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Efficient and Selective Synthesis of Crownopaddlanes Possessing Two Cyclobutane Rings and Exclusive Complexation of Lithium

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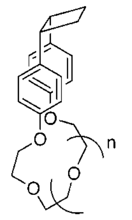
A new type of crown compounds (crownopaddlanes) bearing two cyclobutane rings were efficiently and selectively prepared by means of intramolecular [2 + 2] photocycloaddition of appropriate styrene derivatives, which was successfully carried out in cyclohexane under irradiation through a Pyrex filter. Crownopaddlanes **4a**, **5**, and **6** exclusively and quantitatively extracted Li^+ on the solid−liquid extraction. Upon the competitive extraction, **4a** showed the highest selectivity toward Li^+ over Na^+ and K^+ ($Li^+/Na^+ = 610$, $Li^+/K^+ = 976$). The structural factors working in the complexation of the crownopaddlane were examined by X-ray crystallographic analysis.

Introduction

Ring closure of linear precursors to crown ethers is entropically unfavorable, and their polymerization often cannot be avoided. Some improvements, such as the template effect[1−3] and/or high-dilution techniques,[4,5] have increased the yield of cyclization products. These improvements usually require some additional workup, except for Okahara cyclization.[6] Recently, we developed a new high-yielding photocyclization for crown compounds in which the template effect and high dilution are not crucial. Thus, many "crownophanes"[7] possessing both cyclic polyether and cyclophane moieties have been prepared in high yields (up to 95%) by the [2 + 2] photocycloaddition of α,ω-bis(vinylphenyl)oligo(oxyethylenes). Quite astonishingly, this reaction was accomplished even with a relatively high concentration of precursor olefins (100 mM). This approach has been applied to the synthesis of sophisticated ionophoric materials.

In previous extraction and liquid membrane transport experiments, it has been revealed that crownophanes have specific characteristics in host−guest interactions with many kinds of metal cations[8] and organic compounds.[9] Among the crownophanes, the prototypical crownophane **1b** with five ethereal oxygen atoms exhibited a greater complexing ability toward Li^+ than the conventional lithiophilic 12-crown-4 (**2**) and dibenzo-14-crown-4 (**3**) by solid−liquid extraction[10] and liquid membrane transport.[11] The intriguing high lithiophilicity of **1b** was concluded to be due to its unique structure,[10] and the main cause of the reduced Li^+ selectivity of **2**[12] and **3**[13] has been attributed to 2:1 (host:guest) complexation with larger cations such as Na^+ or K^+. Therefore, if one can strongly prevent the formation of the 2:1 (host:guest) sandwich complex by adding structural factors to **1b**, one should be able to greatly increase its Li^+ selectivity. Generally, to increase the selectivity of crown ethers, one introduces peripheral bulky groups.[14−16] Another structural modification of host molecules which improves the selectivity involves rigidifying or preorganizing them for particular guest molecules. For example, a spherand modified in this manner showed enormous Li^+ affinity



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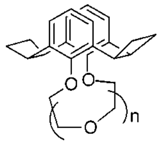
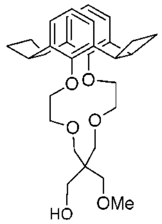
b n = 2



4a n = 2
b n = 3
c n = 4



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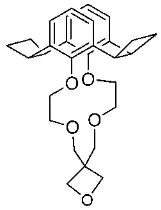

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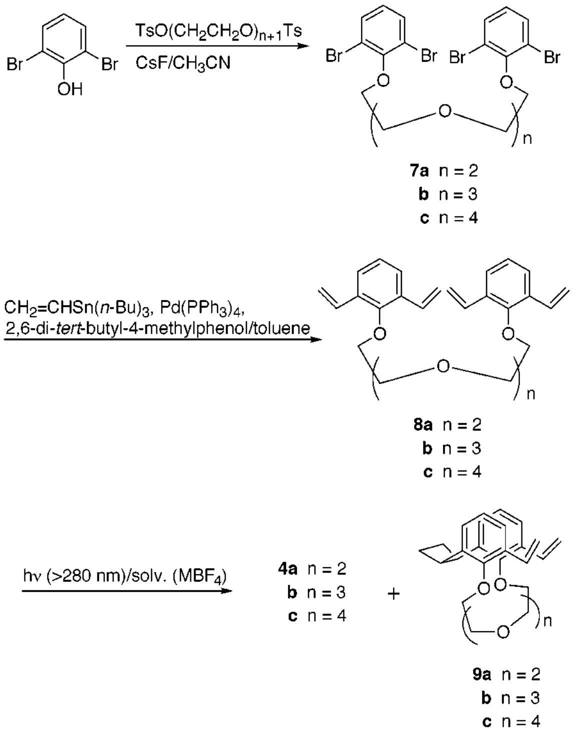
S0022-3263(98)00152-2 CCC: $15.00

Scheme 1



(ΔG = 17 kcal mol^{-1}).[17,18] However, these structural modifications often require multistep syntheses which involve some tedious procedures and meager total yields.

Accordingly, we were prompted to prepare a highly lithiophilic ionophore which optimized the structure of **1b** by [2 + 2] photocycloaddition. Hence, we designed "crownopaddlanes" **4** and **5** with two cyclobutane rings on the basis of the following criteria. First, they must have 12- to 14-membered rings with four ethereal oxygen atoms to accept Li$^+$. Second, they must have large substituents to prevent 2:1 (host:guest) tetrahedrally coordinated complexation with larger cations such as Na$^+$ or K$^+$. Third, they must have sufficiently lipophilic substituents. Fourth, they preferably should have additional ligating groups to improve the binding ability. In this paper we describe the synthesis and lithiophilic properties of **4** and **5** as well as some related compounds.

Results and Discussion

Synthesis of Crownopaddlanes. First, we tried to synthesize crownopaddlanes (**4**), as shown in Scheme 1. α,ω-Bis(2,6-dibromophenyl)oligo(oxyethylenes) (**7**) were easily prepared by the conventional method and converted to the corresponding tetraolefins (**8**) by the Stille reaction.[19] These precursor olefins were irradiated in a variety of solvents with different polarities, as listed in Table 1.

In most cases, the starting material was almost completely consumed under irradiation. In some instances, the yields and conversions were almost the same, while in others they were considerably different. For example, in run 7, the conversion was 96% but the total yield of **4** and **9** was only 50%. In such cases, we usually obtained some polymeric material which was not characterized.

Generally, nonpolar solvents favored the photoreaction. An extraordinarily high yield was obtained in the photoreaction of olefin **8a** in cyclohexane (up to 93%), which was comparable to those of prototypical crownophanes **1a**,**b**.[10] This efficiency was attributed to steric effects due to the high flexibility of C−O bonds in the linkages between two phenoxy groups.[20]

The photoreaction yields are clearly dependent on the polarity of the solvents and on the duration of irradiation. The time course of the reaction of **8b** is illustrated in Figure 1. In cyclohexane, the yield of crownopaddlane **4b** smoothly increased with irradiation time and reached a maximum (up to 97%) at 20 min. At the same time, the conversion approached 100% and **9b**, which is considered to be an intermediate of **4b**, completely disappeared. On the other hand, in acetonitrile (MeCN), although the consumption rate of **8b** was similar to that in cyclohexane, the maximum yield of **4b** was much lower than that in cyclohexane and the photostability of the product in this polar solvent was remarkably low. Furthermore, intermediate **9b** seemed to be long-lived, in contrast to that in cyclohexane. Thus, double photocyclization proceeds efficiently in nonpolar solvents such as cyclohexane, benzene, and toluene. However, the yield in polar solvents such as MeCN was slightly improved by the addition of alkali metal salts (entries 6, 8, and 14−16 in Table 1). The template effect plays a role in the polar solvents and seems to increase product stability.[7]

Synthesis of Crownopaddlanes with a Secondary Ligating Site. Lariat-type crownopaddlane **5** was prepared following a sequence similar to that for **4**. Photocyclization of the precursor tetraolefin was carried out in cyclohexane. The yield of crownopaddlane **6** with an oxetane moiety was slightly lower than that of **4**. Compound **6** was readily converted to lariat-type crownopaddlane **5**.

Single Extraction of Alkali Metal Thiocyanates into CH_2Cl_2 by Crownopaddlanes. The complexing ability of crownophanes toward alkali metal cations was evaluated by solid−liquid extraction and compared with those of **1a**,**b**, **2**, and **3**. This extraction is a simple method for measuring the net complexing ability of ligands since the process does not include dehydration from cations in an aqueous phase. The results of the extraction experiments with crownopaddlanes are summarized in Table 2 together with those of reference crown compounds.

Crownopaddlane **4a** quantitatively and exclusively extracted Li$^+$. This selectivity was not attained with conventional crown ethers **2** and **3**: the former extracted not only Li$^+$ but also Na$^+$ and K$^+$ due to the formation of 2:1 sandwich complexes, as reported previously,[12] while the latter, which is more lithiophilic than **2**,[21] extracted quite a large amount of Na$^+$ as well as Li$^+$. According to a framework examination using a space-filling model, the cavity size of **4a** (ca. 1.2 Å) is quite suitable for Li$^+$. Furthermore, the two bulky cyclobutane blades attached to the aromatic nuclei can effectively prevent it from forming a 2:1 sandwich complex.

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Table 1. Preparation of Crownopaddlanes 4 and 9[a]

		reaction conditions				yield[e] (%)	
entry	olefin	solvent[b]	addn[c]	time[d]/min	conversion[e] (%)	**4**	**9**
1	**8a**	cyclohexane		15	100	84 (93)[f]	6 (6)[f]
2	**8a**	benzene		15	94	61	15
3	**8a**	toluene		15	99	87	3
4	**8a**	MeOH		15	97	56	14
5	**8a**	MeCN		15	94	32	25
6	**8a**	MeCN	$LiBF_4$	15	85	38	17
7	**8a**	MeCN	$NaBF_4$	15	96	18	32
8	**8a**	MeCN	KBF_4	15	98	54	26
9	**8b**	cyclohexane		15	100	92 (93)[f]	7 (6)[f]
10	**8b**	benzene		15	96	71	12
11	**8b**	toluene		15	95	53	9
12	**8b**	MeOH		15	96	58	15
13	**8b**	MeCN		15	94	39	30
14	**8b**	MeCN	$LiBF_4$	15	100	67	1
15	**8b**	MeCN	$NaBF_4$	15	97	75	18
16	**8b**	MeCN	KBF_4	15	97	41	16

[a] A 400 W high-pressure mercury lamp was set at the distance of 5 cm from Pyrex tubes (15 mL) which contained the reaction mixture (10 mL) under a nitrogen atmosphere at room temperature. [b] 2 mM. [c] 60 mM. [d] Around maximum yields (in 15 min). [e] Determined by HPLC and ^1H NMR spectroscopy. [f] Isolated yield under different conditions (see Experimental Section).

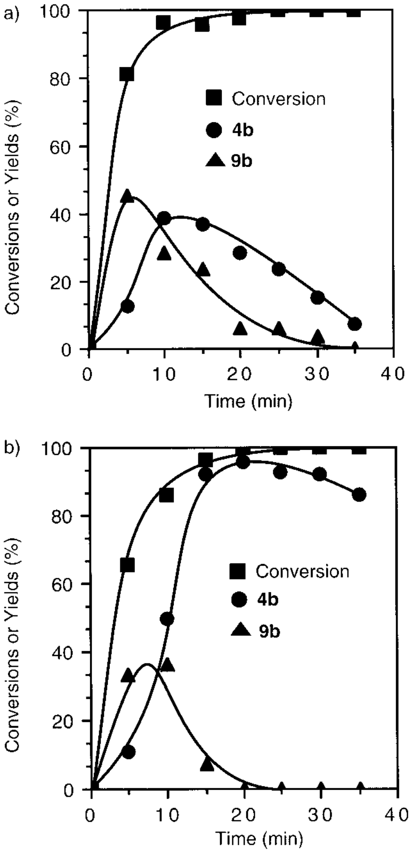

Figure 1. Time course of the photoreaction of **8b** in (a) acetonitrile and (b) cyclohexane.

Moreover, the selectivity showed by **4a** is considerably different from those of paracrownophanes **1**. Ether **1a**, which is similar to **4a**, did not extract any cations at all, while crownophane **1b**, which has five ethereal oxygen atoms, exhibited relatively high Li^+ affinity.[10] This is because **1a** has a cyclic ether ring that is widely expanded by two benzene rings and is too rigid to bind any metal cations, even the small Li^+. Thus, **4a** strongly forces both ends of the ether linkage close together to accept the small cation.

Table 2. Single Extraction of Metal Thiocyanate with Crownopaddlanes in CH_2Cl_2[a]

	percent extraction		
ligand	Li^+	Na^+	K^+
1a	0	0	0
1b	100	24	28
2	100	59	58
3	100	45	0
4a	99	0	0
4b	89	94	42
4c	100	65	70
5	92	0	0

[a] Extraction conditions: Solid phase, a pulverized metal thiocyanate (1.5×10^{-3} mol). Liquid phase, [ligand] = 5.0×10^{-2} M (CH_2Cl_2, 1 mL).

On the other hand, crownopaddlane **4b** with five ethereal oxygen atoms extracted Li^+, Na^+, and K^+, and the order of extractability was $Li^+ \sim Na^+ > K^+$. Compound **4c** with six ethereal oxygen atoms also extracted all of the cations examined in the order $Li^+ > Na^+ \sim K^+$. These results with **4b**,**c** suggest that their cavities are still smaller than those of conventional crown ethers but not small enough to bind Li^+ selectively.

Crownopaddlane **6** with an oxetane residue, which has a cavity corresponding formally to that of 13-crown-4 or 14-crown-4, was practically insoluble in CH_2Cl_2 and could not be used as an extractant. To increase the solubility of **6** and also to increase the number of ligating sites, the oxetane moiety was cleaved with acid catalyst in methanol (MeOH) to afford crownopaddlane **5**. It became soluble and showed high selectivity and efficiency toward Li^+, like **4a**.

Single Extraction of Alkali Metal Thiocyanates into $CHCl_3$ by Crownopaddlanes. In general, extraction coefficients depend on the solvents used in extraction systems due to the solubility and/or distribution constants of complexes formed from ligands and substrates. In a liquid membrane transport system, changing the solvent from CH_2Cl_2 to $CHCl_3$ results in a different transport rate of alkali metal cations.[22] To examine solvent effects on the extraction and to evaluate the complexing ability of crownopaddlane **6**, which was insoluble in CH_2Cl_2, solid−liquid extraction was carried out in $CHCl_3$. The results are shown in Table 3.

All of the ligands showed exclusive selectivity toward Li^+. The efficiency order was **4a** < **6** < **5**, which can be

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Table 3. Single Extraction of Metal Thiocyanate with Crownopaddlanes in $CHCl_3$[a]

	percent extraction		
ligand	Li^+	Na^+	K^+
4a	50	0	0
5	100	0	0
6	87	0	0

[a] Extraction conditions: Solid phase, a pulverized metal thiocyanate (1.5×10^{-3} mol). Liquid phase, [ligand] = 5.0×10^{-2} M ($CHCl_3$, 1 mL).

Table 4. Competitive Extraction of Metal Thiocyanate with Crownopaddlanes[a]

	percent extraction			selectivity	
ligand	Li^+	Na^+	K^+	Li^+/Na^+	Li^+/K^+
3	31.9	0.28	0.16	114	199
4a	48.8	0.08	0.05	610	976
5	72.0	0.84	0.12	86	600

[a] Extraction conditions: Solid phase, a pulverized metal thiocyanate (1.5×10^{-3} mol in each). Liquid phase, [ligand] = 5.0×10^{-2} M (CH_2Cl_2, 10 mL).

explained as follows: crownopaddlane **6** has a more suitable cavity for Li^+ than **4a**, and lariat crownopaddlane **5** has an additional ligating site for stronger complexation.

Competitive Extraction of Alkali Metal Thiocyanates by Crownopaddlanes. Considerable differences are often found between single and competitive extraction[23,24] and the selectivity of competitive extraction is important from a practical point of view because the latter indicates an absolute complexing selectivity for cations contained together in the system.

Competitive extraction was carried out for some representative ligands with Li^+ affinity. As shown in Table 4, the order of the efficiency of Li^+ extraction by crown compounds with four ethereal oxygen atoms was **3** < **4a** < **5**. With regard to selectivity, host **4a** exhibited the highest selectivity toward Li^+ over Na^+ and K^+ ($Li^+/Na^+ = 610$, $Li^+/K^+ = 976$) among the compounds. The selectivity of **5** toward Li^+ over Na^+ was lower than that of **4a**. This is considered to be due to the binding of Na^+ by intramolecular cooperation between the cyclic polyether part and the additional ligating site, namely, a methoxy group.

Crystal Structure of Crownopaddlane 4a. The specific complexation feature mentioned above was examined by X-ray crystallographic analysis. Since we could not prepare a single crystal of the complex between **4a** and lithium salts such as LiSCN, $LiBF_4$, etc., in acetone, we only analyzed a single crystal of **4a**.

As illustrated in Figure 2, the solid-state structure of **4a** was determined to exhibit structural preorganization upon complexation with the smallest group I metal, Li^+; i.e., the polyether ring was curved toward one of the cyclobutane rings, and the cavity diameter of **4a** was ca. 1.22 Å, which is quite appropriate for binding to Li^+. Furthermore, the cyclobutane blades of **4a** may act as a steric barrier to 2:1 sandwich complexation. These results suggest that these factors act cooperatively in the solution and result in the quantitative and exclusive extraction of Li^+.

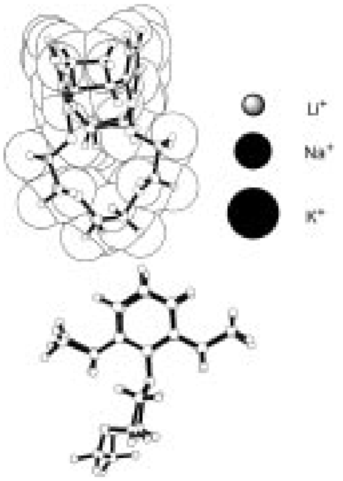

Figure 2. Crystal structure of crownopaddlane **4a**.

Conclusion

Crownopaddlanes were conveniently synthesized by intramolecular [2 + 2] photocycloaddition of the corresponding divinylbenzene derivatives. The host molecule with four ethereal oxygen atoms showed excellent Li^+ selectivity and great efficiency in solid−liquid extraction due to its unique structure.

Experimental Section

General. ^1H NMR spectra were taken at 500 MHz using tetramethylsilane as an internal standard. Elemental analysis was carried out in the Technical Research Center for Instrumental Analysis. Cyclohexane, benzene, and toluene were purified by distillation over Na after prolonged reflux under N_2. Guaranteed reagent grade MeCN, MeOH, and CH_2Cl_2 were distilled before use.

Paracrownophane **1**[10] and dibenzo-14-crown-4 **3**[19] were prepared by the method reported previously. Reagent grade 12-crown-4 **2** was used without further purification. The commercially available highest grades of LiSCN, NaSCN, and KSCN were used. All aqueous solutions were prepared with distilled, deionized water.

Preparation of α,ω-Bis(2,6-divinylphenyl)oligo(oxyethylenes) 7a−c. To a suspension of CsF (50.0 g, 329 mmol) in 100 mL of MeCN, a mixture of 2,6-dibromophenol (30.0 g, 11.9 mmol) and corresponding oligo(ethylene glycol) ditosylate (4.0 mmol) in MeCN (70 mL) was added at room temperature for 1 h under N_2. The mixture was stirred at reflux temperature for 5 h. The suspension was filtered, and the filtrate was concentrated in vacuo. The residue was dissolved in CH_2Cl_2 (1 L) and then successively washed with 10% aqueous NaOH and water and dried over $MgSO_4$. The organic layer was evaporated under reduced pressure to give the desired compounds.

Compound 7a: Yield, 91%; mp 75−76 °C. ^1H NMR ($CDCl_3$): δ 7.50 (d, $J = 8.2$, 4H), 6.85 (t, $J = 8.1$, 2H), 4.22−4.19 (m, 4H), 3.98−3.95 (m, 4H), 3.82 (s, 4H). Anal. Calcd for $C_{18}H_{18}O_4Br_4$: C, 34.99; H, 2.94. Found: C, 35.14; H, 3.01.

Compound 7b: Yield, 97%; viscous liquid. ^1H NMR ($CDCl_3$): δ 7.49 (d, $J = 7.9$, 4H), 6.85 (t, $J = 8.1$, 2H), 4.24−4.16 (m, 4H), 3.99−3.91 (m, 4H), 3.83−3.67 (m, 8H). Anal. Calcd for $C_{20}H_{22}O_5Br_4$: C, 36.29; H, 3.35. Found: C, 36.12; H, 3.30.

Compound 7c: Yield, 78%; viscous liquid. ^1H NMR ($CDCl_3$): δ 7.49 (d, $J = 7.9$, 4H), 6.85 (t, $J = 8.1$, 2H), 4.21−4.17 (m, 4H), 3.96−3.91 (m, 4H), 3.80−3.74 (m, 4H), 3.72−3.66 (m, 8H). Anal. Calcd for $C_{22}H_{26}O_6Br_4$: C, 37.42; H, 3.71. Found: C, 37.47; H, 3.79.

Preparation of α,ω-Bis(Divinylphenyl)oligo(oxyethylenes) 8a−c. A solution of α,ω-bis(2,6-dibromophenyl)-

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oligo(oxyethylenes) (20.2 mmol), tributylvinylstannane (3.90 g, 120 mmol), $Pd(PPh_3)_4$ (5.60 g, 4.86 mmol), and 2,6-di-*tert*-butyl-4-methylphenol (15 mg) in toluene (300 mL) was heated to reflux for 20 h. After the mixture was cooled to ambient temperature, a large excess of 1.2 M aqueous KF solution was added, and the resulting mixture was stirred overnight at the same temperature. The organic layer was separated from the sludge and aqueous layer and then dried over $MgSO_4$. The concentrated crude material was purified by column chromatography (SiO_2, a gradient mixed solution of benzene and acetone) to afford the tetravinyl derivatives.

Compound 8a: Yield, 24%; mp 72−73 °C. ^1H NMR ($CDCl_3$): δ 7.44 (d, J = 8.0, 4H), 7.13−7.06 (m, 6H), 5.75 (d, J = 17.7, 4H), 5.29 (d, J = 11.3, 4H), 3.99−3.95 (m, 4H), 3.85−3.82 (m, 4H), 3.81−3.78 (m, 4H). Anal. Calcd for $C_{26}H_{30}O_4$: C, 76.82; H, 7.44. Found: C, 76.95; H, 7.39.

Compound 8b: Yield, 23%; viscous liquid. ^1H NMR ($CDCl_3$): δ 7.44 (d, J = 7.9, 4H), 7.14−7.04 (m, 6H), 5.74 (d, J = 18.9, 4H), 5.29 (d, J = 12.2, 4H), 3.98−3.94 (m, 4H), 3.82−3.75 (m, 12H). Anal. Calcd for $C_{28}H_{34}O_5$: C, 74.64; H, 7.61. Found: C, 74.83; H, 7.59.

Compound 8c: Yield, 58%; viscous liquid. ^1H NMR ($CDCl_3$): δ 7.44 (d, J = 7.9, 4H), 7.08 (dd, J = 11.3 and 17.7, 4H), 6.96 (t, J = 7.5, 2H), 5.75 (d, J = 17.8, 4H), 5.29 (d, J = 11.2, 4H), 4.09−4.05 (m, 4H), 3.97−3.92 (m, 4H), 3.88−3.84 (m, 4H), 3.81−3.68 (m, 8H). Anal. Calcd for $C_{30}H_{38}O_6$: C, 72.85; H, 7.74. Found: C, 72.97; H, 7.81.

Preparation of Crownopaddlanes 4a−c. Into a 1 L Pyrex flask with a magnetic stirrer and N_2 inlet was placed 2.0 mmol of α,ω-bis(2,6-divinylphenyl)oligo(oxyethylenes) **8** dissolved in cyclohexane (800 mL), and N_2 was bubbled through the solution for 15 min. The solution was irradiated by a 400 W high-pressure Hg lamp. The progress of the reaction was followed by HPLC. After irradiation for 5 h, the solvent was removed by evaporation. The crude reaction product was purified by column chromatography (SiO_2, a gradient solution of benzene and acetone) to afford the crownopaddlanes.

Compound 4a: Yield, 93%; mp 176 °C. ^1H NMR ($CDCl_3$): δ 6.57 (d, J = 7.6, 4H), 6.48 (t, J = 7.5, 2H), 4.52−4.48 (m, 4H), 3.98−3.93 (m, 4H), 3.87−3.76 (m, 4H), 3.65−3.55 (m, 4H,), 2.51−2.28 (m, 8H). Anal. Calcd for $C_{26}H_{30}O_4$: C, 76.82; H, 7.44. Found: C, 76.67; H, 7.48.

Compound 4b: Yield, 93%; mp 143−144 °C. ^1H NMR ($CDCl_3$): δ 6.56 (d, J = 7.3, 4H), 6.47 (t, J = 7.5, 2H,), 4.53−4.44 (m, 4H), 3.89−3.75 (m, 12H), 3.63−3.57 (m, 4H), 2.48−2.26 (m, 8H). Anal. Calcd for $C_{28}H_{34}O_5$: C, 74.64; H, 7.61. Found: C, 74.37; H, 7.64.

Compound 4c: Yield, 29%; mp 85−86 °C. ^1H NMR ($CDCl_3$): δ 6.56 (d, J = 10.0, 4H), 6.47 (t, J = 7.5, 2H), 4.52−4.41 (m, 4H), 3.89−3.51 (m, 20H), 2.46−2.26 (m, 8H). Anal. Calcd for $C_{30}H_{38}O_6$: C, 72.85; H, 7.74. Found: C, 72.78; H, 7.69.

Compounds **9a**,**b** were also obtained as byproducts.

Compound 9a: Yield, 6%; viscous liquid. ^1H NMR ($CDCl_3$): δ 7.23 (d, J = 9.1, 2H), 7.09 (d, J = 9.1, 2H), 6.93−6.81 (m, 4H), 5.61 (d, J = 18.6, 2H), 5.17 (d, J = 11.9, 2H), 4.61−4.53 (m, 2H), 3.99−3.68 (m, 12H), 2.54−2.27 (m, 4H). Anal. Calcd $C_{26}H_{30}O_4$: C, 76.82; H, 7.44. Found: C, 76.77; H, 7.36.

Compound 9b: Yield, 6%; viscous liquid. ^1H NMR ($CDCl_3$): δ 7.22 (d, J = 7.6, 2H), 7.14 (d, J = 7.6, 2H,), 6.94−6.60 (m, 4H), 5.60 (d, J = 17.7, 2H), 5.17 (d, J = 11.3, 2H), 4.58−4.51 (m, 2H), 3.96−3.71 (m, 16H), 2.54−2.31 (m, 4H). Anal. Calcd for $C_{28}H_{34}O_5$: C, 74.64; H, 7.61. Found: C, 74.79; H, 7.58.

Preparation of Crownopaddlane 6. A mixture of 2,6-dibromophenol (30.0 g, 11.9 mmol) and 3,3-bis(*p*-toluenesulfonyloxymethyl)oxetane (15.3 g, 30.0 mmol) in dioxane (360 mL) was added to a suspension of pulverized KOH (7.35 g, 131 mmol) in 100 mL of MeCN at room temperature for 1 h under N_2. The mixture was stirred at reflux temperature for 10 h. The suspension was filtered, and the filtrate was concentrated in vacuo. The residue was dissolved in CH_2Cl_2 (500 mL) and then successively washed with 10% aqueous NaOH and water and dried over $MgSO_4$. The organic layer was evaporated under reduced pressure, and the residue was purified by column chromatography (SiO_2, a gradient solution of benzene and ethyl acetate) to give the desired tetrabromide, a derivative of **7** in Scheme 1. Yield, 33%. ^1H NMR ($CDCl_3$): δ 7.51 (d, J = 8.2, 4H), 6.86 (t, J = 8.1, 2H), 4.52 (s, 4H), 4.24−4.18 (m, 4H), 3.96−3.90 (m, 4H), 3.82 (s, 4H). Anal. Calcd for $C_{21}H_{22}O_5Br_4$: C, 37.42; H, 3.29. Found: C, 37.65; H, 3.34.

A solution of tetrabromide prepared above (5.91 g, 8.77 mmol), tributylvinylstannane (13.9 g, 43.8 mmol), $Pd(PPh_3)_4$ (2.02 g, 1.76 mmol), and 2,6-di-*tert*-butyl-4-methylphenol (15 mg) in toluene (120 mL) was heated to reflux for 20 h. After the mixture was cooled to ambient temperature, a large excess of 1.2 M aqueous KF solution was added, and the resulting mixture was stirred overnight at the same temperature. The organic layer was separated from the sludge and aqueous layer and then dried over $MgSO_4$. The crude material obtained by evaporation of the filtrate was purified by gel permeation chromatography (GPC) using $CHCl_3$ as eluent to afford the tetravinyl derivatives (1.94 g), a derivative of **8** in Scheme 1, as a pale yellow liquid. Yield, 48%. ^1H NMR ($CDCl_3$): δ 7.43 (d, J = 8.0, 4H), 7.14−7.01 (m, 6H), 5.75 (d, J = 17.7, 4H), 5.29 (d, J = 11.3, 4H), 4.57 (s, 4H), 4.01−3.92 (m, 4H), 3.84−3.72 (m, 8H). Anal. Calcd for $C_{29}H_{34}O_5$: C, 75.30; H, 7.41. Found: C, 75.67; H, 7.55.

Into a 1 L Pyrex flask equipped with a magnetic stirrer and N_2 inlet was placed 0.33 g (0.71 mmol) of the precursor olefin dissolved in cyclohexane (700 mL), and N_2 was bubbled through the solution for 30 min. The solution was irradiated by a 400 W high-pressure Hg lamp. The progress of the reaction was followed by HPLC. After irradiation for 1.5 h, the reaction mixture was evaporated. The crude reaction product was purified by GPC using $CHCl_3$ as eluent to afford crownopaddlane **6** (0.19 g). Yield, 58%; mp 199−200 °C. ^1H NMR ($CDCl_3$): δ 6.56 (d, J = 7.3, 4H), 6.47 (t, J = 7.4, 2H), 4.61 (s, 4H) 4.50−4.39 (m, 4H), 4.13 (s, 4H), 3.75−3.54 (m, 8H), 2.48−2.27 (m, 8H). Anal. Calcd for $C_{29}H_{34}O_5$: C, 75.30; H, 7.41. Found: C, 75.39; H, 7.38.

Preparation of Lariat Crownopaddlane 5. A mixture of crownopaddlane **6** (0.40 g, 0.87 mmol), MeOH (2.60 g, 81.3 mmol), and H_2SO_4 (0.05 g) was placed into a 20 mL pressure bottle. The solution was heated at 130 °C for 5 h. The reaction mixture was cooled to room temperature and neutralized with saturated aqueous Na_2CO_3. The crude reaction product obtained after evaporation of the filtrate was purified by GPC using $CHCl_3$ as eluent to afford crownopaddlane **5** (0.23 g). Yield, 53%; mp 150 °C. ^1H NMR ($CDCl_3$): δ 6.57 (d, J = 7.3, 4H), 6.48 (t, J = 7.5, 2H), 4.52−4.42 (m, 4H), 3.97−3.51 (m, 16H), 3.43 (s, 3H), 3.09−3.04 (m, 1H), 2.48−2.22 (m, 8H). Anal. Calcd for $C_{30}H_{38}O_6$: C, 72.85; H, 7.74. Found: C, 72.66; H, 7.85.

Solvent and Additive Effects on the Photocycloaddition. The yields for the photocyclizations were measured under a variety of conditions by using a merry-go-round apparatus. The 15 mL Pyrex test tubes containing a solution of the precursor olefin (2 mmol) in a degassed solvent were set around a 400 W high-pressure Hg lamp at the distance of 5 cm. After irradiation for the prescribed time, the conversion and the yields of products were determined by HPLC and ^1H NMR spectroscopy.

Single Solid−Liquid Extraction of Alkali Metal Cations. A CH_2Cl_2 or a $CHCl_3$ solution of crownophane (5×10^{-2} M, 1.0 mL) and a pulverized metal thiocyanate (1.5×10^{-3} mol) were stirred in a 5.0 mL glass-stoppered test tube with a ground-glass stopper at ambient temperature (18−20 °C) for 24 h. The organic liquid phase was separated and evaporated. The extractability of the ligand was evaluated from the nitrogen content of the residue, which was measured by elemental analysis.

Competitive Solid−Liquid Extraction of Alakali Metal Cations. A CH_2Cl_2 solution of crownophane (5×10^{-2} M, 10 mL) and three pulverized metal thiocyanates (1.5×10^{-2} mol in each) were stirred in a 15 mL glass-stoppered test tube with a ground-glass stopper at ambient temperature (18−20 °C) for 6 h. The organic liquid phase was separated and evaporated in vacuo. The residue was dissolved in 0.1 M HNO_3 for analysis by atomic absorption spectrometry.

Crystallographic Analysis of 4a. A colorless prismatic crystal of $C_{26}H_{30}O_4$ having approximate dimensions of 0.20 × 0.20 × 0.30 mm was mounted on a glass fiber. All measurements were made on a diffractometer with graphite monochromated Cu Kα radiation.

Cell constants and an orientation matrix for data collection, obtained from a least-squares refinement using the setting angles of 25 carefully centered reflections in the range $56.41 < 2\theta < 56.99°$, corresponded to a primitive triclinic cell with dimensions: $a = 9.996(3)$ Å, $b = 14.019(3)$ Å, $c = 7.535(2)$ Å, $V = 1033.4(5)$ A^3, $\alpha = 94.67(2)°$, $\beta = 96.63(3)°$, $\gamma = 98.04(2)°$, $V = 1033.4(5)$ $Å^3$.

For $Z = 2$ and fw = 406.52, the calculated density is 1.31 g/cm^3. On the basis of a statistical analysis of intensity distribution, and the successful solution and refinement of the structure, the space group was determined to be: $P\bar{1}$ (No. 2).

The data were collected at a temperature of 20 ± 1 °C using the $\omega-2\theta$ scan technique to a maximum 2θ value of 120.1°. The ω scans of several intense reflections, made prior to data collection, had an average width at half-height of 0.33° with a takeoff angle of 6.0°. Scans of $(1.68 + 0.30 \tan \theta)°$ were made at a speed of 16.0°/min (in ω). The weak reflections ($I < 10.0\sigma(I)$) were rescanned (maximum of three scans), and the counts were accumulated to ensure good counting statistics. Stationary background counts were recorded on each side of the reflection. The ratio of peak counting time to background counting time was 2:1. The diameter of the incident beam collimator was 1.0 mm, the crystal to detector distance was 235 mm, and the computer controlled detector aperture was set to 9.0 × 13.0 mm (horizontal × vertical).

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Supporting Information Available: Tables listing, for **4a**, crystallographic data, atomic coordinates, anisotropic displacement parameters, bond lengths and angles, torsion angles, and nonbonded contact distances, text describing data collection methods, and figures showing an ORTEP of **4a** and elution results for **4a**−**c**, **5**, and **6** (28 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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