

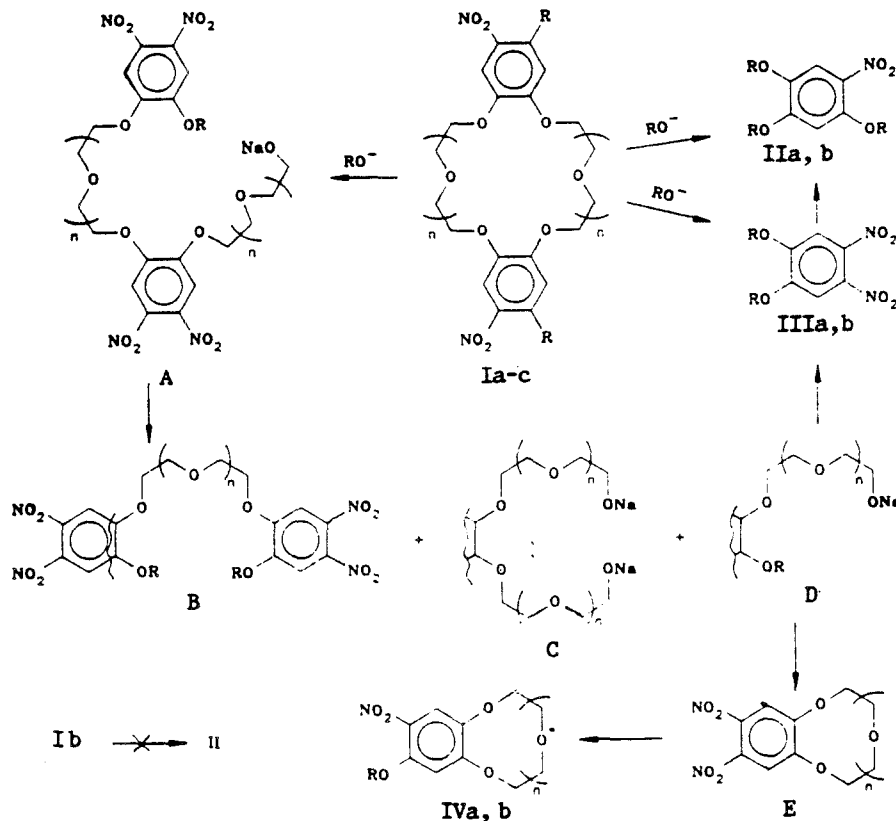
RECYCLIZATION OF TETRANITRODIBENZO-18-CROWN-6 AND TETRANITRODIBENZO-24-CROWN-8 INTO MONOBENZOCROWN ETHERS

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The benzo-9-crown-3 and benzo-12-crown-4 derivatives are formed by reaction of tetranitrodibenzo-18-crown-6 and tetranitrodibenzo-24-crown-8, respectively, with sodium methoxyethoxide in DMSO at 20°C.

Tetranitrodibenzo-18-crown-6 (Ia) is opened by sodium alkoxides in DMSO or DMF at room temperature to form the corresponding trialkoxynitrobenzenes IIa, b [1]. It was found that the o-dinitro derivatives III are intermediates in formation of compounds II. The initial step is mainly opening of the macrocycle, not substitution of the nitro groups [2]. This is confirmed by the fact that compounds of type III are readily converted under the reaction conditions into compounds II whereas crown ether Ib does not react with Na alkoxides at room temperature.

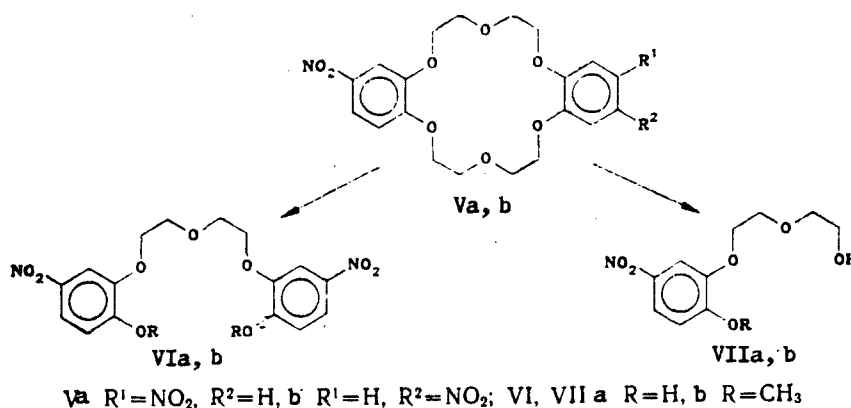


Ia, c R = NO₂, b R = OCH₃; II, III a R = CH₃, b R = C₂H₅; IVa, b R = C₂H₄OCH₃; A-E R = CH₃, C₂H₅, C₂H₄OCH₃; Ia, b, IVa n = 1, Ic IVb n = 2, A-E n = 1, 2

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However, it is difficult to envision conversion of compounds I into the dinitro derivatives III as the result of simultaneous attack of several alkoxides on one of the phenyl rings of Ia. The structures A-E are the most likely intermediates of such a conversion.*

The fact that heating the syn- or anti-dinitrodibenzo-18-crown-6 (Va, b) with Na methoxide or base in DMSO forms compounds VIa, b and VIIa, b in good yield is direct proof that this path is followed. This agrees with the data of [3].



Structures C and D should also participate in nucleophilic substitution reactions. In theory, either substitution of a diethyleneglycol residue and a nitro group to form compounds III and II or a two-step conversion of derivative D into monobenzo-crown ether IV by intramolecular cyclization of D into E with subsequent substitution of the nitro group by an alkoxide can occur.

The path of nucleophilic substitution reactions under otherwise equal conditions is known to depend on the nature of the leaving group. Thus, we used either Na methoxide or ethoxide and the Na salt of methylcellosolve as the alkoxides assuming that the nucleophilicities of the methylcellosolve and diethyleneglycol anions are comparable.

In fact, a compound of type IV could not be isolated among the products from reaction of Ia with Na methoxide. However, benzo-9-crown-3, IVa, is formed in 26% yield by reaction of Ia with the Na salt of methylcellosolve (1:2). The yield of IVa decreases on increasing the relative amount of cellosolve salt. The principal product becomes nitrobenzene II. The nature of the cation does not substantially affect the yield of IVa. Thus, IVa is formed in practically identical yields by using either the Na or Li salts of methylcellosolve.

Under analogous conditions, tetranitrodibenzo-24-crown-8 (Ic) forms benzo-12-crown-4 IVb.

The reaction described can be used preparatively since known syntheses of small-ring monobenzo-crown ethers give very low yields [4].

EXPERIMENTAL

The PMR spectra were obtained on a Tesla BS-467 (60 MHz) instrument. The IR spectra were recorded on a Specord IR-75 instrument. Mass spectra were taken on a Varian MAT-112 spectrometer. Silufol-254 plates were used for TLC. Silica gel 100/250 and acetone-hexane (1:2) eluent were used for column chromatography.

Elemental analyses for C, H, and N for IVa, b, VIa, b, and VIIa, b agreed with those calculated.

9-Nitro-10-[(2'-methoxy)ethoxy]benzo-9-crown-3 (IVa, $\text{C}_{13}\text{H}_{17}\text{O}_7\text{N}$). Compound Ia (0.54 g, 1 mmole) was dissolved in DMSO (100 ml). Sodium methoxyethoxide (0.196 g, 2 mmoles) was added. The mixture was stirred for 2 h at 20°C. Water (500 ml) was added. The solution obtained was extracted with CHCl_3 (3 \times 100 ml). The solvent was distilled off. The product was isolated by column chromatography (50 cm column). Yield 78 mg (26%). mp 56-57°C. IR spectrum (KBr): 1590 (C=C), 1510 (NO_2), 1120 cm^{-1} (C-O-C). PMR spectrum (CDCl_3): 7.12 (2H, m, Ph), 3.96 ppm (15H, m, CH_2O). Mass spectrum: 299 (M^+).

*For simplification, only probable intermediates of opening tetranitrodibenzo-18-crown-6 are given.

12-Nitro-13-[(2'-methoxy)ethoxy]benzo-12-crown-4 (IVb, C₁₅H₂₁O₈N) was obtained analogously to IVa by reaction of Ic (628 mg, 1 mmole) and Na methoxyethoxide (0.196 g, 2 mmoles). Yield 51 mg (15%). mp 61-62°C. IR spectrum (KBr): 1590 (C=C), 1520 (NO₂), 1140 cm⁻¹ (C-O-C). PMR spectrum (CDCl₃): 6.98 (2H, m, Ph), 3.92 ppm (19H, m, CH₂O). Mass spectrum: 343 (M⁺).

1,5-Bis(2'-hydroxy-5'-nitrophenoxy)-3-hydroxypentane (VIa, C₁₆H₁₆O₉N₂). A mixture of syn-dinitrodibenzo-18-crown-6 (Va, 0.45 g, 1 mmole) and NaOH (0.4 g, 10 mmoles) in DMSO (100 ml) was heated on a water bath for 4 h. It was diluted 5 times with water and neutralized with aqueous HCl until the pH was 6-7. The product precipitated, was filtered off, and was washed with water. Yield 0.3 g (78%), mp 186-187°C. IR spectrum (KBr): 3490 (OH), 1505 (NO₂), 1130 cm⁻¹ (C-O-C). PMR spectrum (CDCl₃): 8.15, 7.25 (6H, m, Ph), 4.55 ppm (8H, m, CH₂O). Mass spectrum: 380 (M⁺).

1,5-Bis(2'-methoxy-5'-nitrophenoxy)-3-hydroxypentane (VIb, C₁₈H₂₀O₉N₂) was prepared analogously to VIa by heating Va (0.45 g, 1 mmole) with Na methoxide (0.54 g, 10 mmoles). Yield 0.28 g (74%). mp 138-141°C. IR spectrum (KBr): 1510 (NO₂), 1130 cm⁻¹ (C-O-C). PMR spectrum (CDCl₃): 7.58, 6.84 (6H, m, Ph), 3.86 ppm (14H, m, CH₂O). Mass spectrum: 408 (M⁺).

5-(2'-Hydroxy-5'-nitrophenoxy)-3-hydroxypentan-1-ol (VIIa, C₁₀H₁₃O₆N) was prepared analogously to VIa by heating anti-dinitrodibenzo-18-crown-6 (Vb, 0.45 g, 1 mmole) with NaOH (0.4 g, 10 mmoles). The product was isolated by extraction of the aqueous solution with CHCl₃ (3 × 100 ml). Yield 0.25 g (64%). mp 117-118°C. IR spectrum (KBr): 3480 (OH), 1505 (NO₂), 1140 cm⁻¹ (C-O-C). PMR spectrum (CDCl₃): 7.77, 6.95 (3H, m, Ph), 3.92 ppm (8H, m, CH₂O). Mass spectrum: 243 (M⁺).

5-(2'-Methoxy-5'-nitrophenoxy)-3-hydroxypentan-1-ol (VIIb, C₁₁H₁₅O₆N) was prepared analogously to VIIa by heating Vb (0.45 g, 1 mmole) with Na methoxide (0.54 g, 10 mmoles). Yield 0.26 g (65%). mp 87-89°C. IR spectrum (KBr): 3490 (OH), 1510 (NO₂), 1080 cm⁻¹ (C-O-C). PMR spectrum (CDCl₃): 7.43, 6.71 (3H, m, Ph), 3.82 ppm (11H, m, CH₂O). Mass spectrum: 257 (M⁺).

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