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. 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. In contrast, photo-reversible systems containing a C-C bond cleavage/formation process have been rarely utilized for this purpose. Herein, we report on a synthesis of novel photoresponsive compounds which alter the ring size of crown ether via the formal olefin metathesis 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).  

The cycloreversion of 1 usually requires the drastic reaction conditions [ex., for 1a, flash vacuum pyrolysis at 500 °C] since the reaction involves a thermally forbidden four electron process.  

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 C1-C7 bond weakening due to the effects of through-bond coupling of lone pairs and synergetic capto-dative radical stabilization.  

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.  

Compound (5) has a close structural similarity to 1b concerning the substitution pattern and hence some C1-C7 bond elongation (weakening) can be reasonably expected.  

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) in the presence of BF3*Et2O (CH2Cl2, -20°C) to give the endo adduct (8) in 93% yield.
The anti-stereochemistry of the substituent (R) was confirmed by the 270 MHz $^1$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 ($110^\circ$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 $\leftrightarrow$ 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$^+$).
REFERENCES


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

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