Chemistry of Heterocyclic Compounds, Vol. 36, No. 12, 2000

NITRATION OF BENZO CROWN ETHERS WITH POTASSIUM NITRATE IN POLYPHOSPHORIC ACID

A. D. Grebenyuk, S. A. Andreev, I. A. Stempnevskaya, M. G. Levkovich, and A. K. Tashmukhamedova

A general method for the nitration of benzo crown ethers with potassium nitrate in polyphosphoric acid has been developed. Mono- and dinitro derivatives of benzo-12-crown-4, benzo-15-crown-5, dibenzo-18-crown-6, and dibenzo-24-crown-8 have been prepared. The role of complex formation in the regioselective tendency for the nitration of dibenzo-18-crown-6 has been demonstrated.

Keywords: benzo crown ethers, potassium nitrate, polyphosphoric acid, nitration.

Study of electrophilic substitution in benzo crown ethers has shown that they belong to a specific class of aromatic compounds, the reactivity of which depends on the size of the macrocycle and its conformation under the reaction conditions. The orientation on introduction of one or two substituents also has characteristics which are determined by the combination of steric and electronic factors [1].

Polyphosphoric acid (PPA) is an excellent catalyst, solvent, and reagent for the alkylation and acylation of benzo crown ethers [1-3], and it has been discovered that PPA converts inorganic salts into active electrophiles in reactions with aromatic compounds [4]. We have successfully extended these reactions to benzo crown ethers [5]. Carboxylic acid salts in PPA became acylating agents [6]. The nitration of dibenzo-18-crown-6 (DB18C6) to mixtures of 4',4"- and 4',5"-dinitro-DB18C6 with different concentrations of nitric acid in chloroform and acetic acid has been described [7-9]. In the presence of rare earth, scandium, yttrium, and aluminum nitrates, which form complexes with DB18C6, nitration with 63% nitric acid was successfully carried out selectively, depending on the nature of the metal and the solvent, to give mononitro-DB18C6, and the high melting or low melting isomer of dinitro-DB18C6 [10-12]. Nitration of dibenzo-24-crown-8 (DB24C8) was reported in a review [13] but the melting point of the product was not given. The nitration of some monobenzo crown ethers has also been described. For example, 4'-nitro-B18C6, 4'-nitro-B15C5, and 4',5'-dinitro-B15C5 respectively were obtained from benzo-18-crown-6 (B18C6) and benzo-15-crown-5 (B15C5) with 76% HNO_3 in glacial acetic acid [14]. Mononitro derivatives of B18C6 and B15C5 were synthesized using 58% HNO_3 in acetonitrile [15]. Data on the nitration of benzo-12-crown-4 (B12C4) have been given, but only the 4'-nitro derivative was isolated and purified [16].

The nitration of benzo crown ethers with potassium nitrate in PPA proposed by us is a general method for preparing nitro derivatives of mono- and dibenzo crown ethers. In contrast to aromatic compounds [4] benzo crown ethers are nitrated much easily with self-heating to give mono- and dinitro products. The 4',4"- and 4',5"-isomers were formed from DB18C6 and DB24C8, the 4',5'-dinitro compounds from B15C5 and B12C4.

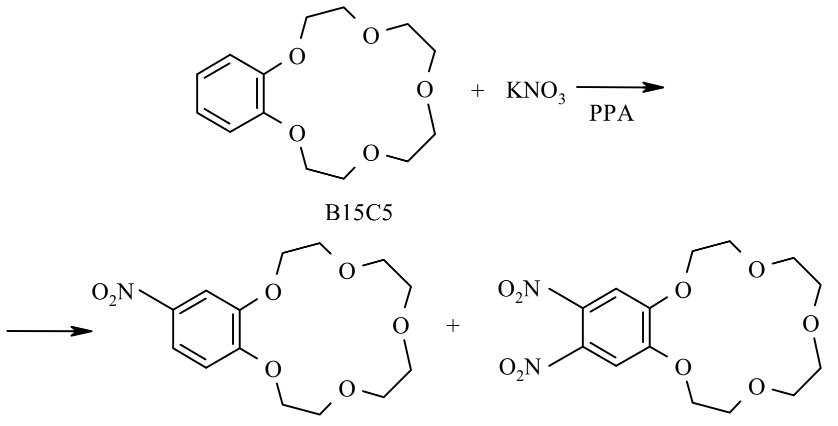
Nitration was carried out with a 20-fold excess (w/w) of PPA over crown ether. The course of the reaction was monitored by TLC. Samples were taken every 5 or 10 minutes during the experiment to provide a complete picture of the course of the reaction. The time when the starting material disappeared from the reaction mixture

---

M. Ulugbek Tashkent State University, Tashkent 700095, Uzbekistan; e-mail: root@tsu.silk.org. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 12, 1688-1696, December, 2000. Original article submitted April 22, 1999; Revision submitted March 26, 2000.

and the time when the mononitro product was converted into the dinitro product were determined. The structures of the compounds obtained were confirmed from IR and ^{1}H NMR spectra.

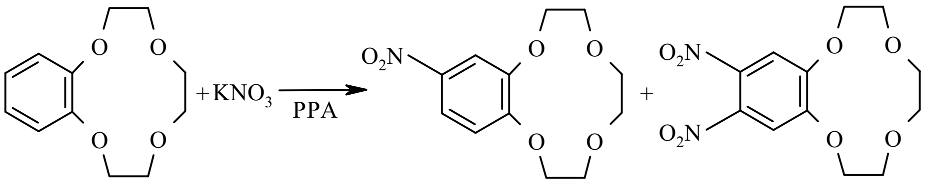
Nitration of B15C5 with potassium nitrate in PPA gave both the mono- (**1**) and dinitro (**2**) derivatives:



B15C5

1 **2**

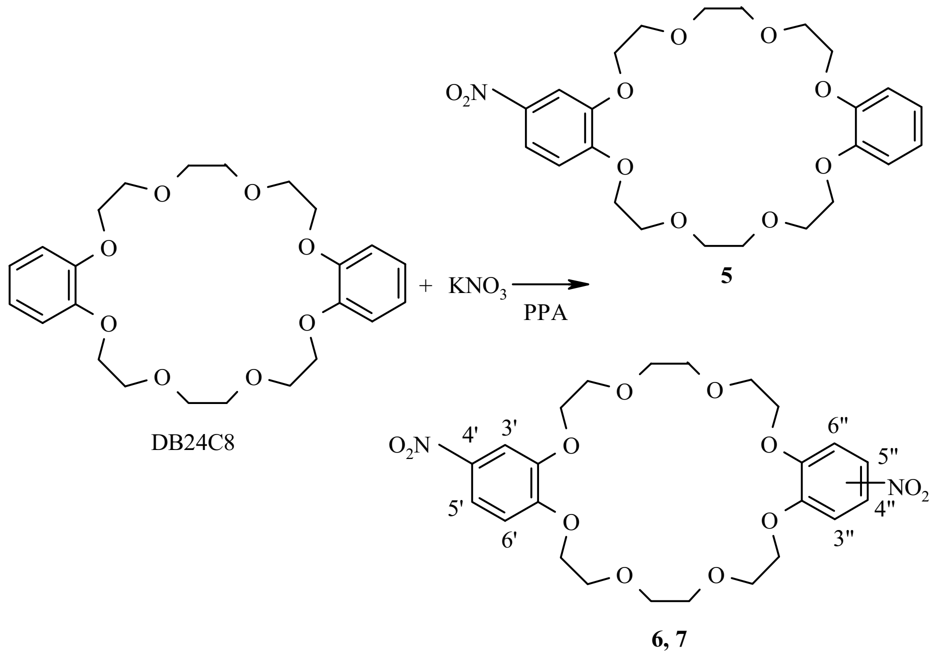
With 1:1 and 1:1.25 molar ratios of B15C5 : KNO$_3$ the basic product was the dinitro derivative **2**; the small amount of the mononitro compound **1** was successfully isolated from its mixture with B15C5 after isolation of compound **2**. With a 2-2.5 molar excess of the nitrating agent an exothermic reaction occurred very rapidly and product **2** was formed in 63% yield. The characteristics of compounds **1** and **2** (mp, ^{1}H NMR spectra) agreed with those cited in the literature [14, 15]. The ether B12C4 appeared to be more reactive than B15C5. When B12C4 and B15C5 were nitrated simultaneously (molar ratio B12C4 : B15C5 : KNO$_3$ 1:1:1) a sample taken from the reaction mixture after 15 min showed that B12C4 was absent. Both mono- (**3**) and dinitro-B12C4 (**4**) were formed in the first minutes with molar ratios B12C4 : KNO$_3$ of 1:1 or 1:1.25.



B12C4 **3** **4**

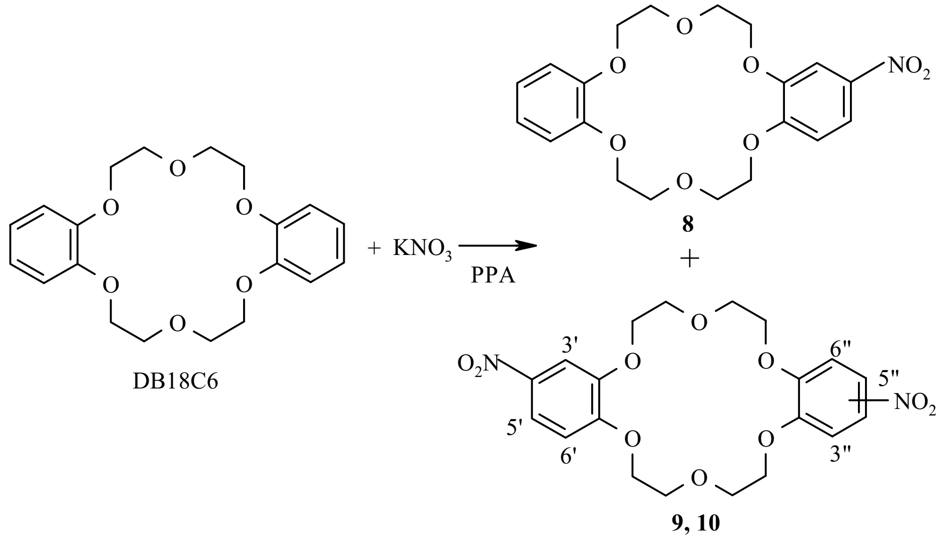
With an excess of potassium nitrate the reaction went very fast to give a 55% yield of compound **4**. With an excess of the substrate (B12C4 : KNO$_3$ 2:1) the basic product was again the dinitro derivative **4**, but the mononitro product **3** was isolated in small yield (~ 5%). In the IR spectrum of compound the symmetric and antisymmetric vibrations of the two nitro groups appear as very intense bands at 1358, 1338, and a doublet centered at 1530 cm^{-1}. This is evidently connected with displacement of the nitro groups out of the plane of the benzene ring which was confirmed by our calculation of the molecular shape by the MNDO method. The decreased conjugation shifts the absorption bands to the higher frequency region [17]. The ^{1}H NMR spectrum has a singlet at 7.41 ppm corresponding to the aromatic protons in positions 3' and 6'.

In the first minutes of the nitration of DB24C8 mono- (**5**) and dinitro-DB24C8 (**6, 7**) are formed:



An attempt to stop the reaction at the stage of formation of compound **5** was not successful. A sample was obtained [15] by nitration of DB24C8 with nitric acid and was described previously [18]. According to ^{1}H NMR spectroscopic results the principal product is a mixture of the 4',4"- and 4',5"-isomers **6** and **7**, separation of which was unsuccessful.

Nitration of DB18C6 with 2 and 2.5-fold excesses of potassium nitrate gave a mixture of 4'-nitro-DB18C6 (**8**) and 4',4"- and 4',5"-dinitro-DB18C6 (**9** and **10**). The structures of compounds **9** and **10** were established by ^{1}H NMR spectroscopy (see below).



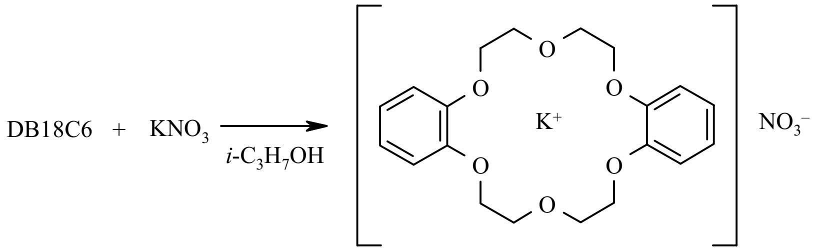
The mixture of isomers **9** and **10** was separated by fractional crystallization [7, 8]. The pure isomer (TLC, ^{1}H NMR spectrum) with mp 242.5-244.5°C was isolated in 30% yield. The principal reaction product (yield ~60%), as in a previous report [8], was the isomer with 198-201°C. Purification from a small amount of the higher melting product (according to ^{1}H NMR spectroscopic data) was not successful. The mononitro compound **8**, which was present in the final product as an impurity, was determined by TLC in the mother liquor. Pure **8**, obtained by the reaction of the complex DB18C6·KNO$_3$ with PPA (see below) was used as the standard.

The question of whether the low melting isomer had structure **9** or **10** had not yet been settled unambiguously. The lower melting isomer had been ascribed [7] the structure 4',5"-dinitro-DB18C6 or the *cis* isomer **10** and the higher melting isomer the structure 4',4"-dinitro-DB18C6 or *trans* isomer **9** (by analogy with geometric isomers). In our view this analogy is impossible because these are typical structures and not geometric isomers.

The low melting 4',4"-isomers, in particular the diacetyl derivative **11** [6] are the predominant products of the acylation of DB18C6 with potassium carboxylates in PPA. The structure of the high melting 4',5"-diacetyl-DB18C6 (**12**) was determined by an counter synthesis [2]. The direction of the process was explained by the pacifying effect of the acyl group on position 5" of the unsubstituted benzene ring in the intermediate monoacetyl-DB18C6 by the "transannular transmission" effect [20, 21]. This effect is aided by the conformation of the macrocycle with spatially close oxygen atoms which is fixed by coordination with the potassium cation. We believe that this is the reason for the predominant formation of the low melting dinitro isomer in the nitration of DB18C6 with potassium nitrate in PPA.

The ^{1}H NMR spectra of the diacetyl and dinitro derivatives of DB18C6 previously obtained with Varian XL-100, XL-200, and Tesla BS-567 spectrometers did not permit the differentiation of the 4',4"- and 4',5"-isomers. In the present work in the ^{1}H NMR spectra of these derivatives, obtained with a Unity-400+ spectrometer (Table 1), the signals of the pairs of protons 5'-H,5"-H (4',4"-isomer) and 5'-H,4"-H (4',5"-isomer) are doublets with different chemical shifts. The positions of the doublet signal of the 3'-H,3"-H protons (4',4"-isomer) also differs from the position of the 3'-H,6"-H protons (4',5"-isomer). The signals of the 4',5"-isomers are shifted to weak field in comparison with the corresponding signals of the 4',4"-isomers. Moreover, a difference in the chemical shifts of the pairs of protons 6'-H,6"-H (4',4"-isomer) and 6'-H,3"-H (4',5"-isomer) was observed. The high melting isomer of dinitro-DB18C6 was similar in the shift of its signals to the high melting diacetyl derivative of DB18C6 which, as mentioned above, was shown to be the 4',5"-isomer **12** by counter synthesis. On the basis of this discussion the structure of the 4',5"-isomer **10** is logically ascribed to the dinitro-DB18C6 melting at 242.5-244.5°C. The sample of dinitro-DB18C6 with mp 198-201°C is a mixture of the 4',4"- and 4',5"-isomers, with the former predominating, according to the ^{1}H NMR spectrum. So acylation [6] and nitration of DB18C6 with the corresponding potassium salts in PPA occurs with a regional preference. Acylation is the more selective process, only the low melting 4',4"-isomer **11** being formed, while the more vigorous nitration occurs less selectively to give a mixture of isomers in which the low melting 4',4"-isomer **9** predominates.

To clarify the influence of coordination on the nitration process we prepared the complexes of potassium nitrate with DB18C6 and its mononitro derivative **8** and studied their behavior in PPA. We obtained the complex of DB18C6 with KNO_3 (**13**) by a method which included heating the components in propanol-2.



13

Complex **13** was dissolved in a 20-fold excess of PPA; an energetic reaction was observed with the formation of the mononitro product **8**, the structure of which was confirmed by mass and ^{1}H NMR spectral data. Thus the introduction of the potassium cation either does not pacify the benzene ring or the pacification is compensated by sharply increased activity of the NO_3^- anion in the crown-separated electron pair from which the nitrating agents is formed.

$$\mathbf{13} \xrightarrow{\text{PPA}} \mathbf{8}$$

TABLE 1. ^{1}H NMR Spectra of the 4',4"- and 4',5"-Isomers of the Dinitro- and Diacetyl Derivatives of DB18C6, δ, ppm, coupling constant (J), Hz

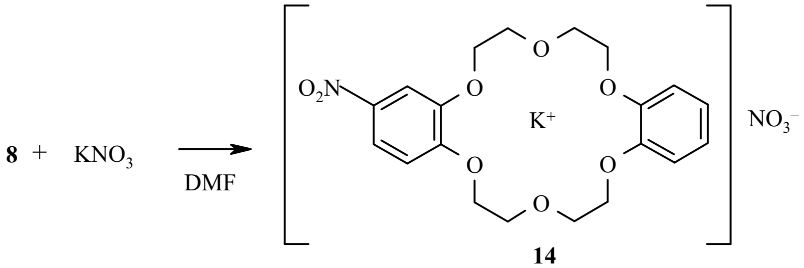
Compound	5'-, 5"-H/5'-, 4"-H 2H, dd	3'-, 3"-H/3'-, 6"-H 2H, d	6'-, 6"-H/6'-, 3"-H 2H, d	4_{α}-OCH$_2$, 8H, m	4_{β}-OCH$_2$, 8H, m
9[*]	7.820 $J_1 = 8.9; J_2 = 2.7$	7.643 $J_2 = 2.6$	6.794 $J_1 = 9.0$	4.169	3.970
10	7.823 $J_1 = 8.9; J_2 = 2.7$	7.640 $J_2 = 2.6$	6.799 $J_1 = 8.9$	4.170	3.970-3.959
11	7.468 $J_1 = 8.3; J_2 = 1.95$	7.413 $J_2 = 1.95$	6.769 $J_1 = 8.42$	4.176-4.124	3.990-3.920
12	7.477 $J_1 = 8.4; J_2 = 2.0$	7.414 $J_2 = 2.0$	6.770 $J_1 = 8.4$	4.176-4.134	3.996-3.930

---

[*] Obtained by subtracting the signals of the protons of compound **10** from the spectrum of the mixture of compounds **9** and **10**.

The process described permits the formation of the 4'-nitro derivative **8**, whereas all the other cases in which a mixture of the crown ether and KNO_3 was used gave simultaneously mononitro-DB18C6 with a considerable quantity of dinitro-DB18C6.

The complex of the nitrocompound **8** with KNO_3 (**14**) was obtained by boiling the reagents in DMF [22].

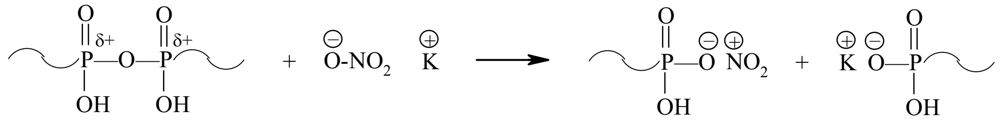


14

When this complex was dissolved in PPA an exothermic reaction also occurred to give 4',4"-dinitro-DB18C6, with mp 217-219°C, close to the literature melting point for the low melting isomer **9**.

$$\mathbf{11} \xrightarrow{\text{PPA}} \mathbf{8}$$

The results of these experiments confirm that coordination with the potassium cation is responsible for the regioselectivity of the nitration. Successful nitration via the complex with KNO_3 clearly showed that the nitrating agent is formed from the nitrate anion. We propose that the formation of the nitronium cation from NO_3^- occurs as a result of attack by the positively charged phosphorus atom of PPA on this anion. The ionized mixed anhydride of nitric and polyphosphoric acids formed is simultaneously a carrier of the nitronium cation and an acceptor of the proton displaced from the benzene ring, which role is played by the polyphosphate anion.



Despite their structural similarity, the benzo crown ethers studied differ markedly in the mobility of the hydrogen in the benzene rings. A characteristic of the benzo crown ethers with potassium nitrate in PPA is the introduction of a second nitro group early in the reaction when a large excess of the crown ether starting material is present. This indicates the greater reactivity of the mononitro benzo crown ethers in comparison with the unsubstituted compounds. The analogous phenomenon observed in the nitration of dibenzodioxin was explained starting from the cation-radical mechanism for the nitration of active aromatic compounds.

EXPERIMENTAL

^{1}H NMR spectra were recorded on BS-567, Tesla, and Unity-400+ spectrometers in $CDCl_3$ with HMDS as internal standard. IR spectra of nujol mulls were recorded on a Perkin Elmer Lambda-16 spectrometer. Mass spectra were obtained on a Kratos MS-25 RF spectrometer. Quantum-chemical calculations were carried out with the HyperHim5 program. The purity of the compounds synthesized was monitored by TLC with 2:1 hexane–acetone as eluent. Neutral aluminum oxide, activity IV, was used for column and thin-layer chromatography. Analyses were carried out with a Karl-Erba EA-1108 analyzer.

Nitration of Benzo Crown Ethers with Potassium Nitrate in PPA (General Method). A mixture of the crown ether and KNO_3 (molar ratio of crown ether: KNO_3 1:2 or 1:1.2) was ground together and added in several portions with stirring to PPA (20-fold weight excess relative to the crown ether). The reaction mixture heated to 40°C and further heating was prevented by cooling with water. At the end of the reaction (according to TLC) the reaction mass was decomposed with water and the product was extracted with chloroform. The extract was washed with water until neutral, dried, and part of the solvent was evaporated. The concentrate was passed through a layer of aluminum oxide to remove oily materials. The pale yellow residue after complete removal of the solvent was recrystallized from ethanol. The residue from the dibenzo crown ethers, after decomposition of the reaction mixture, was filtered, washed with water, dried, and purified by passing a solution in chloroform through a layer of aluminum oxide.

4'-Nitro-B15C5 (1). Yield 5%; mp 91-94°C. Lit. mp 95-95.5°C [15].

4',5'-Dinitro-B15C5 (2). Yield 60%; mp 169-170.5°C. Lit. mp 168°C [14].

4'-Nitro-B12C4 (3). Yield 5%; mp 104-105.5°C. Lit. mp 105-108°C [16].

4',5'-Dinitro-B12C4 (4). Yield 55%; mp 112.5-113.5°C. IR spectrum, ν, cm^{-1}: 1530, 1358, 1338 (NO_2), 1297 ($ArOCH_2$), 1122 (CH_2OCH_2). ^{1}H NMR spectrum, δ, ppm: 7.41 (2H, s, 3'- and 6'-H); 4.20-4.35 (4H, m, 2α-OCH_2); 3.75-3.90 (4H, m, 2β-OCH_2); 3.67 (4H, s, 2γ-OCH_2). Found, %: N 8.71. $C_{12}H_{14}N_2O_8$. Calculated, %: N 8.91.

Mixture of 4',4"- and 4',5"-Dinitro-DB24C8 (6 and 7). Yield 91%; mp 135-140.5°C. IR spectrum, ν, cm^{-1}: 1510, 1341 (NO_2), 1281 ($ArOCH_2$), 1144 (CH_2OCH_2). ^{1}H NMR spectrum, δ, ppm, J, Hz: 7.81 (2H, dd, $J_1 = 9.5$, $J_2 = 3.0$, 5'- and 4"- or 5"-H); 7.65 (2H, d, $J = 3.0$, 3'- and 3"- or 6"-H); 6.80 (2H, d, $J = 9.5$, 6'- and 6"- or 3"-H); 4.0-4.31 (8H, m, 4α-OCH_2); 3.82-4.0 (8H, m, 4β-OCH_2); 3.78 (8H, s, 4γ-OCH_2).

Mixture of 4',4"- and 4',5"-Dinitro-DB18C6 (9 and 10). Yield 97%; mp 168-191°C. The mixture was separated into isomers by boiling in methyl or ethyl cellosolve with subsequent filtration and recrystallization of the poorly soluble isomer **10**. Distillation of methyl cellosolve gave the isomer **9** with isomer **10** as impurity.

4',4"-Dinitro-DB18C6 (9) with a negligible impurity of isomer **10**. Yield 62%; mp 198-201°C. Lit. mp 200-201°C [8], 210-211°C [9], 208-213°C [7], 212-213°C [10]. ^{1}H NMR spectrum, see Table 1.

4',5"-Dinitro-DB18C6 (10). Yield 30%; mp 242-244°C. Lit. mp 247-252°C [7], 257-258°C [9], 249-251°C [12]. ^{1}H NMR spectrum, see Table 1.

Concurrent Reaction of Crown Ethers B15C5 and B12C4 with KNO_3 in PPA. Equimolar amounts of the crown ethers B15C5, B12C4, and KNO_3 were used. The mixture of B15C5 and B12C4 was dissolved in PPA (20-fold mass excess relative to the total mass of the crown ethers) at 70°C. After almost complete dissolution of the substrates the mixture was cooled to room temperature and the potassium nitrate was added with vigorous stirring. A sample was taken for TLC every five minutes. After 15 min B12C4 had completely disappeared from the mixture.

4'-Nitro-DB24C8 (5) (see also [18]). Nitric acid (*d* = 1.37, 0.04 ml, 0.53 mmol) was added to a solution of DB24C8 (0.25 g, 0.56 mmol) in acetonitrile (10 ml) cooled in ice. The mixture was stirred intensively for 32 h and left for 3 days at room temperature. The reaction mixture was poured into ice water (50 ml), the precipitate of product **5** was filtered off, washed with water until neutral, and purified by column chromatography (eluent 2:1 hexane–acetone). Yield 0.09 g (33%); mp 119-120°C. IR spectrum, ν, cm^{-1}: 1515, 1338 (NO_2), 1281 ($ArOCH_2$), 1144 (CH_2OCH_2). ^1H NMR spectrum, δ, ppm, *J*, Hz: 7.85 (1H, dd, J_1 = 8.7, J_2 = 3.5, 5'-H); 7.70 (1H, d, *J* = 3.5, 3'-H); 6.85 (4H, s, 3"-, 4"-, 5"-, and 6"-H); 6.83 (1H, d, *J* = 8.7, 6'-H); 4.00-4.25 (8H, m, 4α-OCH_2); 3.85-4.00 (8H, m, 4β-OCH_2); 3.80 (8H, s, 4γ-OCH_2).

Complex of DB18C6 with Potassium Nitrate (13). DB18C6 (1.09 g, 3 mmol) and KNO_3 (0.61 g, 6 mmol) were ground together and the mixture was boiled for 11 h in propanol-2 (15 ml). The residue after removing the solvent was ground into a powder and extracted with hot chloroform. Crystals of complex **13** separated on cooling the chloroform solution. Yield 0.71 g (53%); mp 192-194°C. Lit. mp 195-196°C [22].

Reaction of Complex 13 with PPA. 4'-Nitro-DB18C6 (8). Finely ground complex **13** (0.59 g, 1.3 mmol) was added to PPA (11.8 g) with vigorous stirring. The reaction mixture heated to 40°C, and was kept at that temperature by cooling with water. After 40 min the reaction was stopped by the addition of ice. The precipitate was filtered off, washed with water until neutral, and dried in the air. According to TLC it consisted of compound **8** with impurities of the initial crown ether and 4',4"(5")-dinitro-DB18C6. The product was purified from the initial crown ether by column chromatography (eluent $CHCl_3$) and from dinitro-DB18C6 impurities by recrystallization from benzene. Yield: 0.44 g (84%) of 4'-nitro-DB18C6 **8**; mp 174-175°C. Lit. mp 173-177°C [12]. Found: M 405. $C_{20}H_{23}NO_8$. Calculated: M 405. ^1H NMR spectrum, δ, ppm, *J*, Hz: 7.85 (1H, dd, J_1 = 9.5, J_2 = 3.7, 5'-H); 7.64 (1H, d, *J* = 3.7, 3'-H); 6.81 (5H, s, 6'-, 3"-, 4"-, 5"-, and 6"-H); 4.05-4.37 (8H, m, 4α-OCH_2); 3.67-4.07 (8H, m, 4β-OCH_2).

Complex of 4'-Nitro-DB18C6 with Potassium Nitrate (14). Hot solutions of 4'-nitro-DB18C6 (0.185 g, 0.46 mmol) in DMF (5 ml) and KNO_3 (0.046 g, 0.46 mmol) in DMF (5 ml) were mixed and heated to boiling. After removal of the solvent in vacuum the clear yellow complex **14** was obtained (0.22 g, 94%); mp 185-188°C. Found, %: N 5.44. $C_{20}H_{23}KN_2O_{11}$. Calculated, %: N 5.53. Decomposition of complex **14** with water gave compound **8**; mp 174-175°C. A mixed melting point with a sample prepared by the reaction of PPA with complex **13** gave no depression.

Reaction of Complex 14 with PPA. 4',4"-Dinitro-DB18C6 (9). Finely ground complex **14** (0.19 g) was added to PPA (4.93 g) with vigorous stirring. The reaction mixture heated up and gained a brown color. After 30 min compound **8** was absent according to TLC data. The mass was stirred for a further 10 min and poured onto ice. The residue was filtered off, washed with water until neutral, dried in air, and dissolved in chloroform. The solution was pushed through a small layer of aluminum oxide to remove the colored impurities. After removal of the solvent, compound **9** was obtained as a light yellow powder (0.11 g, 70%); mp 217-219°C (methyl cellosolve).

REFERENCES

1. B. A. Tashmukhamedov, A. I. Gagel'gans, A. K. Tashmukhamedova, Z. Mirkhodzhaev, M. V. Zamaraeva, A. V. Shkinev, and Sh. K. Norov, *Synthesis, Membrane-active Properties, and Biological Effects of Crown Ethers* [in Russian], Fan, Tashkent (1987), 264.
2. A. K. Tashmukhamedova, I. A. Stempnevskaya, N. Zh. Saifullina, R. A. Abdullaeva, and M. T. Adylbekov, *Bioorgan. Khim.,* **4**, 806 (1978).
3. A. K. Tashmukhamedova, I. A. Stempnevskaya, N. Zh. Saifullina, and M. G. Levkovich, *Khim. Geterotsikl. Soedin.,* 1461 (1986).
4. S. Sastry and N. A. Kudav, *Indian J. Chem.,* **18B**, No. 2, 198 (1979).
5. A. D. Grebenyuk and A. K. Tashmukhamedova, *Dokl. Akad. Nauk Uzbek. Republ.,* No. 6, 32 (1994).
6. A. D. Grebenyuk, I. A. Stempnevskaya, N. J. Sayfullina, and A. K. Tashmukhamedova, *XVIII Int. Symp. Macrocylic Chemistry*, The Netherlands (1993), A-73.
7. W. M. Feigenbaum and R. N. Michel, *J. Polym. Sci. (A-1),* **9**, 817 (1971).

8. E. Shchori, J. Jagur-Grodzinski, and M. Shporer, *J. Am. Chem. Soc.,* **95**, 3842 (1973).
9. V. A. Popova, I. V. Podgornaya, I. Ya. Postovskii, and N. N. Frolova, *Khim.-Farm. Zh.,* **10**, No. 6, 66 (1976).
10. V. S. Kalishevich, D. V. Zagorevskii, A. I. Gren', and O. S. Timofeev, *Dokl. Akad. Nauk Ukr. SSR, Ser. B,* No.2, 34 (1984).
11. V. S. Kalishevich, O. S. Timofeev, N. S. Zakharov, and A. I. Gren', *Zh. Org. Khim.,* **24**, 396 (1988).
12. V. S. Kalishevich, A. I. Gren', and O. S. Timofeev, *Zh. Org. Khim.,* **29**, 179 (1993).
13. J. Bradshaw and P. E. Stott, *Tetrahedron*, **36**, 461 (1980).
14. R. Ungaro, E. El Haj, and J. Smid, *J. Am. Chem. Soc.,* **98**, 5198 (1976).
15. O. V. Ivanov, I. S. Markovich, L. I. Blokhina, S. P. Nikolaenko, M. P. Filatova, and G. V. Vasil'chenko, USSR Inventor's Certificate 1544774; *Ref. Zh. Khim.,* 14N134P (1990).
16. S. Shinkai, T. Ogawa, J. Kusano, O. Manabe, K. Kikukawa, T. Joto, and I. Matsuda, *J. Am. Chem. Soc.,* **104**, 1960 (1982).
17. L. Bellamy, *Infrared Spectra of Complex Molecules* [Russian translation], IL, Moscow (1963), 427.
18. V. T. Loktev, I. L. Mudrakovsky, A. K. Tashmukhamedova, I. A. Stempnevskaya, and I. Yu. Morozova, *J. Magn. Res. Chem.,* **28**, 176 (1990).
19. Yu. A. Simonov, A. A. Dvorkin, S. V. Mendeman, A. I. Gren', and V. S. Kalishevich, *Kristallografiya*, **33**, 878 (1988).
20. A. K. Tashmukhamedova, I. A. Stempnevskaya, and N. Zh. Saifullina, *Dokl. Akad. Nauk Uzbek. SSR.,* No. 8, 35 (1988).
21. A. K. Tashmukhamedova and I. A. Stempnevskaya, *J. Inclusion Phenomena*, **30**, No. 2, 91 (1998).
22. I. A. Alekseeva, V. A. Popova, and I. V. Podgornaya, *Zh. Obshch. Khim.,* **48**, 1630 (1978).
23. A. S. Morkovnik. *Usp. Khim.,* **57**, 254 (1988).