

In this case, the lattice parameters are decreased because the interstitial oxygen are depleted and the ionic radius of Zr is smaller than that of Yb, which are well fitted with the results of X-ray diffraction. The equilibrium constant of Eq. (14) can be expressed by

$$K_3 = [\text{Zr}_{\text{Yb}}^{\bullet}]^3 \cdot [\text{V}_{\text{Yb}}^{\bullet\bullet}]^2 \cdot [h^{\bullet}]^3 \cdot P_{\text{O}_2}^{-3/4} \quad (15)$$

Then the electrical conductivity dependence on oxygen partial pressure can be represented in terms of electronic hole concentration

$$\rho = K_3' \cdot P_{\text{O}_2}^{1/4} \quad (16)$$

where $K_3' = K_3^{1/3} \cdot [\text{Zr}_{\text{Yb}}^{\bullet}]^{-1/3} \cdot [\text{V}_{\text{Yb}}^{\bullet\bullet}]^{-1/3}$. So, the electrical conductivity dependence on oxygen partial pressure ($1/n$) is $1/4$. This value agrees well with the experimental value.

From this agreement, we can conclude that the effectively negatively doubly charged oxygen interstitial and the effectively negatively triply charged metal vacancy are predominant in low and high doping level, respectively and that the charge carrier is electronic hole originated from the metal vacancy in Yb_2O_3 system. The fact that the conductivity decreases as the mole fraction of dopant increases as shown in Figure 6 means that metal vacancy formed from equilibrium (14) moves the equilibrium (2) toward left-hand side. Therefore, heavy Zr^{4+} substitution reduces the charge carrier (electronic hole) concentration, so does electrical conductivity.

Acknowledgement. The present studies were support by the Basic Science Research Institute Program, Ministry of Education, Korea, 1990.

References

1. M. Foex and J. P. Traverse, *Rev. Int. Hautes Temper. Refract.*, **3**, 429 (1966).
2. O. T. Sorensen, "Nonstoichiometric Oxides", Academic press, N. Y., **21** (1981).
3. J. H. Cho, K. H. Chang, K. H. Kim, Y. B. Kim, and J. S. Choi, *J. Kor. Chem. Soc.*, **29**(6), 608 (1985).
4. S. H. Park, Y. Y. Kim, and K. H. Kim, *Bull. Kor. Chem. Soc.*, **11**(4), 339 (1990).
5. Y. H. Kang, J. S. Choi, and K. H. Yoon, *J. Kor. Chem. Soc.*, **18**(1), 23 (1981).
6. C. R. Dutta and K. Barua, *Physica Status Solid(a)*, **71**, K1 81 (1982).
7. V. B. Tare and H. Schmalzried, *Z. Phys. chem.*, **43**, 30 (1964).
8. G. V. Subba Rao, S. Ramdas, P. N. Mehrotra, and C. N. Rao, *J. Solid St. Chem.*, **2**, 377 (1970).
9. J. L. Carpentier, A. Lebrun, F. Perdu, and P. Tellier, *J. Phys. Chem. Solids*, **43**(10), 1003 (1982).
10. L. B. Valdes, *Proc. IRE.*, **42**, 420 (1954).
11. J. B. Nelson and D. P. Riley, *Proc. Phys. Soc. London*, **57**, 160 (1945).
12. P. Kofstad, "Nonstoichiometry, Diffusion and Electrical Conductivity in Binary Metal Oxides", John Wiley & Sons Inc., N. Y., 1972, p. 6.
13. W. Noddack and H. Walch, *Z. Electrochem.*, **63**, 269 (1959).
14. G. V. Subba Rao, S. Ramdas, P. N. Mehrotra, and C. N. Rao, *J. Solid State Chem.*, **2**, 377 (1970).
15. Y. Wilbert, N. Dherbomez, and H. Breuil, *Compt. Rend. Ser. C.*, **280**, 465 (1975).

Syntheses and Phase-transfer Catalytic Activities of Monoazacrown Ethers

Jae Hu Shim*, Kwang Bo Chung, and Masao Tomoi†

Department of Chemical Engineering, Dongguk University, Seoul 100-715

†Department of Applied Chemistry, Faculty of Engineering,

Yokohama National University, Yokohama 240, Japan. Received January 3, 1992

Preparative methods for and catalytic activities of monoaza-18-crown-6 or monoaza-15-crown-5 in the reaction of 1-bromooctane with aqueous KI or NaI were investigated. Monoazacrown ethers were prepared by debenzoylation of N-benzylmonoazacrown ethers, obtained from the reaction of N-benzyl-diethanolamine and oligoethylene glycol ditosylate. The phase-transfer catalytic activity of N-benzylmonoazacrown ethers was higher than that of the corresponding monoazacrown ethers.

Introduction

Since pioneering works by Pedersen¹ a large variety of macrocyclic compounds have been prepared and their cation

complexation properties have been investigated extensively². The aza-crowns have complexation properties that are intermediate between those of the all-oxygen crowns, which strongly complex alkali and alkaline earth metal ions, and

those of the all-nitrogen cyclams, which strongly complex heavy-metal cations. These mixed complexation properties make the aza-crowns interesting to researchers in many areas.

The aza-crowns are important intermediates for the synthesis of cryptands (from di-aza-crown)^{3,4}, nitrogen-pivot lariat crown ethers⁵, and other species requiring one or two nitrogens in the macroring^{6,7}.

In addition, the aza-crowns have important uses as synthetic receptors in molecular recognition processes⁸ and, in some cases, anion complexation properties that are similar to those in certain biological systems⁹⁻¹¹. They have an enhanced complexing ability for ammonium salts^{12,13} and for transition-metal ions^{13,14} over the all-oxygen crown compounds.

There are a number of interesting uses of aza-crowns as catalysts in nucleophilic substitution and oxidation reactions^{15,16}, in the design of chromogenic reagents that are sensitive to alkali and alkaline earth metal cations¹⁷, and in the chromatographic separation of metal cations¹⁷.

This paper reports on the preparation of monoaza-18-crown-6(1,4,7,10,13-pentaoxa-16-azacyclooctadecane) and monoaza-15-crown-5(1,4,7,10-tetraoxa-13-azacyclopentadecane) and their catalytic activity for the halogen exchange reaction of *n*-octyl bromide with potassium- and sodium iodide.

Experimental

Materials. 1-Bromooctane, *p*-cymene were purified by distillation under reduced pressure, and *n*-hexane were refluxed and distilled over sodium wire. *N,N*-Dimethylformamide (DMF) was refluxed and distilled over calcium hydride under reduced pressure. Other reagent and solvents were obtained commercially and used without further purification.

Instruments. IR-spectra were taken using a Shimadzu FT IR-4000 spectrophotometer and frequencies are given in reciprocal centimeter. ¹H-NMR spectra were recorded on a 60 MHz instrument (JNM-PMX 60) using CDCl₃ as solvent and tetramethylsilane as internal standard and chemical shifts are expressed as units relative to tetramethylsilane. Phase-transfer reactions were followed by GLC on a Shimadzu 4C-PT thermal conductivity instrument with a 2 m glass column of Silicone GE SF-96 on Chromosorb W AW DMCS at 170°C.

Phase-transfer Reactions. Halogen exchange reactions were studied at 90°C. In a typical run a 100 ml three-necked flask was charged with 0.02 mol of the catalyst (based on 1-bromooctane), 20 ml of toluene, 0.1 mol of NaI or KI, 15 ml of water, and 0.5 g of *p*-cymene [internal standard for gas-liquid chromatography (GLC)]. The mixture was stirred mechanically at 200 rpm for 1 h to condition the catalyst. 1-Bromooctane (20 mmol) was added at time=zero, the stirring speed was increased to 500-550 rpm, and samples of the organic phase were analyzed periodically by GLC.

N-Benzyl-diethanol Amine. In a 1 l four-necked flask 1.0 mol of diethanolamine and 76 g of potassium carbonate were dissolved in DMF (300 ml). The stirred mixture was heated at 50°C and then benzyl chloride (1.0 mol, 126.6 g) was added to the mixture over 3 h under nitrogen. After the evolution of CO₂ was complete the reaction was stopped. DMF was evaporated, and the resulting viscous oil was di-

stilled under reduced pressure, to give 1 in a 73% yield, bp. 130-132°C/0.5-0.7 torr; IR (neat): 3400 (OH), 2890 cm⁻¹ (NCH₂); ¹H-NMR (CDCl₃): δ=2.57-2.73 (4H, m; NCH₂CH₂), 3.53-3.64 (4H, m; CH₂CH₂O), 3.70 (2H, s; phCH₂), 4.07 (2H, s; OH), 7.33 (5H, s; C₆H₅).

N-Benzylbis (2-(2-hydroxyethoxy))ethyl Amine. Benzyl amine (0.5 mol, 53.5 g), β-chloroethoxyethanol (1.5 mol, 187 g), sodium carbonate (2.0 mol, 212 g) and 500 ml of xylene were added to a 1 l four-necked flask fitted with a Dean-Stark trap, a mechanical stirrer, and a thermometer. The mixture was stirred at 120°C for 24h. The reaction was continued at reflux temperature (150°C) over 3 days on removing produced water. After cooling, salts were separated from the reaction mixture by filtration and washed with ethanol. After evaporation of ethanol the residue was distilled under reduced pressure to give 2 in a 77% yield, bp. 172-178°C/0.5-0.6 torr; IR (neat): 3400 (OH), 2900 (NCH₂), 1100 cm⁻¹ (C-O-C); ¹H-NMR (CDCl₃): δ=2.70-2.87 (4H, m; NCH₂CH₂), 3.63 (12H, s; CH₂CH₂O-CH₂), 3.80 (2H, s; phCH₂), 4.37 (2H, s; OH), 7.40 (5H, s; C₆H₅).

General Procedure for the Preparation of Oligo-ethyleneglycol Ditosylate¹⁸. The glycol (0.5 mol) was dissolved in pyridine (120 ml)-benzene (150 ml) solution and *p*-toluenesulphonyl chloride (211 g, 1.1 mol) added portionwise over 2 h as powder to the stirred and ice-cooled solution. Stirring and cooling was then continued for another 4 h. The mixture was left overnight, then precipitated ditosylate was filtered off and washed on the filter with toluene (100 ml) and water (200 ml). Recrystallization from ethanol (300 ml) gave the pure ditosylate.

Since tetraethyleneglycol ditosylate was liquid, it was isolated in a different manner. After the reaction mixture had been poured on 400 g of ice, the solution was made acidic with conc. hydrochloric acid (200 ml) and extracted with chloroform. The organic layer was washed with sodium carbonate solution and then with water and dried over magnesium sulphate. After evaporation of chloroform at reduced pressure an oil was analyzed.

Diethyleneglycol ditosylate (yield 91%); IR: 1360, 1180 (SO-OC), 1098 (C-O), 910, 820, 780 (S-O-C), 662, 555 cm⁻¹ (Ar-SO₂); ¹H-NMR (CDCl₃): δ=2.44 (6H, s; CH₃), 3.52-3.69 (4H, m; CH₂OCH₂), 3.97-4.17 (4H, m; CH₂OSO₂), 7.26-7.39 (4H, m; CHCCH₃), 7.68-7.82 (4H, m; CHCSO₂).

Triethyleneglycol ditosylate (yield 83%); ¹H-NMR (CDCl₃): δ=2.45 (6H, s; CH₃), 3.52-3.80 (8H, m; CH₂OCH₂), 4.03-4.25 (4H, m; CH₂OSO₂), 7.33-7.47 (4H, m; CHCCH₃), 7.77-7.90 (4H, m; CHCSO₂).

Tetraethyleneglycol ditosylate (yield 72%); ¹H-NMR (CDCl₃): δ=2.40 (6H, s; CH₃), 3.53-3.70 (12H, m; CH₂OCH₂), 3.97-4.17 (4H, m; CH₂OSO₂), 7.13-7.27 (4H, m; CHCCH₃), 7.57-7.73 (4H, m; CHCSO₂).

N-Benzylmonoaza-15-crown-5¹⁹. In a 1 l four-necked flask 0.6 mol of sodium hydride (60 wt.% in mineral oil) was added and washed with hexane twice to remove the mineral oil. Then 300 ml of DMF were added into the flask, and the mixture was stirred at room temperature under nitrogen. A solution of *N*-benzyl-diethanolamine (0.2 mol, 39 g) in DMF (200 ml) and triethyleneglycol ditosylate (0.2 mol, 91.6 g) in DMF (200 ml) were added dropwise to the stirring mixture simultaneously over 5 days. Then the mixture was stirred at room temperature for additional 20 h. DMF was

evaporated from the reaction mixture, the residue was diluted with dichloromethane. The dichloromethane solution was concentrated and diluted with toluene and evaporated.

Benzylcrown was extracted with chloroform in a continuous extraction apparatus. Chloroform was evaporated and the resulting viscous oil was distilled under reduced pressure to give **4** ($m=1$) in a 49% yield, bp. 144-151°C/0.46-0.53 torr; IR (neat): 1100 (C-O-C), 740, 700 cm^{-1} (benzene); $^1\text{H-NMR}$ (CDCl_3): $\delta=2.76$ -2.94 (4H, m; NCH_2CH_2), 3.60 (2H, s; phCH_2), 3.70 (16H, s; $\text{CH}_2\text{CH}_2\text{O}$), 7.42 (5H, s; C_6H_5).

In a similar manner N-benzylmonoaza-18-crown-6 was prepared in a 36% yield, bp. 171-176°C/0.55-0.65 torr; $^1\text{H-NMR}$ (CDCl_3): $\delta=2.70$ -2.88 (4H, m; NCH_2CH_2), 3.53 (2H, s; phCH_2), 3.60-3.71 (20H, m; $\text{CH}_2\text{CH}_2\text{O}$), 7.27 (5H, s; C_6H_5).

Monoaza-15-crown-5¹⁹. In a pressure-resisting bottle of hydrogenolysis apparatus 2 g of 10% Pd/C catalyst and ethanol were charged. After the addition of N-benzylmonoaza-15-crown-5 (32 g) was complete, the mixture was vibrated at room temperature for 14 h at 4.3 kg/cm^2 of hydrogen pressure. Pd/C catalyst was separated from the reaction mixture by filtration, ethanol was evaporated from the filtrate. The residue was distilled under reduced pressure to give **5** ($m=1$) in a 76% yield, bp. 83-85°C/0.25-0.30 torr; mp. 44-47°C; IR (neat): 1100 cm^{-1} (C-O-C); $^1\text{H-NMR}$ (CDCl_3): $\delta=2.64$ -2.87 (5H, m; HNCH_2CH_2), 3.62-3.78 (16H, m; $\text{CH}_2\text{CH}_2\text{O}$).

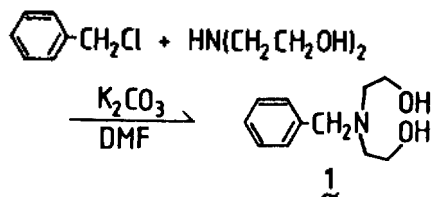
In a similar manner monoaza-18-crown-6 was prepared in a 60% yield, bp. 114-116°C/0.36-0.45 torr; mp. 48-50°C; $^1\text{H-NMR}$ (CDCl_3): $\delta=2.25$ (1H, s; NH), 2.68-2.87 (4H, m; NCH_2CH_2), 3.53-3.68 (20H, m; $\text{CH}_2\text{CH}_2\text{O}$).

Results and Discussion

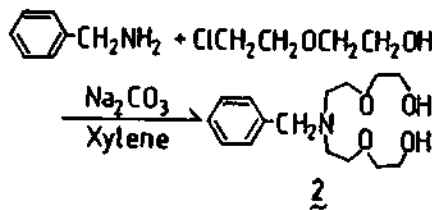
In most cases azacrowns were prepared by the reaction of various aliphatic and aromatic amines and the diiodide derivative of oligoethylene glycol²⁰ or oligoethylene glycol ditosylate and cyanamide²¹. High dilution cyclization of the N-benzyl diethanolamine **1** with oligoethyleneglycol ditosylate **3** ($n=3,4$) gave the N-benzylmonoazacrown ethers **4**. The cyclization step was accomplished by using sodium hydride in DMF. The yield were moderate, depending on the size of the macroring. It was postulated by Greene²² that a template effect was responsible for the moderate yields observed in these ring formation reactions. The yield difference was no doubt due to differences in the template effect during synthesis. The question of the template effect in the synthesis of azacrown ethers has recently been addressed by Frensdorff²³. He concluded that the formation of azacrown ether was assisted by the presence of alkali metal cations, although the effect was less pronounced because the softer N-donor atoms form weaker complexes with the alkali metal cations.

This method was convenient because the two starting materials were readily available (Scheme 1, 3).

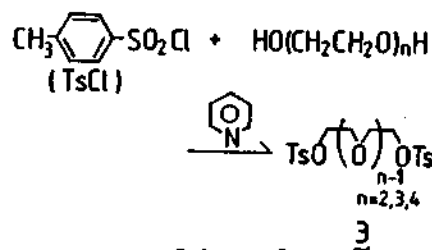
In addition to the N-benzyl diethanol amine, we presented here one new synthetic procedure to prepare N-benzylmonoaza-18-crown-6 (Scheme 5). On the other hand, a convenient two-step synthetic method of diazacrown compounds was established by Bradshaw and his co-workers²⁴. We have extended their method to the formation of N-benzylbis(2-(2-hydroxyethoxy)ethyl) amine **2** (Scheme 2). It was expected that this compound may be useful as a new starting material



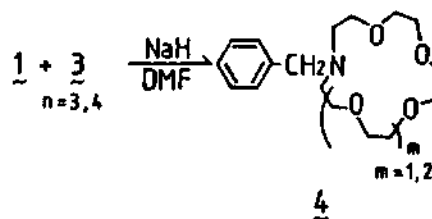
Scheme 1



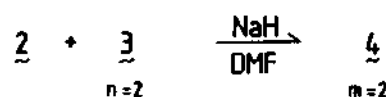
Scheme 2



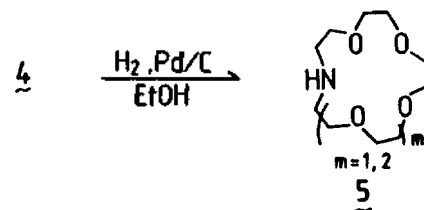
Scheme 3



Scheme 4



Scheme 5



Scheme 6

for macrocyclic polyether synthesis.

In the synthesis of N-benzylmonoaza-18-crown-6, Scheme 5 was a more appealing procedure than Scheme 4 because the yield of two starting material in Scheme 5 was somewhat higher than that in Scheme 4, and especially handling ditosylate compound. In practice, the yield was improved about 10%.

Removal of the benzyl group can be achieved by acid cleavage or reduction^{25,26}. Hydrogenolysis of N-benzyl crown ethers proceeded in essentially good yield to gave the free

Table 1. Reaction of 1-Bromooctane with NaI or KI in the Presence of Crown Ethers

Crown ether	$k_{obsd} \times 10^6$ (s ⁻¹)	
	NaI	KI
N-Benzylmonoaza-15-crown-5	11	7
N-Benzylmonoaza-18-crown-6	31	74
Monoaza-15-crown-5	1.1	0.4
Monoaza-18-crown-6	1.2	6.4

ligand 5 as a white solid.

Phase-transfer Catalytic Activity of Crown Ethers in Halogen Exchange Reaction. The phase-transfer catalytic activity of 15- or 18-membered N-benzyl- and monoazacrown ethers was examined using the nucleophilic displacement reaction of metal iodide in aqueous phase on 1-bromooctane in organic phase as a typical reaction, and was evaluated by pseudo-first-order rate constants (k_{obsd}).



$$k_{obsd} = \frac{-\ln(1 - [I]_t/[X]_0)}{\Delta t}$$

$[I]_t$: concentration of product at time t

$[X]_0$: concentration of substrate at time zero

Δt : total reaction time

Table 1 shows the effects of cavity size of crown ethers and nucleophile structure on k_{obsd} .

N-benzylmonoazacrown ethers had higher activity than monoazacrown ethers. The low activity of monoazacrown ethers is due to the low transfer rate of the complexation of crown ethers with KI or NaI. The reduced transfer must result in less effective contact with substrate, hence lower the rate constants. Catalyst with an 18-membered ring was used rates decreased with a change in salt from KI to NaI, whereas catalyst which bore a 15-membered ring, created the opposite effect. This corresponds to the well-known fact that the 18-membered crown binds K^+ tightly, but Na^+ a little loosely²⁷.

A study on the immobilization of this monoazacrown ether moieties onto the polymer supports is in progress.

References

1. C. J. Pedersen, *J. Am. Chem. Soc.*, **89**, 2495 (1967).

- J. J. Christensen, D. J. Eatough, and R. M. Izatt, *Chem. Rev.*, **74**, 351 (1974).
- B. Dietrich, J. M. Lehn, J. P. Sauvage, and J. Blanzan, *Tetrahedron*, **29**, 1629 (1973).
- J. M. Lehn, *Chem. Res.*, **11**, 49 (1978).
- R. A. Schultz, B. D. White, D. M. Dishong, K. A. Arnold, and G. W. Gokel, *J. Am. Chem. Soc.*, **107**, 6659 (1985).
- H. G. Lohr and F. Vogtle, *Chem. Ber.*, **118**, 905 (1985).
- B. D. White, K. A. Arnold, and G. W. Gokel, *Tetrahedron Lett.*, **28**, 1749 (1987).
- For a review, see: I. O. Sutherland, *Chem. Soc. Rev.*, **15**, 63 (1986).
- M. W. Hosseini, J. M. Lehn, S. R. Duff, K. Gu, and M. P. Mertes, *J. Org. Chem.*, **52**, 1662 (1987).
- J. M. Lehn, *Science* (Washington, D.C.), **227**, 849 (1985).
- P. G. Yohannes, M. P. Mertes, and K. B. Mertes, *J. Am. Chem. Soc.*, **107**, 8288, (1985).
- J. M. Lehn and P. Vierling, *Tetrahedron Lett.*, **21**, 1323 (1980).
- R. M. Izatt, J. S. Bradshaw, S. A. Nielsen, J. D. Lamb, J. J. Christensen, and D. Sen, *Chem. Rev.*, **85**, 271 (1985).
- J. D. Lamb, R. M. Izatt, J. J. Christensen, and D. K. Eatough, In *Coordination Chemistry of Macrocyclic Compound*: G. A. Melson, Ed; Plenum Press: New York, 1979.
- For a review, see: A. R. Kausser, *J. Chem. Soc. Pak.*, **5**, 227 (1983).
- For a review, see: E. Weber, *Kontakte (Merck)*, **38** (1983).
- For a review, see: E. Weber, *Kontakte (Merck)*, **26** (1984).
- J. Dale and P. O. Kristiansen, *Acta Chem. Scand.*, **26**, 1471 (1972).
- G. W. Gokel and B. J. Garcia, *Tetrahedron Lett.*, **4**, 317 (1977).
- M. J. Calverley and J. Dale, *J. Chem. Soc. Commun.*, 684 (1981).
- H. Maeda, Y. Nakatsuji, and M. Okahara, *Tetrahedron Lett.*, **22**, 4105 (1981).
- R. N. Greene, *Tetrahedron Lett.*, 1793 (1972).
- H. K. Frensdorff, *J. Am. Chem. Soc.*, **93**, 600 (1971).
- J. S. Bradshaw and K. E. Krakowiak, *J. Org. Chem.*, **53**, 1808 (1988).
- M. R. Johnson, I. O. Sutherland, and R. F. Newton, *J. Chem. Soc., Perkin Trans.*, **1**, 357 (1979).
- M. R. Johnson, N. F. Jones, and I. O. Sutherland, *J. Chem. Soc., Perkin Trans.*, **1**, 1637 (1985).
- C. J. Pederson and H. K. Frensdorff, *Angew. Chem. Int. Ed. Engl.*, **11**, 16 (1972).