

Photochemical reaction of *ortho*-formylbenzyltrialkylstannanes for the generation of α -oxy-*o*-quinodimethane

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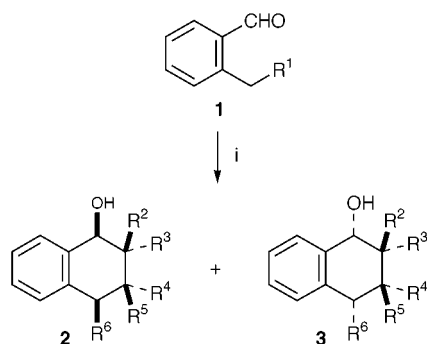
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Irradiation of *o*-formylbenzyltrialkylstannanes in benzene gives α -trialkylstannoxy-*o*-quinodimethanes which are trapped with dienophiles at room temperature to afford cycloadducts with high stereoselectivities, while the corresponding silane and germane gave a different type of *o*-quinodimethane and moderate stereoselectivities in cycloadditions.

o-Quinodimethane intermediates are a useful synthetic tool for the synthesis of condensed cyclic compounds 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 and radical.² In the course of our studies, we focused our attention on the photochemical generation of *o*-quinodimethane intermediates utilizing the characteristics of Group 14 organometallic compounds, since it is known that facile generation of α -hydroxy-*o*-quinodimethanes was achieved by irradiation of *o*-tolualdehyde via a photoenolisation process involving a 1,5-hydrogen shift.³ We present here our investigation on the photoreactions of *o*-formylbenzyltrialkylstannanes, -silane and -germane in the presence of dienophiles.

The tin precursors **1c,d** were easily prepared from *o*-methylbenzyl alcohol in two steps by a method previously reported,^{2b} and the corresponding trimethylsilyl and tributylgermyl derivatives **1a,b** were prepared in a similar way. First, these precursors were irradiated in a benzene solution at room temperature to give the corresponding *o*-quinodimethane intermediates, which were trapped *in situ* with dimethyl fumarate (Scheme 1 and Table 1).



- a** R¹ = SiMe₃, R² = R⁴ = CO₂Me, R³ = R⁵ = H, R⁶ = SiMe₃
b R¹ = GeBu₃, R² = R⁴ = CO₂Me, R³ = R⁵ = H, R⁶ = GeBu₃
c R¹ = SnMe₃, R² = R⁴ = CO₂Me, R³ = R⁵ = R⁶ = H
d R¹ = SnBu₃, R² = R⁴ = CO₂Me, R³ = R⁵ = R⁶ = H
e R¹ = SnBu₃, R² = COMe, R³ = R⁴ = R⁵ = R⁶ = H
f R¹ = SnBu₃, R² = CO₂Me, R³ = R⁴ = R⁵ = R⁶ = H
g R¹ = SnBu₃, R²-R⁵ = -CO-N(Me)-CO-, R³ = R⁴ = R⁶ = H
h R¹ = SnBu₃, R²-R⁵ = -CO-N(Ph)-CO-, R³ = R⁴ = R⁶ = H

Scheme 1 Reagents and conditions: i, dienophile (3 equiv.), hv, PhH, room temp.

Table 1 Photoreaction of **1** with dienophiles

1	Dienophile	Cycloadduct	Yield(%) (2 : 3)
1a	Dimethyl fumarate	2a + 3a	35 (71:29)
1b	Dimethyl fumarate	2b + 3b	45 (53:47)
1c	Dimethyl fumarate	2c + 3c	36 (>99:1)
1d	Dimethyl fumarate	2d + 3d	48 (>99:1)
1d	Dimethyl maleate	2d + 3d	35 (>99:1)
1e	Methyl vinyl ketone	2e + 3e	38 (>99:1)
1f	Methyl acrylate	2f + 3f	21 (>99:1)
1g	<i>N</i> -methylmaleimide	2g + 3g	25 (>99:1)
1h	<i>N</i> -phenylmaleimide	2h + 3h	51 (>99:1)

It has been reported that cycloaddition of α -hydroxy-*o*-quinodimethane with dimethyl fumarate gave the corresponding cycloadduct as a mixture of two stereoisomers (1,2-*cis* and 1,2-*trans*) in a 74:26 ratio.⁴ Compounds **1a,b** also showed similar selectivities. When **1a** was irradiated with dimethyl fumarate, the cycloadduct having a trimethylsilyl group on the benzylic position was isolated as a mixture of two stereoisomers in a 71:29 ratio; **1b** gave a similar result. In these reactions, it is obvious that a 1,5-hydrogen shift proceeds upon photolysis to give *o*-quinodimethane intermediates (**A** in Fig. 1) followed by trapping with the dienophile to afford the cycloadducts **2a**(+**3a**) and **2b**(+**3b**), respectively.

In the case of stannanes **1c,d**, however, the corresponding cycloadducts **2c**(+**3c**) and **2d**(+**3d**) involved no stannyl groups and the stereoselectivity was extremely high.⁵ In a control experiment, it was observed that when 1-hydroxy-4-tributylstannyl-1,2,3,4-tetrahydronaphthalene was irradiated under similar conditions, most of the compound was recovered without loss of the stannyl group. This observation suggests that the formation of **2c**(+**3c**) and **2d**(+**3d**) does not proceed via an α -hydroxy- α' -trialkylstannyl-*o*-quinodimethane such as **A** in Fig. 1. The plausible reactive intermediate would be α -trialkylstannoxy-*o*-quinodimethane **B** (Fig. 1).

That is, it is conceivable that a 1,5-shift of the stannyl group proceeded to give **B**,⁶ which was trapped with the dienophile to give 2,3-dimethoxycarbonyl-1-trialkylstannoxy-1,2,3,4-tetrahydronaphthalene followed by destannylation to give the hydroxy compounds.⁷ Furthermore, the present high stereoselectivities in the cycloadditions can be rationalized by supposing the existence of the intermediate **B**. When **B** approaches the dimethyl fumarate, the 1,2-*cis* *endo* addition **C** would be a favored pathway, since the 1,2-*trans* *exo* addition **D**

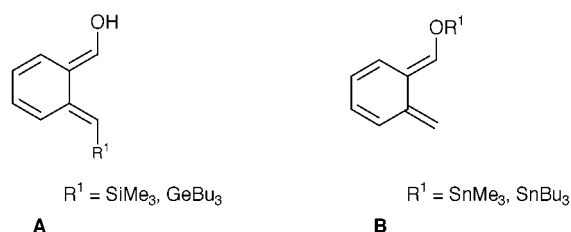


Fig. 1 The structure of *o*-quinodimethanes generated from the silane and germanane (**A**) and the stannane (**B**).

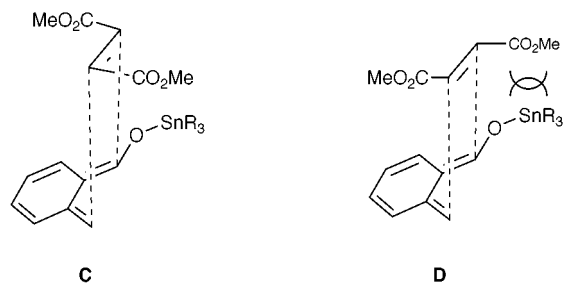


Fig. 2 Transition states for the cycloaddition of *o*-quinodimethane with dimethyl fumarate: 1,2-*cis* endo addition (**C**); 1,2-*trans* exo addition (**D**).

suffers from steric repulsion between the trialkylstannyl group and the ester group (Fig. 2).

We next examined the photoreaction of *o*-formylbenzyltributylstannane with various dienophiles, as shown in Table 1. It is noted that the cycloadditions proceeded with exclusive formation of the 1,2-*cis* isomers in all cases. That dimethyl maleate gave the same cycloadduct (2,3-*trans*) as in the case of dimethyl fumarate could be explained by the following facts. It is known that dimethyl maleate isomerizes to dimethyl fumarate under irradiation conditions, and it is also known that dimethyl fumarate is a more reactive dienophile than dimethyl maleate in Diels–Alder reaction.⁸

In summary, we have shown that the generation of α -trialkylstannoxy-*o*-quinodimethanes was achieved *via* 1,5-shift

of the stannyl group by irradiation of *o*-formylbenzyltrialkylstannanes, and the stereoselectivities of the cycloadditions with dienophiles were extremely high, whereas other precursors without a stannyl group undergo a 1,5-hydrogen shift and showed moderate selectivities in the cycloadditions.

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Notes and references

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- 4 J. L. Charlton and S. Maddaford, *Can. J. Chem.*, 1993, **71**, 827.
- 5 Selected data for **2c**: δ_{H} 2.37 (d, *J* 5.1, 1H), 2.89 (dd, *J* 11.7, 16.6, 1H), 3.12 (dd, *J* 3.4, 11.7, 1H), 3.21 (dd, *J* 5.5, 16.6, 1H), 3.39 (dt, *J* 3.5, 11.7, 1H), 5.12 (dd, *J* 3.5, 5.1, 1H), 7.10–7.40 (m, 4H).
- 6 A similar 1,5-shift of a boron group upon the generation of *o*-quinodimethanes has been reported: G. Kanai, N. Miyaura and A. Suzuki, *Chem. Lett.*, 1993, 845.
- 7 It seems that the destannylation proceeded during the irradiation, since the trialkylstannoxy compound could not be detected after the reaction.
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