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REACTION OF TETRANITRODIBENZO-18-CROWN-6 WITH SODIUM ALKOXIDES

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It is shown that the reaction of tetranitrodibenzo-18-crown-6 with sodium alkoxides in aprotic solvents at room temperature occurs with initial cleavage of the macroheterocycle and formation of an intermediate – substituted o-dinitrobenzene – whereas the reaction in protonated solvents occurs with substitution of the nitro groups. From among other derivatives of dibenzo-18-crown-6 containing azole rings linked to the benzene ring, only the furoxan-containing crown ether is cleaved under similar conditions.

We have previously shown that the reaction of tetranitrodibenzo-18-crown-6 (I) with sodium methoxide or ethoxide in the ratio 1:6 at room temperature occurs with formation of trialkoxynitrobenzene (II) [1]. Since the initial compound I has several reaction centers capable of undergoing nucleophilic substitution, the question has remained open as to which occurs first – substitution of the nitro groups or cleavage of the macroheterocycle.

From the mixture of products formed by reaction of crown ether I with sodium methoxide in the ratio 1:2, in addition to trimethoxynitrobenzene (II) it was possible to isolate o-dinitrobenzene III in 18% yield together with trace amounts of isomers IV. Compound III is readily converted under the reaction conditions to trialkoxynitrobenzene II whereas crown ether IV does not decompose under these conditions. The results obtained show conclusively that cleavage of the macrocycle occurs at the first stage of this reaction (see scheme on following page).

Chromatographic monitoring of the reaction mixture showed that even after 5 min decomposition products II and III are present in it. When the reaction mixture was treated with acid to pH 7, it was also possible to detect diethylene glycol among the reaction products. When the rate of agitation is 120 rpm, the reaction is complete after 20-25 min.

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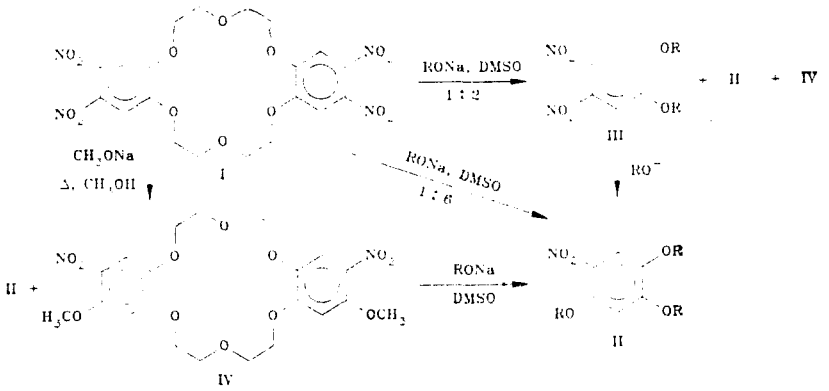
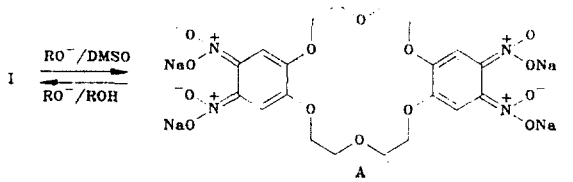


The nature and ratio of the products formed by cleavage of crown ether I with sodium methoxide in many respects depend on the nature of the solvent. Thus, at room temperature the initial substrate I does not react with sodium methoxide in methanol and dioxane. The fact that the reaction occurs extremely readily in DMSO appears to be due to the ability of DMSO to solvate Na^+ cations during the reaction, leading to a sharp increase in nucleophilicity of the "bare" RO^- anions. The validity of the above argument is confirmed by the fact that the reaction can be readily carried out in an aprotic solvent such as DMF.

When the initial crown ether I was boiled in a methanol solution of sodium methoxide, the main reaction product to be isolated was a mixture (68%) of isomeric compounds IV, which it was not possible to separate, and trace quantities of compound II (about 8%).

It should be noted that during the reaction in aprotic solvents, after addition of sodium methoxide the reaction mixture almost instantaneously develops a deep red color, while in methanol there is no change of color. According to the data of the PMR spectra (Fig. 1) the observed change in color may be due to the existence in the first case of an equilibrium mixture of compound I and sodium salts of its aci form of the type A, which are unstable in "acidic" methanol.



It is this equilibrium that possibly also accounts for the fact that in methanol the main reaction is substitution of the nitro groups while in DMSO and DMF the first stage of the reaction ivolves cleavage of the macroheterocycle.

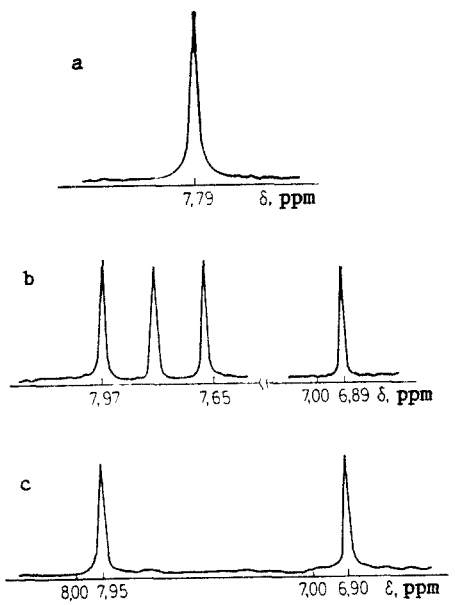


Fig. 1. PMR spectra in DMSO: a) initial; b) 10 min after adding RONa; c) 30 min after adding RONa.

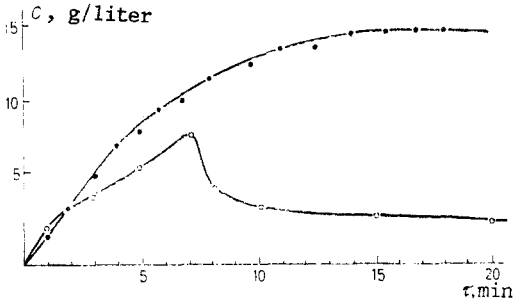
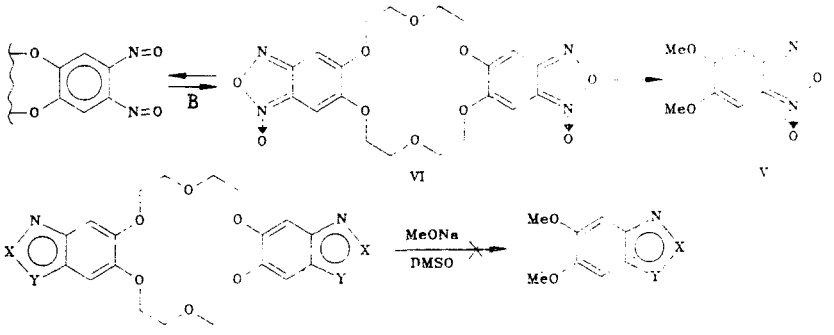


Fig. 2. Results of chromatographic monitoring of the reaction mixture: •) concentration of compound II; o) concentration of compound III.



VII–IX

VII X=CNH_2, Y=S; VIII X=CCH_3, Y=NH; IX X=NEt, Y=N

By diluting aliquots of the reaction mixture of compound I and sodium methoxide in DMSO with methanol, in which the reaction stops, we succeeded by means of GLC in following the change in the relative concentrations of reaction product II and intermediate product III with time. The nature of the curves in Fig. 2 indicates that the conversion of compound I to trimethoxynitrobenzene (II) occurs in at least two stages to give the intermediate III.

In an attempt to carry out the reaction with other derivatives of dibenzo-18-crown-6 (VI-IX) it was found that when crown ether VI was treated with sodium methoxide in DMSO at room temperature it underwent cleavage to give 5,6-dimethoxybenzofuroxan (V).

It should be noted that macroheterocycles VII-IX do not react with sodium methoxide under these conditions. The increased reactivity of compound VI is apparently due, on the one hand, to the greater electron-withdrawing effect of the furoxan ring on the macrocycle in comparison with the other azole rings in crown ethers VII-IX and, on the other hand, it is possibly due to the occurrence in compound VI of cyclic-chain tautomerism of benzofuroxan ⇆ o-dinitrosobenzene of the type B [2], which is responsible for the known similarity of the compound with tetranitrodibenzo-18-crown-6.

EXPERIMENTAL

PMR spectra were obtained on a Tesla BS 497 instrument (100 MHz); IR spectra were recorded on a Specord IR-75 instrument. Mass spectra were recorded on a Varian MAT-112 spectrometer. For TLC Silufol UV-254 plates were used in the system acetone–hexane (1:2). GLC was carried out using a Chrom-5 chromatograph, with P 2100 liquid phase deposited 5% on Inerton Super; column length 1.5 m, helium carrier gas, flame ionization detector.

Crown ethers VII-IX were obtained according to the method in [3], and compound VI according to the method in [4].

To 0.135 g (0.25 mmole) of tetranitrodibenzo-18-crown-6 in 5 ml of dry DMSO was added 0.027 g (0.5 mmole) of sodium methoxide with agitation by means of a magnetic stirrer. After 0.5 h the reaction mixture was diluted with water, pH 7 was reached by adding dilute hydrochloric acid, and the reaction products were extracted with chloroform. The pure compounds were isolated by column chromatography on silica gel. The elemental analysis data for C, H, and N correspond to that calculated.

4,5-Dimethoxy-1,2-dinitrobenzene (III, $C_8H_8N_2O_6$). Yield 18%, mp 123-124°C. IR spectrum (KBr): 1590 (C=C), 1490 cm^{-1} (NO_2). PMR spectrum ($CDCl_3$): 6.17 (2H, s, Ph), 3.01 ppm (6H, s, Me). Mass spectrum: 228 (M^+).

2,14(13)-Dimethoxy-3,13(14)-dinitrodibenzo-18-crown-6 (IV, $C_{22}H_{26}N_2O_{12}$) (mixture of syn- and anti-isomers). Yield 6%, mp 170-175°C. IR spectrum (KBr): 2860 (C–C, 1585 (C=C), 1490 (NO_2), 1110 cm^{-1} (C–O–C). PMR spectrum (DMSO-D_6): 7.70, 7.10 (4H, s, Ph), 3.90 ppm (22H, m, CH_2O). Mass spectrum: 510 (M^+).

5,6-Dimethoxybenzofuroxan (V, $C_8H_8N_2O_4$). To 0.476 g (1 mmole) of compound VI in 200 ml of dry DMSO was added 0.324 g (6 mmole) of sodium methoxide with agitation. After 2 h the reaction mixture was diluted with water, pH 7 was reached by adding dilute hydrochloric acid, and the reaction products were extracted with chloroform. Benzofuroxan V was isolated by column chromatography on silica gel. Yield 70%, mp 150-152°C. IR spectrum (KBr): 3060 (=CH), 1620 (C=C), 1475 cm^{-1} (N–O). PMR spectrum (CD_3COCD_3): 7.08 (2H, s, =CH), 4.00 ppm (6H, s, CH_3O). Mass spectrum: 196 (M^+).

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CHIROPTICAL PROPERTIES OF THE NONPLANAR AMIDE CHROMOPHORE IN N-ACYLAZIRIDINES*

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The optically active 1-acyl-substituted (1R,2R)-2-methyl- and (1R,2S)-2-methoxycarbonylaziridines were synthesized. The nonplanarity of the amide chromophore in them and its high conformational mobility, which was caused by the rotation around the N–C(O) bond, were shown on the basis of the investigation of the CD spectra and the calculations of simple models by the MNDO method. The possible correlation of the sign of the Cotton effect of the long-wave p–π* transition with the intrinsic chirality of the chromophore was studied.

The amide rotation and the inversion of the nitrogen atom in N-acylaziridines, which are rapid in the NMR time scale, were first observed in [2]. The nonplanarity of the amide group of the N-acylaziridines was established in the solid [3] and gas [4, 5] phases. A rule on the weakening of the amide conjugation with the nitrogen atom, included in the strained three-membered ring, was formulated due to the decrease of the p-character of its unshared electron pair [3-6]; it is general for the N-acyl derivatives of aziridines [6], diaziridines [7, 8], and oxaziridines [7]. The amide conjugation with the nitrogen atom of the four-membered heterocycles is weakened less significantly [9]. The nonplanarity of the amide group is also observed in β-lactams [10], crystalline peptides [11], and the rigid bi- and tricyclic structures, which are intensively studied by chiroptical methods [10, 12, 13].

*Communication 64 in the series "Asymmetric Nitrogen," for Communication 63, see [1].

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