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TRIDECALINO-18-CROWN-6. SYNTHESIS OF CYLINDRICAL CROWN ETHER

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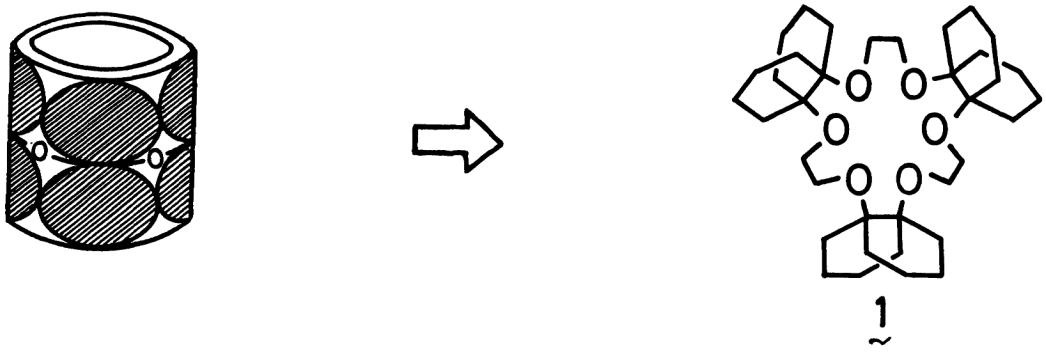
Tridecalino-18-crown-6 being a new type of cylindrical crown ether has been synthesized and found to exhibit high complexing selectivity for K^+/Na^+ as well as high complexing ability for K^+.

Recently, there has been substantial interest in cylindrical system in the field of host guest complex chemistry, since these cylindrical systems are expected to exhibit some significant complexing behavior which is not realized in the monocyclic polyether system.[1] As an approach to novel hosts with high complexing ability as well as high complexing selectivity, we have designed a new type of cylindrical crown ether with the decalin walls.[2] In this paper, we report on a tridecalino-18-crown-6 (1), in which three decalin moieties are arranged alternately in expectation of the efficient embedding effect on complexation.



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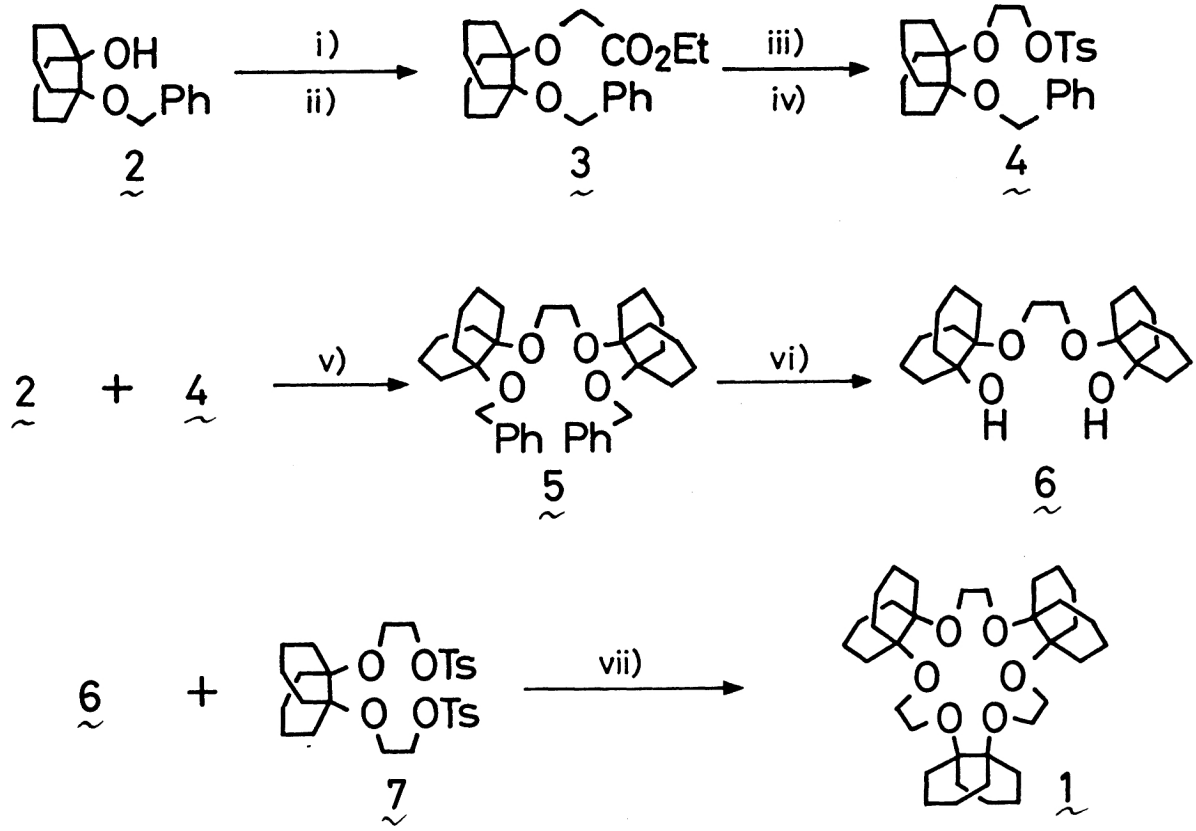
The title compound 1 was synthesized as outlined in Scheme 1. The starting material, decalindiol monobenzyl ether (2), was prepared from decalindiol and benzyl chloride in 58% yield. Williamson synthesis from 2 and chloroacetic acid, followed by esterification, lithium aluminum hydride reduction, and tosylation gave the tosylate 4 in 65% overall yield. The reaction of 2 with 4 produced bis-benzyl ether 5 in 45% yield. The hydrogenolysis of 5 proceeded smoothly in the presence of p-toluenesulfonic acid[3] to give the diol 6. The reaction of equimolecular amounts of 6 and 7[2a] in N,N-dimethylformamide at room temperature under high dilution condition (0.01 mol/L) produced 1 as colorless crystals (mp 197-198 °C) after recrystallization from 1,2-dimethoxyethane, albeit in low yield (1.3%).[4]

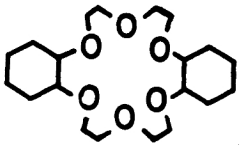


Scheme 1. i) $ClCH_2COOH$, NaH. ii) EtOH, TsOH. iii) LAH. iv) TsCl, C_5H_5N. v) NaH, THF. vi) H_2, TsOH, Pd/C. vii) NaH, DMF.

Table 1. Complexation constants for K^+ and Na^+ [a]

	log Kc [b]	
	K^+	Na^+
18-Crown-6	(5.98)	(4.32)
8 [c]	8.24 (5.41)	6.47 (3.73)
9	9.36 (6.18)	7.25 (4.81)
1	10.07 (7.00)	7.20 (4.22)

a) Extraction method of picrates in water/chloroform system at 25 °C. The values derived from potentiometric titration method of chlorides in methanol/chloroform = 19/1 solvent at 25 °C are given in parentheses.
b) Uncertainty within ±0.03 (±0.05).
c) Cis-syn-cis/cis-anti-cis = 6.9/1 mixture from GLC (SE-30) analysis.



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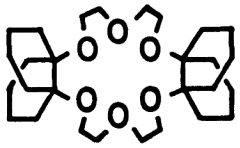

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Complexation constants, Kc, in organic solvent defined for the 1:1 crown ether-cation complex formation for K^+ and Na^+ were measured by both extraction method of picrates in water/chloroform system[5] and potentiometric titration method of chlorides in methanol/chloroform=19/1 solution[2a,6] and then the K^+/Na^+ selectivities, $Kc(K^+)/Kc(Na^+)$, were calculated. Interestingly, the title compound 1 exhibits remarkably higher complexing ability for K^+ compared with those of the other crown ethers with fused cyclohexane rings such as dicyclohexano-18-crown-6 (8)[7] and didecalino-18-crown-6 (9)[2a] as shown in Table 1.

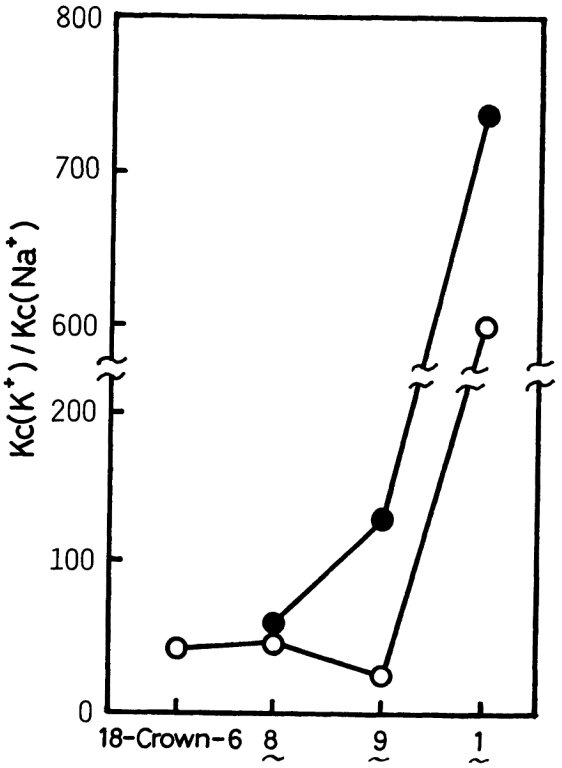

Fig. 1. Selectivities for K^+/Na^+, $Kc(K^+)/Kc(Na^+)$.
● Extraction method.
○ Potentiometric titration method.

On the other hand, Kc of 1 for Na^+ is at comparable level with those of 8 and 9. As a result, the K^+/Na^+ selectivity of 1 is greater than those of 8 and 9.[8]

Thus, the high complexing selectivity and the high complexing ability of 1 are ascribed to the embedding effect of the decalin walls on the coordinated cation, by which it is buried deeply in the lipophilic cylinder and, therefore, shielded from the attack of solvent in the decomplexation process. In addition, it is noted that the crown ether ring is forced into the favorable conformation for complexation by introduction of the decalin walls.[9]

References

1) For example, see: F. Kotzyba-Hibert, J. M. Lehn, and K. Saigo, J. Am. Chem. Soc., 103, 4266 (1981); D. M. Walba, R. W. Richards, S. P. Shrwood, and R. C. Haltiwanger, ibid., 103, 6213 (981).

2) As preliminary experiments, we have reported on quasi-cylindrical crown ethers with one or two decalin walls. a) K. Kobiro, Y. Tanaka, K. Okubo, Y. Hiramatsu, K. Kakiuchi, Y. Tobe, and Y. Odaira, Chem. Lett., 1983, 1507; b) K. Kobiro, K. Kakiuchi, Y. Tobe, and Y. Odaira, ibid., 1984, 487.

3) T. Miyazaki, S. Yanagida, A. Itoh, and M. Okahara, Bull. Chem. Soc. Jpn., 55, 2005 (1982).

4) All new compounds gave satisfactory elemental analyses and spectral data. Selected data for 1 are as follows: MS m/z 588 (M^+); ^{13}C NMR ($CDCl_3$, 56 °C) δ 21.7 (t, 6C), 23.0 (t, 6C), 30.8 (t, 12C), 61.7 (t, 6C), 78.0 (s, 6C).

5) K. Kimura, T. Maeda, and T. Shono, Talanta, 26, 945 (1976).

6) H. K. Frensdorff, J. Am. Chem. Soc., 93, 600 (1971).

7) This compound is available from Aldrich Chemical Co.

8) Concerning K^+/Na^+ selectivity in methanol, the values reported were 540 for cryptand type crown ether (Y. Nakatsuji, T. Mori, and M. Okahara, J. Chem. Soc., Chem. Commun., 1984, 1046) and 398 for dibenzo-30-crown-10 (Ref. 6), respectively.

9) The results of X-ray crystal structure analysis of 1 are now submitted for publication to J. Chem. Soc., Dalton Trans. and, as expected, it has been shown that three decalin moieties, which are oriented perpendicular to the ring plane of the crown ether, form the apparent cylinder wall and coordinated cation is buried in it.

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