

Macrocycle opening in crown ethers

2.* Template effect in macrocycle opening in formyl derivatives of benzocrown ethers under the action of amines with the formation of podands

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Macrocycle opening in derivatives of benzocrown ethers under the action of amines is affected by the nature of the heteroatoms in the macrocycle, the nature of the functional group in the benzene ring of the crown ether, and the length, branching, and number of hydrocarbon radicals at the amine nitrogen atom. A distinguishing feature of this reaction is the template effect of MeNH_3^+ , Me_2NH_2^+ , Na^+ , and K^+ ions.

Key words: 4'-formylbenzocrown ethers; macrocycle opening; alkylamines; podands; complex formation.

Earlier we have shown that formyl derivatives of benzocrown ethers enter into the reaction of nucleophilic opening of macrocycle under the action of methylamine and methylammonium chloride to form open-chain analogs of crown ethers (podands).¹ It was proposed that the ability of a crown ether macrocycle to form complexes with methylammonium cation effects significantly the course of this reaction. In this connection it was interesting to find a correlation between the structure of the starting crown compounds and alkylamines, on the one hand, and the template effect² of organic and inorganic cations under conditions of the macrocycle opening reaction, on the other hand.

The 4'-formylbenzocrown ethers (**1a–e**) and oxime of 4'-formylbenzo-15-crown-5 ether required for this study were obtained by the described by us method.³

It was found that heating of formylbenzocrown ethers **1a–e** with an ethanolic solution of R^1NH_2 and $\text{R}^1\text{NH}_3^+\text{Cl}^-$ followed by hydrolyzing the reaction mixture with a dilute acid results in podands (**2a–h**) in up to 94 % yields (Scheme 1, Table 1).

We assume that interaction of an amine and its hydrochloride with **1a–e** affords initially immonium derivatives of crown-containing benzaldehydes (**3**) which are activated to a greater extent towards nucleophilic substitution into the *para*-position than the starting compounds. Then, compound **3** and R^1NH_3^+ may form complex (**4**) where the formation of a hydrogen bond with the oxygen atom in the *para*-position to the immonium group promotes the addition of R^1NH_2 to give Meisenheimer σ -complex (**5**) and, simultaneously, fa-

vors elimination of the alkoxy group with the formation of podand **6**.

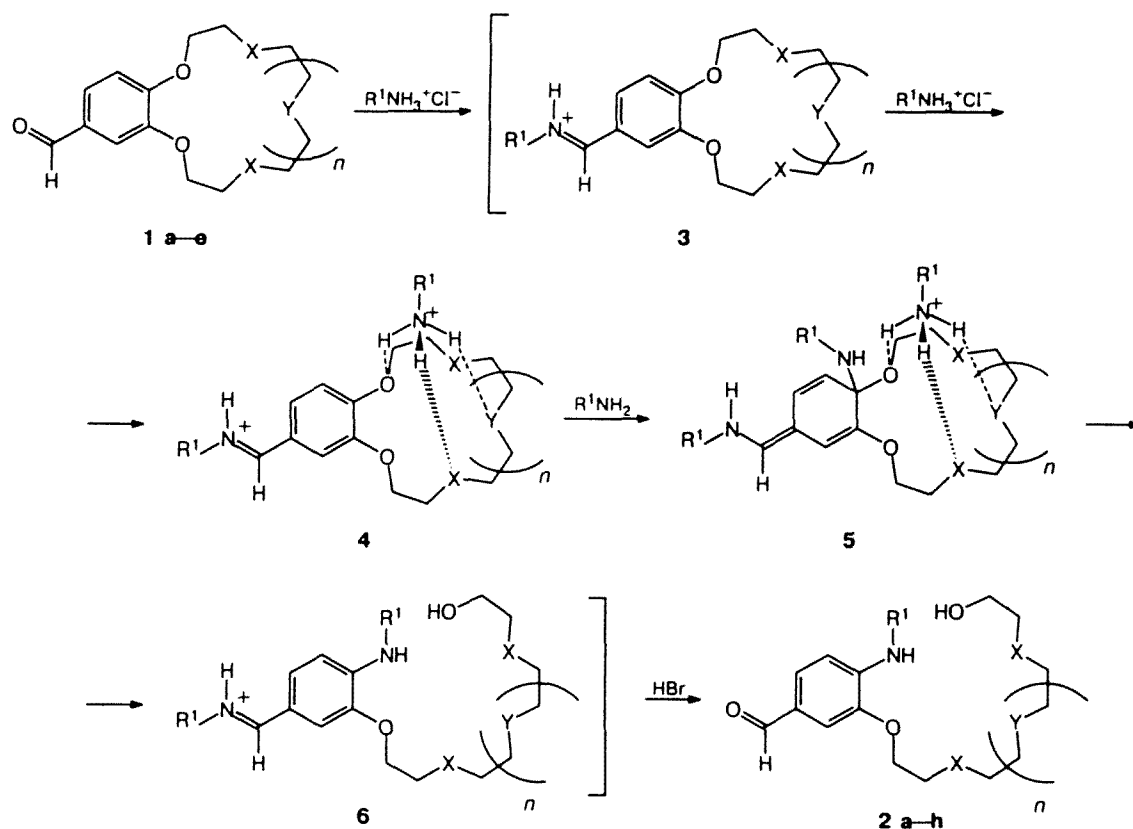
Analyzing the dependence of the degree of transformation of 4'-formylbenzo-15-crown-5 ether (**1a**) into podand **2a** under the action of MeNH_2 and $\text{MeNH}_3^+\text{Cl}^-$ on temperature and reaction time, we found out that 20 h is sufficient for the complete transformation of **1a** at 200 °C. The increase in the reaction time to 60 h has practically no effect on the yield of **2a**, indicating the high thermostability of **2a** or its immonium derivative **6** under these conditions. In other words, all side processes of this reaction occur, probably, at the steps which precede the opening of the macrocycle.

It is known that crown ethers readily form complex compounds with ammonium ions where the "host" and "guest" molecules are linked by hydrogen bonds.^{4,5} If complexation really effects the rate of nucleophilic macrocycle opening in **1a–e**, one may observe the dependence of the degree of transformation on the stability of complex **4**. However, there are no literature data on complexation of **1a–e** with $\text{R}^1\text{NH}_3^+\text{Cl}^-$ in ethanol. The analysis of complexation of their structural analogs with ammonium salts shows that the complexation constants for dithiacrown compounds are lower than those for full oxygen analogs of the latter,⁶ the complexation constants for azacrown ethers are approximately equal or a little higher than those for oxygen crown ethers,⁷ and the complexation constants for 18-crown-6 derivatives are, as a rule, somewhat higher than those for 15-crown-5 derivatives.⁸

In order to study these regularities, we carried out a series of experiments over a period of time which is known to be insufficient for complete transformation of **1a–e** into the reaction products (10 h) under compara-

* For Part I see Ref. 1.

Scheme 1

**Table 1.** Conditions of macrocycle opening in 4'-formylbenzocrown ethers **1a-e** and oxime **10** under the action of amines (200 °C) and yields of podands **2a-i**

Start- ing com- pound	Reac- tion time /h	Amine	Salt	Recovery of start- ing com- pound (%)	Degree of trans- formation (%)	Yield (%) ^a
1a	60 ^b	MeNH ₂	MeNH ₃ ⁺ Cl ⁻	59	2a (36)	2a (88)
1a	10	MeNH ₂	MeNH ₃ ⁺ Cl ⁻	36	2a (60)	2a (94)
1a	20	MeNH ₂	MeNH ₃ ⁺ Cl ⁻	0	2a (80)	2a (80)
1a	60	MeNH ₂	MeNH ₃ ⁺ Cl ⁻	0	2a (77)	2a (77)
1b^c	10	MeNH ₂	MeNH ₃ ⁺ Cl ⁻	60	2b (34)	2b (83)
1c^c	10	MeNH ₂	MeNH ₃ ⁺ Cl ⁻	18	2c (54)	2c (65)
1d^c	10	MeNH ₂	MeNH ₃ ⁺ Cl ⁻	33	2d (59)	2d (89)
1e^c	10	MeNH ₂	MeNH ₃ ⁺ Cl ⁻	68	2e (26)	2e (82)
1a	60	EtNH ₂	EtNH ₃ ⁺ Cl ⁻	0	2f (13)	2f (13)

Start- ing com- pound	Reac- tion time /h	Amine	Salt	Recovery of start- ing com- pound (%)	Degree of trans- formation (%)	Yield (%) ^a
1a	60	<i>n</i> -PrNH ₂	<i>n</i> -PrNH ₃ ⁺ Cl ⁻	0	2g (15)	2g (15)
1a	60	<i>i</i> -PrNH ₂	<i>i</i> -PrNH ₃ ⁺ Cl ⁻	-3 ^d	2h (-1) ^d	—
1a	60	<i>t</i> -BuNH ₂	<i>t</i> -BuNH ₃ ⁺ Cl ⁻	54	0	0
1a	40	Me ₂ NH	Me ₂ NH ₂ ⁺ Cl ⁻	30	2i (39)	2i (55)
1a	60	MeNH ₂	Without a salt	72	2a (18)	2a (63)
1a	60	MeNH ₂	Na ⁺ Br ⁻	15	2a (41)	2a (48)
1a	60	MeNH ₂	K ⁺ Br ⁻	49	2a (25)	2a (50)
10	60	MeNH ₂	MeNH ₃ ⁺ Cl ⁻	1a (0)	2a (54)	2a (54)
10	60	MeNH ₂	Without a salt	1a (51)	2a (2)	2a (2)

^a Calculated with respect to **1a-e** which entered the reaction. ^b The reaction temperature was 170 °C. ^c Compounds **1b-e** completely enter the reaction within 40 h to afford podands **2b-e** in 58–80 % yields. ^d The ratio and yields of the reaction products were found from ¹H NMR spectra.

ble conditions. We found out that 4'-formylbenzodithia-15(18)-crown-5(6) ethers **1b,e** enter the reaction of macrocycle opening under the action of MeNH₂ and MeNH₃⁺Cl⁻ to form podands **2b,e** much less readily (degree of transformation ~30 %) than compound **1a**

(degree of transformation 60 %). This may result from the fact that sulfur atoms cannot take part in complexation and from the decrease in the number of oxygen atoms in **1b,e** which are capable of forming hydrogen bonds with MeNH₃⁺Cl⁻. On the contrary, the formyl

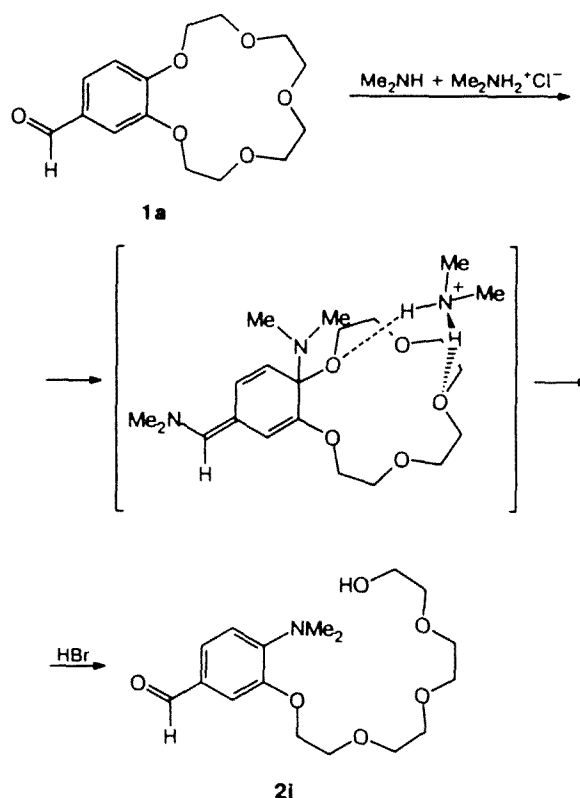
derivative of *N*-methylbenzoaza-15-crown-5 ether **1c** appeared to be more reactive under these conditions (recovery of the starting compound was 18 %) than **1a**, although their degrees of transformation into podands **2c** and **2a** are comparable (54 % and 60 %, respectively). This result can probably be explained either by competitive intramolecular nucleophilic attack by the nitrogen atom of the crown ether macrocycle in the *para*-position to the activating group, affording side products, or by the thermal lability of **1c**. It should be noted that in our experiments we did not find substantial differences in reactivity between derivatives of 15-crown-5 **1a,b** and 18-crown-6 **1d,e**, which indicates the decisive role of the nature of the heteroatoms which form the macrocycle.

One may expect that the increase in the length and branching of the hydrocarbon radical in R^1NH_2 and $R^1NH_3^+Cl^-$ will result in the increase in the volume of amine and in the decrease in the ability of the corresponding ammonium cation to form complexes with crown-containing compounds. Actually, it was found experimentally that using alkyl substituents R^1 instead of $R^1 = Me$ leads to a significant decrease in the yield of podands down to ~14 % for $R^1 = Et$, *n*-Pr (**2f,g**) and to 1 % for $R^1 = i$ -Pr (**2h**). In the case of $R^1 = t$ -Bu, the corresponding podand was not found at all (Table 1). All reactions were accompanied by strong resinification. However, these results can hardly be explained only by the decrease in the ability of alkylammonium cations for complexation or by a simple increase in the volume of R^1 which may interfere with the approach of the amine to the reaction center (Scheme 1). At the same time, they indicate the thermal instability of the intermediates formed from **1a** and reagents in the course of macrocycle opening at high temperature.

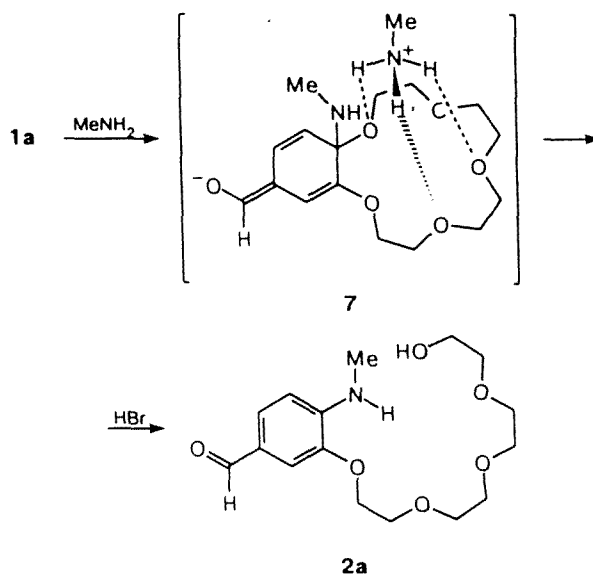
Indeed, in the case of the reaction of **1a** with Me_2NH and $Me_2NH_3^+Cl^-$ (Scheme 2) we observed a higher degree of transformation and yield of the end product **2i** in a shorter reaction time as compared with reagents based on alkylamines (except transformation of **1a** into **2a**). This is the case in spite of the significant steric hindrance which is observed as such amine (branching at the nitrogen atom) approaches the reaction center, and in spite of the lesser expected stability of the complex of the 4 type (see Ref. 9) (only two hydrogen bonds with the crown ether fragment, instead of three, can be formed).

To separate the effect of activation of the nucleophilic macrocycle opening in **1a**, which is due to the formation of the complex with $MeNH_3^+$ **4**, from a similar effect related with the formation of the immonium derivative **3**, we carried out the reaction of **1a** with $MeNH_2$ in the absence of $MeNH_3^+Cl^-$ (Scheme 3). In spite of the fact that the degree of transformation is not high (Table 1), podand **2a** is formed in 63 % yield, unlike the case of 4-methoxybenzaldehyde where the nucleophilic substitution of methoxy group under similar conditions does not proceed at all.¹⁰ One may assume that **1a** directly enters the reaction under study,

Scheme 2



Scheme 3



although the aldehyde group probably activates the nucleophilic opening of macrocycle to a lesser extent than the immonium group in compound **3**. The structure of intermediate **7** formed may be similar to that of **5**, but the concentration of **7** in the reaction mixture is prob-

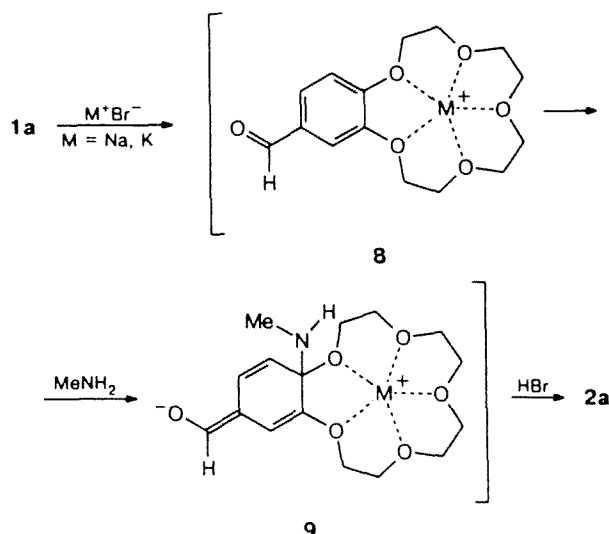
ably low and this decreases the effectiveness of the reaction.

If our proposal about participation of intermediate **7** in this reaction is valid, the addition of sodium and potassium salts, which are known to form more stable complexes with derivatives of 15-crown-5 ether,^{4,5} may noticeably increase the degree of transformation of **1a** into **2a**. We chose sodium and potassium bromides as salts since their solubility in ethanol is relatively high and the nucleophilicity of bromine anion is low as compared with MeNH₂.

The degree of transformation of **1a** into **2a** in these reactions was significantly higher in the case of NaBr (Table 1), which may result from the better fit of the sodium cation diameter to the size of the cavity of 15-crown-5 ether fragment of **1a** as compared with potassium cation.

Based on these data one may assume that complex **8**, which is to a larger extent activated for nucleophilic attack by MeNH₂ than **1a**, is initially formed in the reaction mixture from **1a** and M⁺. Intermediate **9** is formed as the result of the addition of MeNH₂, and the metal cation located in the cavity of the crown ether fragment favors elimination of the alkoxy residue with the formation of the end product (Scheme 4).

Scheme 4



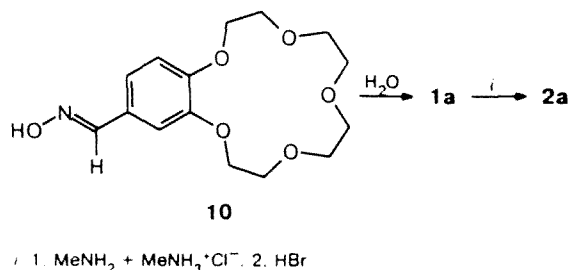
It was interesting to try to use the oxime group as an activating group for the nucleophilic opening of macrocycle (Scheme 5). It was shown that the reaction of MeNH₂ and MeNH₃⁺Cl⁻ with the oxime of 4'-formylbenzo-15-crown-5 ether (**10**) affords podand **2a** in 54 % yield. Two more compounds were isolated from the reaction mixture. They are the products of transformation of the oxime group without opening of macrocycle. This direction of the reaction will be analyzed in a separate paper. When the reaction of **10** with MeNH₂

Table 2. Mass spectra of compounds **2b,c,e-g**, and **i**

Compound ^a	Molecular formula	<i>m/z</i> (<i>I</i> _{rel} (%)) ^b	Found: $[M]^+$ Calculated: <i>M</i>
2b	C ₁₆ H ₂₅ NO ₄ S ₂	359 (14), 343 (25), 209 (89), 181 (100), 178 (29), 150 (34), 149 (48), 109 (28), 105 (88), 87 (29), 61 (50)	359.11986 359.12247
2c	C ₁₇ H ₂₈ N ₂ O ₅	340 (2), 278 (15), 266 (19), 265 (100), 219 (13), 195 (11), 150 (14), 133 (13), 132 (82), 100 (97), 72 (20)	340.20151 340.19979
2e	C ₁₈ H ₂₉ NO ₅ S ₂	403 (17), 372 (12), 255 (11), 254 (13), 253 (100), 225 (63), 150 (11), 149 (24), 105 (36), 87 (16), 61 (16)	403.14967 403.14868
2f	C ₁₇ H ₂₇ NO ₆	341 (77), 253 (7), 213 (7), 209 (10), 176 (9), 165 (49), 164 (39), 150 (28), 148 (14), 89 (37), 48 (100)	341.18496 341.18380
2g	C ₁₈ H ₂₉ NO ₆	355 (84), 326 (28), 240 (12), 179 (32), 178 (35), 176 (41), 164 (11), 150 (46), 148 (24), 89 (41), 48 (100)	355.19995 355.19945
2i^c	C ₁₇ H ₂₇ NO ₆	341 (75), 192 (51), 177 (20), 166 (33), 165 (100), 163 (31), 162 (43), 151 (25), 150 (36), 148 (23), 89 (44)	341.18268 341.18380

^a For mass spectra of **2a**, and **2d** see Ref. 1. ^b The peak of the molecular ion and the 10 most intense peaks are given. ^c According to ¹H NMR data, the sample of **2i** contains 29 % of **2a** since an aqueous solution of Me₂NH of "pure" grade was used which contains an admixture of MeNH₂.

Scheme 5



was carried out in the absence of MeNH₃⁺Cl⁻, **2a** was formed in 2 % yield only, and 4'-formylbenzo-

Table 3. IR and ^1H NMR spectra of compounds **2b,c,e—g**, and **i**

Compound ^a	IR (KBr, thin film), ν/cm^{-1}	^1H NMR ($\text{CDCl}_3\text{—CCl}_4$, 1:1), δ (J/Hz)
2b	3396 (NH, OH) 1663 (C=O)	2.77 (m, 4 H, 2 CH_2S); 2.82 (t, 2 H, CH_2S , $J = 6.3$); 3.00 (d, 3 H, MeN, $J = 5.3$); 3.04 (t, 2 H, CH_2S , $J = 6.5$); 3.69 (m, 4 H, 2 CH_2O); 3.76 (t, 2 H, CH_2O , $J = 5.9$); 4.29 (t, 2 H, CH_2O , $J = 6.5$); 5.17 (br.q, 1 H, NH, $J = 5.3$); 6.59 (d, 1 H, H-3, $J = 8.1$); 7.29 (s, 1 H, H-6); 7.40 (d, 1 H, H-4, $J = 8.1$); 9.70 (s, 1 H, CH=O)
2c	3356 (NH, OH) 1661 (C=O)	2.29 (s, 3 H, MeN); 2.60 (m, 4 H, 2 CH_2N); 2.89 (d, 3 H, MeNH, $J = 5.7$); 3.47—3.65 (m, 8 H, 4 CH_2O); 3.77 (m, 2 H, CH_2O); 3.92 (br.s, 1 H, OH); 4.17 (m, 2 H, CH_2O); 5.58 (br.q, 1 H, NH); 6.48 (d, 1 H, H-3, $J = 7.9$); 7.19 (s, 1 H, H-6); 7.29 (d, 1 H, H-4, $J = 7.9$); 9.60 (s, 1 H, CH=O)
2e	3388 (NH, OH) 1663 (C=O)	2.65—2.81 (m, 6 H, 3 CH_2S); 2.96 (d, 3 H, MeN, $J = 5.2$); 2.99 (t, 2 H, CH_2S , $J = 6.4$); 3.56—3.73 (m, 10 H, 5 CH_2O); 4.25 (t, 2 H, CH_2O , $J = 6.4$); 5.13 (br.q, 1 H, NH, $J = 5.2$); 6.53 (d, 1 H, H-3, $J = 8.1$); 7.24 (s, 1 H, H-6); 7.33 (d, 1 H, H-4, $J = 8.1$); 9.63 (s, 1 H, CH=O)
2f	3372 (NH, OH) 1732 ^b , 1663 (C=O)	1.32 (t, 3 H, Me, $J = 7.2$); 2.81 (br.s, 1 H, OH); 3.29 (m, 2 H, CH_2N); 3.58—3.83 (m, 12 H, 6 CH_2O); 3.89 (m, 2 H, CH_2O); 4.23 (m, 2 H, CH_2O); 5.28 (br.s, 1 H, NH); 6.58 (d, 1 H, H-3, $J = 8.2$); 7.29 (s, 1 H, H-6); 7.38 (d, 1 H, H-4, $J = 8.2$); 9.68 (s, 1 H, CH=O)
2g	3372 (NH, OH) 1731 ^b , 1663 (C=O)	1.02 (t, 3 H, Me, $J = 7.4$); 1.69 (m, 2 H, MeCH_2); 3.21 (q, 2 H, CH_2N , $J = 8.0$); 3.58—3.80 (m, 12 H, 6 CH_2O); 3.83—3.97 (m, 2 H, CH_2O); 4.15—4.27 (m, 2 H, CH_2O); 5.32 (br.t, 1 H, NH); 6.58 (d, 1 H, H-3, $J = 8.2$); 7.29 (s, 1 H, H-6); 7.38 (d, 1 H, H-4, $J = 8.2$); 9.67 (s, 1 H, CH=O)
2i	3360 (OH) 1726 ^b , 1665 (C=O)	2.95 (s, 6 H, Me_2N); 3.54—3.75 (m, 12 H, 6 CH_2O); 3.89 (m, 2 H, CH_2O); 4.21 (m, 2 H, CH_2O); 6.84 (d, 1 H, H-3, $J = 8.2$); 7.31—7.37 (m, 2 H, H-6, H-4); 9.75 (s, 1 H, CH=O)

^a For IR and ^1H NMR spectra of **2a** and **2d** see Ref. 1. ^b Weak signal attributed by us to vibrations of the C=O group of the complexes of podands **2a,d,f,g**, and **i** with KBr from the support.

15-crown-5 ether (**1a**) was the main product of the reaction (Table 1).

These results allowed us to conclude that **10** probably undergoes hydrolysis in the course of the reaction with the formation of **1a** which, after that, is transformed into **2a** according to the mechanism shown in Scheme 1. It should be noted that this conclusion does not agree with the statement of the authors¹⁰ about the activation of the nucleophilic substitution under the action of MeNH_2 by the oxime group itself as demonstrated by the example of *p*-methoxybenzaldehyde oxime.

The structure of compounds obtained was established using ^1H NMR, IR, and mass spectroscopy involving high resolution mass spectrometry (Tables 2 and 3). It should be noted that the IR spectra of podands **2a,d,f,g**, and **i**, along with the main absorption band of C=O group at 1663 cm^{-1} , contain the low-intensity band at $1726\text{—}1732\text{ cm}^{-1}$. We consider that this band corresponds to the valence vibrations of the C=O group of the part of the podand, which forms a complex with KBr from the support. This conclusion is confirmed by the absence of the corresponding absorption band in the

case of podands **2b,c** and **e** for which lower constants of complexation with KBr may be expected.

Thus, the nucleophilic opening of the macrocycle in derivatives of benzocrown ethers under the action of amines depends on the nature of the heteroatoms which compose the macrocycle, the nature of the functional group in the benzene fragment of the crown compound, and the length and branching of hydrocarbon radicals at the amine nitrogen atom. The distinguishing feature of the influence of MeNH_3^+ , Me_2NH_2^+ , Na^+ and K^+ ions on the reaction studied is their template effect, i.e., the organic or inorganic cation bound in complex with benzocrown ether acts directly on the reaction center of the reacting molecule favoring the addition of amine, and then elimination of the alkoxy residue with the formation of podand.

Experimental

^1H NMR spectra were obtained on Bruker AC-200p and Bruker AMX-400 spectrometers using $\text{CDCl}_3\text{—CCl}_4$ (1 : 1) as a solvent and SiMe_4 as the internal standard. Mass spectra

were obtained on a Varian MAT-311A instrument at an ionization energy of 70 eV using direct injection of samples into the ionization source. IR spectra were recorded on a Shimadzu IR-435 spectrophotometer in thin films. The reactions were monitored by TLC on DC-Alufolien Aluminiumoxid 60 F₂₅₄ neutral (Type E) plates.

Synthesis of podands 2a–e (general procedure). To 4'-formylbenzocrown ether **1a–e** (0.676 mmol) or oxime **10** were added MeNH₃⁺Cl[−] (0.46 g, 6.76 mmol) (or without this compound), NaBr or KBr (2.03 mmol) (or without these compounds), and a 41 % solution of MeNH₂ in abs. EtOH (7 mL), and the reaction mixture was heated for 10–60 h at 170 or 200 °C (a bath with Wood's alloy) in a sealed tube. The tube was then opened, and the solvent was evaporated *in vacuo*. Aqueous HBr (30 : 1, 30 mL) was added to the dry residue in the case of the reaction with **1a–e**, or water (30 mL) in the case of oxime **10**, and the mixture was kept for 1 h. Dilute KOH was then added until pH ~10 was attained, and the mixture was extracted with chloroform. The extract was concentrated *in vacuo*, and the residue was purified by column chromatography on Al₂O₃ (L 40/250, alkaline or neutral, Chemapol, eluent was benzene–EtOH, 30 : 1), or, in the case of oxime **10**, on silica gel (L 40/250, Chemapol, gradient elution from benzene to MeOH up to 11 % of the latter), to give podands **2a–e** as light yellow oils.

Synthesis of podands 2f,g and i (general procedure). To 4'-formylbenzocrown ether **1a** (0.20 g, 0.676 mmol) were added ethyl-, *n*-propyl, or dimethylamine hydrochloride (6.76 mmol) and, respectively, 14 % solution of EtNH₂ in abs. EtOH (7 mL), *n*-PrNH₂ (3.52 mmol) in 6 mL of abs. EtOH or 40 % solution of Me₂NH in abs. EtOH (5 mL). The reaction mixture was heated for 40 or 60 h at 200 °C (a bath with Wood's alloy) in a sealed tube. The tube was then opened, and the solvent was evaporated *in vacuo*. Aqueous HBr (30 : 1, 30 mL) was added to the dry residue and the mixture was kept for 1 h. Dilute KOH was then added until

pH ~10 was attained, and the mixture was extracted with chloroform. The extract was concentrated *in vacuo*, and the residue was purified by column chromatography on silica gel (L 40/100, Chemapol, gradient elution from benzene to EtOH up to 5 % of the latter) to give podands **2f,g** and **i** as light yellow oils.

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Received September 15, 1995