CHEMISTRY LETTERS, pp. 369-372, 1983.

PREPARATION AND CHARACTERIZATION OF UNSYMMETRICAL BIS(BENZOCROWN ETHER)S : PREFERENTIAL COMPLEXATION WITH RUBIDIUM CATION

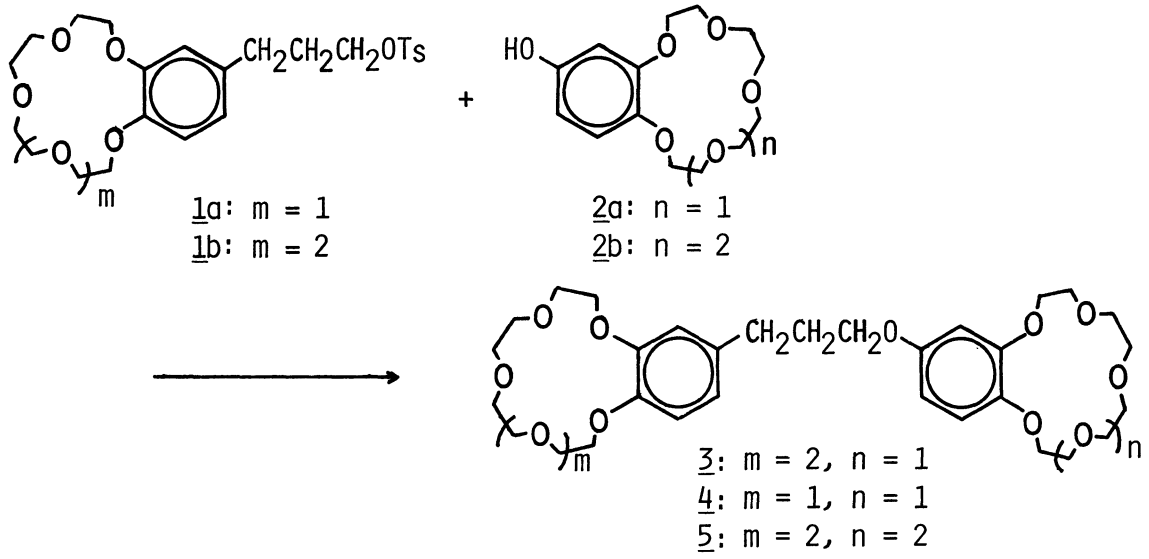
Toshihiko IKEDA, Akito ABE, Kiyoshi KIKUKAWA, and Tsutomu MATSUDA*

Department of Organic Synthesis, Faculty of Engineering, Kyushu University, Hakozaki, Higashi-ku, Fukuoka 812

New unsymmetrical and pseudo-symmetrical bis(benzocrown ether)s (3, 4, and 5) were synthesized. The unsymmetrical crown ether 3 showed preferential complexation with Rb^+ over other alkali metal cations in solvent extraction (CH_2Cl_2-H_2O) and in the behaviour as PVC membrane electrode, as compared to 4 and 5.

In recent years, synthetic ionophores, crown ethers,[1] have become of interest in the application in many fields such as solvent extraction,[2],[3] colorimetry,[4] and neutral carriers[5] in ion-selective electrode. A bis(crown ether), specially, is an interesting compound because of its increased ability of complex-formation with cationic species due to the co-operative effect of the two crown ether rings, and various types of symmetrical bis(crown ether)s have been synthesized and characterized so far. The complexing property of a crown ether is supposed to be responsible for its structure (hole size) and the kind of coordination atoms. Therefore, we got interested in the property of unsymmetrical bis(crown ether)s consisting of two crown ethers of different hole sizes and/or coordination atoms. In this paper, we wish to report the synthesis of an unsymmetrical bis(benzocrown ether) (3) and pseudo-symmetrical (4) and (5) connected by unsymmetrical linkage, trimethyleneoxy group, and then their complexing properties with alkali metal cations (Na^+, K^+, Rb^+, and Cs^+) in solvent extraction (CH_2Cl_2-H_2O) and PVC membrane electrodes based on 3-5 as neutral carriers.

To a mixture of 4'-hydroxybenzo-15-crown-5 (2a)[6] (1.1 mmol), sodium hydroxide (3.0 mmol), dimethylsulfoxide (5 ml) and dioxane (15 ml) under nitrogen atomosphere at 70 °C, a solution of 4'-tosyloxypropylbenzo-18-crown-6 (1b)[7] (1.2 mmol) in dioxane (5 ml) was added in small portions for 3 h. After stirring of the mixture for more 18 h at 80-90 °C, precipitates formed were filtered and washed with chloroform. The filtrate was concentrated under reduced pressure to give an oil. Column chromatography (Al_2O_3-$CHCl_3$) gave pure 3. Similar procedure gave 4 and 5 from the corresponding 1 and 2, respectively. Yields and analytical data of 3, 4 and 5 are as follows; (Calcd. values in parenthesis). 3, 55%, mp 100.1-100.9 °C, C, 62.15%; H, 7.64% (C, 62.25%; H, 7.60%). 4,53%, mp 102.8-103.9 °C, C, 62.66%; H, 7.52% (C, 62.83%; H, 7.48%). 5,41%, mp 36.2-37.8 °C, C, 61.81%; H, 7.90% (C, 61.75%; H, 7.70%).



Solvent extraction was carried out from an aqueous alkali metal picrate solution with methylene chloride solution containing bis(benzocrown ether), according to Pedersen's[8] procedure. An absorption maximum of the picrate salt complex in the resulting methylene chloride solution was also measured, which affords some information as to the nature of the resulting complex. The results are shown in Table 1 and 2. Increased extraction of K^+ with 4 and of Cs^+ with 5 as compared with those in the corresponding monobenzocrown ethers are reasonably ascribed to the formation of 2:1 sandwich-type complex.[9] It is noteworthy that the extractability of 3 is best for Rb^+. It may be due to the co-operative effect of the crown rings of different sizes. The formation of sandwich-type complexes with the cations from K^+ to Cs^+ are supported by the large red shifts[10] of the absorption maxima in Table 2.

Table 1. Extraction of Alkali Metal Picrates with Various Crown Ether Derivatives

Crown Ether	Picrate Salt Extracted (%)[a]			
	Na^+	K^+	Rb^+	Cs^+
B15C5[b]	2.6	14.2	11.2	7.7
B18C6[b]	3.3	54.1	27.2	15.8
3	6.8	64.6	79.0	72.3
4	7.1	77.9	57.6	17.6
5	7.1	74.5	57.9	81.7

a) The values were calculated based on picric acid in aqeous phase. Solvent extraction conditions are as follows, $CH_2Cl_2 = H_2O = 10$ ml, [Picric acid] = 7×10^{-5} M(mol/dm^{-3}), [Metal hydroxide] = 0.01 M, and [Crown unit] = 3.5×10^{-4} M.

b) Benzo-15-crown-5, Benzo-18-crown-6. Ref 10.

Table 2. Absorption Maxima of Bis(benzocrown ether)s - Alkali Metal Picrate Complex in CH_2Cl_2

Bis(benzocrown ether)	λ_{max} (nm)			
	Na^+	K^+	Rb^+	Cs^+
none[a]	352	358	361	362
3	368	372	378	379
4	368	378	378	379
5	b)	370	376	377

a) THF solution. Ref 10.

b) The absorption spectrum was too broad to determine the absorption maximum.

Table 3. Electrode Properties of PVC Membranes Containing Bis(benzocrown ether)s

Bis(benzocrown ether)	Electrode	Maximal slope/ mV $decade^{-1}$	k_{MN}[a]			
			Na^+	K^+	Rb^+	Cs^+
3	Rb^+	55	2×10^{-3}	2×10^{-1}	-	6×10^{-1}
4	K^+	56	5×10^{-4}	-	2×10^{-1}	6×10^{-3}
5	Cs^+	60	1×10^{-3}[b]	6×10^{-2}	4×10^{-2}	-

a) Mixed solution method in the presence of the foreign ion of constant concentrations. Na^+ : 1×10^{-1} M(mol/dm^{-3}), K^+ : 1×10^{-2} M, Rb^+ : 1×10^{-2} M, Cs^+ : 1×10^{-3} M in electrode 3, 1×10^{-1} M in electrode 4.

b) Separate solution method.

The selectivity coefficients of 3-5 as neutral carriers in PVC membrane electrodes were evaluated by mixed solution method, except for Na^+ selectivity in electrode 5 The electrochemical cell constructed was as follows; Ag, AgCl|0.001 M MCl|PVC membrane|measured solution|AgCl, Ag. Preparation of the PVC membranes and their conditioning were carried out according to Kimura's report.5) The results are summarized in Table 3. The selectivity coefficients of 3-5 decrease in the following orders, respectively; $Rb^+ > Cs^+ > K^+ > Na^+$ in 3, $K^+ > Rb^+ > Cs^+ > Na^+$ in 4, $Cs^+ > K^+ > Rb^+ > Na^+$ in 5. These trends of responce of the electrodes are inherently similar to those in extractabilities, indicating that the selectivities of the PVC membrane electrodes are controlled by the complexing property of the crown ether.11) Although the Rb^+ selectivity of 3 is not so large, the results support that combination of different crown rings in a bis(crown ether) is promising to control cation-selectivity which may be unable to expect in symmetrical bis(crown ether)s. The chemistry of various unsymmetrical bis(crown ether)s is now in progress.

This work was supported partly by a Grant-in-Aid for Scientific Research No. 56470077 from the Ministry of Education.

References

1) L. M. Kolthoff, Anal. Chem., 51, 1R (1979).
2) P. R. Danesi, H. Meider-Gorican, R. Chiarizia and G. Scibona, J. Inorg. Nucl. Chem., 37, 1479 (1975).
3) Y. Takeda and H. Goto, Bull. Chem. Soc. Jpn., 52, 1920 (1979).
4) M. Takagi, H. Nakamura, Y. Sanui, and K. Ueno, Anal. Chim. Acta., 126, 185 (1981).
5) K. Kimura, H. Tamura, and T. Shono, J. Electroanal. Chem., 105, 335 (1979).
6) F. Wada, R. Arata, T. Goto, K. Kikukawa, and T. Matsuda, Bull Chem. Soc. Jpn., 53, 2061 (1980).
7) Prepared from the reaction of 4'-hydroxypropylbenzo-18-crown-6* with p-toluensulfonyl chloride in pyridine. * K. Kikukawa, A. Abe, F. Wada, and T. Matsuda, Bull. Chem. Soc. Jpn., in press.
8) C. J. Pedersen, Fed. Pro., Fed. Am. Soc. Exp. Biol., 27, 1305 (1968).
9) M. Bourgoin, K. H. Wong. J. Y. Hui. and J. Smid, J. Am. Chem. Soc., 97, 3462 (1975).
10) F. Wada, Y. Wada, T. Goto, K. Kikukawa, and T. Matsuda, Chem Lett., 1980, 1189.
11) W. E. Morf, D. Amman, E. Pretsch, and W. Simon, Pure and Applied Chemistry, 36, 421 (1973).

(Received January 12, 1983)