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Communications

A New Mode for the Generation of *o*-Xylylene by *peri*-Selenium Participation from 8,13-Dihydrobenzo[*g*]naphtho[1,8-*bc*][1,5]diselenonin under Irradiation

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Summary: A new cyclic bis-selenide containing both benzylic methylene groups and a naphthalene ring, 8,13-dihydrobenzo[*g*]naphtho[1,8-*bc*][1,5]diselenonin (1), was stable in the dark; however, the C–Se bond of 1 was readily cleaved to form *o*-xylylene (2) and naphtho[1,8-*cd*]-1,2-diselenole (3) under the scattered light in the laboratory. The *o*-xylylene generated from 1 under the scattered light or UV irradiation (254 nm) was trapped by several dienophiles.

The highly reactive molecule, *o*-xylylene (*o*-quinodimethane, 2), has received considerable interest from the theoretical, structural, and synthetical point of view.^{1–5} We have previously reported that the multicenter selenide participation of cyclic polyselenaethers can produce the diselena dication or the hypervalent species.⁶ Recently, we showed that 1,8-bis(methylseleno)naphthalene and

naphtho[1,8-*bc*]-1,5-diselenocin underwent *Se*-dealkylation (*i.e.*, the cleavage of C_{sp3}–Se bond) to form the naphtho 1,8-diselenide moiety upon treatment with benzoyl peroxide.⁷ This behavior, in which a diselenide (–SeSe–) bond is produced by 1,8-diselenonaphthalene derivatives, has prompted us to study the generation of reactive species induced by *peri*-selenium interaction. We have now found that a new cyclic bis-selenide containing both benzylic methylene groups and a naphthalene ring, 8,13-dihydrobenzo[*g*]naphtho[1,8-*bc*][1,5]diselenonin (1), undergoes facile C–Se bond scission, quantitatively, to *o*-xylylene (2) and naphtho[1,8-*cd*]-1,2-diselenole (3) under photoirradiation.

The cyclic bis-selenide 1 was stable in the dark; however, in organic solvents such as dichloromethane, chloroform, carbon tetrachloride, and acetonitrile, 1 decomposed under the scattered light in the laboratory. The UV–vis spectrum of 1 in CHCl₃ shows an absorption at λ_{max} 298 nm (ε = 8.0 × 10³). When a chloroform solution of 1 was irradiated by UV lamp (254 nm) at room temperature under an Ar atmosphere in a UV–vis cell, new absorptions appeared at λ_{max} 261 nm and 377 nm, which are assignable to naphtho[1,8-*cd*]-1,2-diselenole (3).⁸ This observation suggests that a cleavage of the carbon–selenium bond occurred to generate the *o*-xylylene intermediate and 1,8-diselenide 3.

The *o*-xylylene generated from 1 under the scattered light or UV irradiation could be trapped by several

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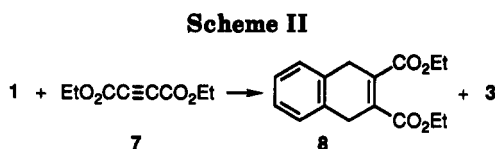
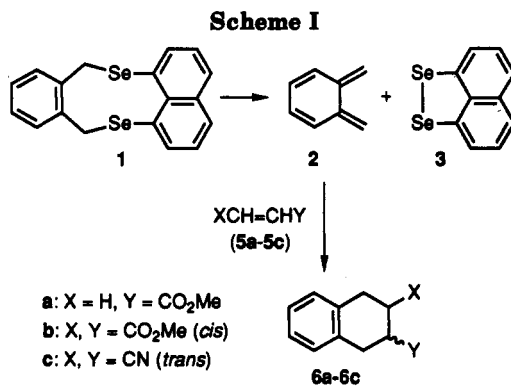
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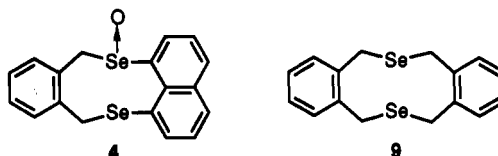
(8) (a) The absorption of the diselenide 3 may be overlapped with the reported λ_{max} = 373 nm of *o*-xylylene in a low-temperature matrix,² whereas *o*-xylylene is rapidly decayed at room temperature. (b) The same result was obtained on the photolysis of 1 in air.



dienophiles (electron deficient olefins and acetylene) to produce the cycloadduct. A typical procedure is as follows. The mixture of bis-selenide **1** (102 mg, 0.26 mmol) and methyl acrylate (**5a**) (67 mg, 0.78 mmol) in CHCl₃ was allowed to react at room temperature for 48 h under the scattered light in the laboratory. After removal of the solvent, the residue was chromatographed on silica gel to afford the cycloaddition product **6a** (97% yield)⁹ and 1,8-diselenide **3** (96% yield) (Scheme I). This reaction was greatly accelerated by irradiation with 254-nm UV light, *i.e.*, the cycloaddition was complete in 3 h. The addition reaction of **1** to olefins and acetylene did not take place in the dark. The olefins (**5a-5c**) and acetylene (**7**) are efficient traps for the reactive intermediate **2** generated by photolysis of **1** (Schemes I and II). Yields of adducts (**6b**, **6c**) and **8** with these olefins and acetylene are as follows: *cis*-**6b** (94%)⁹ and **3** (97%) from dimethyl maleate (**5b**) with **1**; *trans*-**6c** (99%)⁹ and **3** (98%) from fumaronitrile (**5c**) with **1**; **8** (87%) and **3** (84%) from diethyl acetylenedicarboxylate (**7**) with **1** (Scheme II). The generality of this reaction is illustrated by the finding that *o*-xylylene is generated and produces cycloadducts in such excellent yields. No addition products were obtained from olefins (**5a-5c**) and acetylene **7** with the diselenide **3**. In the absence of dienophiles, 1,2:5,6-dibenzocyclooctadiene and spiro[di-*o*-xylylene] derived from *o*-xylylene in a 1:1 ratio² and 1,8-diselenide **3** were produced upon photolysis of **1**.

In contrast to **1**, the monoselenoxide, 8,13-dihydrobenzo[*g*]naphtho[1,8-*bc*][1,5]diselenonin 7-oxide (**4**), was stable in chloroform under the scattered light, although the UV-vis spectrum of **4** in CHCl₃ exhibits an absorption at λ_{max} 297 nm, which is similar to that of **1**. Accordingly, the reaction of the selenoxide **4** with the olefin **5c** did not proceed under the scattered light in the laboratory, *i.e.*, none of the cycloaddition product was obtained. This observation suggests that the cleavage of the carbon-selenium bond of **1** may be facilitated by the lone pair-lone pair repulsion between the two selenyl groups leading

to *o*-xylylene. The existence of a *peri*-selenium interaction in **1** has been reported in an electrochemical oxidation.¹⁰



We therefore performed an electrochemical oxidation by cyclic voltammetry (CV).¹¹ The cyclic voltammogram of **1** in CH₃CN showed a reversible oxidation wave at +0.17 V vs Ag/0.01 M AgNO₃. The oxidation potential of **1** is lower than those of 1,8-bis(benzylseleno)naphthalene (+0.46 V) and dibenzyl selenide (+0.98 V), which are irreversible.¹² Our facile oxidation and the electrochemically-reversible oxidation of **1** are attributed to the destabilization of **1** by transannular lone pair-lone pair repulsion and the stabilization of the oxidized species by neighboring-selenium participation.

Thus, the transannular selenium-selenium interaction of **1** promotes electron transfer from the selenide. The formation of *o*-xylylene may be rationalized by a mechanism involving photoinduced electron transfer from **1** to the excited state, which undergoes cleavage of the C-Se bond.

This facile C-Se bond scission of **1** under scattered light seems to be quite rare in alkyl and aryl selenides, since there are only a few known examples of the photochemical cleavage of a σ bond between selenium and carbon atoms.^{13,14} The results described herein represent a new method for the generation of *o*-xylylene by photoinitiated cleavage of C-Se bond under mild conditions from organoselenium compounds. Attempts to understand the mechanism of C-Se bond scission of **1** under the scattered light and to extend this type of chemical behavior are underway.

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Supplementary Material Available: Experimental procedures and spectral data for compounds **1**, **4**, and **8** (2 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

(11) The cyclic voltammeteries for all selenides were measured in CH₃CN containing 0.1 M NaClO₄ as supporting electrolyte using a glassy carbon working electrode, platinum counter electrode, and Ag/0.01 M AgNO₃ in CH₃CN reference electrode (scan rate: 50 mV/s).

(12) Normally, the cyclic voltammogram for dialkyl or diaryl selenides shows an irreversible oxidation wave, although the electrochemistry of organoselenium compounds is little known. In general, since the cation radicals and dications of heteroatoms having alkyl groups would be expected to deprotonate or react with nucleophiles very rapidly, the lifetime of these species is short, resulting in the irreversible oxidation wave.

(13) Bis-selenide, 3,4,8,9-dibenzo-1,6-diselenacyclodecane (**9**),^{5a} unlike the naphthalene derivative, was stable under the scattered light in the laboratory.

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