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MACROHETEROCYCLES.

7.* SYNTHESIS AND EXTRACTION CAPACITY OF SOME DIBENZO-18-CROWN-6-DERIVATIVES

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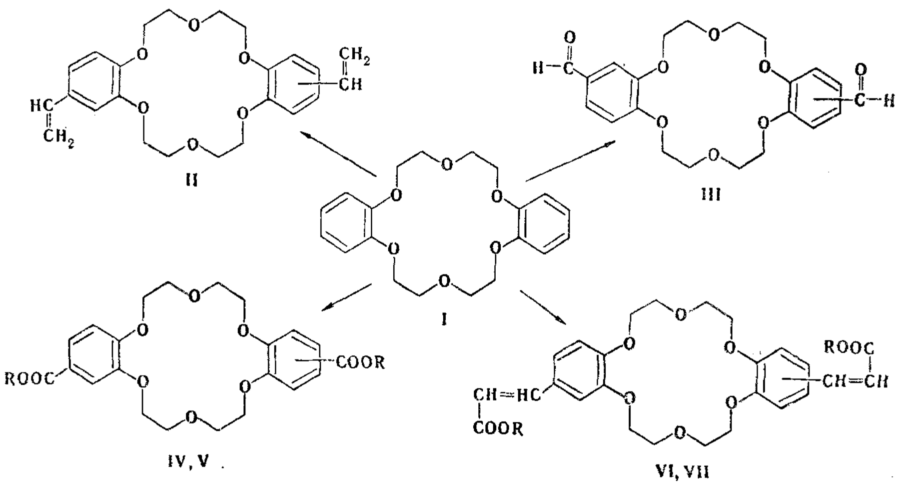
Derivatives that contain vinyl, formyl, acetyl, carboxy, carbethoxy, β-carboxyvinyl, or β-carbethoxyvinyl groups in the benzene rings were synthesized from dibenzo-18-crown-6. The ability of the synthesized crown ethers to extract picrates of alkali metals from the aqueous phase to the chloroform phase was investigated.

The unique ability of macrocyclic polyethers (crown ethers) to form stable complexes with ions of alkali and alkaline earth metals and to solubilize inorganic salts in nonpolar solvents has led to their wide use as catalysts for interphase transfer, extractants, materials for ion-selective detectors, analytical reagents, and model systems for the study of the transport of ions through biological membranes [2, 3]. One of the most accessible and effective complexones with a broad spectrum of activity is dibenzo-18-crown-6 (I). In order to study the effect of various substituents on the complexing ability of dibenzo-18-crown-6 we obtained a number of its new derivatives (II-VII).



IV, VI R=H; V, VII R=C_2H_5

4,4'(5')-Divinylbenzo-18-crown-6 (II) was synthesized by acylation of crown ether I with acetic acid in polyphosphoric acid (PPA) [4] with subsequent reduction of 4,4'(5')-diacetyldibenzo-18-crown-6 (VIII) with sodium borohydride and dehydration of the resulting 4,4'(5')-bis(α-hydroxyethyl)dibenzo-18-crown-6 (IX) via the following scheme:

See [1] for Communication 6.

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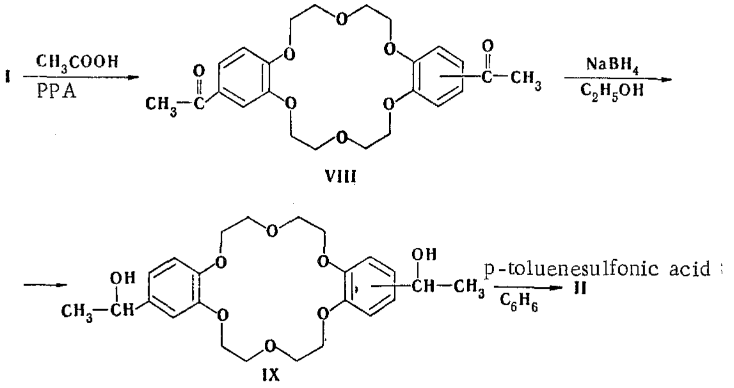
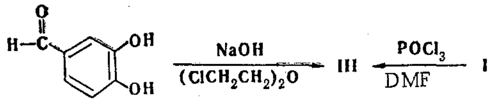


In contrast to the method of reduction of ketone VIII with lithium aluminum hydride proposed in [5], the use of sodium borohydride is more convenient in a preparative respect and leads to an increase in the yield of the desired compound.

4,4'(5')-Divinylbenzo-18-crown-6 (II) is an extremely interesting substance for the synthesis from it of polymeric materials that have complexing properties. Such polymers were recently obtained on the basis of vinylbenzo-15-crown-5 and vinylbenzo-18-crown-6 [6]. These polymers have a linear structure and are soluble in many organic solvents. The presence of two vinyl groups in II opens up the possibility for the synthesis from it of crosslinked homopolymers or copolymers that should be less soluble and consequently can be used as new chromatographic materials and convenient heterogeneous catalysts for interphase transfer.

4,4'(5')-Diacetyldibenzo-18-crown-6 (VIII) is a convenient starting compound for the synthesis of various derivatives of crown ether I. Thus we obtained 4,4'(5')-dicarboxydibenzo-18-crown-6 (IV) by oxidation of VIII with sodium hypobromite. Diethyl ester V was obtained by the reaction of the chloride of acid IV with ethanol.

4,4'(5')-Diformylbenzo-18-crown-6 (III) was synthesized by two methods:



The reaction of 3,4-dihydroxybenzaldehyde with sym-dichloroethyl ether (Chlorex) in butanol in the presence of sodium hydroxide leads to III in ∿20% yield. In this connection, we studied the possibility of obtaining dialdehyde III by direct formylation of crown ether I under the conditions of the Vilsmeier reaction. The yield in this case reaches 40%; however, the difficulties that arise during its isolation make this method less acceptable.

The reaction of III with malonic acid and subsequent decarboxylation under the conditions of the Knoevenagel reaction leads to the formation of acid VI, the diethyl ester of which (VII) was obtained in the same way as ester V.

The properties and spectral characteristics of the synthesized compounds are presented in Tables 1 and 2. In the PMR spectra the signal of the protons of the polyether ring is observed in the form of a complex multiplet at 3.30-4.50 ppm. The spin–spin coupling constants of the protons attached to the C=C bonds in VI and VII are 16.0 Hz, which makes it possible to assign a trans configuration to them.

TABLE 1. Characteristics of Dibenzo-18-crown-6 Derivatives (II-VII)

Compound	mp, °C	Found, %		Empirical formula	Calc., %		Yield, %
		C	H		C	H	
II	135—140	69,8	6,7	$C_{24}H_{28}O_6$	69,9	6,8	47
III	205—207	63,4	5,8	$C_{22}H_{24}O_8$	63,5	5,8	40
IV	301—303	58,9	5,3	$C_{22}H_{24}O_{10}$	58,9	5,4	75
V	152—155	61,8	6,3	$C_{26}H_{32}O_{10}$	61,9	6,4	60
VI	278—280	62,5	5,7	$C_{26}H_{28}O_{10}$	62,4	5,6	71
VII	120—123	64,9	6,5	$C_{30}H_{36}O_{10}$	64,8	6,5	62

TABLE 2. Spectral Characteristics of Dibenzo-18-crown-6 Derivatives (II-VII)

Compound	UV spectrum, λ_{max}, nm (log ε)	IR spectrum, ν, cm^{-1}	PMR spectrum, δ, ppm ($CDCl_3$)
II	214 (4,47); 262 (4,26); 298 (3,82)	1630 (C=C); 1140 (C—O—C)	6,86 (2H, d); 6,76 (4H, s) ArH; 6,55 (2H, q); 5,46 (2H, q); 5,02 (2H, q); $CH=CH_2$; 4,20—3,75 (16H, m) OCH_2
III	209 (4,20); 231 (4,37); 275 (4,18); 308 (4,00)	1690 (C=O); 1140 (C—O—C)	9,70 (2H, s) HCO; 7,37 (2H, d); 7,22 (2H, s); 5,76 (2H, d) ArH; 4,23—3,73 (16H, m) OCH_2
IV*	218 (4,48); 257 (4,16); 289 (3,83)	3410 (O—H); 1700 (C=O); 1210 (C—OH); 1130 (C—O—C)	7,41 (2H, d); 7,23 (2H, s); 6,60 (2H, d) ArH; 4,07—3,33 (16H, m) OCH_2
V	221 (4,60); 262 (4,30); 294 (4,00)	1710 (C=O); 1220 ($C—OC_2H_5$); 1140 (C—O—C)	7,70—7,37 (4H, m); 6,77 (2H, d) ArH; 4,50—3,53 (20H, m) OCH_2; 1,18 (6H, t) CH_3
VI*	217 (3,74); 234 (3,76); 294 (3,80); 318 (4,14)	3420 (O—H); 1690 (C=O); 1630, 1600 (CH=CH-*trans*); 1180 (C—OH); 1140 (C—O—C)	8,02—6,33 (6H, m) ArH; 7,03 (2H, d); 5,92 (2H, d) CH=CH; 4,07—3,33 (16H, m) OCH_2
VII	217 (4,17); 234 (4,14); 294 (4,20); 321 (4,27)	1710 (C=O); 1640, 1605 (CH=CH-*trans*); 1180 ($C—OC_2H_5$); 1140 (C—O—C)	7,00—6,60 (6H, m) ArH; 7,47 (2H, d); 6,13 (2H, d) CH=CH; 4,33—3,36 (16H, m) OCH_2; 3,53 (4H, q) CH_2; 1,13 (6H, t) CH_3

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*The PMR spectra were recorded in the form of solutions in trifluoroacetic acid.

TABLE 3. Percentage of Extraction of the Picrates of Alkali and Alkaline Earth Metals by Dibenzo-18-crown-6 Derivatives (I-III, V, VII-IX)

Compound	Cation										
	Li^+	Na^+	K^+	Rb^+	Cs^+	NH_4^+	$t\text{-}Bu—\overset{+}{N}H_3$	Mg^{2+}	Ca^{2+}	Sr^{2+}	Ba^{2+}
I	0,2	1,0	20,5	11,2	2,3	2,5	3,3	0,3	0,0	0,0	3,1
II	0,0	0,0	18,8	13,8	5,9	4,5	3,0	0,1	0,2	0,9	2,2
III	0,0	0,0	1,2	0,0	0,0	0,0	0,0	0,2	0,0	0,1	0,0
V	0,0	0,2	5,5	4,8	1,6	1,0	1,4	0,0	0,0	0,0	0,0
VII	0,0	2,7	6,7	6,3	5,9	2,3	3,8	0,0	0,0	0,0	0,0
VIII	0,0	1,9	5,7	1,6	0,0	0,0	0,0	0,9	0,9	1,1	0,8
IX	0,0	0,4	23,7	14,0	7,7	6,9	6,5	3,5	0,6	1,2	3,1

To evaluate the complexing ability of the compounds obtained we studied the extraction by them of picrates of alkali and alkaline earth metals from the aqueous phase to the chloroform phase. Preliminary experiments showed that in the absence of a crown ether one does not observe any appreciable extraction of the picrates of the metals into chloroform and that one also does not observe distribution of the crown ethers into the aqueous layer. The concentration of the salt in the aqueous phase after the establishment of equilibrium was determined spectrophotometrically at λ = 354 nm. The percentage of extraction of the ions of alkali and alkaline earth metals, which was calculated from the formula $[(D_1 - D_2)/D_1]\cdot 100\%$, where D_1 and D_2 are the optical densities of the aqueous solution of the salt before and after extraction, is presented in Table 3.

It is apparent from the data presented in Table 3 that the introduction of electronegative substituents in the aromatic ring leads to a sharp decrease in the complexing ability of the crown ether. At the same time, the presence of a vinyl group has virtually no effect on the extraction capacity of II in comparison with crown ether I. The introduction of an α-hydroxyalkyl group in the aromatic ring leads to a certain increase in the extraction capacity of IX; this is possibly associated with the ability of the alcohol groups to solvate the gegenion (the picrate anion).

EXPERIMENTAL

The individuality of the compounds obtained was monitored by thin-layer chromatography (TLC) on Silufol UV-254 plates. The UV spectra in methanol were recorded with a Specord

UV-vis spectrophotometer. The IR spectra of KBr pellets were recorded with a Perkin–Elmer 580B spectrometer. The PMR spectra were recorded with a Tesla BS-467 spectrometer (60 MHz) with hexamethyldisiloxane as the internal standard.

4,4'(5')-Diacetyldibenzo-18-crown-6 (VIII). A 28-g (0.48 mole) sample of acetic acid was added at 70°C to a solution of 20 g (0.054 mole) of dibenzo-18-crown-6 in 200 g of PPA, and the mixture was heated at 80-100°C for 1 h, after which it was cooled and diluted with water. The resulting precipitate was removed by filtration, washed with water, and recrystallized from ethanol to give 34.4 g (70%) of a product with mp 197-200°C.

4,4'(5')-Bis(α-hydroxyethyl)dibenzo-18-crown-6 (IX). A 17.2-g (0.04 mole) sample of VIII was added in portions to a mixture of 700 ml of ethanol and 8.6 g (0.23 mole) of sodium borohydride, and the mixture was stirred at room temperature for 1 h, at 60°C for 1 h, and allowed to stand overnight. Acidified water was added, and the mixture was filtered. The filtrate was evaporated to a volume of 100 ml and extracted with chloroform. The chloroform solution was evaporated to give 15 g (87%) of a product with mp 179-183°C.

4,4'(5')-Divinyldibenzo-18-crown-6 (II). A mixture of 15 g (0.033 mole) of crown ether IX, 700 ml of benzene, and a catalytic amount of p-toluenesulfonic acid (PTSA) was refluxed for 10 h with a Dean–Stark adapter. It was then cooled to room temperature, 5-10 drops of pyridine were added, and the mixture was filtered. The filtrate was washed with 200 ml of water, and the organic layer was evaporated to a volume of 100 ml, and the concentrate was added slowly to 200 ml of hexane. The resulting precipitate was removed by filtration.

4,4'(5')-Diformyldibenzo-18-crown-6 (III). A) A mixture of 4 g (0.1 mole) of sodium hydroxide and 13.8 g (0.1 mole) of 3,4-dihydroxybenzaldehyde in 60 ml of n-butanol was refluxed for 30 min in a nitrogen atmosphere, after which a solution of 7.8 g (0.055 mole) of sym-dichloroethyl ether (Chlorex) in 8 ml of n-butanol was added in the course of 2 h, and the mixture was refluxed for 1 h. Another 4 g (0.1 mole) of sodium hydroxide was added, and the mixture was refluxed for 1 h. A solution of 7.8 g (0.055 mole) of Chlorex in 8 ml of n-butanol was then added in the course of 2 h, and the mixture was refluxed for 16 h. A 2-ml sample of concentrated HCl was added dropwise, 14 ml of n-butanol was removed by filtration, and distillation was continued with the continuous addition of water until the temperature of the vapors reached 100°C. The mixture was cooled, and the resulting precipitate was removed by filtration and recrystallized from toluene to give 4.2 g (20%) of the product.

B) A mixture of 3.6 g (0.01 mole) of crown ether I, 3.1 g (0.02 mole) of phosphorus oxychloride, and 4.5 g (0.06 mole) of dimethylformamide (DMF) was refluxed for 2 h, after which it was poured over 50 g of ice. A 20% solution of sodium hydroxide was added until the mixture gave an alkaline reaction with litmus paper, and the resulting precipitate was removed by filtration and recrystallized from benzene. The dialdehyde was isolated by column chromatography on silica gel (100/160 μ) by means of elution with chloroform–acetone (3:5).

4,4'(5')-Dicarboxydibenzo-18-crown-6 (IV). A 4.8-g (0.03 mole) sample of bromine was added with stirring and cooling with ice water to a solution of 4 g (0.1 mole) of sodium hydroxide in 20 ml of water in such a way that the temperature of the reaction mixture did not exceed 10°C. It was then cooled to 0°C, and a suspension of 2.2 g (0.005 mole) of VIII in 20 ml of dioxane was added in portions. At the end of the addition, the mixture was stirred at room temperature for 1 h and evaporated *in vacuo*. The residue was dissolved in water, and a 20% solution of NaOH was added until the mixture gave an alkaline reaction with litmus paper. The mixture was filtered, and the filtrate was acidified with concentrated HCl until it gave an acidic reaction with litmus paper, and the resulting precipitate was removed by filtration and recrystallized from methanol.

4,4'(5')-Bis(β-acryloyl)dibenzo-18-crown-6 (VI). A 0.78-g (0.002 mole) sample of dialdehyde III and two drops of piperidine were added to a solution of 0.5 g (0.005 mole) of malonic acid in 4 ml of pyridine, and the mixture was refluxed for 25 h. It was then poured over a mixture of ice and hydrochloric acid, and the resulting precipitate was removed by filtration and recrystallized from ethanol.

4,4'(5')-Dicarboxydibenzo-18-crown-6 Diethyl Ether (V). A mixture of 0.9 g (0.002 mole) of acid IV, 5 g (0.04 mole) of thionyl chloride, and 10 ml of dry benzene was refluxed until hydrogen chloride evolution ceased. The mixture was filtered, and the filtrate was evaporated with a rotary evaporator. The residue was refluxed in a mixture of 10 ml of dry benzene and 2 ml of dry ethanol for 2 h, after which the mixture was cooled and filtered, and the filtrate was poured into 30 ml of hexane. The resulting precipitate was removed by filtration.

4,4'(5')-Bis(β-acryloyl)dibenzo-18-crown-6 Diethyl Ester (VII). This compound was similarly obtained from 0.2 g (0.0004 mole) of acid VI, 1 g (0.008 mole) of thionyl chloride, and 0.5 ml of dry ethanol.

Extraction of Picrates of Alkali and Alkaline Earth Metals by I-III, V, and VII-IX. A 1-ml sample of a $1 \cdot 10^{-3}$ M aqueous solution of the picrate of the corresponding metal and 0.4 ml of a $5 \cdot 10^{-3}$ M solution of the ligand in chloroform that had been previously saturated with water was stirred vigorously with a magnetic stirrer for 5 min. After centrifugation, a 0.1-ml sample of the aqueous layer was removed and treated with 2.9 ml of distilled water, and the optical density of the resulting solution was measured at 354 nm.

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SYNTHESIS AND IR SPECTRA OF SOME 2-AMINOBENZOXAZOLE DERIVATIVES

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A large number of 5-nitro-, 6-nitro-, 5-chloro-, and 6-bromo-2-aminobenzoxazoles were synthesized by the reaction of benzoxazoline-2-thiones with various amines. It was shown by IR spectroscopy that all of the compounds exist in the amino form in solution, whereas the 5-substituted compounds exist in the imino form in the solid state, and the 6-substituted compounds exist simultaneously in the two forms.

In our previous research we developed a new method for the preparation of thiourea derivatives that contain a 2-hydroxyphenyl grouping as a substituent [1, 2] by the reaction of benzoxazoline-2-thione with ammonia. These compounds proved to be interesting in a chemical respect, and this compelled us to develop a method for the preparation of derivatives of 2-aminobenzoxazole and 2-imino-3-alkylbenzoxazoline [3, 4]. We showed that 2-aminobenzoxazole derivatives exist in various tautomeric forms in the solid form and in solution [5], whereas 2-imino-3-methylbenzoxazoline derivatives have an anomalously high frequency of the azomethine group in the IR spectra [6]. In addition, some of the 2-aminobenzoxazole derivatives have the properties of stabilizers of rubber mixtures [7] and are inhibitors of metal corrosion.

We became interested in the effect of substituents in the aromatic ring of 2-aminobenzoxazoles on the state of the tautomeric equilibrium. We obtained several derivatives of 2-amino-5-nitrobenzoxazole, 2-amino-6-nitrobenzoxazole, 2-amino-5-chlorobenzoxazole, and 2-

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