

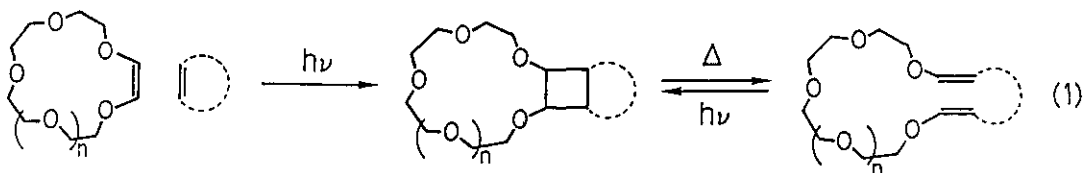
# Design and Synthesis of Photoresponsive Crown Ethers via Olefin Metathesis

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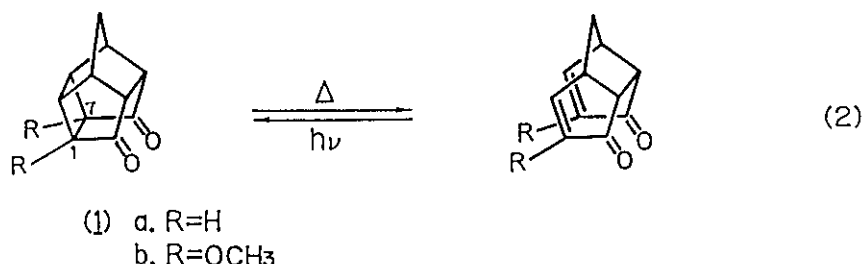
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**Abstract** - Crowned cage compounds (5 and 9), prepared from crowned p-benzoquinone and cyclopentadienes by the sequence of the Diels-Alder reaction and photochemical [2+2] cycloaddition, constitute a new class of photoresponsive systems based on 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.<sup>1</sup> 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.<sup>1-5</sup> In contrast, photo-reversible systems containing a C-C bond cleavage/formation process have been rarely utilized for this purpose.<sup>6</sup> Herein, we report on a synthesis of novel photoresponsive compounds which alter the ring size of crown ether via the formal olefin metathesis<sup>7</sup> as outlined in eq 1.



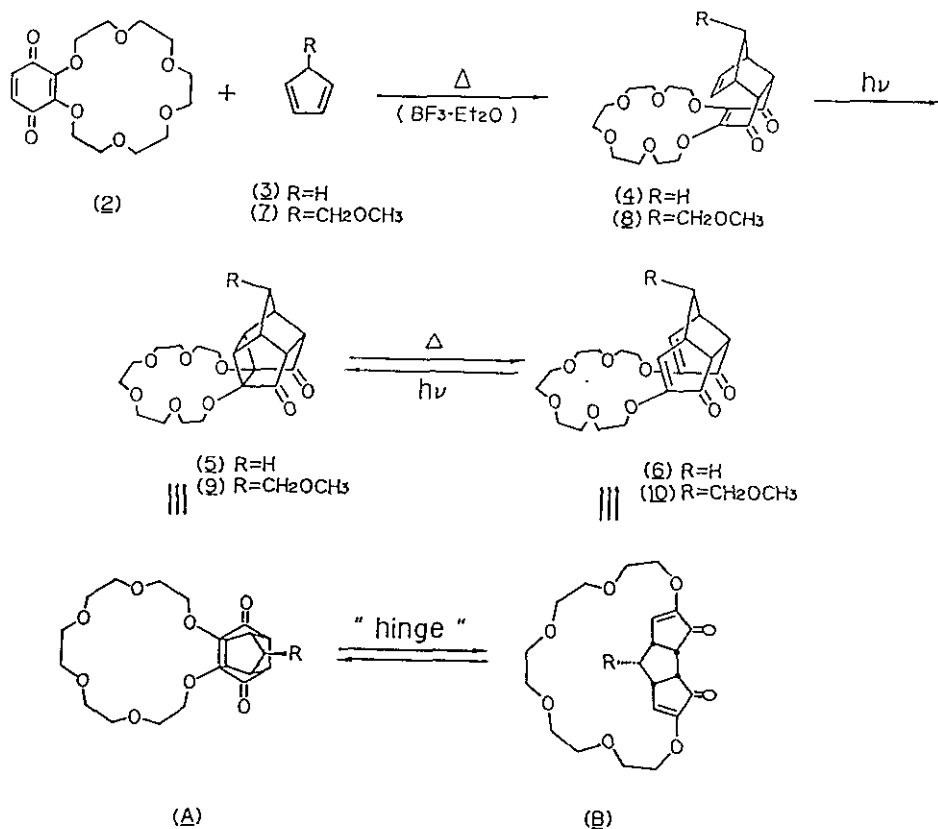
As a promising candidate of such chromophores, we have chosen the Cookson's cage compounds (1) which are known to undergo the reversible [2+2] cycloreversion/cycloaddition reaction (eq 2).<sup>8</sup>



The cycloreversion of 1 usually requires the drastic reaction conditions [ex., for 1a, flash vacuum pyrolysis at 500 °C]<sup>8</sup>, since the reaction involves a thermally forbidden four electron process.<sup>9</sup> 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<sub>1</sub>-C<sub>7</sub> bond weakening due to the effects of through-bond coupling of lone pairs and synergetic capto-dative radical stabilization.<sup>10</sup>

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<sup>11</sup>. Compound (5) has a close structural similarity to 1b concerning the substitution pattern and hence some C<sub>1</sub>-C<sub>7</sub> bond elongation (weakening) can be reasonably expected.<sup>10</sup> 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)<sup>12</sup> in the presence of BF<sub>3</sub>·Et<sub>2</sub>O (CH<sub>2</sub>Cl<sub>2</sub>, -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 <sup>1</sup>H 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<sup>-4</sup>M in benzene) exhibited specific selectivity for Rb<sup>+</sup> (diameter; 2.98Å) among alkali metal ions (Na<sup>+</sup>, K<sup>+</sup>, Cs<sup>+</sup>).<sup>13</sup>

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13. The experiments were also carried out for compounds 4 and 5, which exhibited little selectivity among alkali metal ions.

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