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Photoresponsive Complexation of Metal Cations with an Azobenzene–Crown–Azobenzene Bridge Immobilized in Polymer Supports

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Polymer supports that carry various functional groups have attracted much attention in recent years. In particular, the applications of polymer supports to "three-phase test", "triphase catalysis", and immobilization of crown ethers are the most noteworthy achievements that demonstrate the usefulness of polymer supports not only in the syntheses but also in the clarification of the reaction mechanisms.[1-14] The object of our investigation has been to control the binding ability of crown ethers by light. We and others have reported that a photoresponsive crown ether that combines within a molecule both a crown ether and a photoresponsible chromophore changes its conformation in response to photoirradiation, resulting in a change in the complexation ability.[15-19] The finding has been applied to the photocontrol of solvent extraction and ion transport across membranes. It occurred to us that polymer supports may be useful to induce the conformational change of crown ethers by light. The distance between the 4- and 4′-positions of *trans*-azobenzene is 9.0 Å, while that of *cis*-azobenzene is 5.5 Å. When a molecule containing both a crown ether and an azobenzene is immobilized in a polymer support, the contraction of the azobenzene moiety due to the photoinduced trans-to-cis isomerization would be compensated by the elongation of the crown ether moiety. With this object in view, we synthesized and immobilized an azobenzene–24-crown-8–azobenzene bridge on cross-linked polystyrene beads and attempted to photocontrol the complexation ability of the immobilized dibenzo–24-crown-8 unit toward cesium ion.

Dinitrodibenzo–24-crown-8 (mixture of cis and trans) was reduced by catalytic hydrogenation (Pd–carbon), and the resultant diaminodibenzo–24-crown-8 was diazotized in $NaNO_2$/HCl. The subsequent treatment of the diazo compound with sodium phenoxide gave a key intermediate (**1**) involving the azobenzene–24-crown-8–azobenzene unit. The disodium salt of **1** was treated with *p*-chloromethylated polystyrene (3.2% cross-linked, 4 mequiv of Cl/g)[20] and benzyl chloride in *N*,*N*-dimethylformamide (DMF) to give a polymer-supported crown ether and its monomeric analogue (**3**), respectively (Scheme I). **3** (mp of cis–trans mixture, 120–138 °C) was identified by elemental analysis and IR. The styrene unit that reacted with **1** was estimated to be 4.8 mol % on the basis of elemental analysis. The remaining chloromethyl groups were converted to the ethoxy groups by treatment with sodium ethoxide in tetrahydrofuran.[21] The polystyrene beads (**2**) thus obtained were used in the following experiments. That two terminal azophenoxide groups of **1** reacted with the polymeric chloromethyl groups was evidenced by the following facts: (i) the color change of the resin from yellow (azophenol) to red (azophenoxide) was not observed even in strongly basic solution; (ii) no ash was detected in elemental analysis; (iii) in the solution after treatment with acetic acid, no Na^+ ion was detected by atomic absorption spectroscopy.

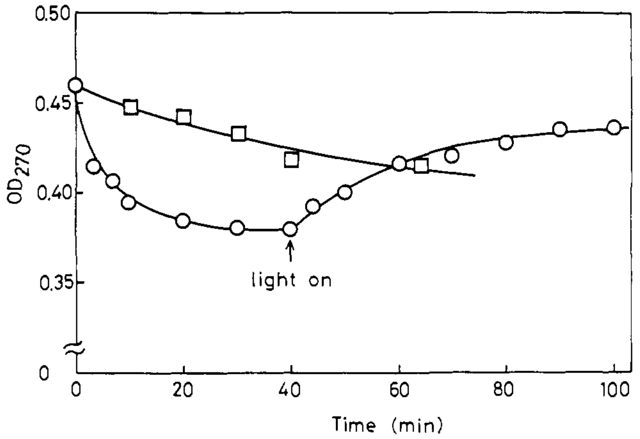

Figure 1. Influence of photoirradiation on the binding of cesium *p*-nitrobenzoate to **2**. The reaction solution (7.7 mL of DMF) contains 100 mg (0.0145 mmol of crown ether) of **2** and 0.0145 mmol of cesium *p*-nitrobenzoate: (○) 0 → 40 min in the dark and then photoirradiated after 40 min; (□) photoirradiated for 1 h in the absence of cesium *p*-nitrobenzoate and then mixed (time 0) with cesium *p*-nitrobenzoate in the dark.

When the monomeric analogue **3** (2.00×10^{-5} M) in DMF (λ_{max} 366 nm) was photoirradiated with a 500-W high-pressure Hg lamp (no filter), the photostationary state was attained within 1 min and the percent cis compound calculated on the basis of the assumption that the absorbance (366 nm) of *cis*-**3** is negligible in comparison to that of *trans*-**3** was 32%. The first-order rate constant for the thermal cis-to-trans isomerization at 30 °C was 0.0101 min^{-1} and was slightly suppressed by the addition of Cs^+ (0.0071 min^{-1} at $[C_{11}H_{23}CO_2Cs] = 2.50 \times 10^{-4}$ M).

To 3.85 mL of DMF containing **2** (100 mg, 0.0145 mmol of crown) was added 3.85 mL of a DMF solution of cesium *p*-nitrobenzoate (0.0145 mmol). The solution was maintained at 30 °C and stirred at a constant speed, and the aliquot (100 μL) was withdrawn at appropriate time intervals. The withdrawn sample was diluted to 3 mL and subjected to spectral analysis. The fraction of cesium ions bound to the polymer beads was estimated spectrophotometrically by measuring the concentration of remaining *p*-nitrobenzoate in the solution at 270 nm. The typical results are illustrated in Figure 1.

When **2** was mixed with the DMF solution of cesium *p*-nitrobenzoate in the dark, the concentration of cesium *p*-nitrobenzoate in the solution decreased rapidly and reached an equilibrium within 20 min. The time dependence could be approximated by a first-order rate equation with $k = 0.156$ min^{-1}. Since the "concentration" of the crown ether is equal to that of cesium *p*-nitrobenzoate, Cs^+ bound to **2** is readily estimated to be 17%. When this solution was subjected to photoirradiation with a 500-W

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(1) Rebek, J., Jr.; Trend, J. E. *J. Am. Chem. Soc.* **1979**, *101*, 737.
(2) Rebek, J., Jr. *Tetrahedron* **1979**, *35*, 723.
(3) Regen, S. L. *J. Am. Chem. Soc.* **1976**, *98*, 6270.
(4) Regen, S. L.; Besse, J. J.; McLick, J. *J. Am. Chem. Soc.* **1979**, *101*, 116.
(5) Regen, S. L.; Bolikal, D. *J. Am. Chem. Soc.* **1981**, *103*, 5248.
(6) Regen, S. L. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 421.
(7) Farrall, M. J.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **1978**, *100*, 7998.
(8) Fréchet, J. M. J. *J. Macromol. Sci., Chem.* **1981**, *A15*, 877.
(9) Fréchet, J. M. J. *Tetrahedron* **1981**, *37*, 663.
(10) Molinari, H.; Montanari, F.; Tundo, P. *J. Chem. Soc., Chem. Commun.* **1977**, 639.
(11) Montanari, F.; Tundo, P. *Tetrahedron Lett.* **1979**, 5055.
(12) Warshawsky, A.; Kalier, R.; Deshe, A.; Berkovitz, H.; Patchornik, A. *J. Am. Chem. Soc.* **1979**, *101*, 4249.
(13) Tomoi, M.; Abe, O.; Ikeda, M.; Kihara, K.; Kakiuchi, H. *Tetrahedron Lett.* **1978**, 3031.
(14) Tomoi, M.; Kihara, K.; Kakiuchi, H. *Tetrahedron Lett.* **1979**, 3485.
(15) (a) Shinkai, S.; Ogawa, T.; Nakaji, T.; Kusano, Y.; Manabe, O. *Tetrahedron Lett.* **1979**, 4569. (b) Shinkai, S.; Nakaji, T.; Nishida, Y.; Ogawa, T.; Manabe, O. *J. Am. Chem. Soc.* **1980**, *102*, 5860.
(16) (a) Shinkai, S.; Ogawa, T.; Kusano, Y.; Manabe, O. *Chem. Lett.* **1980**, 283. (b) Shinkai, S.; Nakaji, T.; Ogawa, T.; Shigematsu, K.; Manabe, O. *J. Am. Chem. Soc.* **1981**, *103*, 111.
(17) Asano, T.; Okada, T.; Shinkai, S.; Shigematsu, K.; Kusano, Y.; Manabe, O. *J. Am. Chem. Soc.* **1981**, *103*, 5161.
(18) Yamashita, I.; Fujii, M.; Kaneda, T.; Misumi, S. *Tetrahedron Lett.* **1980**, 541.
(19) Shiga, M.; Takagi, M.; Ueno, K. *Chem. Lett.* **1980**, 1021.

(20) Cross-linked *p*-chloromethylated polystyrene was kindly supplied by Mitsubishi Kasei Co. Ltd.
(21) When the polystyrene resin that was not treated with sodium ethoxide was photoirradiated by a Hg lamp, we noticed that further cross-linking takes place. This is probably due to photoreaction of the chloromethyl group.

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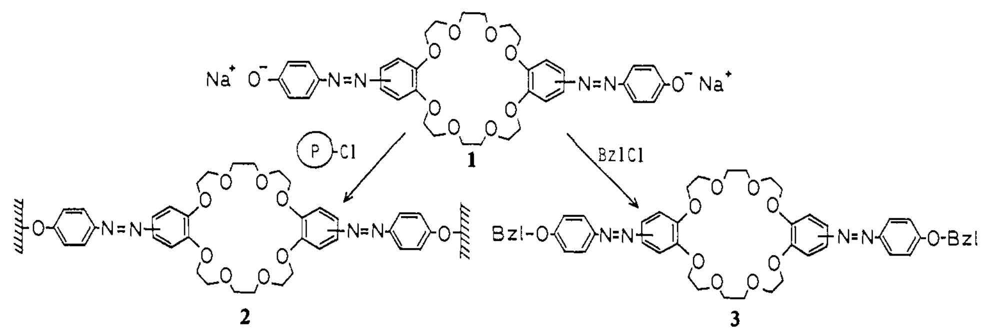
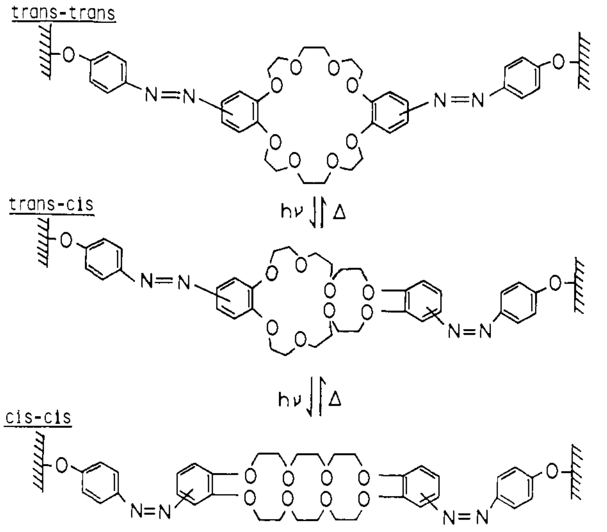
Scheme I



Scheme II



high-pressure Hg lamp (no filter), which induces the trans-to-cis isomerization of the azobenzene moiety, the concentration of cesium *p*-nitrobenzoate increased gradually and reached a new equilibrium where only 5% of Cs^+ was bound to **2**. On the other hand, when **2** in DMF was photoirradiated for 1 h and then mixed with the DMF solution of cesium *p*-nitrobenzoate in the dark, the absorbance of cesium *p*-nitrobenzoate decreased slowly and reached an equilibrium that was comparable with that attained in the dark (i.e., 17% binding). The time dependence which was also approximated by a first-order rate equation with $k = 0.0142$ min^{-1} is thus assumed to reflect the thermal cis-to-trans isomerization of the azobenzene moiety immobilized in the polymer support. It is of interest that the rate constant for the thermal isomerization in the polymer support (0.0142 min^{-1}) is very similar to that of the monomeric analogue (**3**) in the homogeneous solution (0.0101 min^{-1}). Finally, we photoirradiated **2** in DMF for 1 h and kept photoirradiating after mixing with the DMF solution of cesium *p*-nitrobenzoate. The decrease of OD_{270} was very slow (data not shown in Figure 1) and reached an equilibrium comparable with that of the final stage of the first experiment (i.e., 5% binding). The same photoirradiation effect was obtained when the concentration of cesium ion in the DMF solution was followed by an atomic absorption spectrophotometer.

The foregoing results consistently suggest that, as shown in Scheme II, the photoinduced trans-to-cis isomerization of the azobenzene moiety is capable of changing the conformation of the crown ether into a more stretched one which has poor ion-binding ability relative to the normal crown ether. Therefore, the binding ability of the crown ether immobilized as the azobenzene–crown–azobenzene bridge in the polymer support can be controlled by an on–off light switch. This conclusion suggests that the polymer support is useful as a "fixed point" to induce the conformational changes of immobilized functional molecules.[22] Since the surface of the polymer beads may be regarded as one side of the polymer membrane, we believe that this concept is applicable to the photocontrol of ion transport across the polymer membrane.

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Registry No. **1**·2Na, 81456-74-8; **3**, 81456-75-9; cesium *p*-nitrobenzoate, 81456-99-7.

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[22] A referee raised a question whether the 3.2% cross-linked polymer really acts as a "fixed point". Several our subsequent experiments support that the answer is yes: (i) the binding of K^+ in DMF is not subject to the photoirradiation effect; (ii) the photoirradiation effect appears clearly in DMF (not a good solvent for polystyrene resin) but is not clear in good solvents (e.g., *o*-dichlorobenzene and tetrahydrofuran); (iii) the photoirradiation effect is reproducible more clearly in highly cross-linked polystyrene resins; (iv) the solvent extraction of Cs^+ with monomeric **3** is scarcely affected by photoirradiation.

Generation and Rearrangement of the 2-Oxobicyclo[2.2.1]heptane-6,7-diyl Diradical via Nitrogen Extrusion from the Azoalkane 2,3-Diazatricyclo[4.3.0.$0^{4,9}$]non-2-en-8-one

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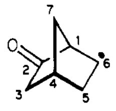
The diradical 2-oxobicyclo[2.2.1]heptane-6,7-diyl (**1**) has the



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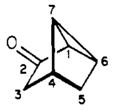

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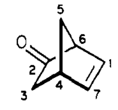

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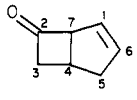

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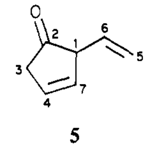

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options of cyclizing into tricyclo[3.2.0.$0^{2,7}$]heptan-3-one (**2**), of rearranging into 2-norbornenone (**3**) and bicyclo[3.2.0]hept-2-en-7-one (**4**), respectively, via C-1 to C-6 and C-1 to C-7 acyl 1,2-shifts, or of fragmenting into 2-vinylcyclopent-3-enone (**5**).[1] Presently we report on the generation of diradical **1** via the thermal and photochemical denitrogenation of azoalkane **6** (eq 1) and show that diradical **1** indeed affords the isomeric ketones **2**–**4**. The

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[†] On leave of absence from the University of Padova, Italy.

(1) Schuster, D. I. In "Rearrangements in Ground and Excited States"; de Mayo, P., Ed.; Academic Press: New York, 1980; Vol. 3, pp 167–279.