_3}}]^- M^+ \longrightarrow Bu_3Sn^- M^+ + Me_3SiF$$



When a THF solution of α,α'-dibromoxylene **1a**, dimethyl fumarate (**3a**, 2.0 eq.) $Me_3SiSnBu_3$ (2.0 eq.), and TASF (2.0 eq.) was stirred at 0°C for 1h, the desired tetrahydronaphthalene derivative **4a**[4l] was obtained in 25% yield along with the quinodimethane dimer **5**[5] (24% yield, Table I, entry 1). The formation of the *o*-quinodimethane dimer **5** indicates that *o*-quinodomethane **2** is generated from **1a** and $Me_3SiSnBu_3$ in the presence of TASF, and the reaction of **2** with **3a** would proceed *via* [4+2] cycloaddition. The yield was improved when the reaction was carried out in DMF in the presence of CsF instead of TASF (entry 2). The use of 3.0 eq. of $Me_3SiSnBu_3$ and CsF increased the yield of the desired product **4a** (93% yield, entry 5).[6] For the solvent, CH_2Cl_2 can be used, but longer reaction times were required (entry 6).

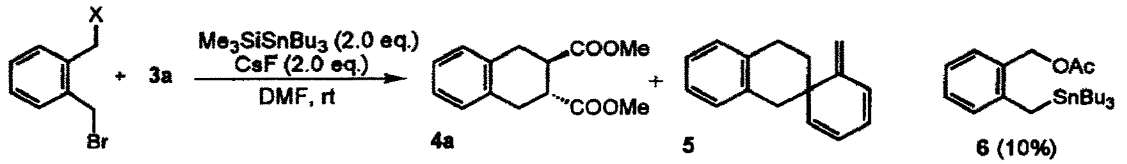


The effect of the leaving group was examined and the results are shown in Table II. For the formation of *o*-quinodimethane **2** from **1** and stannyl anion, generated from $Me_3SiSnBu_3$ and CsF, the reactivity of compound **1b** (X=OTf) was almost same as that of compound **1a** (X=Br). However, the reaction of compound **1d** (X=OAc) with $Me_3SiSnBu_3$ in the presence of CsF did not afford the desired product, and the stannylated compound **6**, the dehalogenation product **7** and the Michael addition product **8** were obtained in 10%, 25%, and 18% yields, respectively.

Table I. Reaction of α,α'-Dibromo-*o*-xylene with $Me_3SiSnBu_3$-F^-

entry	F^-	solvent	temp	time (hr)	products^a 4a (%)	5 (%)
1	TASF (2.0 eq.)	THF	0 °C	1	25	24
2	CsF (2.0 eq.)	DMF	0 °C	1	40	trace
3	CsF (1.1 eq.)	DMF	rt	2	58	trace
4	CsF (2.0 eq.)	DMF	rt	1	73	trace
5	CsF (3.0 eq.)	DMF	rt	1	93	trace
6	CsF (3.0 eq.)	CH_2Cl_2	rt	120	78	trace

^{a} isolated yields.



4a

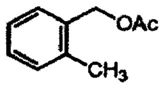
5

6 (10%)

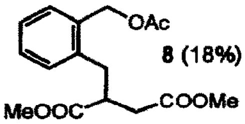
1a X = Br
1b = OTf
1c = $OCOCF_3$
1d = OAc

Table II. Effect of the Leaving Group

entry	X	4a (%)	5 (%)
1	Br (1a)	73	trace
2	OTf (1b)	70	8%
3	$OCOCF_3$ (1c)	56	—



7 (25%)

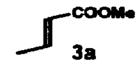
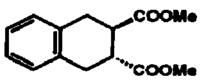
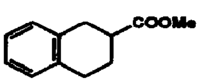
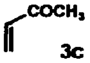
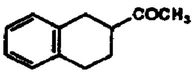
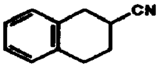
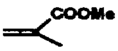
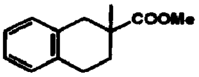
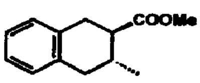
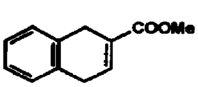
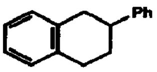
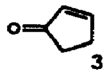
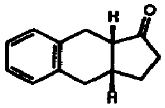


8 (18%)

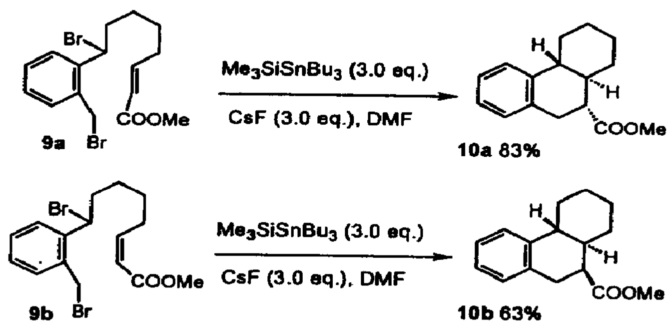
On the basis of the above results, the reaction of **1a** with the various dienophiles **3** was carried out in the presence of $Me_3SiSnBu_3$ and CsF. The results are summarized in Table III. The yields of the [4+2] cyclization products **4a**~**4e** were good to moderate (entries 1~5). The reaction of **1a** with methyl propiolate **3g**, styrene **3h** and cyclopentenone **3i** as the dienophiles afforded the desired cyclized products **4g**, **4h**, and **4i**, respectively.

Subsequently, the intramolecular cyclization reaction was carried out. For the starting materials, E- and Z-α,β-unsaturated esters **9a** and **9b** were selectively prepared.[10] The reaction of **9a** with $Me_3SiSnBu_3$ in the presence of CsF proceeded smoothly to give the tricyclic ester **10a** in high yield. The stereochemistry of **10a** was determined by comparison with the reported spectral data.[11] The reaction of the Z-isomer **9b** with stannyl anion also afforded the desired product **10b** in 61% yield as a single isomer, whose stereochemistry was determined by X-ray analysis and the results are shown in Fig 1.

Table III. Reaction of 1a with the various dienophiles

entry	dienophiles	$Me_3SiSnBu_3$ (eq.)	time (hr)	products[a] 4 (%)			5 (%)
1	 3a	3.0	1		4a[4l]	93	trace
2	 3b	3.0	0.5		4b[4g]	87	trace
3	 3c	3.0	1		4c[7]	86	trace
4	 3d	2.0	1		4d[4g]	59	1
5	 3e	2.0	2		4e[8]	45	5
6	 3f	2.0	2		4f[4l]	15	22
7	 3g	2.0	2		4g	36	20
8	 3h	3.0	4		4h[9]	30	14
9	 3i	3.0	2		4i	22	6

[a] Isolated yield.



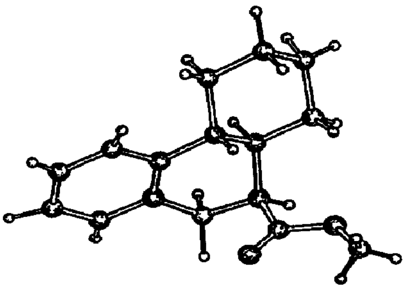


Figure 1. X-ray crystal structure of 10b.

The most remarkable characteristic for the formation of *o*-quinodimethane from α,α'-dibromoxylene **1a** and Me3SiSnBu3 in the presence of CsF is as follows. The starting material is readily available, the reaction proceeds even at 0 °C (usually at room temperature) and the reaction time is very short. Thus, the stereochemistry of the cyclized product could be controlled.

Further studies are now in progress.

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6. The reaction of **1a** with dimethyl fumarate (**3a**, 2eq.) in the presence of Bu3SnLi (3eq.), generated from Bu3SnH and LDA, did not afford the desired product **4a**.
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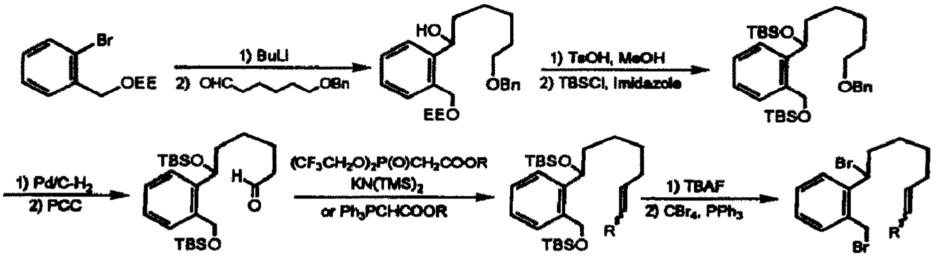
10. The starting materials **9a** and **9b** were prepared as follows.



11. The corresponding ethyl ester of **10a** was synthesized in 81% yield. The spectral data of the ethyl ester agreed with those reported by Nicolau, K. C.; Barnette, W. E.; Ma, P. *J. Org. Chem.* **1980**, *45*, 1463.

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