

A VERSATILE SYNTHESIS OF OLIGOCROWN COMPOUNDS WITH HYDROXYL GROUPS AT THE HINGE*

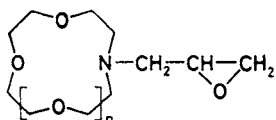
Martin BĚLOHRADSKÝ, Petr HOLÝ, Ivan STIBOR and Jiří ZÁVADA

*Institute of Organic Chemistry and Biochemistry,
Czechoslovak Academy of Sciences, 166 10 Prague 6*

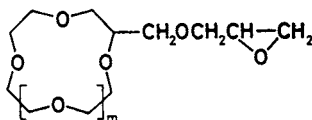
Received April 25th, 1987

Oxirane ring-opening reaction of N-(2,3-epoxy-1-propyl) azacrowns Ia–Ic and 4,5-epoxy-2'-oxapentylcrowns IIa–IIe with mono- and diamines (including mono- and diazacrowns) afforded array of new di-, tri-, and tetracrown compounds with hydroxyl groups placed at the hinge.

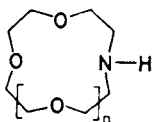
Molecules bearing two or more pendant crown units attracted a considerable attention in recent years^{1–6}. Ability to encapsulate a variable number of metal ions makes such compounds interesting on its own right but appealing also to other areas of investigation, *e.g.*, metal ion separation and catalysis.



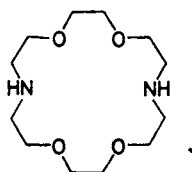
Ia, $n = 1$
Ib, $n = 2$
Ic, $n = 3$



IIa, $m = 1$ II d, $m = 4$
II b, $m = 2$ II e, $m = 5$
II c, $m = 3$



III a, $n = 1$
III b, $n = 2$
III c, $n = 3$



IV

* Part VII in the series Chemistry of Multidentate Ligands; Part VI: Collect. Czech. Chem. Commun. 52, 2500 (1987).

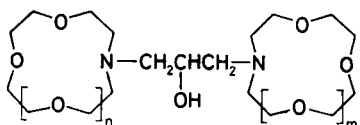
Aiming to provide a wider access to the intriguing ligands we prepared⁷ previously macrocyclic building blocks *Ia–Ic* and *IIa–IIe* designed to allow anchoring the crown moieties – *via* the pendant oxirane group – at single as well as multiple nucleophilic sites.

In this paper we made use of the methodology in the reaction with amines including azacrowns *IIIa–IIIc* and *IV*. Main attention was given to synthesis of dicrown homologous series required for complexation studies⁸.

RESULTS AND DISCUSSION

S_N2 reaction of epoxides with amines is well-known^{9,10}. When the epoxide group is in a terminal position, the nucleophilic attack takes place usually at the primary carbon atom.

In accordance with the prevailing experience, the reaction of the epoxycrowns *Ia–Ic* as well as *IIa–IIe* with azacrowns *IIIa–IIIc* afforded always a uniform product which was assigned structure of dicrown compound *Va–Vf* or *Vla–Vlo*, respectively. The reaction of the same epoxycrowns with morpholine took an analogous course, yielding the corresponding “mini” dicrown compounds *VIIa–VIIc* and *VIIIa–VIIIe*, respectively.



Va, $n=1$, $m=1$

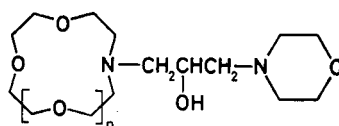
Vb, $n=1$, $m=2$

Vc, $n=1$, $m=3$

Vd, $n=2$, $m=2$

Ve, $n=2$, $m=3$

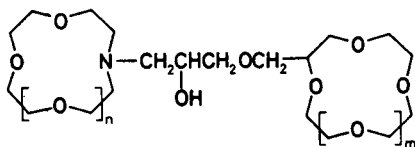
Vf, $n=3$, $m=3$



VIIa, $n=1$

VIIb, $n=2$

VIIc, $n=3$



VIa, $n=1$, $m=1$

VIb, $n=1$, $m=2$

VIc, $n=1$, $m=3$

VId, $n=1$, $m=4$

VIe, $n=1$, $m=5$

VI f, $n=2$, $m=1$

VIg, $n=2$, $m=2$

VIh, $n=2$, $m=3$

VIi, $n=2$, $m=4$

VIj, $n=2$, $m=5$

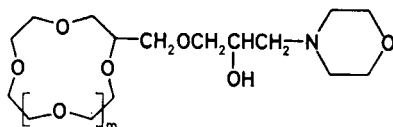
VIk, $n=3$, $m=1$

VI l, $n=3$, $m=2$

VI m, $n=3$, $m=3$

VI n, $n=3$, $m=4$

VI o, $n=3$, $m=5$



VIIIa, $m=1$

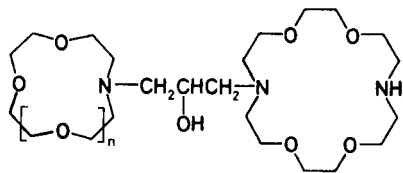
VIIIb, $m=2$

VIIIc, $m=3$

VIIId, $m=4$

VIIIe, $m=5$

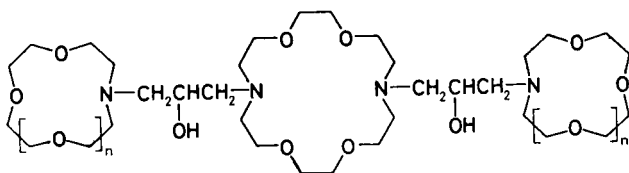
The reaction of the epoxides *Ia–Ic* and *IIa–IIe* with an equimolar amount of the diazacrown *IV* yielded a mixture of the di- and tricrown compounds *IXa–IXc* and *Xa–Xc*, or *XIa–XIc* and *XIIa–XIIc*, respectively, which could be separated



IXa, $n = 1$

IXb, $n = 2$

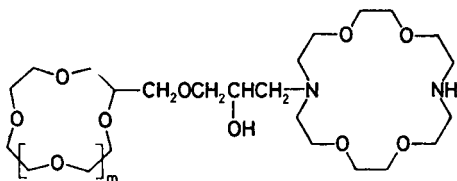
IXc, $n = 3$



Xa, $n = 1$

Xb, $n = 2$

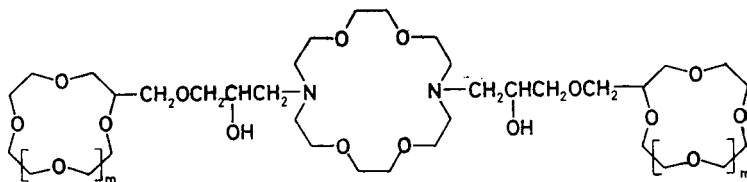
Xc, $n = 3$



XIa, $m = 1$

XIb, $m = 2$

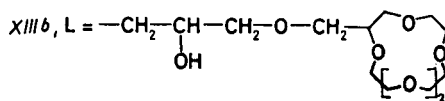
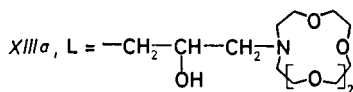
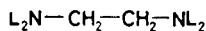
XIc, $m = 3$



XIIa, $m = 1$

XIIb, $m = 2$

XIIc, $m = 3$



by a flash chromatography. When the reaction was performed with an excess of the epoxide reagent, the tricrown compounds were obtained predominantly. Similarly, the tetracrown compounds *XIIIa,b* were the main products in the reaction of ethylenediamine with an excess of the epoxide *Ib* and *IIB*, respectively.

TABLE I
Dicrown compounds *V*

Compound ^a	Yield ^b , % (method) ^c (composition of CH ₃ OH-NH ₄ OH eluent)	Formula (mol. wt.)	Calculated ^d /found		
			% C	% H	% N
<i>Va</i>	81 (<i>A</i>), 91 (<i>B</i>) (10 : 1)	C ₁₉ H ₃₈ N ₂ O ₇ (406.5)	52.38	8.79	6.11
			52.05	8.90	6.29
<i>Vb</i>	77 (<i>A</i>) (8 : 1)	C ₂₁ H ₄₂ N ₂ O ₈ (450.6)	52.57	8.82	5.57
			53.05	8.82	5.70
<i>Vc</i>	64 (<i>A</i>) (4 : 1)	C ₂₃ H ₄₆ N ₂ O ₉ (494.6)	52.73	8.85	5.12
			53.30	9.07	5.35
<i>Vd</i>	57 (<i>A</i>), 67 (<i>B</i>) (8 : 1)	C ₂₃ H ₄₆ N ₂ O ₉ (494.6)	52.73	8.85	5.12
			52.69	8.59	5.47
<i>Ve</i>	71 (<i>A</i>) (3 : 1)	C ₂₅ H ₅₀ N ₂ O ₁₀ (538.7)	52.86	8.87	4.74
			52.67	9.05	5.18
<i>Vf</i>	55 (<i>A</i>), 73 (<i>B</i>) (2 : 1)	C ₂₇ H ₅₄ N ₂ O ₁₁ (582.7)	52.98	8.89	4.41
			53.25	8.95	4.67

^a Mass spectrum, *m/z* (%), found for *Va*: M⁺ = 406 (0.1), 188 (100), 214 (27), 218 (23), 100 (15), 56 (13); *Vb*: M⁺ = 450 (1), 232 (100), 258 (93), 214 (87), 188 (69), 218 (62); *Vc*: M⁺ = 494 (1), 214 (100), 276 (98), 302 (95), 188 (95), 218 (70); *Vd*: M⁺ = 494 (0.2), 258 (100), 232 (89), 262 (56), 56 (32), 100 (14); *Ve*: M⁺ = 538 (1), 276 (100), 258 (84), 302 (74), 232 (69), 262 (51); *Vf*: M⁺ = 582 (1), 302 (100), 276 (98), 306 (57), 45 (32), 56 (27). ^b After flash chromatography.

^c For method *A*, *B* see Experimental. ^d Calculated for a monocarbonate.

TABLE II
Dicrown compounds VI

Compound ^a	Yield ^b , % (composition of CH ₃ OH-NH ₄ OH eluent)	Formula (mol. wt.)	Calculated ^c /found		
			% C	% H	% N
<i>VIa</i>	91 (10 : 1)	C ₂₀ H ₃₉ NO ₉ (437·5)	52·70	8·41	3·07
			53·05	8·65	2·74
<i>VIb</i>	97 (10 : 1)	C ₂₂ H ₄₃ NO ₁₀ (481·6)	52·89	9·08	2·80
			53·06	8·83	2·59
<i>VIc</i>	74 (3 : 1)	C ₂₄ H ₄₇ NO ₁₁ (525·6)	53·02	9·08	2·58
			53·06	9·07	2·70
<i>VIId</i>	74 (6 : 1)	C ₂₆ H ₅₁ NO ₁₂ (569·7)	53·14	9·09	2·38
			53·26	8·80	2·09
<i>VIe</i>	79 (5 : 1)	C ₂₈ H ₅₅ NO ₁₃ (613·8)	53·30	9·09	2·22
			52·81	8·73	1·96
<i>VIIf</i>	92 (8 : 1)	C ₂₂ H ₄₃ NO ₁₀ (481·6)	52·89	9·08	2·80
			53·05	8·87	2·62
<i>VIg</i>	81 (7 : 1)	C ₂₄ H ₄₇ NO ₁₁ (525·6)	53·02	9·08	2·58
			52·59	8·80	2·38
<i>VIh</i>	79 (4 : 1)	C ₂₆ H ₅₁ NO ₁₂ (569·7)	53·14	9·09	2·38
			52·74	8·88	2·16
<i>VIi</i>	80 (5 : 1)	C ₂₈ H ₅₅ NO ₁₃ (613·8)	53·30	9·09	2·22
			53·76	8·89	1·92
<i>VIj</i>	81 (6 : 1)	C ₃₀ H ₅₉ NO ₁₄ (657·8)	53·32	9·10	2·07
			53·99	8·95	1·80
<i>VIk</i>	75 (6 : 1)	C ₂₄ H ₄₇ NO ₁₁ (525·6)	53·02	9·08	2·58
			52·45	8·74	2·32
<i>VIl</i>	67 (4 : 1)	C ₂₆ H ₅₁ NO ₁₂ (569·7)	53·14	9·09	2·38
			52·83	8·76	2·03
<i>VIIm</i>	50 (1 : 1)	C ₂₈ H ₅₅ NO ₁₃ (613·8)	53·30	9·09	2·22
			52·79	8·80	1·92
<i>VIIn</i>	57 (4 : 1)	C ₃₀ H ₅₉ NO ₁₄ (657·8)	53·32	9·10	2·07
			53·28	8·91	1·90
<i>VIo</i>	50 (3 : 1)	C ₃₂ H ₆₃ NO ₁₅ (701·9)	53·39	9·10	1·95
			53·44	8·55	1·70

^a Mass spectrum, m/z (%), found for *VIa*: M^+ = 437 (2), 188 (100), 45 (14), 100 (11), 56 (8), 158 (8), 218 (4), 292 (3), 405 (2); *VIb*: M^+ = 481 (1), 188 (100), 45 (12), 100 (8), 158 (7), 56 (6), 218 (4), 336 (3), 406 (1), 450 (1); *VIc*: M^+ = 525 (0·5), 188 (100), 45 (5), 100 (4), 292 (4), 158 (3),

The structure assigned to the individual compounds were confirmed by ^1H NMR as well as mass spectra. All the novel compounds are hygroscopic and absorb carbon dioxide. Unless precautions were taken to avoid contact with atmosphere, the elemental analyses corresponded to monohydrates for the compounds with one nitrogen atom, to monocarbonates for the compounds with two nitrogens and to dicarbonates for the compounds with four nitrogens. Such a pattern of behaviour is accountable by different basicities of the involved nitrogen atoms^{8,11,12}.

EXPERIMENTAL

Separation and analytical techniques employed in this study were analogous as described previously⁷.

Dicrown Compounds *Va*–*Vf*

A) An equimolar mixture of an epoxide *Ia*–*Ic* and an appropriate monoazacrown *IIIa*–*IIIc* (3 mmol each) was stirred under nitrogen at 80°C for 8 h. The product was isolated by a flash chromatography on a silicagel column (eluent CH_3OH –aq. NH_4OH). Data are summarized in Table I.

B) (one-pot synthesis of the symmetrical compounds *Va*, *f*, *d*, from *IIIa*–*IIIc* and epichlorohydrine involving *in situ* preparation of the epoxides *Ia*–*Ic*): Epichlorohydrine (0.2 ml; 2.55 mmol) was heated with an appropriate monoazacrown *IIIa*–*IIIc* (5.5 mmol) under nitrogen at 90°C for 2.5 h. Isolation by a flash chromatography afforded products which were identical with the corresponding ones obtained by the procedure *A*.

Dicrown Compounds *VIa*–*VIo*

Equimolar amounts of an appropriate epoxide *IIa*–*IIe* and monoazacrown *IIIa*–*IIIc* (3 mmol each) were heated under nitrogen at 100°C for 20 h. The products were isolated by flash chromatography analogously as described above. Data are summarized in Table II.

←
218 (3), 336 (1); *VIId*: M^+ = 569 (2), 188 (100), 45 (25), 87 (22), 89 (13), 100 (12), 158 (7), 424 (6), 494 (4); *VIe*: M^+ = 613 (0.5), 188 (100), 45 (28), 87 (15), 89 (15), 133 (12), 177 (5), 218 (3), 468 (2); *VIIf*: M^+ = 481 (1), 232 (100), 45 (15), 56 (7), 87 (5), 100 (5), 202 (4), 262 (4), 575 (2), 188 (2); *VIg*: M^+ = 525 (0.5), 232 (100), 45 (15), 56 (7), 87 (5), 100 (5), 202 (4), 262 (4), 175 (2), 188 (2); *VIh*: M^+ = 569 (0.5), 232 (100), 45 (15), 87 (9), 100 (5), 262 (4), 258 (4), 202 (3), 144 (2), 380 (1); *VIi*: M^+ = 613 (0.7), 232 (100), 45 (14), 87 (5), 89 (3), 100 (3), 202 (2), 262 (2), 424 (1); *VIj*: M^+ = 657 (0.5), 232 (100), 45 (16), 87 (6), 89 (4), 59 (4), 73 (3), 100 (3), 202 (2), 262 (2), 468 (1); *VIk*: M^+ = 525 (0.5), 276 (100), 45 (11), 100 (5), 56 (5), 246 (3), 188 (2), 306 (2), 524 (1); *VIl*: M^+ = 569 (0.5), 276 (100), 45 (8), 100 (4), 56 (3), 87 (3), 232 (2), 246 (2), 306 (1), 568 (1); *VIIm*: M^+ = 613 (0.5), 276 (100), 45 (19), 87 (9), 100 (6), 232 (4), 56 (4), 188 (2), 246 (2), 306 (1); *VIIn*: M^+ = 657 (0.5), 276 (100), 45 (10), 100 (4), 87 (3), 246 (2), 188 (2), 306 (2), 424 (1); *VIo*: M^+ = 701 (0.5), 276 (100), 45 (6), 87 (3), 100 (3), 246 (2), 306 (2), 468 (1), 318 (1).^b After flash chromatography. ^c Calculated for a monohydrate.

"Mini" Dicrown Compounds *VIIa–VIIc* and *VIIIa–VIIe*

A) An appropriate epoxide *Ia–Ic* (*IIa–IIe*) was dissolved in an excess of morpholine (1 ml; 11 mmol) and heated under nitrogen at 80°C for 8 h. The solvent was taken off *in vacuo* and the product was isolated by a short-path distillation (Kugelrohr) or by flash chromatography. Data are given in Table III.

B) (applicable only for the compounds *VIIa–VIIc*): N-(2,3-Epoxy-1-propyl)morpholine (0.29 g; 2 mmol) was heated with an appropriate monoazacrown *IIIa–IIIc* (2 mmol) at 80°C for 9 h. Products were isolated by a short-path distillation (Kugelrohr). Data are given in Table III.

TABLE III
"Mini" dicrown compounds *VII* and *VIII*

Compound ^a	Yield ^b , % (method) (composition of CH ₃ OH–NH ₄ OH eluent)	Formula (mol. wt.)	Calculated ^c /found		
			% C	% H	% N
<i>VIIa</i>	93 (B)	C ₁₅ H ₃₀ N ₂ O ₅ (318.4)	50.51	8.48	7.36
			51.00	8.80	7.32
<i>VIIb</i>	96 (B)	C ₁₇ H ₃₄ N ₂ O ₆ (362.5)	50.93	8.55	6.59
			50.76	8.82	6.43
<i>VIIc</i>	94 (B)	C ₁₉ H ₃₈ N ₂ O ₇ (406.5)	51.28	8.60	5.98
			51.61	8.76	6.25
<i>VIIIa</i>	93 (A) (20 : 1)	C ₁₆ H ₃₁ NO ₇ (349.4)	52.22	9.04	3.81
			52.63	8.81	4.19
<i>VIIIb</i>	71 (A) (10 : 1)	C ₁₈ H ₃₅ NO ₈ (393.5)	52.54	9.06	3.40
			52.20	8.75	3.14
<i>VIIIc</i>	72 (A) (7 : 1)	C ₂₀ H ₃₉ NO ₉ (437.5)	52.70	8.41	3.07
			53.20	8.71	2.69
<i>VIIId</i>	64 (A) (8 : 1)	C ₂₂ H ₄₃ NO ₁₀ (481.6)	52.89	9.08	2.80
			53.28	8.76	2.61
<i>VIIIe</i>	62 (A) (10 : 1)	C ₂₄ H ₄₇ NO ₁₁ (525.6)	53.02	9.08	2.58
			53.50	8.72	2.57

^a Mass spectrum, *m/z* (%), found for *VIIa*: M⁺ = 318 (1), 188 (100), 100 (88), 214 (85), 126 (56), 218 (55), 56 (50), 130 (30), 176 (17), 300 (13); *VIIb*: M⁺ = 362 (1), 232 (100), 258 (78), 100 (68), 126 (59), 262 (38), 56 (34), 130 (24), 344 (8); *VIIc*: M⁺ = 406 (0.5), 232 (100), 100 (46), 45 (39), 56 (27), 144 (24), 114 (24), 276 (20), 126 (18), 130 (13); *VIIIa*: M⁺ = 349 (1), 100 (100), 45 (17), 87 (13), 175 (7), 130 (4), 188 (1), 249 (1); *VIIIb*: M⁺ = 393 (1), 100 (100), 45 (23), 87 (16), 130 (16), 145 (11), 293 (7), 160 (7), 263 (6); *VIIIc*: M⁺ = 437 (1), 100 (100), 57 (80), 87 (60), 130 (7), 145 (5), 189 (5), 175 (4), 160 (3); *VIIIe*: M⁺ = 525 (2), 100 (100), 45 (19), 87 (8), 130 (5), 144 (4), 160 (2), 495 (2), 204 (2), 507 (2). ^b After flash chromatography. ^c Calculated for a dicarbonate *VII* or a monohydrate *VIII*.

TABLE IV
Di- and tricrown compounds IX–XII

Compound ^a	Yield ^b , % (composition of CH ₃ OH–NH ₄ OH eluent)	Formula (mol. wt.)	Calculated ^c /found		
			% C	% H	% N
<i>IXa</i>	46 (4 : 1)	C ₂₃ H ₄₇ N ₃ O ₈ (493·6)	52·82	9·05	7·70
			52·70	9·11	7·27
<i>Xa</i>	12 (4 : 1)	C ₃₄ H ₆₈ N ₄ O ₁₂ (724·9)	50·93	8·55	6·60
			50·92	8·83	6·32
<i>IXb</i>	21 (3 : 1)	C ₂₅ H ₅₁ N ₃ O ₉ (537·7)	52·95	9·06	7·12
			53·39	9·38	6·80
<i>Xb</i>	20 (3 : 1)	C ₃₈ H ₇₆ N ₄ O ₁₄ (813·0)	51·27	8·61	5·98
			50·74	8·80	6·05
<i>IXc</i>	27 (2 : 1)	C ₂₇ H ₅₅ N ₃ O ₁₀ (581·7)	53·06	9·07	6·63
			52·51	9·00	6·68
<i>Xc</i>	8 (1 : 1)	C ₄₂ H ₈₄ N ₄ O ₁₆ (901·1)	51·55	8·65	5·47
			51·32	8·61	5·64
<i>XIa</i>	26 (9 : 1)	C ₂₄ H ₄₈ N ₂ O ₁₀ (524·6)	52·07	8·39	4·86
			51·92	8·38	4·77
<i>XIIa</i>	28 (9 : 1)	C ₃₆ H ₇₀ N ₂ O ₁₆ (786·9)	52·97	8·65	3·34
			52·94	8·36	3·60
<i>XIb</i>	25 (4 : 1)	C ₂₆ H ₅₂ N ₂ O ₁₁ (568·7)	52·23	8·60	4·51
			51·78	8·91	4·69
<i>XIIb</i>	34 (4 : 1)	C ₄₀ H ₇₈ N ₂ O ₁₈ (875·1)	53·11	8·70	3·02
			52·85	8·66	3·14
<i>XIc</i>	38 (2 : 1)	C ₂₈ H ₅₆ N ₂ O ₁₂ (612·8)	52·39	8·79	4·21
			51·82	8·88	4·12
<i>XIIc</i>	16 (2 : 1)	C ₄₄ H ₈₆ N ₂ O ₂₀ (963·1)	53·24	8·74	2·76
			53·55	8·78	2·66

^a Mass spectrum, m/z (%), found for *IXa*: M^+ = 493 (2), 188 (100), 305 (95), 214 (79), 218 (77), 275 (70), 301 (46), 56 (46), 100 (42), 45 (28); *Xa*: M^+ = 724 (1), 188 (100), 276 (61), 214 (61), 218 (52), 45 (50), 100 (45), 275 (39), 56 (38), 289 (25); *IXb*: M^+ = 537 (1), 232 (100), 305 (87), 258 (80), 262 (65), 275 (56), 301 (46), 56 (33), 100 (25), 474 (22); *Xb*: M^+ = 812 (2), 232 (100), 258 (54), 262 (40), 580 (35), 56 (21), 45 (17), 100 (17), 275 (14), 550 (12); *IXc*: M^+ = 581 (1), 276 (100), 305 (71), 302 (59), 275 (47), 301 (45), 306 (45), 56 (19), 100 (18), 518 (13); *Xc*: M^+ = 900 (1), 276 (100), 306 (32), 302 (30), 45 (17), 100 (16), 277 (16), 56 (14), 188 (5), 232 (5); *XIa*: M^+ = 524 (2), 275 (100), 276 (28), 45 (25), 100 (21), 114 (20); 192 (19), 318 (18), 289 (14), 463 (8); *XIIa*: M^+ = 786 (1), 537 (100), 275 (86), 45 (39), 538 (28), 144 (28), 100 (25), 276 (24), 289 (24), 317 (14); *XIb*: M^+ = 568 (1), 275 (100), 45 (88), 56 (38), 100 (38), 114 (30), 276 (25), 114 (23),

Di- and Tricrown Compounds *IXa–IXc* and *XIIIa–XIIIc*

Equimolar amount of the epoxide *Ia–Ic* (*Ila–Ilc*) and the diazacrown *IV* (2 mmol each) were heated under nitrogen at 100°C for 3 h and the resulting mixture of di- and tricrown compounds was separated by a flash chromatography (silicagel; eluent CH₃OH–aq. NH₄OH). Data are given in Table IV.

Tetracrown Compounds *XIIIa,b*

Prepared from ethylenediamine (30 mg; 0.5 mmol) and a fourfold excess of the epoxide *Ib* (*IIlb*) under the same conditions as described above. Data are given in Table V.

TABLE V

Tetracrown compounds *XIII*

Compound ^a	Yield ^b , % (composition of CH ₃ OH–NH ₄ OH eluent)	Formula (mol. wt.)	Calculated ^c /found		
			% C	% H	% N
<i>XIIIa</i>	65	C ₅₄ H ₁₀₈ N ₆ O ₂₀ (1 161.5)	52.32	8.78	7.40
	(3 : 2)		52.52	8.39	7.54
<i>XIIIb</i>	87	C ₅₈ H ₁₁₂ N ₂ O ₂₈ (1 285.5)	52.98	8.59	2.09
	(6 : 1)		52.72	8.53	2.01

^a Mass spectrum, *m/z* (%), found for *XIIIa*: M⁺ = 1 160 (1), 232 (100), 258 (53), 262 (43), 100 (21), 56 (21), 45 (18), 305 (21), 580 (18), 635 (11); *XIIIb*: M⁺ = 1 284 (0.1), 45 (100), 87 (95), 336 (86), 642 (35), 59 (35), 219 (23), 101 (23), 131 (19), 362 (18). ^b After flash chromatography.

^c Calculated for dicarbonate *XIIIa* and monocarbonate *XIIIb*.

REFERENCES

- Smid J. in the book: *Progress in Macrocyclic Chemistry* (R. M. Izatt and J. J. Christensen, Eds), Vol. 2, Chapt. 3. Wiley, New York 1981.
- Sinta R., Lamb B., Smid J.: *Macromolecules* 16, 1382 (1983).
- Kimura K., Maeda T., Shono T.: *Anal. Lett.*, A 11, 821 (1978).
- Weber E.: *Angew. Chem., Int. Ed.* 22, 616 (1983).
- Wong K. H., Ng H. L.: *J. Coord. Chem.* 11, 49 (1981).
- Sakamoto H., Kimura K., Koseki Y., Matsuo M., Shono T.: *J. Org. Chem.* 51, 4974 (1986).

←
317 (16), 192 (14); *XIIb*: M⁺ = 874 (4), 581 (100), 45 (63), 582 (34), 144 (28), 275 (28), 87 (23), 100 (18), 114 (16), 331 (16); *XIc*: M⁺ = 612 (2), 275 (100), 45 (33), 317 (28), 276 (26), 192 (24), 100 (18), 85 (18), 114 (18), 130 (13); *XIIc*: M⁺ = 962 (1), 625 (100), 626 (32), 45 (19), 144 (17), 87 (13), 331 (10), 89 (9), 100 (8), 114 (7). ^b After flash chromatography. ^c Calculated for monocarbonate (*IX*, *XI*, *XII*) or dicarbonate (*X*).

7. Bělohradský M., Holý P., Stibor I., Závada J.: Collect. Czech. Chem. Commun. 52, 2500 (1987).
8. Závada J., Koudelka J., Holý P., Bělohradský M.: Unpublished results.
9. Parker R. E., Issacs N. C.: Chem. Rev. 59, 737 (1959).
10. Bartok M., Lang K. L. in the book: *Small Ring Hetrocycles* (A. Hassner, Ed.), Part 3, Chapt. 1. Wiley, New York 1985.
11. Gero A.: J. Org. Chem. 76, 5158 (1954).
12. Gero A.: J. Org. Chem. 76, 5159 (1954).

Translated by the author (J.Z.).