JOURNAL OF THE CHEMICAL SOCIETY

Chemical Communications

Number 16
1984

A New Type of Macrobicyclic Polyether: Synthesis and Complexation of Alkali Metal Cations

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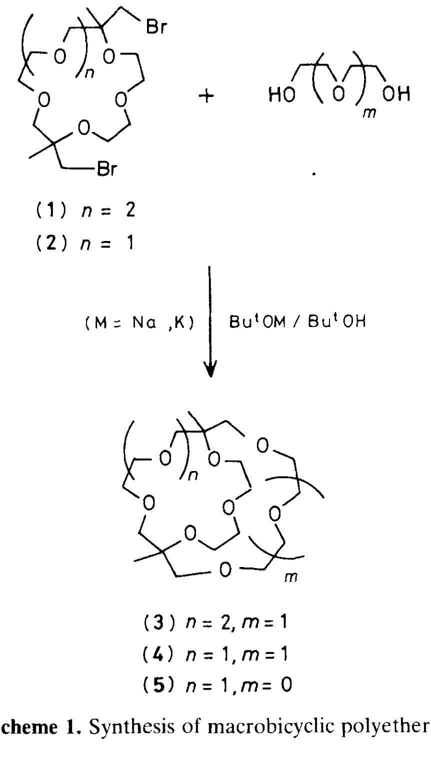
Macrobicyclic polyethers with novel ring structures have been synthesized and found to complex with Na^+ and K^+ in accordance with the relative sizes of the cavity and the cation.

Although macrobicyclic polyethers with carbon bridgeheads are interesting from the viewpoint of complexation with alkali metal cations,[1] the number of structures of this type seems to be relatively limited[2] in comparison with the cryptands containing bridgehead nitrogen atoms.[3] We now report a novel synthetic method for preparing such compounds with various ring sizes, together with their complexation with Na^+ and K^+.

The starting material, (**1**) was obtained from diethylene glycol bis(2-methylallyl) ether and ethylene glycol in two steps by the procedure reported previously.[4] The *cis* and *trans* stereoisomers of (**1**) were separated by silica gel column chromatography and their structures were inferred by comparing the ^{13}C n.m.r. data† and the elution order with those of (**2**).[4]



(**1**) $n = 2$
(**2**) $n = 1$

(**3**) $n = 2, m = 1$
(**4**) $n = 1, m = 1$
(**5**) $n = 1, m = 0$

Scheme 1. Synthesis of macrobicyclic polyethers.

A solution of (**1**) (*cis* isomer) and diethylene glycol in Bu^tOH was refluxed for 30 h in the presence of Bu^tOK to give the macrobicyclic polyether (**3**) as a colourless liquid in 14% yield [b.p. 150 °C at 0.005 Torr (Kugelrohr); δ ($CDCl_3$) 1.11 (s, 6H) and 3.52—3.88 (m, 32H); ν_{max} (neat) 2870, 1470, 1360, 1300, 1250, and 1120 cm^{-1}; *m/z* 422(M^+, 33%), 333(5), 316(4), 276(8), 171(29), 159(30), 103(53), 101(93), 89(42), 87(36), 73(42), 57(6), 45(100), and 43(50)]. In a similar manner, (**4**) and (**5**) were prepared by the reaction of (**2**) (a 1 : 1 mixture of *cis* and *trans* isomers) with diethylene glycol and ethylene glycol, respectively [(**4**): yield 20%; *m/z* 378 (M^+, 31%) and 45(100); (**5**): yield 17%; *m/z* 334(M^+, 51%) and 45(100)] (Scheme 1).

The stability constants at 25 °C in methanol determined by the potentiometric titration method[5] are shown in Table 1, together with some reference data.

It is well known that 18-crown-6 displays a high selectivity

Table 1. Stability constants (K) for 1 : 1 complexation of macrobicyclic polyethers.

Compound	Molecular structure (ring size)	Log K Na^+	Log K K^+	Selectivity $K(K^+)/K(Na^+)$
(**3**)	20,18,18	4.33	7.06	540
(**4**)	18,17,15	5.38	5.94	3.6
(**5**)	15,15,14	4.26	2.66	0.025
18-Crown-6		4.30 (4.32)[a]	6.02 (6.10)[a]	52 (60)[a]
15-Crown-5		3.31 (3.23)[b]	3.34 (3.43)[b]	1.1 (1.6)[b]

[a] Ref. 5. [b] Ref. 6.

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† ^{13}C N.m.r. data ($CDCl_3$, δ p.p.m.) *trans* isomer of (**1**): 19.797 (CH_3–), 37.326 ($BrCH_2$–); *cis* isomer: 19.894 (CH_3–), 37.254 ($BrCH_2$–).

for K^+/Na^+ complexation and this is interpreted in terms of the sizes of the cavity and the cation. Compound (**3**) can be considered to possess two 18- and one 20-membered rings and so the cavity size of (**3**) is well suited to K^+ and results in high K^+/Na^+ selectivity. On the other hand, the stability constants of (**5**), which consists of two 15- and one 14-membered rings, for Na^+ and K^+ demonstrate that the cavity size of (**5**) is too small to effectively accommodate K^+ by three-dimensional co-ordination. Compound (**4**), which possesses ring sizes between (**3**) and (**5**), shows the highest stability constant for Na^+ among the host molecules examined in this study. However, the selectivity for Na^+ and K^+ is rather low since (**4**) has an 18-crown-6 ring structure suitable for K^+. From these results, it is clear that the three macrobicyclic polyethers (**3**)—(**5**) display a selectivity for alkali metal cations corresponding to their cavity sizes. Therefore, this approach can be applied to the synthesis of a variety of macrobicyclic polyethers having different ring structures by selecting appropriate starting materials and this is expected to enable molecular design for specific cations.

Received, 27th March 1984; Com. 425

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