Tandem Cyclizations of Benzopyranylidenetungsten(0) Complexes with Electron-Rich Dienes for the Stereoselective Synthesis of Polycyclic Carbon Skeletons

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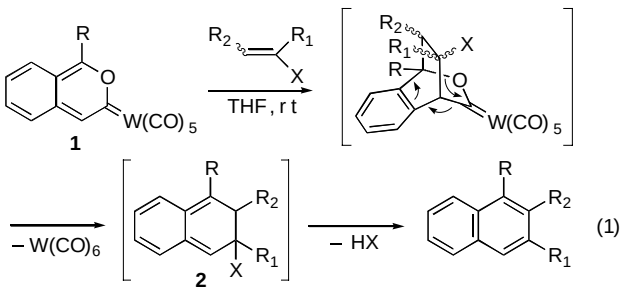
o-Quinodimethanes, generated by the Diels-Alder reactions of benzopyranylidenetungsten(0) complexes with electron-rich dienes, further undergo intramolecular cyclizations to afford novel polycyclic compounds.

Recently, we have reported the novel synthesis of pentacarbonylbenzopyranylidenetungsten(0) complexes **1** via the dienone-electrocyclization of vinylidene intermediates generated by treatment of *o*-ethynylphenyl ketones with $W(CO)_5$(thf).[1] Furthermore, these complexes underwent inverse electron-demand Diels-Alder reaction with electron-rich alkenes such as vinyl ethers and enamines to give the corresponding naphthalene derivatives in good yield (eq 1).[1] In this reaction, elimination of $W(CO)_6$ occurs smoothly from the initial Diels-Alder adducts to generate the *o*-quinodimethane-type intermediates,[2] which eliminate an alcohol or an amine to give the products. Since *o*-quinodimethanes are known to be highly reactive as a diene component in the Diels-Alder reaction, we expected that the intermediate **2** could be utilized for further carbon-carbon bond formations. In this paper is described the tandem cyclization approach for the stereoselective synthesis of novel polycyclic compounds employing electron-rich dienes as a dienophile in the Diels-Alder reaction with **1**.



(1)

When the benzopyranylidene complex **1a** (R=Ph) was treated with 2-methoxyfuran (3 equiv) in THF at room temperature, a benzonorcaradiene **3a**[3] was obtained as a single diastereomer in good yield accompanied by a small amount of a naphthalene derivative **4a** (Table 1, entry 1). Screening of the reaction conditions revealed that the benzonorcaradiene derivative was selectively produced in the presence of triethylamine (10 mol%), while the addition of TsOH gave the naphthalene in good yield (entries 2 and 3).[4] Thus, either **3a** or **4a** could be obtained selectively by employing the appropriate additive. As shown in Table 1, *s*- and *n*-alkyl-substituted benzopyranylidene complexes **1b** and **1c** also gave either of these two types of products depending on the additive.

The reaction mechanisms and the effect of the additives could be explained as follows: The Diels-Alder reaction between **1** and the less-hindered olefinic moiety of 2-methoxyfuran proceeded to afford the cycloadduct **5**. Elimination of $W(CO)_6$ from **5** readily occurred at room temperature, giving the highly reactive quinodimethane-type intermediate **6**.[5] Then, protonation of the vinyl ether moiety of the resulting quinodimethane **6** and successive C–O bond cleavage preferentially proceeded in the presence of TsOH to afford the corresponding naphthalene derivative **4** (Scheme 1, path b). On the contrary, the use of triethylamine prevented this reaction and intramolecular nucleophilic attack of the ketene acetal moiety to the quinodimethane unit occurred with formation of a three-membered ring to give the benzonorcaradiene derivative **3** (path a).

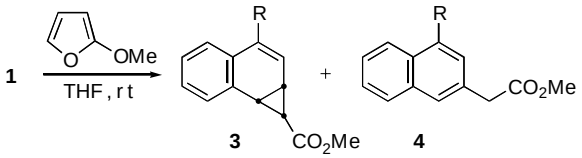
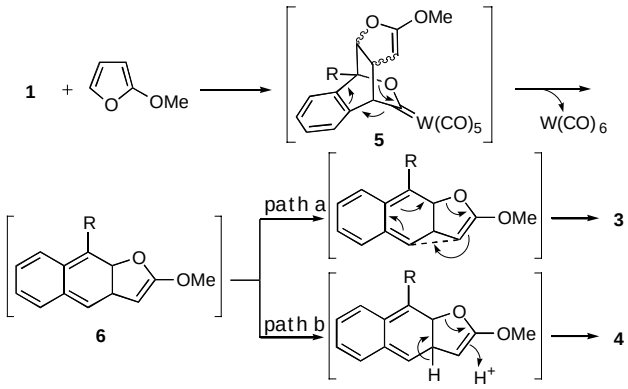


Table 1. Reactions of **1** with 2-methoxyfuran

Entry	R	Additive[a]	Time/h	Yield(**3**+**4**/%)	**3** : **4**
1	Ph (**1a**)	none	6	89	97 : 3
2	Ph	TsOH	2	87	1 : >99
3	Ph	Et_3N	0.5	86	>99 : 1
4	*i*-Pr(**1b**)	none	0.12	80	87 : 13
5	*i*-Pr	TsOH	0.3	80	10 : 90
6	*i*-Pr	Et_3N	0.3	91	>99 : 1
7	*n*-Pr(**1c**)	TsOH	0.05	72	1 : >99
8	*n*-Pr	Et_3N	0.05	80	97 : 3

[a]10 mol%



Scheme 1.

Next, 3-*t*-butyldimethylsiloxy-1-methoxy-1,3-butadiene[6] (**7**) (5 equiv) was employed as another diene component instead of 2-methoxyfuran. Treatment of **1a** with **7** in THF at room temperature exclusively gave a novel polycyclic compound **8a** as a single diastereomer (Table 2, entry 1). The structure of **8a** as well as its stereochemistry was confirmed by X-ray crystallographic analysis.

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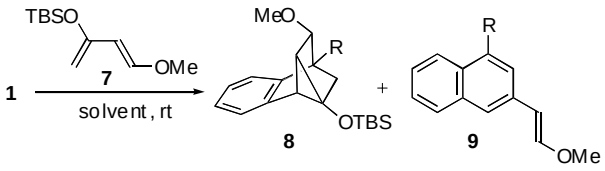


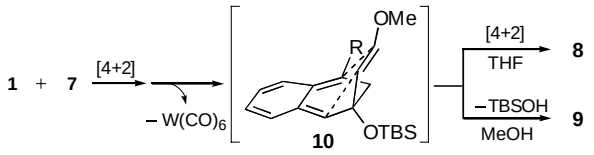
Table 2. Reactions of **1** with siloxydiene **7**[a]

Entry	R	Solvent	Time/h	Yield(**8**+**9**/%)	**8** : **9**
1	Ph (**1a**)	THF	22	94	>99 : 1
2	Ph	MeOH	2.6	69	30 : 70
3	*i*-Pr (**1b**)	THF[b]	15	72	>99 : 1
4	*i*-Pr	MeOH	0.2	86	1 : >99
5	*n*-Pr (**1c**)	THF	1.2	77	>99 : 1
6	*n*-Pr	MeOH	0.1	79	4 : 96

[a] The reactions were performed in 0.03 M solution of **1** unless otherwise noted. [b] 0.003 M THF solution of **1**.

In this reaction, the use of methanol as solvent dramatically changed the reaction pathway, giving the vinylnaphthalene derivative **9a**. Again, either **8** or **9** were selectively produced by choosing the appropriate conditions.

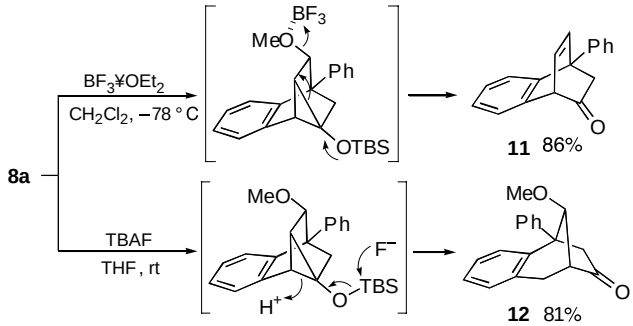
The reaction pathway was considered to be as follows (Scheme 2): The Diels-Alder reaction between **1** and the silyl enol ether moiety of **7** followed by elimination of $W(CO)_6$ gave the quinodimethane intermediate **10**. The reaction in methanol proceeded in a similar manner as path b in Scheme 1. In aprotic solvent (THF), intramolecular Diels-Alder-type reaction of **10** preferentially occurred with formation of a three-membered ring to give **8**. Although intramolecular [4 + 2] cycloaddition reaction of 1,3,6-triene derivatives is not so common and most of the reported examples required high reaction temperature,[7] the present reaction proceeded under very mild conditions (neutral conditions at room temperature) probably due to the high reactivity of the *o*-quinodimethane moiety.[8]



Scheme 2.

Finally, transformation of the product **8a** to synthetically useful intermediates was investigated (Scheme 3). Ring opening of the cyclopropane with elimination of the MeO group readily proceeded by the reaction of **8a** with $BF_3 \cdot OEt_2$ to afford **11** in good yield. On the other hand, treatment of **8a** with tetrabutylammonium fluoride (TBAF) promoted the cleavage of the other C–C bond of the cyclopropane, giving **12** as a sole product. Thus, **8a** could be converted to two types of compound having a bicyclo[2.2.2]octane or bicyclo[3.2.1]octane skeleton by carrying out the reaction under acidic or basic conditions, respectively.

In conclusion, the benzopyranylidenetungsten complexes underwent smooth tandem cyclization with electron-rich dienes to give the novel polycyclic compounds with high stereoselectivity through the *o*-quinodimethane intermediates. Substituted naphthalenes were also prepared selectively by slight adjustment of the reaction conditions.



Scheme 3.

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References and Notes

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2 J. L. Segura and N. Martin, *Chem. Rev.*, **99**, 3199 (1999).
3 The structure of **3** was determined as follows: the reaction of **1a** and **1c** with 2-trimethylsiloxyfuran gave the benzonorcaradiene carboxylic acids as a single diastereomer, whose relative stereochemistries were determined by X-ray analyses. Then the carboxylic acids were treated with $TMSCHN_2$ to give the methyl esters, of which ^{1}H-NMR spectra completely agreed with those of **3a** and **3c**. The stereochemistry of **3b** was assigned based on the similarity of its NMR spectrum with those of **3a** and **3c**.
4 Representative experimental procedure (Table 1, entry 3): To a THF solution (1.0 mL) of **1a** (49.6 mg, 0.09 mmol) was added a THF solution (1.0 mL) of triethylamine (1.0 mg, 0.01 mmol) and 2-methoxyfuran (26 μL, 0.28 mmol) at room temperature. After 0.5 h, the reaction mixture was evaporated, and the resulting crude materials were purified by preparative TLC to afford **3a** (22.0 mg, 86% yield).
5 Similar reactions of benzopyranones normally require high reaction temperature or an acid catalyst. For the Diels-Alder reaction of pyrone derivatives, see: D. W. Jones and A. M. Thompson, *J. Chem. Soc., Perkin Trans. 1*, **1993**, 2533; D. A. Bleasdale and D. W. Jones, *J. Chem. Soc., Perkin Trans. 1*, **1991**, 1683; P. I. Van Broeck, D. J. Vanderzande, E. G. Kiekens, and G. J. Hoornaert, *J. Chem. Soc., Perkin Trans. 1*, **1991**, 639; K. Afarinkia, V. Vinader, T. D. Nelson, and G. H. Posner, *Tetrahedron*, **48**, 9111 (1992).
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8 In marked contrast to the present reaction, α,α-diallyl-*o*-quinodimethane was reported to undergo 1,5-hydrogen shift instead of intramolecular Diels-Alder reaction; B. D. Lenihan and H. Shechter, *J. Org. Chem.*, **63**, 2072 (1998).