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A NOVEL METHOD FOR THE GENERATION OF 2,3-NAPHTHOQUINODIMETHANES UTILIZING SAMARIUM(II) IODIDE-PROMOTED ALLENE SYNTHESIS

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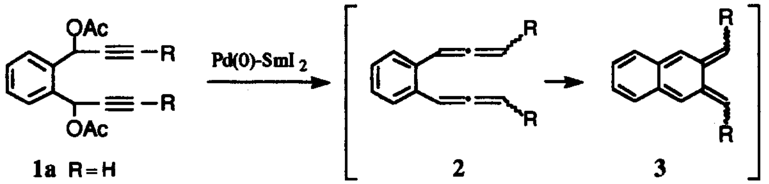
Key Words: 2,3-naphthoquinodimethane; Pd(0)-SmI$_2$ system; allene synthesis; cycloaddition; 1,2-diphenyl-naphtho[b]cyclobutene; [1,5] hydrogen shift

Abstract: *2,3-Naphthoquinodimethanes are easily generated from o-bis(α-acetoxypropargyl)benzene derivatives with SmI$_2$ in the presence of palladium catalyst under mild conditions. The reactions of the quinodimethane intermediates were found to follow the different paths depending on the acetylenic substituents of substrates.*

o-Quinodimethanes have been of intense interest not only from the structural and theoretical point of view but also because of their synthetic utility as effective dienes in Diels-Alder reaction for the construction of polycyclic compounds.[1] Therefore, a number of methods for the generation of these intermediates have so far been developed: e.g., (i) reductive, proton-induced, or anion-triggered 1,4-elimination reactions,[2] (ii) thermal or photochemical extrusion reactions and reverse Diels-Alder processes of cyclic precursors,[3] (iii) ring-opening reactions of benzocyclobutenes and related compounds,[4] etc. Among them, 6π-electron cyclization of *o*-diallenylbenzenes,[5] for the formation of which strong bases were required, has attracted our attention because we recently developed a mild and convenient method for the formation of allenes from the corresponding propargylic acetates by using the Pd(0)-SmI$_2$-proton donor system.[6] Thus, we attempted to apply our allene synthesis to the generation of *o*-naphthoquinodimethanes (3). (Eq. 1)

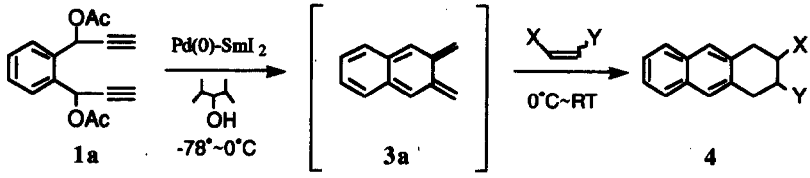


(1)

1a R=H
1b R=Ph
1c R=(CH$_2$)$_5$CH$_3$

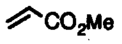
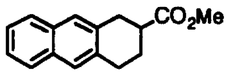
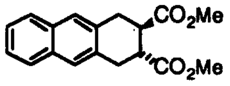
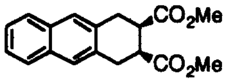
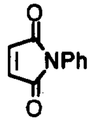
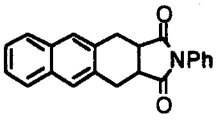
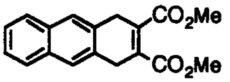
The precursors, bis-propargylic acetates (**1a-c**), were easily prepared from *o*-phthalaldehyde in two steps (LiC≡CR; Ac$_2$O, DMAP) in 70-80% overall yields as mixtures of diastereoisomers (1:1, 1:2, and 1:9, respectively).

First, the reduction of *o*-bis(1'-acetoxy-2'-propynyl)benzene (**1a**) was examined and the postulated *o*-naphthoquinodimethane intermediate (**3a**)[7] was tried to trap with various dienophiles. (Eq. 2) As expected, the convenient one-pot reaction afforded the corresponding Diels-Alder adducts (**4a-e**)[8] in satisfactory yields (Table 1) except for the reaction with dimethyl acetylenedicarboxylate (entry 5). A typical procedure is as follows: A SmI_2-THF solution (0.1 mol dm^{-3}, 9.25 mL, 0.925 mmol) was added slowly to a solution of **1a** (50.0 mg, 0.185 mmol), $Pd(PPh_3)_4$ (22.0 mg, 10 mol%), and 2,4-dimethyl-3-pentanol (58.0 μL, 0.407 mmol) in THF (4 mL) at -78°C. The mixture was stirred for 30 min at the same temperature and then gradually warmed to 0°C over several hours, while being monitored by TLC. After completion of the reduction, a solution of dimethyl fumarate (80.0 mg, 0.555 mmol) in THF (2 mL) was added and the whole mixture was stirred at 0°C for 2 h and then at room temperature for 12 h. To the reaction mixture was added hexane (2 mL) and silica gel (ca. 1 g). The resulting suspension was stirred for 10 min and then passed through a pad of silica gel. The filtrate was concentrated and purified by preparative TLC on silica gel to give **4b** (33.2 mg, 60%) as a white solid.



(2)

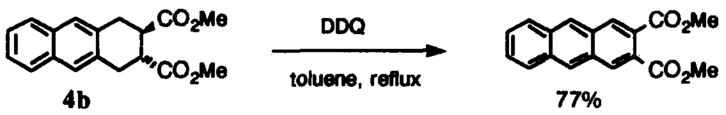
Table 1. One-Pot Conversion of **1a** to the Cycloadducts (**4a** - **4e**)[a)]

Run	Dienophile	Major product		Yield (%)
1			(**4a**)	57
2			(**4b**)	60
3			(**4c**)	48[b)]
4			(**4d**)	59
5	$MeO_2C—\equiv—CO_2Me$		(**4e**)	17

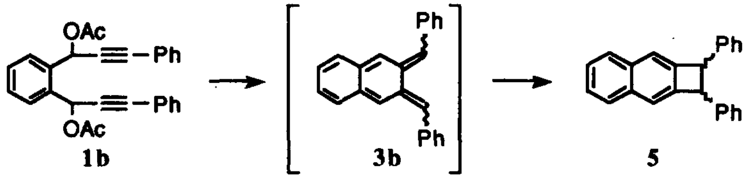
a) For the reaction conditions, see the text. b) A mixture of diastereomers: *cis/trans* =72/28.

The concomitant formation of the cycloadduct (**4b**) in the reaction with dimethyl maleate (entry 3) would be due to the partial isomerization of the starting maleate to fumarate prior to the cycloaddition under the reaction conditions.[9]

The cycloadduct **4b** could easily be converted into dimethyl 2,3-anthracenedicarboxylate[8] in good yield.



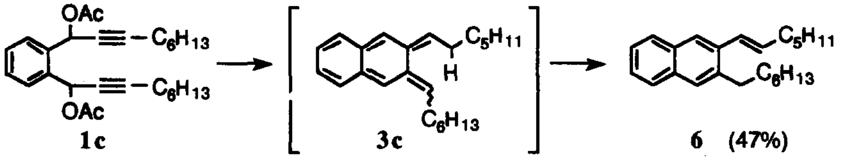
The reduction of phenylacetylene derivative (**1b**) also proceeded smoothly, however, the corresponding [4+2] cycloadduct with methyl acrylate was not detected at all. A mixture of *trans*- and *cis*-diphenylnaphtho[*b*]cyclobutene[5c,8,10] (**5**, *trans/cis*=92/8) was isolated as the result of intramolecular [2+2] cycloaddition of the *o*-naphthoquinodimethane intermediate (**3b**).[11] (Eq. 3) When the reduction was performed at room temperature and then the mixture was stirred at 65°C for several hours without methyl acrylate, a mixture of the diastereoisomers (*trans/cis*=84/16) was obtained in 66% yield. The pure *trans*-**5** was, upon being allowed to stand for 30 days at room temperature, isomerized to give an equilibrium mixture of the stereoisomers (*trans/cis*=80/20),[12] indicating that cleavage and regeneration of the cyclobutene ring takes place thermally and/or photochemically probably through a radical process.[5c-d,13]



(3)

-30°C→RT 59% (*trans/cis*= 92/8)
RT→65°C 66% (*trans/cis*= 84/16)

Also, the reaction of bis-alkynic compound (**1c**) with methyl acrylate did not give the corresponding Diels-Alder adduct under the standard conditions; the major product was 1-alkenyl-2-alkylnaphthalene (**6**)[8] which would be stemmed from the corresponding naphthoquinodimethane (**3c**) via [1,5] hydrogen shift.[5d,14] (Eq. 4)



(4)

In conclusion, the present reductive method, which is characterized by ready availability of open chain precursors and mild reaction conditions, was found to provide a new route to *o*-naphthoquinodimethanes.[15]

References and Notes

1. Reviews: a) Fishwich, C. W. G.; Jones, D. W. "*ortho-Quinonoid Compounds*" in " *The Chemistry of Quinonoid Compounds*", Vol. II; Patai, S.; Rappoport, Z. Ed.; John Wiley & Sons Ltd. **1988**, chapter

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4. For a review, see Wada, Y.; Tago, T.; Nishimura, J. *J. Synth. Org. Chem., Jpn.* **1992**, *50*, 616.
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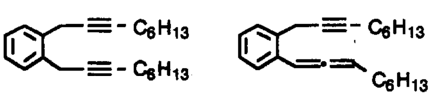
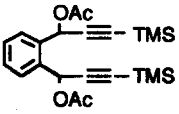
6. Tabuchi, T.; Inanaga, J.; Yamaguchi, M. *Tetrahedron Lett.* **1986**, *27*, 5237.
7. Sondheimer and his co-workers have tried to isolate the *o*-diallenylbenzene intermediate (**2**, R=H) and obtained it in >80% purity. See reference 5a.
8. Satisfactory spectral and analytical data were obtained.
9. In fact, dimethyl fumarate (ca. 15%) was detected in the recovered dienophile. It has been reported that the cycloaddition was at least 95% stereospecific when the reaction was conducted under neutral conditions; see reference 5a.
10. Cava, M. P.; Hwang, B.; Van Meter, J. P. *J. Am. Chem. Soc.* **1963**, *85*, 4031.
11. It is not clear from the isomeric ratio of the products whether the process involves biradicaloid species because the precursor can be a mixture of meso and racemic diallennylbenzenes. For mechanistic consideration, see references 5c and 5d.
12. MM2 calculations of *trans*-**5** and *cis*-**5** were carried out based on the reported data of the X-ray crystallographic analysis of naphtho[*b*]cyclobutene [Crawford, J. L.; Marsh, R. E. *Acta Cryst.* **1973**, *B29*, 1238]. The energy difference between the two isomers was calculated to be 0.99 kcal/mol. We thank Mr. Y. Yokoyama for carrying out the above calculations.
13. Leigh, W. J.; Zheng, K. *J. Am. Chem. Soc.* **1991**, *113*, 4019.
14. In this reaction, a mixture of diacetylene and acetylene-allene derivatives (19:81) was also isolated as minor products (27% yield). Also, in the reduction of bistrimethylsilylacetylene derivative (**1**, R=TMS), the corresponding acetylenic compounds were selectively obtained and no cyclized product derived from the corresponding naphthoquinodimethane intermediate was detected.





15. A part of this work was presented at the 9th Symposium of Rare Earth Society of Japan, May, Kyoto (1991).

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