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EFFECT OF POSITION OF ELECTRON-DONATING SIDEARM OF 16-CROWN-5 ON COMPLEXATION TOWARD Na^+ AND K^+

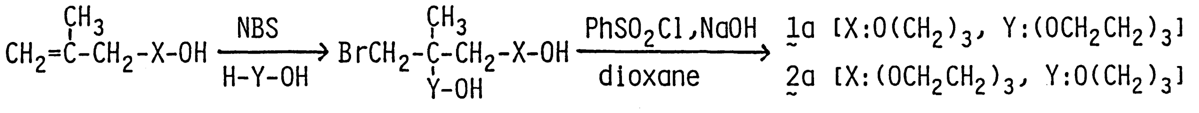
Yohji NAKATSUJI, Masayuki YONETANI, and Mitsuo OKAHARA*
Department of Applied Chemistry, Faculty of Engineering, Osaka University,
Yamada-oka 2-1, Suita, Osaka 565

Several 16-crown-5 derivatives having an electron-donating sidearm were newly prepared and their stability constants toward Na^+ and K^+ were measured. The difference in the position of the sidearm was disclosed to change remarkably the complexation property of such type of compounds.

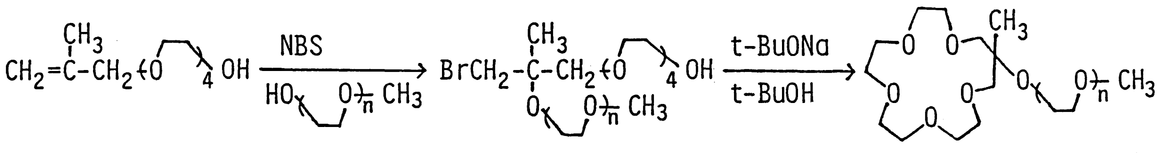
The complexing ability and the selectivity of crown ethers toward metal cations are known to depend mainly on the fitness of sizes of the crown cavity and the cation, but the modification of ring size has its own limit in adjusting the complexation property. As one of the trials to control the complexing ability, both an electron-donating sidearm and an alkyl group were introduced on the same carbon of 15-crown-5 and the methyl lariat ethers thus obtained were found to have the better complexing ability and selectivity than the original 15-crown-5.[1,2] For the purpose of clarifying the role of the electron-donating sidearm for the complexation in more detail, 16-crown-5 is considered to be advantageous as the parent crown ring, because it has an interesting ring structure due to the presence of a trimethylene moiety and affords several isomers, which may have different complexation properties, by changing the position of the sidearm.

Although the selective complexation property of some 16-crown-5 derivatives toward Na^+ was recently reported,[3,4] we synthesized several new 16-crown-5 ethers having an electron-donating sidearm and investigated their coordination modes toward Na^+ and K^+ by measuring the stability constants.

The important key intermediates, 3-bromomethyl-3-methyl-16-crown-5 (**1a**, log $K(Na^+)$:3.31, log $K(K^+)$:2.40, $K(Na^+)/K(K^+)$=8.1) and 2-bromomethyl-2-methyl-16-crown-5 (**2a**, log $K(Na^+)$:2.59, log $K(K^+)$:2.00, $K(Na^+)/K(K^+)$=3.9), were prepared *via* intramolecular cyclization[5] of the corresponding bromomethyl methyl oligoethylene glycols, which were obtained by the bromoalkoxylation of diol mono (2-methylallyl)ethers, in 26% and 24% yields, respectively. (Eq. 1) The reaction of **1a** or **2a** with appropriate sodium alkoxides almost quantitatively gave the objective methyl lariat ethers (**1b**, **1c**, **2b**, and **2c**). The 16-crown-5 derivatives having an electron-donating sidearm and a methyl group at the central carbon of the trimethylene moiety (**3b**, **3c**) were prepared according to Eq. 2.



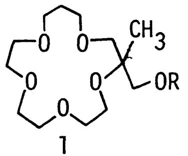
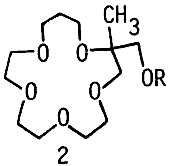
$$CH_2{=}\overset{CH_3}{\overset{|}{C}}{-}CH_2{-}X{-}OH \xrightarrow[H\text{-}Y\text{-}OH]{NBS} BrCH_2{-}\underset{Y\text{-}OH}{\overset{CH_3}{C}}{-}CH_2{-}X{-}OH \xrightarrow[dioxane]{PhSO_2Cl,\,NaOH} \begin{array}{l}\mathbf{1a}\ [X{:}O(CH_2)_3,\ Y{:}(OCH_2CH_2)_3]\\ \mathbf{2a}\ [X{:}(OCH_2CH_2)_3,\ Y{:}O(CH_2)_3]\end{array} \quad (1)$$



(2)

3 (b:n=1, c:n=2)

Table 1. Stability Constants[a)] of 16-Crown-5 Ethers toward Na^+ and K^+

	Compound	R	log K(Na^+)	log K(K^+)	K(Na^+)/K(K^+)
 1	1b	CH_2CH_2OMe	3.60	2.87	5.4
	1c	$(CH_2CH_2O)_2Me$	3.94	3.40	3.5
 2	2b	CH_2CH_2OMe	3.00	2.37	4.3
	2c	$(CH_2CH_2O)_2Me$	3.04	2.76	1.9
	3b	CH_2CH_2OMe	3.62	3.51	1.3
	3c	$(CH_2CH_2O)_2Me$	3.48	4.22	0.2
	15-crown-5		3.31	3.34	0.9
	16-crown-5		3.51	2.63	7.6

a) Determined by potentiometric titration in MeOH at 25 °C.

A large difference between 1 and 2 in the stability constants for both cations is observed. A CPK model examination of compounds 2 suggests that a steric hindrance between the sidearm and the nearest methylene group of trimethylene unit distorts the conformation for the effective coordination, while such type of steric hindrance does not exist in 1 or the methyl lariat ethers having 15-crown ring.[1)] Compounds 1a-1c have higher Na^+ selectivity than the corresponding 15-crown-5 derivatives [K(Na^+)/K(K^+)=1.4, 2.8, and 0.8, respectively],[1)] reflecting the characteristics of 16-crown-5 ring.[3,4)]

On the other hand, 3b and 3c, which are inferred to have the larger three dimensional cavity formed by the ring and the sidearm than 1 or 2, show almost the same complexing ability as 16-crown-5 for Na^+. However, they show a good affinity for the larger K^+ owing to the effective coordination of the sidearm and, as a result, 3c displays K^+ selectivity conversely.

Consequently, these findings strongly indicate that the consideration of the substitution site of the sidearm is important for the molecular design of host molecules having the crown ring of low symmetry.

References

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