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A NEW TYPE OF CYLINDRICAL MACROCYCLIC POLYETHERS. SYNTHESIS AND CATION-COMPLEXING ABILITY OF DIDECALINO- AND DECALINO-CYCLOHEXANO-18-CROWN-6

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Didecalino- and decalino-cyclohexano-18-crown-6, being a new type of cylindrical macrocyclic polyethers, have been synthesized and found to exhibit excellent complexing abilities toward potassium and sodium cations.

Increasing interest is being shown in cylindrical macrotricyclic polyazacrownethers[1)] capable of binding a variety of guests in a toposelective manner in the field of host-guest chemistry, while the synthesis of a cylindrical macrotricyclic polyether composed of two crownether rings fused by the tetrahydroxymethylethylene unit has been recently reported.[2)]

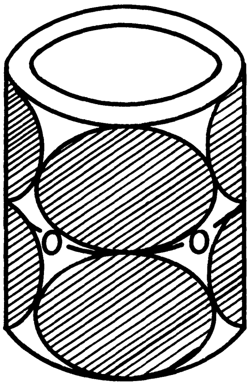

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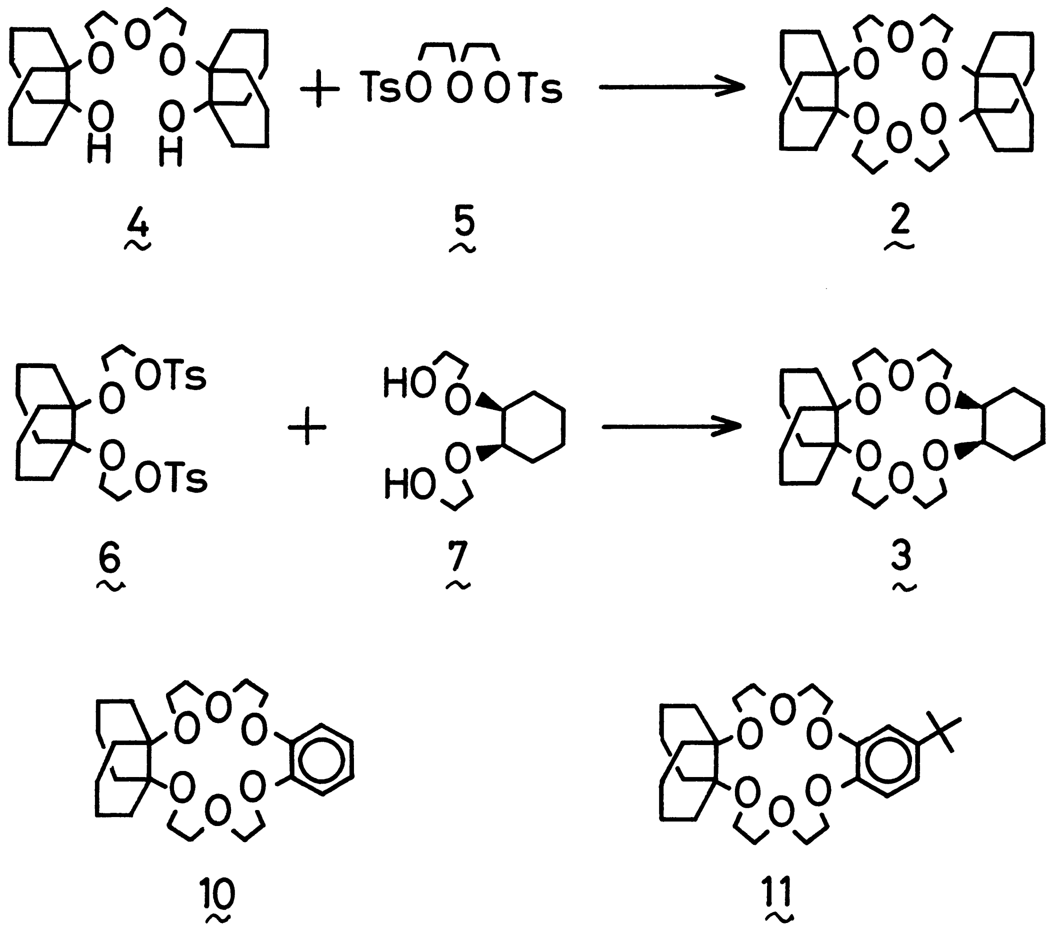
Fig. 1.

In this connection, we have begun a program directed toward the chemistry of a new type of cylindrical polyether (1) constructed by several appropriate *cis*-fused bicyclic alkane moieties, as shown in Fig. 1. The examination of CPK molecular models indicates that such systems come to bear great resemblance in shape to cylindrical molecules, with increasing the number of *cis*-fused bicyclic alkane moieties forming the surrounding wall. Accordingly, the above cylindrical systems may be expected to exhibit novel and useful catalytic activity. Taking the complexation with alkali metal cations as an example, the coordinated cation to the hydrophilic interior crownether ring may be embedded strongly into the central cavity by the lipophilic bicyclic alkane moieties spread out above and below the crownether ring.

As an entry to such novel systems, we wish to report here the synthesis of two simple analogues of general structure type 1, that is, didecalino- and decalino-cyclohexano-18-crown-6, (2 and 3), which possess two alicyclic alkane moieties fused onto opposite sides of crownether ring, and then their prominent complexing properties with alkali metal cations (Na^+, K^+, and Cs^+), in comparison with those of the reference 18-crown-6 derivatives.

Cyclization of 1,2,10,11-didecalino-3,6,9-trioxaundecane-1,11-diol (**4**)[4] and diethyleneglycol ditosylate (**5**) with NaH in THF under high dilution conditions produced didecalino-18-crown-6 (**2**) (colorless plates, mp 178-179 °C, 33%).[3] Moreover, the reaction of equimolecular quantities of 4,5-(decalino)-3.6-dioxaoctane-1,8-diol ditosylate (**6**)[4] and 4,5-(*cis*-cyclohexano)-3,6-dioxaoctane-1,8-diol (**7**)[4] with NaH in DMF under similar conditions gave decalino-cyclohexano-18-crown-6 (**3**) (colorless viscous oil, 26%). The synthetic approach is summarized below in Scheme 1.[5]

Scheme 1.



The complexing abilities of the present novel crownethers, (**2** and **3**), toward potassium and sodium cations were examined according to the method using ion selective electrodes[6] and compared with those of 18-crown-6 (**8**), dicyclohexano-18-crown-6 (**9**),[7] decalino-benzo-18-crown-6 (**10**),[8] decalino-(*tert*-butylbenzo)-18-crown-6 (**11**),[8] and dibenzo-18-crown-6 (**12**), as summarized in Table 1.

Table 1. Stability constants in methanol at 25 °C.

Macrocyclic polyether	log K_1'	
	K^+	Na^+
2	6.18$^{a)}$	4.81$^{a)}$
3	5.95	4.34
8	6.10$^{b)}$ (5.98)$^{a)}$	4.32$^{b)}$
9$^{c)}$	5.41	3.73
10	5.55	4.49
11	5.47	4.59
12	5.00$^{b)}$	4.36$^{b)}$

a) $MeOH/CHCl_3$=19/1 (v/v) *b*) Ref. 6. *c*) Ref. 7.

Several interesting observations can be made from the above data. First, the natural trend of stronger K^+ than Na^+ binding observed in a series of common 18-crown-6 derivatives is also shown for all of these compounds. Second, the substitution of benzene or cyclohexane moiety for one decalin one evidently increases the complexing abilities toward both alkali metal cations.

Moreover, in order to obtain further informations about the embedding effect of two decalin moieties and, especially, to foreknow their feasibilities for application of the present novel crownethers in phase transfer catalysis,[9] solvent extraction was carried out from aqueous alkali metal picrate solutions containing **2** and **3** according to Pedersen's procedure,[10] as shown graphically in Fig. 2. For the purpose of shedding light on the effect of alicyclic substituent, solvent extraction was concurrently attempted for **9** which has been known as the best phase transfer catalyst found to date in 18-crown-6 series.[11]

Interestingly, the extraction efficiency of both **2** and **3** were very high and they showed much more preferential complexation with these metal cations, particularly K^+ and Na^+, over **9**.

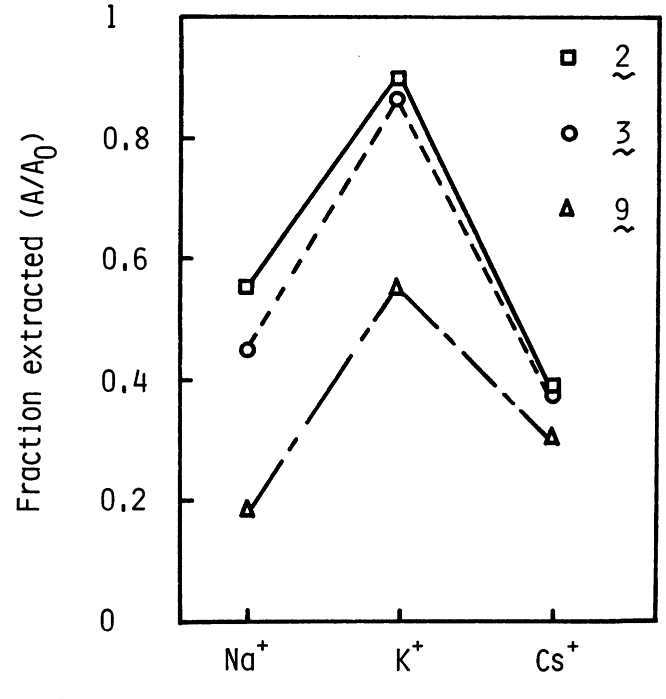


Fig. 2. Extraction of picrates into methylene chloride by polyethers. Picrate concentration $[A_0]=7\times10^{-5}M$. Polyether concentration $[Cr_0]=7\times10^{-5}M$. Metal hydroxide concentration $[MOH]=1\times10^{-1}M$.

From these results, it has been proved that, in a new type of cylindrical macrocyclic polyethers, the incorporation of somewhat flexible decalin moieties (bicyclo[4.4.0]decane framework) into an 18-crown-6 host results in the significant improvement of binding properties toward alkali metal cations.

The study on applications of **2** and **3** in phase transfer catalysis is now in progress and will be published elsewhere.

References

1) F. Kotzyba-Hibert, J. M. Lehn, and P. Vierling, *Tetrahedron Lett.*, 1980, 941, and references cited therein.
2) D. M. Walba, R. M. Richards, S. P. Sharwood, and R. C. Haltiwanger, *J. Am. Chem. Soc.*, 103, 6213 (1981).
3) To a suspension of oil-free NaH (67 mmol) in THF (150 ml) under nitrogen atmosphere at room temperature, a solution of **4** (3.4 mmol) and **5** (3.4 mmol) in THF (50 ml) was added in small portions over 3h and was stirred for 50h at room temperature. Thereafter, since decomposition of **5** takes place gradually in the above reaction system, the necessary quantity of **5** (13.2 mmol) was divided into three parts and added at intervals of about 50h with continuous stirring at room temperature. After addition of a small quantity of water to quench the reaction, followed by removal of THF under reduced pressure, the residue was extracted with CH_2Cl_2. After drying and then removal of the solvent, the remaining semisolid was chromatographed on silica gel to give **2**.
4) The key "two-arm" compounds, **4**, **6**, and **7**, were prepared as follows. **4** was prepared from the reaction of *cis*-9,10-dihydroxydecalin and **5** with NaH in DMF in 75% yield. **6** and **7** were prepared in considerable yields from *cis*-9,10-dihydroxydecalin and *cis*-1,2-dihydroxycyclohexane, respectively, by a procedure similar to that used for the synthesis of 4-(*tert*-butyloxymethyl)-3,6-dioxaoctane-1,8-diol: F. Montanari and P. Tundo, *J. Org. Chem.*, 47, 1298 (1982). **4** is colorless powder; mp 89-90 °C. **6** is colorless needles; mp 97-99 °C, and **7** colorless oil; bp 118 °C(0.3 mm).
5) All new compounds gave satisfactory elemental analyses and spectral data. Selected data for **2** and **3** are as follows:
2: MS(*m/e*) 480(M^+); ^{13}C NMR ($CDCl_3$, 56 °C) δ 22.6 (t, 8C), 29.8 (t, 8C), 60.6 (t, 4C), 71.5 (t, 4C), 77.4 (s, 4C).
3: MS(*m/e*) 426(M^+); ^{13}C NMR ($CDCl_3$, 56 °C) δ 22.2 (2t, 6C), 27.7 (t, 2C), 30.1 (t, 4C), 60.6 (t, 2C), 68.4 (t, 2C), 71.0 (t, 2C), 71.4 (t, 2C), 77.0 (s+d, 4C).
6) H. K. Frensdorff, *J. Am. Chem. Soc.*, 93, 600 (1971).
7) Mixture of *cis-syn-cis* and *cis-anti-cis* isomers available from Aldrich Chemicals Co.
8) Details of syntheses and their physical properties will be reported shortly.
9) G. W. Gokel, D. M. Dishong, and C. J. Diamond, *J. Chem. Soc., Chem. Commun.*, 1980, 1053.
10) a) C. J. Pedersen and H. K. Frensdorff, *Angew. Chem., Int. Ed. Engl.*, 11, 16 (1972); b) C. J. Pedersen, *Fed. Proc.*, 27, 1035 (1968). The values of fraction extracted for **9** are somewhat smaller than those reported in the literature 10b). This may be attributed to the difference in the ratio of the isomers.7)
11) a) W. P. Weber and G. W. Gokel, "Phase Transfer Catalysis in Organic Synthesis", Springer-Varlag, Berlin, 1977; b) C. M. Starks and C. Liotta, "Phase Transfer Catalysis", Academic Press, New York, 1978.

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