Action of 2,4-Dinitrophenylhydrazine on Compound (IIIb). To a solution of 0.4 g of 2,4-dinitrophenylhydrazine in 2 ml of DMF is added a solution of 0.2 g of compound (IIIb) in 0.5 ml of DMF and 2 drops of conc. HCl. The precipitate of dinitrophenylhydrazine is filtered off after 4 h.

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13-AMINO-1,4,7,10-BENZOTETRAOXA-15-CYCLODODECENE

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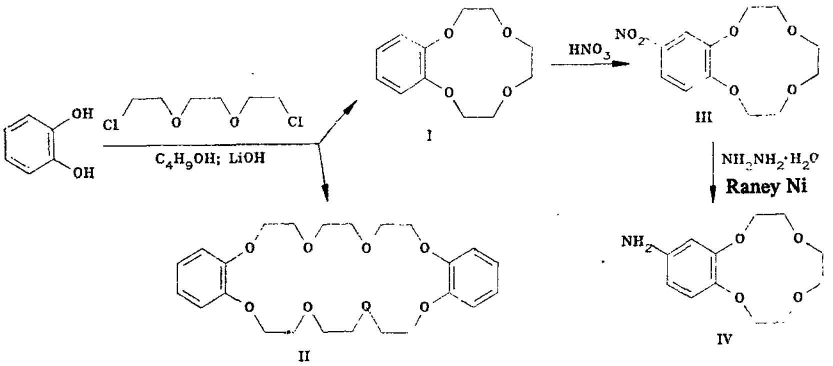
A separation was performed for benzo-12-crown-4 and dibenzo-24-crown-8 obtained as a mixture by the reaction of pyrocatechol with 1,8-dichloro-3,6-dioxaoctane. Nitro and amino derivatives of benzo-12-crown-4 were obtained.

13-Amino-1,4,7,10-benzotetraoxa-15-cyclododecene (IV) is a starting material for the synthesis of derivatives with substitution in the benzene ring. Product IV was obtained by the following scheme:



A matrix synthesis of benzo-12-crown-4 (I) by the reaction of pyrocatechol with 1,8-dichloro-3,6-dioxaoctane under high dilution conditions gave dibenzo-24-crown-8 (II). The separation of these macrocycles through their nitro derivatives was described by Shinkai et al. [1]. We have been able to separate I and II using the high solubility of I in ether.

The purity of the compounds obtained was confirmed by mass spectral analysis. The molecular ions with m/z 224 and 448 correspond to the molecular masses of I and II. The high stability of the molecular peaks relative to electron impact is characteristic of crown ethers containing aromatic rings, and the fragmentation, which is analogous to the

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decomposition of pure 18-crown-6, involves the loss of neutral C_2H_4O fragments (in the case of II, after molecular decomposition into two symmetrical halves), unequivocally confirms the structural assignments of these compounds.

Benzo-12-crown-4 was nitrated by nitric acid in glacial acetic and chloroform [2]. Amine IV was obtained for the first time in the crystalline state by the reduction of nitro compound III by hydrazine hydrate in the presence of Raney nickel. Oily 4'-aminobenzo-12-crown-4 described by Pacey et al. [3] was synthesized by the reduction of a mixture of the nitro derivatives of crown ethers I and II and is a mixture of the corresponding amines.

EXPERIMENTAL

The mass spectra were taken on an LBK 2091 mass spectrometer using direct inlet into the ion source and 70 and 14-15 eV ionizing energy in order to establish compound purity. The PMR spectra were measured on a Varian XL-100-12 spectrometer at 100 MHz with TMS as the internal standard. The IR spectra were taken on a UR-20 spectrometer in KBr pellets.

Benzo-12-crown-4 (I) and Dibenzo-24-crown-8 (II). A mixture of 44.0 g (0.4 mole) pyrocatechol, 600 ml 1-butanol, 35.6 g (0.85 mole) lithium hydroxide in 100 ml water, and 74.8 g (0.4 mole) 1,8-dichloro-3,6-dioxaoctane was heated at 100°C for 30 h, acidified with concentrated hydrochloric acid, and filtered. The solvent was distilled off the filtrate. A sample of 150 ml heptane was added to the residue and the mixture was heated at 80-90°C for 5 h. The extract was removed and cooled to 20°C. The solvent was decanted and 50 ml ether was added to the oily residue. The precipitate of dibenzo-24-crown-8 was filtered off and washed with ether to given 7.0 g product (7.8%), with mp 111-112°C (mp 113-114°C [1]) and mass spectrum with m/z 448. Removal of ether from the filtrate gave 9.0 g (10%) benzo-12-crown-4 as a yellow oil with mass spectrum m/z 224.

13-Nitro-1,4,7,10-benzotetraoxa-15-cyclododecane (III). A nitrating mixture consisting of 3.5 ml nitric acid (d = 1.42) and 10 ml glacial acetic acid was added dropwise with vigorous stirring to a solution of 4.48 g (0.02 mole) I in 100 ml chloroform and 70 ml glacial acetic acid. The reaction mass was stirred for 1 h at 20°C, heated at a reflux for 3 h, cooled, and poured into 300 ml water. The organic layer was separated, washed with water, and evaporated to yield 1.5 g (30%) III with mp 108-109°C (105-108°C [2]).

13-Amino-1,4,7,10-benzotetraoxa-15-cyclodecene (IV). A sample of 2.5 ml (0.05 mole) hydrazine hydrate was added dropwise with vigorous stirring to a solution of 2.2 g (0.008 mole) III in 100 ml dimethylformamide at 40-50°C and then about 1 g Raney nickel was added. The reaction mass was stirred for 4 h at 100°C and filtered. The solvent was distilled off the filtrate. The residue was extracted with chloroform. Removal of the solvent gave 1.5 g (62.5%) IV, mp 84-85°C. PMR spectrum (in $CDCl_3$), δ: 6.32 (1H, d, 11-CH), 6.24 (1H, d.d., 12-CH), 6.34 (1H, d, 14-CH) ($J_{11,12}$ = 8.0 Hz, $J_{12,14}$ = 2.5 Hz), 4.00-4.16 (4H, m, 2,9-CH_2), 3.80-3.94 (4H, M, 3,8-CH_2), 3.80 (4H, s, 5,6-$(CH_2)_2$), 4.50 ppm (2H, s, NH_2). IR spectrum: 3425, 3340, 3207 (NH_2), 1225 ($C{-}O{-}C^{asym}_{arom}$), 1038 ($C{-}O{-}C^{sym}_{arom}$), 1123 ($C{-}O{-}C^{asym}_{aliph}$), 924, 909 cm^{-1} ($C{-}O{-}C^{sym}_{aliph}$). Found: C 60.6; H 7.4; N 5.5%. Calculated for $C_{12}H_{17}NO_4$: C 60.2; H 7.1; N 5.8%.

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