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Design and Synthesis of Photoresponsive Crown Ethers via Olefin Metathesis

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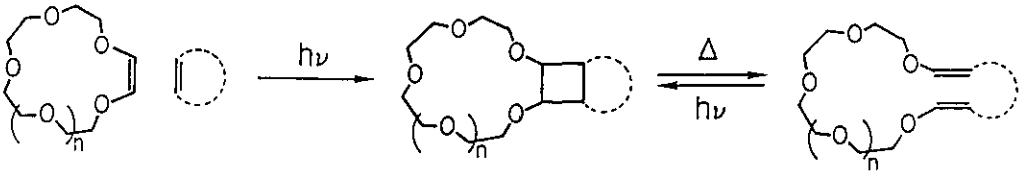
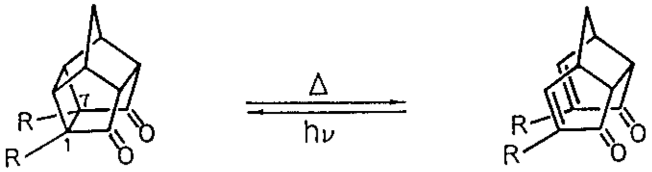
Abstract - Crowned cage compounds (5 and 9), prepared from crowned p-benzoquinone and cyclopentadienes by the sequence of the Diels-Alder reaction and photochemical [2+2] cycloaddition, constitute a new class of photoresponsive systems based on the reversible [2+2] cycloreversion/cycloaddition.

Photoresponsive crown ethers are of current interest for their latent ability to perform the selective ion extraction and ion transport due to the photocontrolled complexation with metal ions.[1] These functions stem from the conformational change of the crown ether moiety induced by the reversible photochemical reaction of the attached chromophores. A number of systems have been considered as candidates for the chromophore causing a reversible structural change. Especially azobenzene derivatives have been widely employed owing to the facile photochemical E/Z isomerism.[1-5] In contrast, photo-reversible systems containing a C-C bond cleavage/formation process have been rarely utilized for this purpose.[6] Herein, we report on a synthesis of novel photoresponsive compounds which alter the ring size of crown ether via the formal olefin metathesis[7] as outlined in eq 1.



(1)

As a promising candidate of such chromophores, we have chosen the Cookson's cage compounds (1) which are known to undergo the reversible [2+2] cycloreversion/cycloaddition reaction (eq 2).[8]



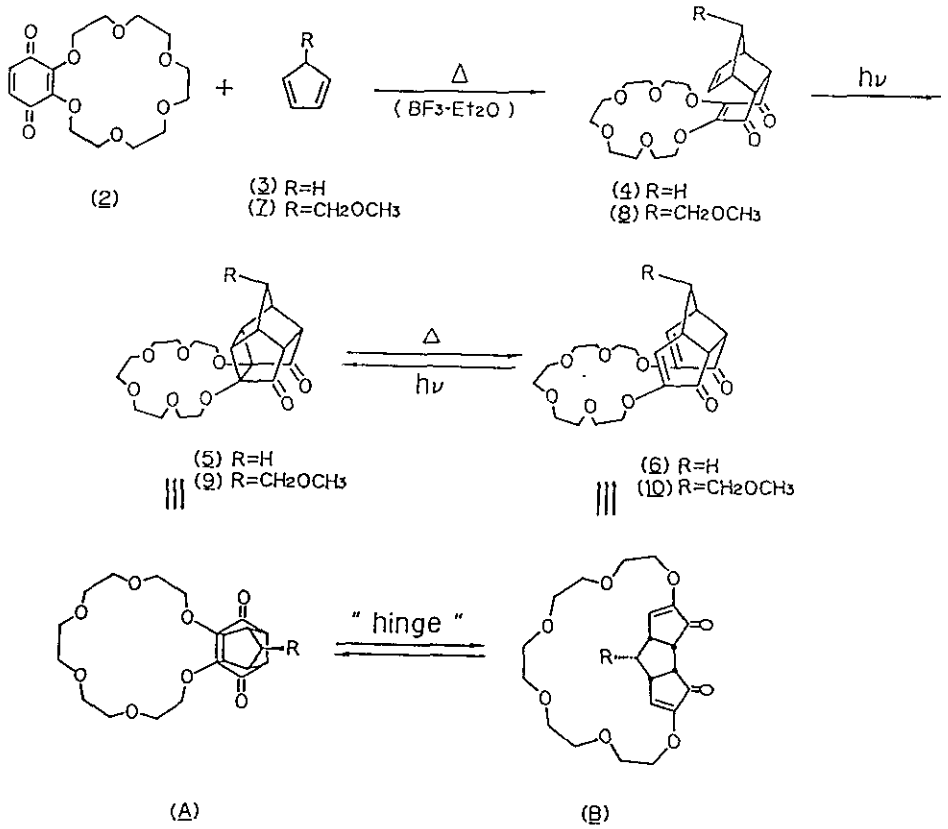
(2)

(1) a. R=H
b. R=OCH_3

The cycloreversion of **1** usually requires the drastic reaction conditions [ex., for **1a**, flash vacuum pyrolysis at 500 °C][8], since the reaction involves a thermally forbidden four electron process.[9] However, our previous studies revealed that the similar reaction of the dimethoxy derivative (**1b**) proceeded under the much milder conditions (95 °C) because of the C_1-C_7 bond weakening due to the effects of through-bond coupling of lone pairs and synergetic capto-dative radical stabilization.[10]

On the basis of these studies we investigated the thermal reaction of crowned cage compound (**5**), which was recently synthesized by the Diels-Alder reaction of crowned p-benzoquinone (**2**) and cyclopentadiene (**3**) followed by photochemical [2+2] cycloaddition[11]. Compound (**5**) has a close structural similarity to **1b** concerning the substitution pattern and hence some C_1-C_7 bond elongation (weakening) can be reasonably expected.[10] Actually, when **5** was heated in benzene at 80 °C (3 h), the cycloreversion took place rapidly to provide **6** in a quantitative yield. Conversely, compound (**6**) was smoothly converted into **5** by irradiation in chloroform with a high-pressure Hg-lamp through a Pyrex filter. This cycloreversion/cycloaddition process was repeated several times with no remarkable loss (decomposition) of the materials.

These results may represent a general method to synthesize more functionalized host compounds since the variously substituted cyclopentadienes are readily available. For example, **2** reacted with 5-methoxymethylcyclopentadiene(**7**)[12] in the presence of $BF_3 \cdot Et_2O$ (CH_2Cl_2, -20°C) to give the endo adduct (**8**) in 93% yield.



Scheme 1

The anti-stereochemistry of the substituent (R) was confirmed by the 270 MHz ^1H nmr (NOESY spectra) which showed the remarkable NOE coupling between the olefin protons and methylene protons in R. Irradiation of **8** afforded a quantitative yield of **9** which in turn readily underwent the thermal cycloreversion (110°C, 3 h) to give **10**. A clean photochemical reconversion of **10** into **9** was also confirmed. Molecular-model inspection indicated that the above reversible processes induced a large structural change ($A \rightleftharpoons B$) including the ring size, direction of two carbonyl groups, and the position of R group. Especially, the proximity of the methoxymethyl group and the crown ring in **10** suggested its potential utility as the capping functionality.

It is noteworthy that preliminary extraction experiments for compound (**6**) (10^{-4}M in benzene) exhibited specific selectivity for Rb^+ (diameter; 2.98Å) among alkali metal ions (Na^+,K^+,Cs^+).[13]

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