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The Preparation of Photoresponsive Cyclobutanocrown Ethers by Means of Intramolecular [2+2]Photocycloaddition

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The reaction of *o*-bis(3-hydroxy-1-oxapropyl)benzene (**7b**) with 3,3′-(trimethylenedi-4,1-phenylene)bis[2-propenoyl chloride] gave 8,9-benzo-4,7,10,13-tetraoxa[16.3]paracyclopha-1,8,15-triene-3,14-dione (**8b**) in a 6.5% yield, together with its dimer in a 12.3% yield. Also, 5,6-benzo-4,7-dioxa[10.3]paracyclopha-1,5,9-triene-3,8-dione (**8a**) and 11,12-benzo-4,7,10,13,16,19-hexaoxa[22.3]paracyclopha-1,11,21-triene-3,20-dione (**8c**) were obtained by the same method in 7.0 and 8.0% yields, together with their respective dimers (**9a**: 6.0%, **9c**: 10.8%). X-Ray analysis of **8b** revealed the two double bonds to be trans and the distances between the two olefinic carbon atoms (C_{17}–C_{35}) and (C_{18}–C_{34}) to be 5.341(11) and 5.906(9) Å respectively. These distances are too long for intramolecular [2+2]photocycloaddition to occur in the crystalline state. However, the irradiation of the solutions of the crown ethers **8a** and **8b** in acetonitrile by Pyrex-filtered UV light (>300 nm) gave two intramolecular [2+2]photocycloadducts, cyclobutanocrown ethers **10a** and **10b**, in 95.7 and 91.8% yields respectively. Subsequently, **10a** and **10b** were transformed to **8a** and **8b** in 37 and 29% yields respectively upon irradiation with 220 nm UV light. The structures of **10a** and **10b** were confirmed to be the *β*-form.

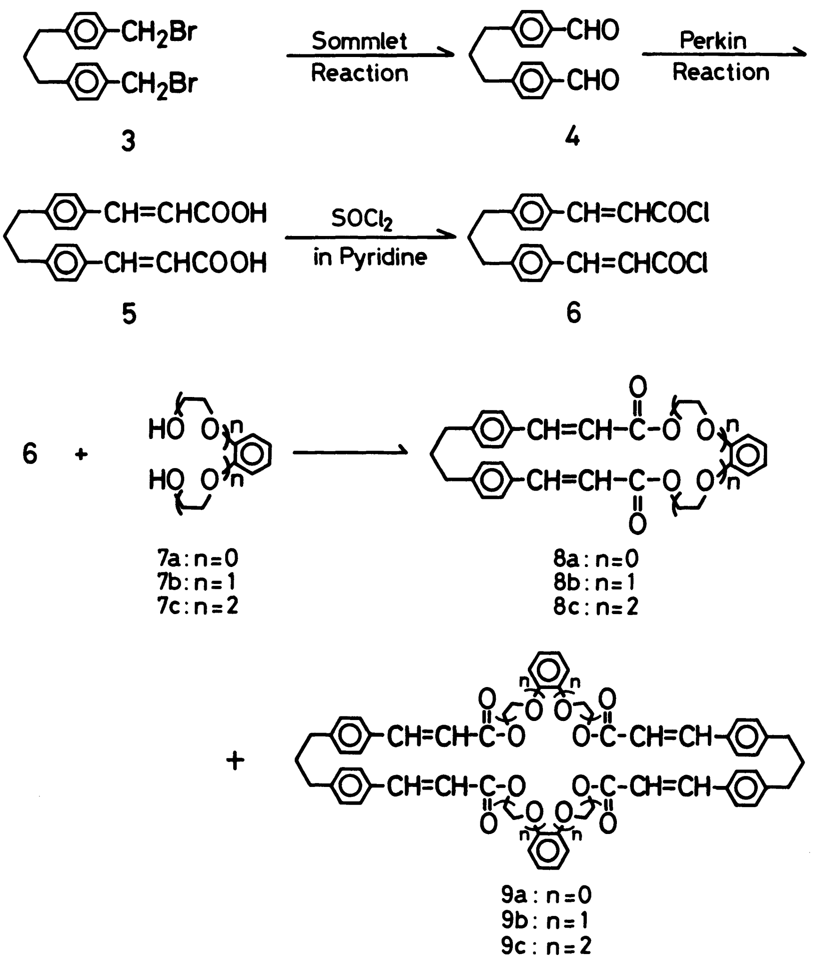
Both intermolecular and intramolecular [2+2]photocycloadditions of a large number of olefinic compounds have recently been investigated extensively by many research groups from the points of view of molecular design and the synthetic method for novel organic compounds.[1] Several kinds of photoresponsive crown ethers have been investigated by several research groups with the aim of controlling the extraction ability of crown ethers by light or thermal means.[2–4] It is well-known that macrocyclic polyethers can be complexed with various metal ions, although the corresponding open chain polyethers show poor complexing abilities.[5] Recently, several kinds of cyclobutanocrown ethers formed by the intramolecular [2+2]photocycloaddition of open-chain polyethers which contain two vinyl or vinyloxy groups at both terminals have received much attention in connection with the synthetic method for crown ethers.[6–9] However, these reports did not discuss the possibility of a photoreversible cleavage of the cyclobutanocrown ethers in order to control the complexing abilities. Egerton et al.[10] reported that the irradiation of cinnamic acid with >300 nm UV light gave a dimer by means of intermolecular [2+2]photocycloaddition, while the irradiation of the dimer with 200 nm UV light gave, on the contrary, the corresponding starting monomer. In connection with this finding, we ourselves reported on the syntheses of cyclobutanocrown ethers by means of the intramolecular [2+2]photocycloaddition of *α*,*ω*-dicinnamoyl polyethylene glycol derivatives **1** with >300 nm UV light and their photoreversible reactions with 220 nm light.[11] However, the rates of the intramolecular [2+2]photocycloaddition of the dicinnamates were extremely slow (e.g., the half-life periods of **1a**, **1b**, and **1c** were 590.7, 98.7, and 105.9 min respectively), and the structures of the main cycloadducts **2** were of the *δ*-form which is disadvantageous for complexation with metal cations. We will, therefore, present in this paper the syntheses of new types of photoresponsive cyclobutanocrown ethers **10** by means of the intramolecular [2+2]photocycloaddition of **8** and their photoreversible cleavage reaction in order to deal with the above problems.

1a: n=0
1b: n=1
1c: n=2

2a: n=0
2b: n=1
2c: n=2

Results and Discussion

Syntheses of 8. Compound **6** was prepared by the following methods. Dialdehyde **4** was obtained in a 95% yield as a pale yellow oil by the Sommelet reaction of the corresponding dibromide **3** according to the method in the literature.[12] The reaction of **4** with malonic acid in the presence of piperidine in pyridine gave **5** in a 91% yield as a colorless powder. The carboxyl groups of **5** were chlorinated with thionyl chloride to give **6** in a 71% yield.[13] The condensation of **6** with **7a** gave **8a** in a 7.0% yield, together with its dimer **9a** in a 6.0% yield. Also, **8b**, **8c**, **9b**, and **9c** were obtained by the same method. The structures of these products were established by their ^{1}H NMR and elemental analysis and mass spectral data and/or gel-permeation chromatography. As is shown in Fig. 1, the ^{1}H NMR spectrum of **8b** showed the signals of the trimethylene protons at δ 2.72(t, J=5.8 Hz, 4H) and 2.24—2.17(m, 2H) respectively, and the signals of the *p*-phenylene protons as a pair in the A_2B_2 pattern at δ 6.95(d, J=8.2 Hz, 4H) and 6.71(d, J=8.2 Hz, 4H) together with the signals of the olefinic protons as a pair in the A_2B_2 pattern at δ 7.52(d,



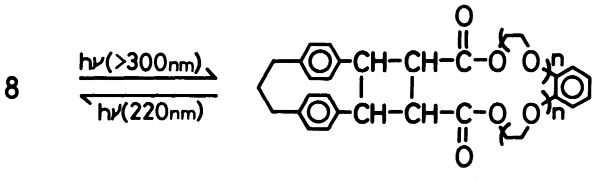
3 4 5 6

7a: n=0
7b: n=1
7c: n=2

8a: n=0
8b: n=1
8c: n=2

9a: n=0
9b: n=1
9c: n=2

J=16.0 Hz, 2H) and 6.24(d, J=16.0 Hz, 2H). However, the signals of the *p*-phenylene protons of the dimers **9a—c** shifted upfield (ca. 0.50 ppm) compared with those of its monomers as a result of decreases in the anisotropic effect of the opposite aromatic rings upon each other. Furthermore, the parent peaks of the dimers of the mass spectra could not be obtained, although the M^+ values of the corresponding monomers agreed well with the calculated values. We then examined the gel-permeation chromatography of **9a—c**. Compounds **9a—c** had a longer retention time than the corresponding compounds **8a—c**. The molecular weights of **9a—c**, which were calculated from the retention times using the calibration curves, were nearly all consistent with the expected values of the dimers.



10a: n=0
10b: n=1
10c: n=2

Conversion of 8 to 10. The intramolecular [2+2]-photocycloaddition of **8a—c** was carried out as follows, while the yields were calculated from the intensity of the absorption band at 275 nm in the steady state. The irradiation of **8b** in acetonitrile for 1 h with a 450W high-pressure mercury lamp through a Pyrex filter in the absence of any sensitizer gave **10b** in a 91.8% yield (isolated yield: 71.3%). The irradiation of **8a** (0.25 h) also yielded **10a** in a 95.7% yield (isolated yield: 18%). It is well known that the trans–cis isomerization of the carbon–carbon double bonds in ethyl cinnamate generally competes with the photodimerization.[1] In the above photoreaction, however, the isolated intramolecular [2+2]photocycloadducts were β-isomers, as will be described below, although very tiny side reaction products were observed by means of TLC. Therefore, the intramolecular [2+2]photocycloaddition of **8a** and **8b** can be said to proceed because of the proximity of the two carbon–carbon double bonds prior to the trans–cis isomerization of the carbon–carbon double bonds. However, **10c** could not be obtained because the irradiation of **8c** gave many tiny products. The solutions of **8a** and **8b** were measured by means of their UV spectra at appropriate intervals during irradiation. The change in the UV spectra of **8b** is

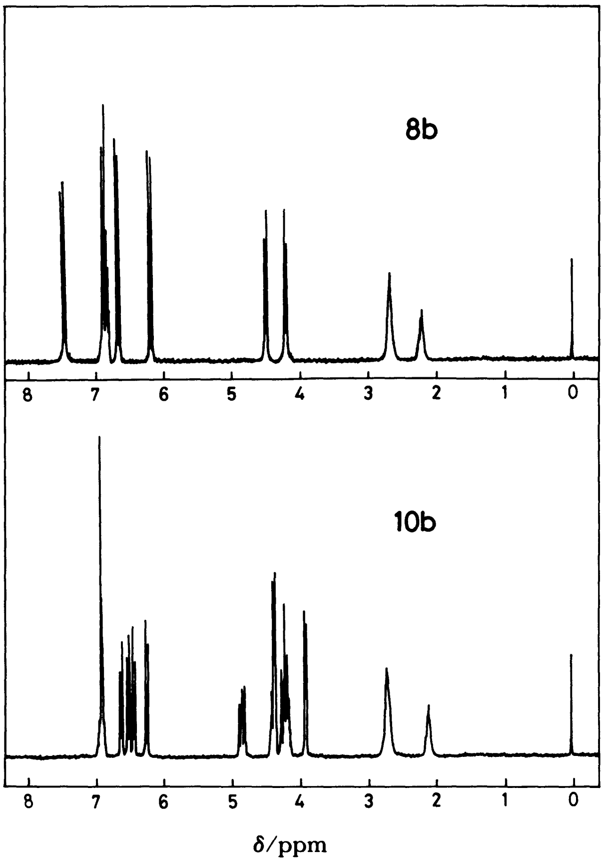


Fig. 1. 400 MHz ^{1}H NMR spectra of **8b** and **10b**.

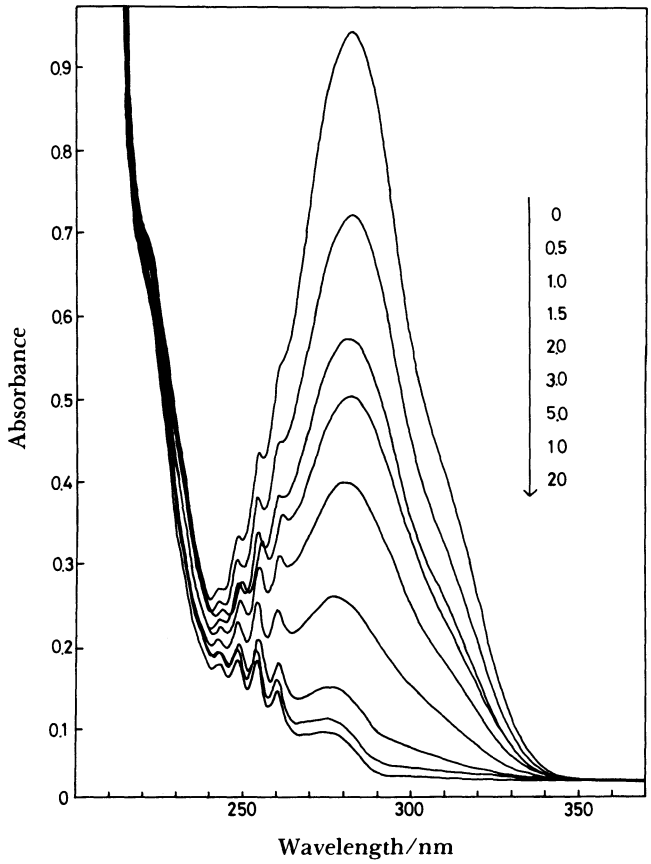


Fig. 2. Spectral changes of **8b** to **10b** in acetonitrile (4×10^{-5} mol dm^{-3}). The numbers beside the arrow are the elapse of irradiation time (min).

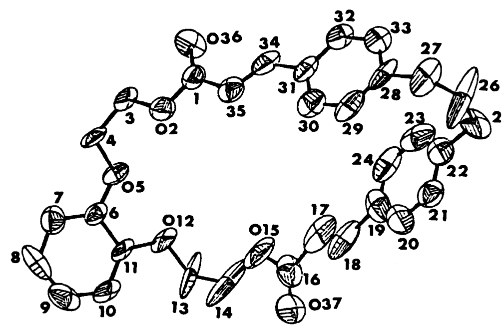


Fig. 3. **ORTEP** drawing of the molecule **8b** with atomic numbering scheme.

shown in Fig. 2. The half-life periods of the intramolecular [2+2]photocycloaddition of **8a** and **8b** were only 29 min and 40 s respectively; these values are very fast compared with those of the corresponding open-chain dicinnamates **1a** and **1b**. The difficulty in the ring closure of **8c** to **10c** is due to the longer intramolecular distance between the two double bonds compared with those of **8a** and **8b**. Therefore, the photoreaction of **8c** caused the intramolecular [2+2]-photocycloaddition, together with other side reactions (for example, trans–cis isomerization, intramolecular [2+2]photocycloaddition of the cis isomerized products, the intermolecular addition of **8c**, and the cleavage of ester groups). The template-type intramolecular [2+2]photocycloaddition of **8** in the presence of the alkali metal ion was also determined; however, the yields were not improved. This fact agrees with the finding that **8** lacks any extraction ability, as will be described below, because if **8** were complexed with an alkali metal cation, the rate of photocyclization would be improved due to the approach of the two double bonds.

Structures of 8 and 10. In order to investigate this problem in more detail, the structure of **8b** was confirmed by means of single crystal X-ray analysis. The conformation of **8b** is illustrated in Fig. 3 together with its atomic numbering, while the selected bond distances and bond angles are summarized in Tables 1 and 2 respectively. As is shown in Fig. 3, the two double bonds are trans and are situated in such positions relative to each other as to make the ring closure possible. The torsion angles of C_{16}–C_{17}–C_{18}–C_{19} and C_{33}–C_{34}–C_{35}–C_{36} are −179.8(5) and 179.7(5)° respectively. Also, the torsion angles of O_2–C_3–C_4–O_5 and C_{12}–C_{13}–C_{14}–C_{15} are −73.7(4) and −24.8(11)° respectively. The two benzene rings are face-to-face, albeit slightly distorted, and the dihedral angle is 20.6(2)°. The distances between the two olefinic carbon atoms (C_{17}–C_{35} and C_{18}–C_{34}) are 5.341(11) and 5.906(9) Å respectively. These values are significantly

Table 1. Fractional Atomic Coordinates ($\times 10^4$) and Thermal Parameters, with Estimated Standard Deviations in Parentheses

Atom	x	y	z	B_{eq}/Å^2	Atom	x	y	z	B_{eq}/Å^2
C(1)	2148(4)	7594(5)	7683(5)	5.7	C(20)	−2890(4)	4316(5)	5991(5)	6.4
O(2)	2850(3)	6489(3)	7785(3)	5.9	C(21)	−3501(4)	5187(5)	5396(5)	6.2
C(3)	3606(4)	6642(5)	8629(5)	5.9	C(22)	−3749(4)	6535(5)	5807(5)	6.4
C(4)	4353(4)	5342(5)	8569(5)	5.7	C(23)	−3367(5)	6932(5)	6837(5)	7.3
O(5)	3638(3)	4447(3)	9162(3)	5.5	C(24)	−2761(4)	6022(6)	7411(5)	7.4
C(6)	4112(4)	3124(5)	8996(4)	4.6	C(25)	−4427(5)	7467(6)	5141(6)	9.4
C(7)	5276(4)	2648(5)	8555(5)	5.7	C(26)	−3869(6)	8064(10)	4220(7)	17.7
C(8)	5646(5)	1285(6)	8387(5)	7.5	C(27)	−2846(5)	8456(7)	3772(5)	9.4
C(9)	4868(5)	425(5)	8656(5)	7.8	C(28)	−1934(4)	8367(6)	4528(5)	6.8
C(10)	3716(5)	876(5)	9114(5)	6.9	C(29)	−1126(4)	7243(6)	4442(5)	6.8
C(11)	3331(4)	2221(5)	9300(4)	5.0	C(30)	−310(4)	7181(5)	5151(5)	6.3
O(12)	2216(3)	2782(3)	9755(3)	6.7	C(31)	−272(4)	8269(5)	5946(4)	5.3
C(13)	1427(6)	1957(8)	10229(9)	15.6	C(32)	−1093(5)	9407(5)	6025(5)	6.9
C(14)	551(7)	1894(8)	9990(7)	14.6	C(33)	−1905(5)	9449(6)	5321(5)	7.5
O(15)	−121(3)	2933(4)	9524(4)	9.0	C(34)	585(4)	8312(5)	6709(5)	5.9
C(16)	−729(4)	2459(6)	8750(5)	7.2	C(35)	1353(4)	7336(5)	6874(5)	5.5
C(17)	−1374(5)	3691(7)	8334(6)	9.8	O(36)	2167(3)	8637(4)	8240(4)	9.1
C(18)	−1815(5)	3576(7)	7545(5)	8.4	O(37)	−773(3)	1307(4)	8523(4)	9.0
C(19)	−2508(4)	4696(6)	6986(5)	6.7					

Table 2. Bond Lengths (Å) and Angles(°), with Estimated Standard Deviations in Parentheses

Bond length	(l/Å)	Bond length	(l/Å)	Bond angle	(ϕ/°)	Bond angle	(ϕ/°)
C(1)-O(2)	1.325(7)	C(17)-C(18)	1.140(9)	O(2)-C(1)-C(35)	111.8(4)	C(18)-C(19)-C(20)	116.9(5)
C(1)-C(35)	1.484(8)	C(18)-C(19)	1.555(9)	O(2)-C(1)-O(36)	121.1(6)	C(18)-C(19)-C(24)	125.4(5)
C(1)-O(36)	1.201(7)	C(19)-C(20)	1.362(8)	C(35)-C(1)-O(36)	127.0(6)	C(20)-C(19)-C(24)	117.7(5)
O(2)-C(3)	1.460(7)	C(19)-C(24)	1.366(8)	C(1)-O(2)-C(3)	115.1(3)	C(19)-C(20)-C(21)	123.6(6)
C(3)-C(4)	1.471(8)	C(20)-C(21)	1.365(8)	O(2)-C(3)-C(4)	107.0(4)	C(20)-C(21)-C(22)	119.3(5)
C(4)-O(5)	1.434(6)	C(21)-C(22)	1.383(7)	C(3)-C(4)-O(5)	106.8(4)	C(21)-C(22)-C(23)	117.5(5)
O(5)-C(6)	1.363(6)	C(22)-C(23)	1.402(8)	C(4)-O(5)-C(6)	115.3(3)	C(21)-C(22)-C(25)	118.1(4)
C(6)-C(7)	1.383(8)	C(22)-C(25)	1.499(9)	O(5)-C(6)-C(7)	124.7(5)	C(23)-C(22)-C(25)	124.4(6)
C(6)-C(11)	1.397(7)	C(23)-C(24)	1.372(8)	O(5)-C(6)-C(11)	115.4(5)	C(22)-C(23)-C(24)	121.3(6)
C(7)-C(8)	1.375(9)	C(25)-C(26)	1.353(11)	C(7)-C(6)-C(11)	119.9(5)	C(19)-C(24)-C(23)	120.6(5)
C(8)-C(9)	1.356(9)	C(26)-C(27)	1.345(11)	C(6)-C(7)-C(8)	119.4(5)	C(22)-C(25)-C(26)	120.1(7)
C(9)-C(10)	1.368(10)	C(27)-C(28)	1.513(9)	C(7)-C(8)-C(9)	119.7(7)	C(25)-C(26)-C(27)	142.7(13)
C(10)-C(11)	1.361(8)	C(28)-C(29)	1.367(9)	C(8)-C(9)-C(10)	121.7(6)	C(26)-C(27)-C(28)	117.9(5)
C(11)-O(12)	1.354(7)	C(28)-C(33)	1.385(8)	C(9)-C(10)-C(11)	119.7(6)	C(27)-C(28)-C(33)	119.5(6)
O(12)-C(13)	1.390(9)	C(29)-C(30)	1.382(9)	C(6)-C(11)-C(10)	119.5(6)	C(27)-C(28)-C(29)	121.6(5)
C(13)-C(14)	1.136(13)	C(30)-C(31)	1.393(8)	C(6)-C(11)-O(12)	115.6(5)	C(29)-C(28)-C(33)	118.9(5)
C(14)-O(15)	1.428(10)	C(31)-C(32)	1.388(8)	C(10)-C(11)-O(12)	124.8(6)	C(28)-C(29)-C(30)	120.5(6)
O(15)-C(16)	1.354(7)	C(31)-C(34)	1.474(8)	C(11)-O(12)-C(13)	118.6(4)	C(29)-C(30)-C(31)	120.9(6)
C(16)-C(17)	1.524(9)	C(32)-C(33)	1.374(9)	O(12)-C(13)-C(14)	126.1(11)	C(30)-C(31)-C(32)	118.2(4)
C(16)-O(37)	1.185(7)	C(34)-C(35)	1.299(8)	C(13)-C(14)-O(15)	125.5(11)	C(30)-C(31)-C(34)	124.8(6)
				C(14)-O(15)-C(16)	113.2(4)	C(32)-C(31)-C(34)	117.0(5)
				O(15)-C(16)-C(17)	106.1(4)	C(31)-C(32)-C(33)	120.2(6)
				O(15)-C(16)-O(37)	124.7(7)	C(28)-C(33)-C(32)	121.3(7)
				C(17)-C(16)-O(37)	129.1(6)	C(31)-C(34)-C(35)	127.8(6)
				C(16)-C(17)-C(18)	120.0(8)	C(1)-C(35)-C(34)	119.4(5)
				C(17)-C(18)-C(19)	127.9(9)		

longer than the value of 4.0 Å for the compounds in which intermolecular [2+2]photocycloaddition in the crystalline state occurred.[1] Indeed, the attempted intramolecular [2+2]photocycloaddition of **8** in the solid state failed. These facts suggest that the intramolecular [2+2]photocycloaddition of **8b** in the solution occurred after the distance between the two double bonds was closed within 4.0 Å due to the molecular flexibility of **8** in the solution. The respective configurations of the photoadducts were elucidated by a comparative ^{1}H NMR study of **10a,b** and the corresponding starting materials **8a** and **8b**. As is shown in Fig. 1, the ^{1}H NMR spectrum of **10b** showed the signals of the trimethylene protons at δ 2.11 (bs, 2H) and 2.71 (bs, 4H), the signals of the oxyethylene protons at δ 4.23—4.27 (m, 4H) and 4.84—4.88 (m, 4H), and the signals of the methine protons of the cyclobutane ring at δ 3.92 (m, 2H) and 4.38 (m,

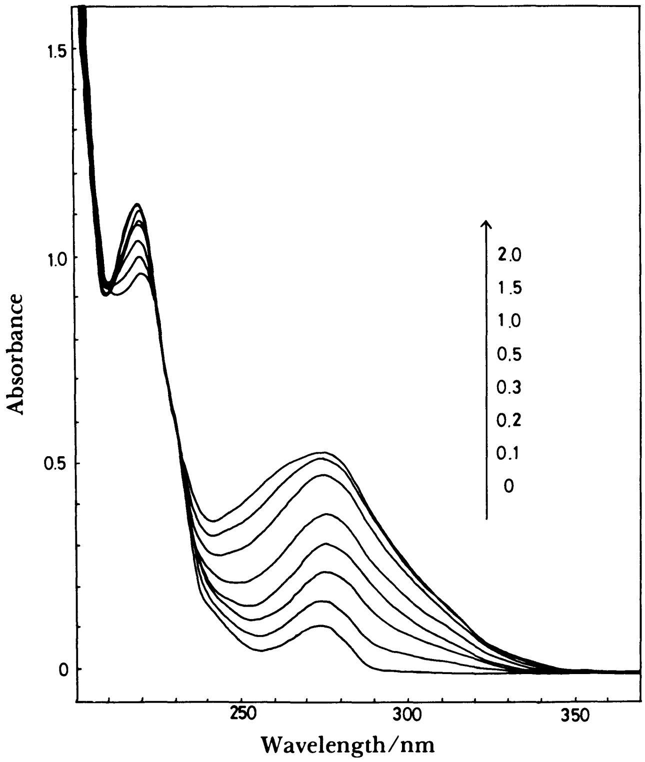


Fig. 4. Spectral changes of **10b** to **8b** in acetonitrile (4×10^{-5} mol dm^{-3}). The numbers beside the arrow are the elapse of irradiation time (h).

2H) as the AA′BB′ pattern, together with the aromatic ring protons, due to the *p*-phenylene groups and the catechol moiety, at δ 6.26—6.66 (two pairs of A_2B_2, 8H) and 6.95 (A_2B_2, 4H) respectively. The aromatic protons of the *p*-phenylene groups shifted upfield (ca. 0.3—0.5 ppm) compared with those of the starting material **8b**. This upfield shift and the two pairs of *p*-phenylene protons in the A_2B_2 pattern suggest that the two benzene rings are opposite each other in the solution. Furthermore, the chemical shifts and the split pattern of the cyclobutane ring protons are consistent with those of the dimethyl β-toluxinate reported by Ben-Efrain et al.[14] Also, the trimethylene group of **8a**—**c** is too short to allow the formation of a δ-isomer. Therefore, these intramolecular [2+2]-photocycloadducts must be β-isomers.

Photoreversible Reaction between 10 and 8. An acetonitrile solution of the pure **10b** was irradiated with a 220 nm UV light. As is shown in Fig. 4, the UV spectra of the solution were then measured at appropriate intervals. The absorption band at 275 nm increased with the UV irradiation of the solution, and a steady state was attained within 2 h. The structures of the irradiated products were confirmed by a direct comparison of the values of TLC and the spectral data with those of authentic samples. The irradiation of the pure **10a** was also carried out by the same method. The photoreversible cleavages of **10a** and **10b** gave **8a** and **8b** in 37 and 29% yields respectively, calculated from the intensities of the absorption bands at 275 nm in the steady state. Also, the yields of the reversible reactions (**8**⟷**10**) were measured by means of irradiation by >300 nm and 220 nm UV lights one after the other. As has been described above, the irradiation of acetonitrile solutions of **8a** and **8b** with >300 nm UV light gave **10a** and **10b** in 95.7 and 91.8% yields respectively. The subsequent irradiation of the above irradiated mixtures of **8a** and **8b** with 220 nm UV light gave **8a** and **8b** in 39.0 and 22.0% yields respectively. Furthermore, one more irradiation of the above solutions with >300 nm UV light gave **10a** and **10c** in 43.8 and 54.0% yields respectively. The absolute concentrations of **8** and **10** under the photoirradiation were derived from these values of the UV spectra. The yields of **10**→**8** are relatively low compared with those of **8**→**10**. The results suggest that, in the photoreaction of **10**→**8**, the cleavage (Fashion A) of the C–C single bonds in the cyclobutane ring[10] occurred together with the cleavage (Fashion B) of the C–C bonds, as is shown in Fig. 5, although another cleavage cannot be ruled out. The above results imply that the photoreversible reaction of **10**⟷**8** can be controlled by UV light, although the yields of the reversible reactions are relatively low because of the side reactions.

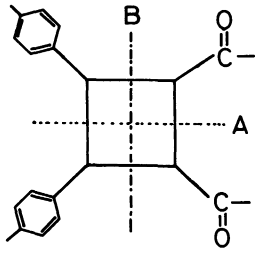


Fig. 5.

Extraction Abilities of 8 and 10. The extraction abilities of **8** and **10** toward alkali and alkaline earth metal cations were examined according to Pedersen's method.[15] These results are summarized in Table 3. An irradiated mixture of **8c** was used instead of pure **10c**, because **10c** could not be isolated, as has been described above. Compound **8c** and the irradiated mixture of **8c** showed a significant extraction ability toward alkali and alkaline earth metal ions, although the extraction ability of **8b** and **10b** toward these metal ions was negligible. The insignificant extraction ability of **8b** and **10b** may be attributed to the smaller number of oxygen atoms which can effect the complexing ability. Only two oxygen atoms of the four in the crown ether moiety of **8b** can contribute to the complexing ability, for the electron density of the two oxygen atoms of the ester groups is lower than that of the ether-linkage oxygen atom. Also, the negligible extraction ability of **10b** can be ascribed to the same reason, although a CPK model suggests that the hole size of **10b** would fit better than that of **8b** to

Table 3. Extraction of Metal Picrates from the Aqueous to the Organic Phase(%)

Compd	Li^+	Na^+	K^+	Rb^+	Cs^+	Mg^{2+}	Ca^{2+}	Sr^{2+}	Ba^{2+}
8b	0	0	0	0	0	0	0	0	0
10b	0	0	0	0	0	0	1	0	0
8c	1	1	3	4	3	3	4	3	5
Irradiated mixtures of **8c**	8	7	7	7	7	7	7	7	5

incorporate the guest metal ions. In **8c** there are four ether-linkage oxgen atoms. Therefore, the extraction ability of **8c** is higher than that of **8b**, although the values are relatively poor because of the presence of the ester moieties in the macrocycle, as has been described in a previous paper.[11] The extraction ability of the irradiated mixture of **8c** is slightly higher than that of **8c**. However, the reason for this higher extraction ability has not been defined, for the irradiated mixture contain several products as has been described above. The above results suggest that the photoreversible crown ethers **8** and **10** showed low or negligible extraction abilities and could not, therefore, control the extraction ability toward alkali and alkaline earth metal ions.

Experimental

The melting points are uncorrected. The UV spectra were obtained on a Hitachi 330 spectrometer. The IR spectra were measured on a JASCO IRA-2 Diffraction Grating Infrared Spectrometer. The ^1H NMR spectra were obtained on a JEOL GX400 Spectrometer, with TMS as the internal standard. For the irradiation of **8** on a preparative scale, the solution was charged with dry nitrogen for 10 min and then internally irradiated with an USHIO high-pressure mercury lamp (HPL)(UM-452). Also, the photocleavage of **10** to **8** was carried out by means of a 220 nm UV light using a grating monochromator (Model JASCO CT-10), with a 500W xenon lamp (JASCO PS-X500) and a band width of 0.5 nm. The gel-permeation chromatography was carried out on a Hitachi 635 high-pressure liquid chromatograph using a Hitachi Gelpack W-520 apparatus as the GLC column (10.7X30 mm L). Chloroform was used as the eluting solvent. UV was detected at 254 nm.

Materials. *o*-Bis(2-hydroxyethoxy)benzene (**7b**),[16] and *o*-bis[2-(2-hydroxyethoxy)ethoxy]benzene (**7c**),[17] and 1,3-bis-(*p*-formylphenyl)propane (**4**)[12] were prepared according to the methods in the literature. The other reagents employed were either commercial or prepared by the usual methods. The solvents were purified by distillation.

3,3′-(Trimethylenedi-4,1-phenylene)bis[2-propenoic acid] (5): A solution of 1,3-bis(*p*-formylphenyl)propane (**4**) (6.25 g, 24.8 mmol) and malonic acid (18.0 g, 182.7 mmol) in dry pyridine (60 cm^3) was refluxed for 8 h in the presence of piperidine (2.2 cm^3). The reaction mixture was cooled to room temperature and then was added to a mixture of ice (100 g) and concentrated hydrochloric acid (80 cm^3). The resulting precipitate was filtered, washed with water, and dried. Recrystallization from acetic acid gave **5** in a 91% yield as a white powder. Mp 262.0—266.0 °C. Found: C, 73.42, H, 6.22%. Calcd for $C_{21}H_{20}O_4\cdot 1/4CH_3COOH$: C, 73.42, H, 5.98%. MS (70 eV) *m/z* 336 (M^+). ^1H NMR (DMSO-d_6) δ=7.57 (d, *J*=16.0 Hz, 2H), 7.69—7.06 (A_2B_2 pattern, m, 8H), 6.44 (d, *J*=16.0 Hz, 2H), 1.75 (bs, 2H), and 2.14—1.60 (m, 4H).

3,3′-(Trimethylenedi-4,1-phenylene)bis[2-propenoyl chloride] (6): A mixture of thionyl chloride (20 cm^3) and **5** (1.50 g, 4.5 cm^3) was stirred for 2 h at 30—35 °C. The excess of thionyl chloride was removed in vacuo, and the residual solid was used for the next reaction without further purification.

Reaction of 6 with 7. Compound **6** (1.90 g, 5.1 mmol) in benzene (100 cm^3) and **7a** (1.01 g, 5.1 mmol) in benzene (100 cm^3) were added to a benzene solution (400 cm^3) containing pyridine (9 cm^3) at the same rate over a period of 27 h and then refluxed further for 15 h. The reaction mixture was cooled and evaporated, and the residue was extracted with chloroform. The extract was washed with aqueous 10% hydrochloric acid and water, dried, and evaporated in vacuo. The residue was chromatographed on silica gel, using chloroform as the eluent. The first fraction was collected and concentrated. The recrystallization of the residual oil from benzene–hexane gave **8a** in a 7.0% yield as colorless needles. Mp 240.0—242.0 °C. Found: C, 80.00, H, 5.74%. Calcd for $C_{27}H_{22}O_4\cdot 1/2C_6H_6$:C, 80.15, H, 5.62%. ^1H NMR ($CDCl_3$) δ=7.63 (d, *J*=16.0 Hz, 2H), 6.37 (d, *J*=16.0 Hz, 2H), 7.28 (s, 4H), 6.97 (d, *J*=8.2 Hz, 4H), 6.75 (d, *J*=8.2 Hz, 4H), 2.76 (t, *J*=5.8 Hz, 4H), and 2.25—2.16 (m, 2H). Crude **9a** was obtained from the second fraction. Recrystallization from toluene gave **9a** in a 6.0% yield as a colorless powder. Mp 245.0—247.0 °C. Found: C, 78.12, H, 5.52%. Calcd for $C_{54}H_{44}O_8\cdot 1/2H_2O$: C, 78.15, H, 5.46%. ^1H NMR ($CDCl_3$) δ=7.80 (d, *J*=16.0 Hz, 2H), 7.31—7.26 (A_2B_2 pattern, 4H), 7.41 (d, *J*=8.2 Hz, 4H), 7.14 (d, *J*=8.2 Hz, 4H), 2.62 (t, *J*=7.8 Hz, 4H), and 1.90 (q, *J*=7.8 Hz, 2H).

Compounds **8b**, **8c**, **9b**, and **9c** were obtained by a method similar to that described above.

8b. Yield, 6.5%. Mp 213.0—214.0 °C. Found: C, 74.50, H, 6.25%. Calcd for $C_{31}H_{30}O_6$: C, 74.68, H, 6.07%. MS (70 eV) *m/z* 471 (M^+). ^1H NMR ($CDCl_3$) δ=7.52 (d, *J*=16.0 Hz, 2H), 6.24 (d, *J*=16.0 Hz, 2H), 6.95—6.86 (A_2B_2 pattern, 4H), 6.95 (d, *J*=8.2 Hz, 4H), 6.71 (d, *J*=8.2 Hz, 4H), 2.72 (t, *J*=5.7 Hz, 4H), 2.24—2.17 (m, 2H), 4.56 (t, *J*=4.3 Hz, 4H), and 4.27 (t, *J*=4.3 Hz, 4H).

9b. Yield, 12.3%, Mp 193.5—194.5 °C. Found: C, 74.81, H, 6.01%. Calcd for $C_{62}H_{60}O_{12}$: C, 74.63, H, 6.07%. ^1H NMR ($CDCl_3$) δ=7.53 (d, *J*=16.0 Hz, 2H), 6.38 (d, 16.0 Hz, 2H), 7.06—6.91 (A_2B_2 pattern, 4H), 7.42 (d, *J*=8.2 Hz, 4H), 7.10 (d, *J*=8.2 Hz, 4H), 2.52 (t, *J*=7.6 Hz, 4H), 1.84—1.74 (q, *J*=7.6 Hz, 2H), 4.46 (t, *J*=4.9 Hz, 4H), and 4.26 (t, *J*=4.9 Hz, 4H).

8c. Yield, 8.0%. Mp 111.0—112.5 °C. Found: C, 70.43, H, 6.51%. Calcd for $C_{35}H_{38}O_8\cdot 1/2H_2O$: C, 70.57, H, 6.43%. MS

(70 eV) *m/z* 586 (M^+). ^{1}H NMR ($CDCl_3$) δ=7.55 (d, *J*=16.0 Hz, 2H), 6.27 (d, *J*=16.0 Hz, 2H), 6.97—6.86 (A_2B_2 pattern, 4H), 7.07 (d, *J*=8.2 Hz, 4H), 6.77 (d, *J*=8.2 Hz, 4H), 2.71 (t, *J*=6.0 Hz, 4H), 2.19 (m, 2H), 4.36 (t, *J*=4.9 Hz, 4H), 4.21 (t, *J*=4.9 Hz, 4H), 3.93 (t, *J*=4.8 Hz, 4H), and 3.87 (t, *J*=4.8 Hz, 4H).

9c. Yield, 10.8%. Mp 145.5—146.5 °C. Found: C, 71.43,H, 6.75%. Calcd for $C_{70}H_{76}O_{16}$: C, 71.65, H, 6.53%. ^{1}H NMR ($CDCl_3$) δ=7.64 (d, *J*=16.0 Hz, 2H), 6.39 (d, *J*=16.0 Hz, 2H), 6.93—6.88 (A_2B_2 pattern, 4H), 7.37 (d, *J*=8.0 Hz, 4H), 7.11 (d, *J*=8.0 Hz, 4H), 2.58 (t, *J*=7.6 Hz, 4H), 1.87 (q, *J*=7.6 Hz, 2H), 4.37 (t, *J*=4.8 Hz, 4H), 4.18 (t, *J*=4.8 Hz, 4H), 3.90 (t, *J*=4.8 Hz, 4H), and 3.87 (t, *J*=4.9 Hz, 4H).

Gel-Permeation Chromatography. Compounds **8a**, **8b**, **8c**, **9a**, **9b**, and **9c** were submitted to gel-permeation chromatography. The retention times were 12.83, 11.89, 11.48, 10.84, 10.40, and 10.13 min respectively. The molecular weights of **8** and **9** were obtained from the calibration curves of the polyethylene glycols and epoxy resins of known molecular weights.

Preparation of 10 by the Photoreaction of 8. A solution of **8b** in acetonitrile (4×10^{-5} M; 1 M=1 mol dm^{-3}) was irradiated internally with a high-pressure mercury lamp (450 W) through a Pyrex filter at the temperature of running water for 1.0 h. The solvent was then evaporated, and the residue was chromatographed on silica gel, using chloroform as the eluent. The first fraction was concentrated and recrystallized from acetonitrile to give **10b** as white leaves. Yield, 71.3%. Mp 218.0—219.0 °C. Found: C, 74.39, H, 6.46%. Calcd for $C_{31}H_{30}O_6$: C, 74.68, H, 6.06%. MS (70 eV) *m/z* 498 (M^+). ^{1}H NMR ($CDCl_3$) δ=6.98—6.92 (m, A_2B_2 pattern, 4H, aromatic H), 6.66—6.26 (m, two pair of A_2B_2 pattern, 8H, aromatic H), 4.90—4.16 (m, 8H, $-OCH_2-$), 4.40—4.36 (m, 2H, C_α-H), 3.95—3.90 (m, 2H, C_β-H), 2.71 (bs, 4H, $-CH_2-$), and 2.11 (bs, 2H, $-CH_2-$).

10a was also obtained by the method described above. Yield, 18%. Mp 148.0—150.0 °C. Found: C, 78.40, H, 5.39%. Calcd for $C_{27}H_{22}O_4$: C, 79.01, H, 5.40%. MS (70 eV) *m/z* 410 (M^+). ^{1}H NMR ($CDCl_3$) δ=7.49—7.37 (m, A_2B_2 pattern 4H, aromatic H), 6.55 (d, *J*=8.1 Hz, 4H, aromatic H), 6.33—5.99 (m, A_2B_2 pattern, 4H, aromatic H), 4.66—4.63 (m, 2H, C_α-H), 3.53—3.49 (m, 2H, C_β-H), 2.77—2.59(m 4H, $-CH_2-$), and 2.12—2.04 (m, 2H, $-CH_2-$).

Photoreversible Cleavage of 10. An acetonitrile solution of **10** (4.0×10^{-5} M) was placed in a quartz cell (1×1×4 cm) and irradiated at room temperature with a 220 nm UV light using a grating monochromater with a xenon lamp (500 W). The UV spectral changes were recorded during irradiation and a steady state was attained within 2 h. The solution was then checked on thin-layer chromatography, using chloroform as the eluent, and the results were compared with the R_f values of authentic samples **8a** and **8b**. The photoreversible yields of **10** were calculated from the intensity of the absorption band at 275 nm in the steady state. The yields of **8a** and **8b** were 37 and 29% respectively.

Photoreversible Reaction between 8 and 10. An acetonitrile solution of **8** (4.0×10^{-5} M) was irradiated by means of high-pressure mercury lamp through a Pyrex filter at the temperature of running water for 1 h. The yields of the irradiated products, **10a** and **10b**, were 95.7 and 91.8% respectively. A part of this solution was placed in a quartz cell (1×1×4 cm) and irradiated at 220 nm UV light, using a grating monochromator with a 500 W xenon lamp, for 2 h. The photoreversible yields of **8a** and **8b** were 39.0 and 20.0% respectively. Furthermore, the solutions were irradiated again with 300 nm UV light to give **10a** and **10b** in 43.8 and 54.0% yields respectively. These values were calculated from the intensity of the absorption band at 275 nm in the steady state. The structures of the irradiated product **10a** and **10b**, and of the photoreversible products, **8a** and **8b**, were confirmed by a comparison of the R_f values of the silica-gel TLC, the melting points, and the spectral data of the authentic samples.

Solvent Extraction. Equal volumes (5 cm^3) of dichloromethane containing 7×10^{-4} M of crown ethers **8b** and **8c** and a photoirradiated mixture of **8b** and **8c**, and an aqueous solution containing 1×10^{-1} M metal nitrate and 7×10^{-5} M picric acid were agitated. The solution was then separated by the use of a centrifugal separator. The upper solution was then withdrawn, and its electronic spectrum was recorded. A similar extraction was performed with pure dichloromethane. Similar extraction abilities were calculated by means of the following equation:

$$\text{Extraction ability}=(A_0-A)/A_0\times100.$$

A_0 was the absorbance in the absence of metal nitrate, while A was the absorbance in its presence.

X-Ray Crystallography. A crystal with dimensions of 0.4×0.2×0.15 mm was used for the X-ray crystallography. The crystal data are as follows: $C_{31}H_{30}O_6$, Mw=498.6, triclinic, $P\bar{1}$, a=11.880(1), b=10.085(1), c=11.480(1) Å, α=93.65(1), β=78.60(1), γ=82.62(1)°, U=1331.5 Å^3, Z=2, D_x=1.24 g cm^{-1}, μ(Cu $K\alpha$)=6.6 cm^{-1}. The intensity data for $2\theta<128°$ were recorded on a Rigaku AFC-5R apparatus with graphite monochromatized Cu $K\alpha$ irradiation. A total of 4440 independent reflections was corrected for Lorentz and polarization factors, but not for absorption. The structure was solved by direct methods using MULTAN84,[19] and refined by block diagonal least-square methods. The positions of the hydrogen atoms were estimated using standard geometry. The final refinements, with anisotropic temperature factors for the non-hydrogen atoms and isotropic temperatures for the hydrogen atoms, were lowered R values 0.113 (R_w=0.096, $w=1/\sigma2(F_o)$, 3125 observed reflections within $F_o\geq2\sigma(F_o)$). The parameters for the bond lengths, angles, and structure factors (observed and calculated) are kept at the Chemical Society of Japan (Document No. 8804).

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References

1) M. Hasegawa, *Chem. Rev.*, **83**, 507 (1983).

2) S. Shinkai, T. Minami, Y. Kusano, and O. Manabe, *J. Am. Chem. Soc.*, **104**, 1967 (1982); S. Shinkai, T. Nakaji, T.

Ogawa, K. Shigematsu, and O. Manabe, *J. Am. Chem. Soc.*, **103**, 111 (1981).

3) H. Sasaki, A. Ueno, J. Anzai, and T. Osa, *Bull. Chem. Soc. Jpn.*, **59**, 1953 (1986).

4) M. Irie and M. Kato, *J. Am. Chem. Soc.*, **107**, 1024 (1985).

5) F. de Jhon and D. N. Reinhouldt, "Stability and Reactivity of Crown-ether Complexes," Academic Press, New York (1981).

6) K. Mizuno, T. Hashizume, and Y. Otsuji, *J. Chem. Soc., Chem. Commun.*, **1983**, 977.

7) M. Kimura, M. Kishimoto, and S. Morosawa, 48 th National Meeting of the Chemical Society of Japan, April **1983**, Kyoto, Abstr., No. 1E32.

8) M. Shirai, A. Ueda, and M. Tanaka, *Makromol. Chem.*, **186**, 493 (1985); M. Shirai, J. Orikata, and M. Tanaka, *Makromol. Chem., Rapid Commun.*, **4**, 65 (1983); *J. Polym. Sci., Polym. Chem. Ed.*, **23**, 463 (1985).

9) K. Hiratani and S. Aiba, *Bull. Chem. Soc. Jpn.*, **57**, 2657 (1984).

10) P. L. Egerton, E. Pitts, and A. Reiser, *Macromolecules*, **14**, 95 (1981); P. L. Egerton, E. M. Hyde, J. Trigg, A. Payne, P. Begnon, M. V. Mijovic, and A. Reiser, *J. Am. Chem. Soc.*, **103**, 3895 (1981).

11) S. Akabori, Y. Habata, M. Nakasawa, Y. Yamada, Y. Shindo, T. Sugimura, and S. Sato, *Bull. Chem. Soc. Jpn.*, **60**, 3453 (1987).

12) J. N. Ashley, H. J. Barber, A. J. Evins, G. Newberg, and A. D. H. Self, *J. Chem. Soc.*, **1942**, 103 (A42).

13) R. C. Fuson and J. T. Walker, *Org. Synth.*, Coll. Vol. 2, 169 (1984).

14) D. A. Ben-Efraim and B. S. Green, *Tetrahedron*, **30**, 2357 (1974).

15) C. J. Pedersen, *Federation Proceedings*, **27**, 1305 (1968).

16) R. E. Rinndfusz, P. M. Ginnings, and V. L. Harnack, *J. Am. Chem. Soc.*, **42**, 163 (1920).

17) S. Kopolow, T. E. Hegen Esch, and J. Smid, *Macromolecules*, **6**, 133 (1973).

18) P. Main, G. Germain, and M. M. Woolfson, "MULTAN84: A System of Computer Programs for the Automatic Solution of Crystal Structures from X-Ray Diffraction Data," Universities of York, England, and Louvain, Belgium (1984).