Generation of the furan analogue of *ortho*-quinodimethane by 1,4-elimination of 3-acetoxymethyl-2-tributylstannylmethylfuran

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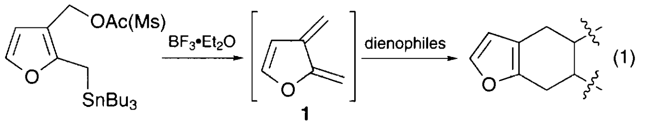
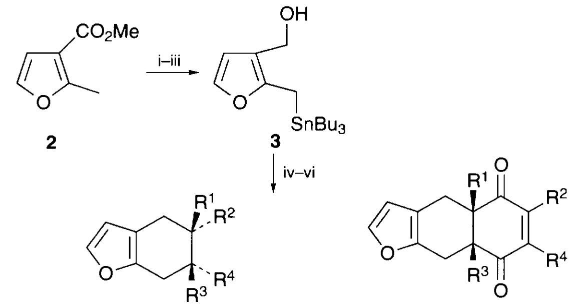
2,3-Dimethylene-2,3-dihydrofuran is generated *in situ* by boron trifluoride induced 1,4-conjugative elimination of tributylstannylmethyl acetate and then trapped with dienophiles to give the corresponding Diels–Alder cycloadducts.

ortho-Quinodimethanes have been widely utilized in the construction of polycyclic aromatic compounds.[1] The study of their heterocyclic analogue has recently attracted attention.[2] Flash vacuum pyrolysis is a typical procedure for the generation of 2,3-dimethylene-2,3-dihydrofuran,[3a–c] described as furan-based *ortho*-quinodimethane. Another method is the 1,4-conjugative elimination of the acetoxy and trimethylsilyl groups induced by fluoride ion.[3d] However, the former method required specific experimental conditions, and the latter can only be applied to secondary acetoxy compounds. In addition, systematic studies relating to the reactivity of 2,3-dimethylene-2,3-dihydrofuran towards various dienophiles have not been reported. We now report a new and convenient method for the generation of the furan analogue of *ortho*-quinodimethane **1** *via* the 1,4-conjugative elimination of 3-(acetoxymethyl)-2-(tributylstannylmethyl)furan induced by boron trifluoride diethyl etherate, and its Diels–Alder reaction with some dienophiles [eqn. (1)].



Mono-bromination of a commercially available compound **2** was effective by photolysis with NBS in 80% yield. A mixture of the obtained monobromide and tributylstannyl chloride in THF was treated with zinc powder at room temperature to afford a tributylstannyl derivative in 90% yield,‡ which was reduced with LAH to give alcohol **3** in 71% yield. Treatment of the acetate or mesylate of **3** with boron trifluoride diethyl etherate ($BF_3{\cdot}Et_2O$) successfully induced 1,4-conjugative elimination in the appropriate solvents at 0 °C,[4]§ and in the presence of excess amounts of dienophiles **4a**, **d–h** afforded the corresponding Diels–Alder adducts **5a**, **d–h** in 66–95% yields (one-pot procedure) (Scheme 1 and Table 1). However, in the case of acrylonitrile **4b** and dimethyl maleate **4c**, the expected Diels–Alder adducts were not obtained under the above reaction conditions, and the dimer[3a] *via* the homo-coupling of **1** was isolated (40–43% yields). We then modified our Diels–Alder reaction in two steps as follows: the acetate or mesylate of **3** was treated with 2 equiv. of $BF_3{\cdot}Et_2O$, and the mixture was stirred for 20 min. The generated **1** was distilled along with the solvent under appropriate reduced pressure at ambient temperature into a cold trap (−78 °C), which contained 10 equiv. of the dienophile **4b** or **c** in ether. The distillate was gradually warmed to room temperature with stirring over 12–14 h. The expected Diels–Alder adducts **5b** and **c** were obtained in 66–80% yields, respectively (two-pot procedure). Cyclohexenone **4i** and cyclopentenone **4j**, less reactive dienophiles, however, did not afford the [4 + 2] cycloadducts with compound **1** under various reaction conditions either in the one-pot or in the two-pot procedures.



5a R¹ = R² = R³ = H, R⁴ = CO₂Me
b R¹ = R² = R³ = H, R⁴ = CN
c R¹ = R⁴ = CO₂Me, R² = R³ = H
d R¹ = R³ = H, R² = R⁴ = CO₂Me
6a R¹ = R³ = R⁴ = H, R² = CO₂Me
5e R¹ = R² = R³ = R⁴ = H
f R¹ = R³ = H, R² = R⁴ = Me
g R¹ = R² = H, R³ = R⁴ = Me
h R¹ = R³ = H, R²—R⁴ = C₄H₄
6g R¹ = R² = Me, R³ = R⁴ = H

Scheme 1 *Reagents and conditions*: i, NBS/CCl_4; ii, Zn/Bu_3SnCl/THF; iii, LAH/Et_2O; iv, AcCl(MsCl)/Py; v, 10 equiv. **4a–h**; vi, 2 equiv. $BF_3{\cdot}Et_2O$

Table 1 Results of Diels–Alder reaction of **1** and **4a–j**

Dienophile **4**	*t*/h	Product (Yield, %)
a methyl acrylate	1.5–2.0	**5a** + **6a** (90–95)[a,e,f]
b acrylonitrile	12–14	**5b** (72–80)[b,d,f,7]
c dimethyl maleate	3–4	**5c** (66–70)[b,d]
d dimethyl fumarate	12–18	**5d** (86–90)[b]
e 1,4-benzoquinone	8–15	**5e** (82–86)[b]
f 2,3-dimethyl-1,4-benzoquinone	8–10	**5f** (75–79)[b]
g 2,6-dimethyl-1,4-benzoquinone	11–19	**5g** + **6g** (66–69)[b,e,f]
h 1,4-naphthoquinone	6–7	**5h** (84–91)[b]
i 2-cyclohexen-1-one	6–11	Dimer (30–31)[c,g]
j 2-cyclopenten-1-one	6–11	Dimer (31–40)[c,g]

[a] In PhH, MeCN, or CH_2Cl_2. [b] In PhH or MeCN. [c] In PhH, MeCN, CH_2Cl_2, or Et_2O. [d] Two-pot procedure. [e] **5a**:**6a** = 10:1; **5g**:**6g** = 10:1.7 (Determined by ^1H NMR). [f] The structures of **5a**, **b** and **g** were determined on the basis of their NMR spectra. [g] ^1H and ^{13}C NMR data of the dimer were identical with those reported.[3a]

The regioselectivities were observed in the Diels–Alder reaction of **1** with **4a**, **b** and **g**. When **4a** and **g** were used as dienophiles, **5a** and **g** were obtained with selectivities of 10:1 and 10:1.7, respectively. In the case of **4b**, cycloadduct **5b** was obtained as the sole product. These regioselectivities obtained are explained by molecular orbital calculations.¶

Footnotes

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‡ Stannylation of the lithium anion derived from **2** with tributylstannyl chloride gave 2-bis(tributylstannylmethyl)-3-methoxycarbonylfuran as a major product (47% yield) along with the desired monostannyl compound (14–17%). This result was in contrast to the silylation of **2**.[3d]

§ Trifluoroacetic acid did not induce the 1,4-conjugative elimination of both the acetate and mesylate of **3**, although benzene-based *ortho*-quinodimethane was generated from a similar system with this reagent.

¶ The obtained regioselectivity agreed with that predicted by orbital coefficients values, calculated with 3-21G basis set by use of software packages SPARTAN version 4.0 Wavefunction, Inc., Irvine, CA, USA. The calculated results indicate that the cycloaddition of **1** with **4a** or **b** proceeds *via* a 'normal' Diels–Alder reaction with high selectivity due to the large difference between the orbital coefficients, while that of **4g** proceeds as an 'inverse' Diels–Alder reaction with low selectivity due to the small difference between the orbital coefficients.

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Received, 18th July 1996; Com. 6/05029H