# Potassium Fluoride-induced 1,4-Elimination of *o*-[(Trimethylsilyl)methyl]benzyl Acetates: A Versatile Generation of *o*-Quinodimethanes

Ryoichi Kuwano* and Takenori Shige

*Department of Cheistry, Graduate School of Sciences, Kyushu University, 6-10-1 Hakozaki, Higashi-ku, Fukuoka 812-8581*

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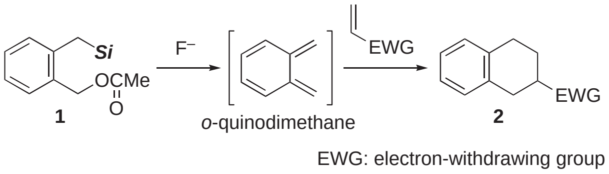
*o*-Quinodimethane interemediate was generated from *o*-[(trimethylsilyl)methyl]benzyl acetate with potassium fluoride. The *o*-quinodimethane in hand reacted with electron-deficient olefins, affording [4+2] cycloadducts, tetrahydronaphthalenes.

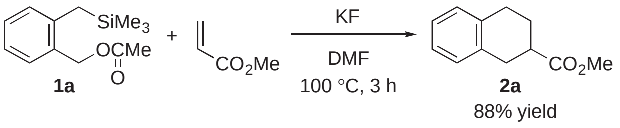
Cycloaddition of olefins to *o*-quinodimethane[1] intermediates has offered a versatile and straightforward access to 1,2,3,4-tetrahydronaphthalene skeletons.[2] A variety of methods for in situ generation of *o*-quinodimethane have been developed,[3–7] and have been utilized for the syntheses of steroids[8] and other natural products to date.[9] In particular, fluoride-induced 1,4-elimination from $\alpha'$-heterosubstituted $\alpha$-silyl-*o*-xylenes is an important and versatile method for the preparation of *o*-quinodimethane.[10–13] The 1,4-elimination occurred under mild conditions compared with other methods, e.g. thermal ring-opening of benzocyclobutenes.[14] The generation of *o*-quinodimethane from the $\alpha$-silyl-*o*-xylenes, however, has been conducted in the presence of either tetrabutylammonium fluoride or cesium fluoride, which are expensive and hard to handle in air because of their hygroscopicity.

Herein, we report a new protocol for the generation of *o*-quinodimethanes via 1,4-elimination of *o*-(silylmethyl)benzylic acetates (**1**).[12,15] Potassium fluoride, which is handled with ease in air and is an inexpensive fluoride source,[16] was employed for the induction of 1,4-elimination. The *o*-quinodimethenes reacted with electron-deficient olefins to give the corresponding tetrahydronaphthalenes **2** (Scheme 1).



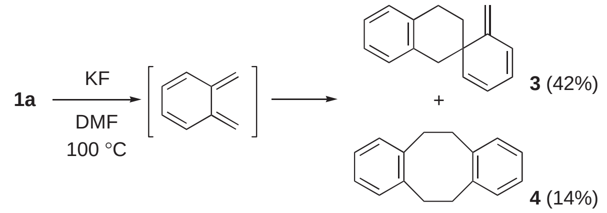
**Scheme 1.**

A mixture of *o*-[(trimethylsilyl)methyl]benzyl acetate (**1a**) with methyl acrylate in DMF was heated at 100 °C in the presence of KF. The resulting mixture afforded methyl 1,2,3,4-tetrahydronaphthalene-2-carboxylate (**2a**) in 88% yield (Scheme 2).[17] When tetrabutylammonium fluoride was used as a fluoride source, **2a** was obtained in trace amount (2%), and 2-methylbenzyl acetate resulting from protodesilylation was generated in 50% yield.[18] The desired product **2a** was formed by use of KF even at room temperature (26% at 48 h), while the reaction afforded 2-methylbenzyl acetate in 40% yield.[19] This observation may indicate that the KF-induced activation of silyl group occurs even at room temperature but the following 1,4-elimination of the acetoxy group seems to compete with the protodesilylation. No consumption of **1a** was observed in any solvents other than DMF. Lewis basicity of DMF may assist the activation of C–Si bond by KF.[20]



**Scheme 2.**

When **1a** was treated with KF in the absence of any dienophile, a mixture of spiro-di-*o*-xylylene **3** and [2,2]orthocyclophane **4** was obtained as seen in Scheme 3. Although the formation of **4** might result from thermally forbidden [4,4] cycloaddition of *o*-quinodimethane, the observation is consistent with Errede's results.[21]



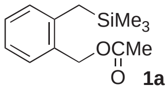
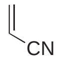
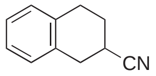
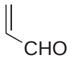
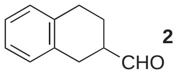
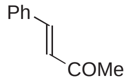
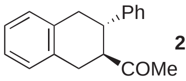
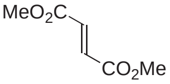
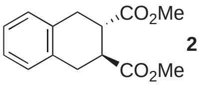
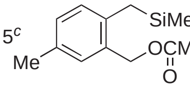
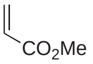
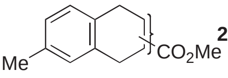
**Scheme 3.**

The *o*-quinodimethane intermediate generated from **1a** reacted with acrylonitrile as well as with methyl acrylate, and the cycloaddition product **2b** was obtained in high yield (Table 1, Entry 1). Unexpectedly, acrolein was not so reactive toward the *o*-qunodimethane intermediate (Entry 2). The reactions of electron-deficient trans-olefins, *trans*-benzalacetone, and dimethyl fumarate, afforded [4+2] cycloadducts **2d** and **2e** in good yields, respectively (Entries 3 and 4). In contrast, no cycloaddition of *o*-quinodimethane was observed when cis-olefins such as maleic anhydride and dimethyl maleate were employed as a dienoplile.[22] Use of acetylenedicarboxylate resulted in a complex mixture.[22] The reaction of 4-methyl-*o*-quinodimethane precursor **1b** with methyl acrylate gave a mixture of two regioisomeric [4+2] cycloadducts with no selectivity (Entry 5).

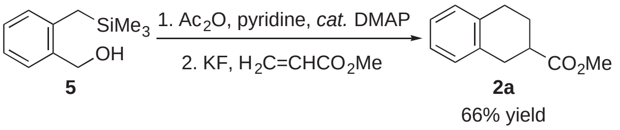
The *o*-quinodimethane precursor **1a** was prepared with acetylation of benzylic alcohol **5**, which was readily synthesized from *o*-methylbenzyl alcohol.[11b] We attempted the one-pot generation of *o*-quinodimethane from **5** (Scheme 4). After **5** was treated with acetic anhydride, methyl acrylate and KF were added to the resulting solution containing **1a**. Heating the mixture at 100 °C for 1 h produced **2a** in 66% yield.[23]

In summary, we have developed a new method for generating *o*-quinodimethane intermediates from **1**. Potassium fluoride, which is an inexpensive and tractable fluoride source, was employed to activate the silyl group and induced 1,4-elimination providing the reactive intermediate. The *o*-quinodimethane in

**Table 1.** Cycloaddition of *o*-quinodimethane with dienophiles[a]

| Entry | **1** | Dienophile | Product (yield/%)[b] |
|---|---|---|---|
| 1 |  **1a** |  |  **2b** (81) |
| 2[c] | |  |  **2c** (26) |
| 3 | |  |  **2d** (63) |
| 4 | |  |  **2e** (77) |
| 5[c] |  **1b** |  |  **2f** (68)[d] |

[a]Reactions were conducted on a 1 mmol scale in DMF (20 mL) at 100 °C for 3 h. **1**/dienophile/KF was 1/1.25/1.5. [b]Isolated yield. [c]The reactions were conducted for 1 h. [d]Yield of the mixture of methyl 5- and 6-methyl-1,2,3,4-tetrahydronaphthalene-2-carboxylates (*ca.* 1:1).



**Scheme 4.** One-pot synthesis of tetrahydronaphthalene from **3**.

hand reacted with electron-deficient dienophiles to give tetrahydronaphthalenes.

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