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SYNTHESES OF ESTER-TYPE BIS-12-CROWN-4 ETHERS AND THEIR COMPLEXING ABILITIES TOWARD SODIUM CATION

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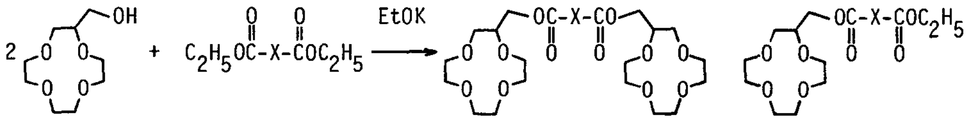
Abstract: Ester-type bis-12-crown-4 ethers with flexible crown rings were synthesized and found to have a good selective complexing ability to sodium cation when a suitable linking moiety was present.

So-called bis-crown ethers which have a unique structure composed of two crown ether rings are expected to show the interesting character due to the peculiar cation inclusion mode and the resultant specific complexing ability toward metal cations(1,2). One of the authors has been developing ion selective electrodes using bis-benzocrown ethers as a neutral carrier(2). Bis-crown ethers of benzo-type, however, may sustain respectable influences of benzene ring, i.e., unfavorable electron withdrawing effect and rigidity due to the catechol moiety(3,4). In order to design a bis-crown ether with a better complexing ability, the flexible crown ethers, including no fused benzene ring, are desirable for use. Sodium selective neutral carrier for a selective electrode has long been requested but only one case concerning tris(amido-ether) type ligands is reported by Simon(5).

New synthetic methods for preparing hydroxymethyl crown ethers were recently reported(6). In view of developing a new Na^+ selective neutral carrier, we attempted the synthesis of bis-12-crown-4 ethers which might have a high complexing selectivity toward sodium cation.



(I) (IIb-d) (IIIb-d), (IVc)

X; b: $>C(C_2H_5)_2$, c: $>C(CH_3)(C_{12}H_{25})$, d: $-C_2H_4-$

Bis-crown ethers (IIIb-d), which might be stereoisomeric mixtures, were prepared by trans-esterification from hydroxymethyl-12-crown-4(I) and dibasic acid diethyl esters(IIb-d). Thus, I (2.17g, 10.5mmol) and potassium metal (0.02g, 0.5mmol) were dissolved in 2 ml of ethanol and then IIb (0.94g, 5.0mmol) was added. The solution was heated to 80°C to evaporate off the ethanol. The reaction mixture was further heated at the same temperature over a period of

24 hr. The completion of reaction was monitored by GLC (silicone gum SE30, 10% on Celite 545, 280°C). Compounds IIIb-d, viscous liquids, were purified by silica gel column chromatography (hexane-acetone). Oxalic bis-crown ether (IIIa, X:-) was prepared from oxalic dichloride and I, and was purified by recrystallization from methanol, fine crystals, mp 141-143°C. Complexing abilities of resulting bis-12-crown-4 ethers toward sodium and potassium cations in methanol at 25°C were measured by Frensdorff's method(3) and selectivities toward sodium cation were calculated as a function of the linking moiety of dibasic acid.

As shown in the Table, the high Na^+ preference was achieved by connection of two 12-crown-4 rings. The complexing ability and its selectivity to sodium cation depend upon the length of linking moiety. Malonates represented high preferences toward sodium cation, and substituents on the methylene carbon of malonic group are the second important factor. Bis(12-crown-4-methyl) dodecylmethylmalonate(IIIc) was the best Na^+-selective ligand in this study and the selectivity over potassium cation is 34. The effect of stereo chemistry due to the presence of a chiral center on the 12-crown-4 ether ring seems to be small from the inspection of the CPK model.

The effect of ring size and linking moiety on complexation with cations are under investigation.

Table Complex Stability Constant and Selectivity to Na^+ over K^+ (MeOH, 25°C)

Ligand	logK'(Na)	logK'(K)	K'(Na)/K'(K)
oxalate (IIIa)	1.5_9	1.7_2	0.7
diethylmalonate (IIIb)	3.25	1.82	27
dodecylmethylmalonate (IIIc)	3.26	1.7_3	34
succinate (IIId)	2.88	1.90	9.5
12-crown-4	1.2	1.3	0.8
12-crown-4-methyl ethyl dodecylmethylmalonate (IVc)	0.8	1.2	0.4
15-crown-5	3.3	3.3	1.0

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