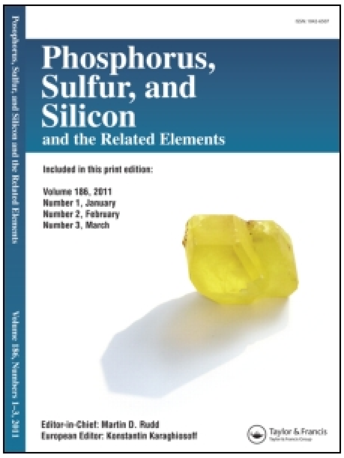

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Synthesis of Cyclobutacyclophanes Containing Group 16 Elements by Intramolecular (2π 2π) Photocycloaddition

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SYNTHESIS OF CYCLOBUTACYCLOPHANES CONTAINING GROUP 16 ELEMENTS BY INTRAMOLECULAR ($2\pi + 2\pi$) PHOTOCYCLOADDITION

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Abstract The benzophenone-sensitized intramolecular ($2\pi + 2\pi$) photocycloaddition of bis(4-vinylphenylmethyl)sulfide and selenide in benzene afforded cyclobutacyclophanes containing sulfur and selenium in good yields. However, the photoreaction of bis(4-vinylphenylmethyl)telluride under similar conditions did not give the corresponding cyclophane compound.

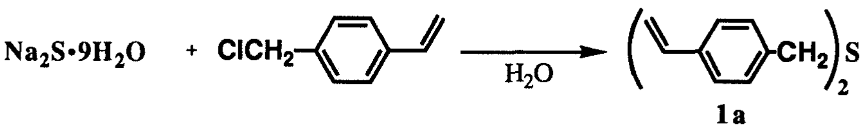
INTRODUCTION

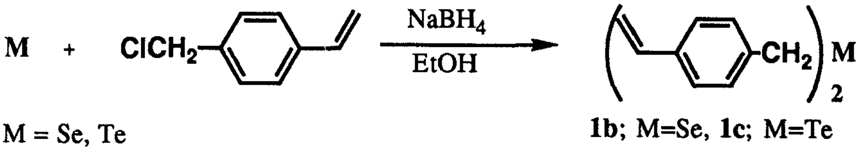
The construction of heteracyclophanes is a subject of current interest from synthetic and structural viewpoints. Nishimura et al. reported the synthesis of cyclobutaoxacyclophanes having crown ether units.[1] We reported the synthesis of cyclobutacyclophanes and spiro compounds containing group 14 elements.[2] These cyclophanes have been prepared by the intramolecular ($2\pi + 2\pi$) photocycloaddition. However, little is known about the preparation of cyclobutaheteracyclophanes containing group 16 elements except oxygen. We now report the convenient synthesis of cyclobutacyclophanes containing sulfur and selenium by the intramolecular ($2\pi + 2\pi$) photocycloaddition of bis(4-vinylphenylmethyl)sulfide and selenide.

RESULTS AND DISCUSSION

Preparation of Bis(4-vinylphenylmethyl)sulfide, Selenide, and Telluride (**1a-c**)

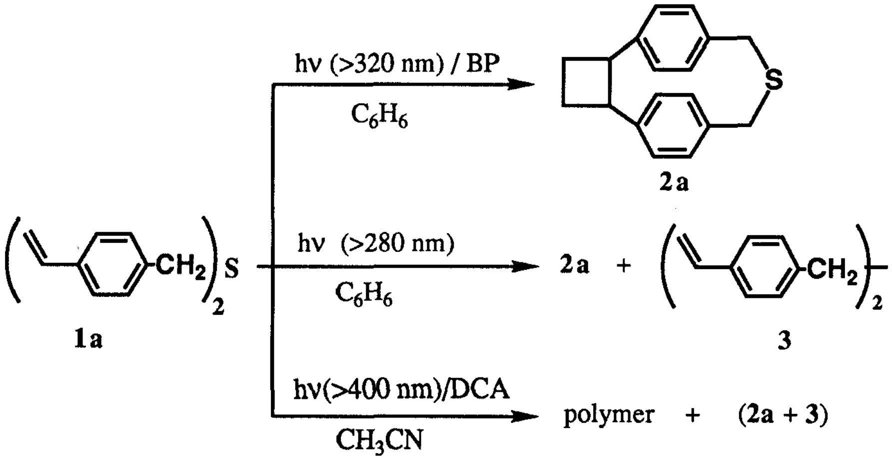
Bis(4-vinylphenylmethyl)sulfide (**1a**) was prepared by stirring a mixture of 1-chloromethyl-4-vinylbenzene and $Na_2S\cdot 9H_2O$ in H_2O at room temperature. Recrystallization from EtOH gave **1a** as colorless powder; mp 72-73 °C. Bis(4-vinylphenylmethyl)selenide (**1b**) was prepared according to the Barton method[3] as follows: A mixture of selenium powder and $NaBH_4$ in EtOH was stirred for one night at room temperature under nitrogen atmosphere. The solution was cooled to 0 °C and then 1-chloromethyl-4-vinylbenzene was added. After stirring at room temperature for one night, the mixture was worked up by the usual manner. Recrystallization from CH_2Cl_2-EtOH gave **1b** as colorless powder; mp 77-78 °C. Similarly, treatment of powdered tellurium and $NaBH_4$ in EtOH under nitrogen atmosphere followed by addition of 1-chloromethyl-4-vinylbenzene afforded bis(4-vinylphenylmethyl)telluride (**1c**). However, **1c** was unstable and could not be isolated in pure form. Prolonged stirring of the reaction mixture resulted in the reductive cleavage of **1c**, giving 1-methyl-4-vinylbenzene in 31 % yield. Under aerobic conditions, **1c** was oxidized to 4-vinylbenzaldehyde in 41 % yield.[4] The structures of **1a-c** were determined by spectral properties (especially ^1H NMR spectra) and elemental analyses.



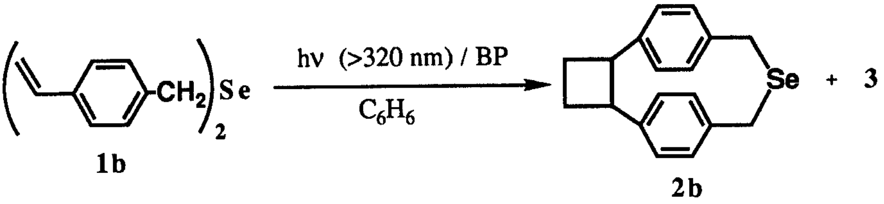


Intramolecular (2π + 2π) Photocycloaddition of **1a-c**

Irradiation of a benzene solution containing **1a** in the presence of benzophenone (BP; E_T=287 kJ/mol) with >320 nm light under nitrogen atmosphere afforded the intramolecular (2π + 2π) photocycloadduct **2a** in a nearly quantitative yield.[5] This photoreaction was also sensitized by other triplet sensitizers such as acetophenone (AP; E_T=308 kJ/mol) and Michler's ketone (MK; E_T=259 kJ/mol). Irradiation of **1a** through a Pyrex filter with >280 nm light in the absence of triplet sensitizers afforded **2a** and 1,2-bis(4-vinylphenyl)ethane **3** in a 5:6 ratio, but prolonged irradiation gave insoluble polymer. Irradiation of an acetonitrile solution of **1a** in the presence of 9,10-dicyanoanthracene (DCA), an electron-transfer sensitizer, gave insoluble polymer as a major isolable product along with small amounts of **2a** and **3**. Irradiation of **2a** in the presence of DCA in acetonitrile resulted in the formation of **1a** and insoluble polymer. The quantum yield for the formation of **1a** from **2a** is much larger than that for the formation of **2a** from **1a** in the DCA-sensitized photoreactions.



The BP-sensitized intramolecular photocycloaddition of **1b** in benzene afforded a mixture of the cycloadduct **2b** and the coupling product **3** in a 3:2 ratio in good yields. In this case, **2b** was not isolated in pure form. However, the formation of **2b** was confirmed by the 270 MHz ^1H NMR and GC mass analyses of the reaction mixture. In the absence of triplet sensitizers, only the coupling product **3** was produced accompanying precipitation of metallic selenium. The photoreaction **1c** in the presence and absence of BP did not give the corresponding cyclophanes, but gave **3** and metallic tellurium as major products.



The advantages of this methodology are; (1) a new type of cyclobutacyclophanes containing sulfur and selenium can be synthesized in good yields under neutral and mild conditions; (2) the high-dilution is not required for this intramolecular photocycloaddition ([**1**]= 0.01-0.05 mol/dm^3). Cyclobutacyclophanes **2a-b** may be converted into cyclobuta[2.2]cyclophanes by desulfurization or deselenation.

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5. Spectral properties of cyclobutanes: **2a**: mp 136-138 °C; ^{1}H NMR(270 MHz, $CDCl_3$), δ 3.78(s, 4H), 2.49-2.57(m, 4H), 4.11-4.17(m, 2H), 6.46(ABq, $\Delta\nu$=124 Hz, J=8 Hz, 4H, ArH), 6.70(ABq, $\Delta\nu$=40 Hz, J=8 Hz, 4H, ArH); **2b**: ^{1}H NMR(270 MHz, $CDCl_3$), δ 3.91(s, 4H), 2.44-2.53(m, 4H), 4.12-4.17(m, 2H), 6.40(ABq, $\Delta\nu$=124 Hz, J=8 Hz, 4H, ArH), 6.72(ABq, $\Delta\nu$=46 Hz, J=8 Hz, 4H, ArH).