

SHORT
COMMUNICATIONS

Nitration Mechanism of Dibenzo-18-crown-6 with Potassium Nitrate in Polyphosphoric Acid Alkylation with Substituted Phenacyl

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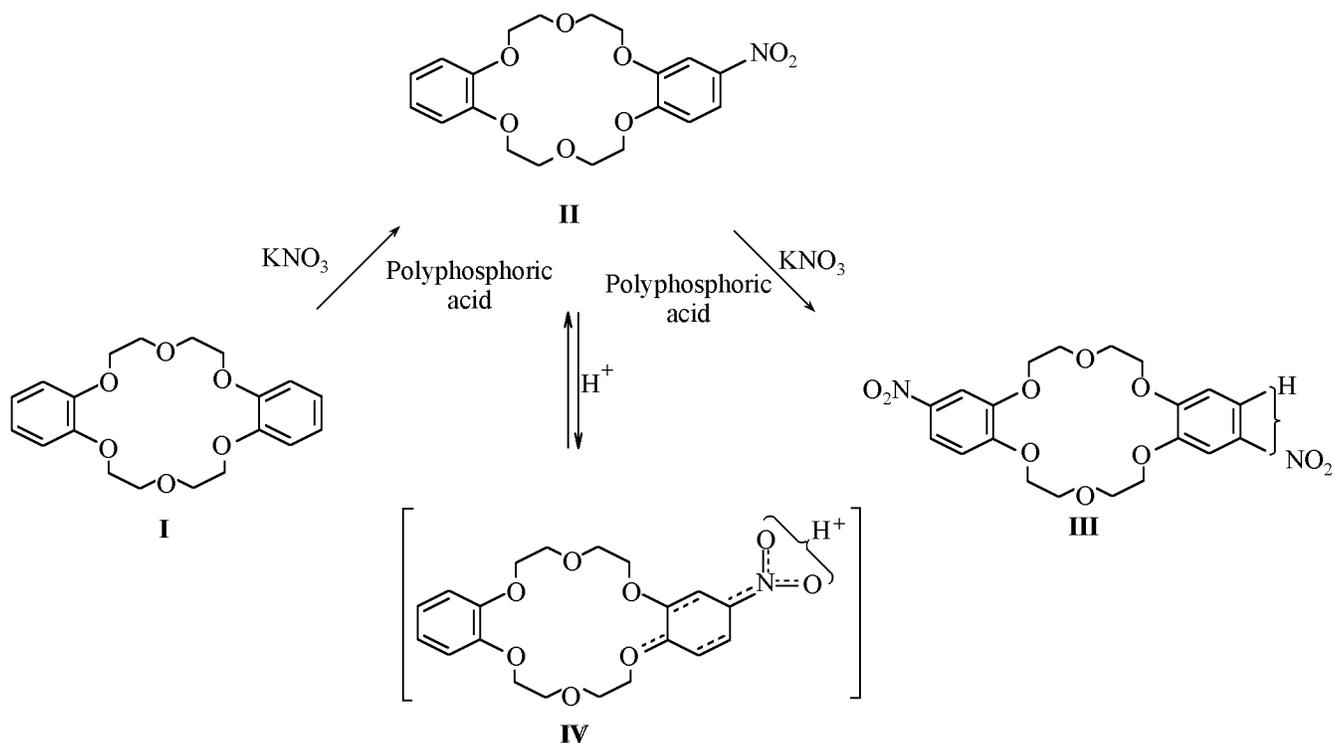
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In the course of investigation of benzo-crown ethers nitration with potassium nitrate in polyphosphoric acid we observed certain features of the reaction characteristic of the processes whose mechanism included a stage of one-electron oxidation. The exothermic process is accompanied with appearance of green color that further turns brown. In some case NO_2 evolution was observed.

In nitration of dibenzo-18-crown-6 (DB18C6) dinitro derivatives appear just at the start of reaction. This phenomenon was observed in nitration of di-

benzodioxine, a structural analog of DB18C6, and it was attributed to the higher reactivity of the cation-radical of mononitrodibenzodioxine in the limiting stage of the reaction [2].

The process of DB18C6 (I) nitration was studied by means of electronic spectroscopy. The nature and composition of the reaction product depends on the n value of the molar ratio KNO_3 -DB18C6 similarly to nitration of dibenzodioxine [3]. At n 2.5 in some time after reagents mixing appears green color that soon disappears. The analysis of the visible spectrum of the

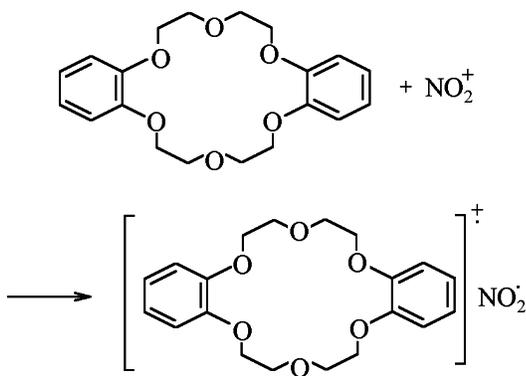


reaction mixture indicates that in this case the reaction is irreversible and results in a mixture of dinitro derivatives of DB18C6 (**III**).

At n 1.2 the green color also appears and further becomes brown. The visible spectrum contains a band of dinitro derivatives of DB18C6 **III** (λ_{\max} 440 nm), a stronger band of mononitro derivative **II** with a maximum at 430 nm, and a band at 630 nm arising presumably from one-electron transition from the π -electron system of the benzene ring in the substrate to nitronium cation that in this case operates as an oxidant.

At the above reagents ratio the electronic spectrum contains also a wide absorption band at 505 nm alongside the classical $\pi-\pi^*$ and $n-\pi^*$ bands of an aromatic ring with nitro group substituent. The same band was observed in the spectrum of mononitro DB18C6 derivative (**II**) recorded in the polyphosphoric acid. This fact indicates that in the solution in the polyphosphoric acid of mononitro-DB18C6 (**II**) exists an equilibrium between the initial substrate and a structure with quinoid-like nitro-substituted benzene ring **IV** which arises from protonation of the system. Formation of such structure was proved for the monoacetyl-DB18C6 [4].

At n the reaction mixture becomes green and thus remains for several weeks. In the electronic spectrum is observed a strong band of cation-radical of DB18C6 (**V**). The lack of bands corresponding to mono and dinitro derivatives indicates that under these conditions the cation-radical is the only reaction product as shows also the TLC analysis of reaction products obtained after quenching of the reaction mixture.



In order to prove the radical nature of the reaction product we recorded ESR spectra of the reaction mixture obtained at n 0.4. The spectra contain a

signal with poorly resolved superfine structure (g 2.0094). The position of the signal and its superfine structure remain unchanged for weeks.

Cation-radical of DB18C6 (**V**) also forms at treating compounds of DB18C6 in acetonitrile with a solution of SbCl_5 in this solvent. In 5 min after mixing the reagents the reaction mixture gets dark-green, and then precipitate dark crystals of hexachloroantimonate of DB18C6 cation-radical. The study of this crystalline product by ESR showed that it is 100% radical species. However no well-resolved superfine structure was observed in the ESR spectrum of the compound.

A fundamental possibility of formation of cation-radicals from benzo-crown ethers in solution was revealed in the ESR study of photoinduced one-electron transfer from substrates to dichlorocycloquinone [5]. However we have not found published examples on cation-radicals formation from benzo-crown ethers as intermediates in electrophilic substitution reactions.

The formation of dinitro derivative of DB18C6 (**III**) since the beginning of the reaction disregarding the deficit of the nitrating agent evidences a competition for NO_2 -radical between the cation-radical of DB18C6 (**V**) and cation-radical of mononitro-DB18C6, and the latter wins the competition due its higher reactivity.

Hexachloroantimonate of cation-radical of DB18C6. A solution of 0.6 g (1.67 mmol) of dibenzo-18-crown-6 in 14 ml of dry acetonitrile preliminary distilled on P_2O_5 was treated with 1.2 g (4.17 mmol) of SbCl_5 in 14 ml of acetonitrile. The precipitate was filtered off, washed with dry acetonitrile, and dried, Yield 0.8 g (69%).

Electron absorption spectra were registered on SF4A device. ESR spectra were measured of spectrometer Bruker ER 200D-SRC. Polyphosphoric acid was prepared along procedure [6]. SbCl_5 was obtained as in [7].

Spectroscopic measurements were performed on solutions prepared as follows: In 2 g of solution of 0.05 g (0.13 mmol) of DB18C6 in polyphosphoric acid was dissolved an appropriate weight of potassium nitrate: 0.035 g (n 2.5), 0.017 g (n 1.2), and 0.006 g (n 0.4).

ESR spectra of reaction mixtures were recorded in thin capillaries. The ESR spectrum of hexachloroantimonate of cation-radical of DB18C6 was measured both in crystalline state and in acetonitrile solution.

REFERENCES

1. Grebenyuk, A.D. and Tashmukhamedova, A.K., *Dokl. Akad. Nauk RUz.*, 1994, no. 6, pp. 32–34.
2. Morkovnik, A.S., *Usp. Khim.*, 1988, vol. 57, no. 2, pp. 254–262.
3. Morkovnik, A.S., Belinskii, E.Yu., Dobaeva, N.M., and Okhlobystin, O.Yu., *Zh. Org. Khim.*, 1982, vol. 18, no. 2, pp. 378–385.
4. Tashmukhamedova, A.K. and Stempnevskaya, I.A., *J. of Inclusion Phenomena and Molecular Recognition in Chem.*, 1998, vol. 30, no. 2, pp. 91–98.
5. Davies, A.G. and Ng K.M., *Austral. J. Chem.*, 1995, vol. 48, pp. 167–173.
6. Gardner, P.D., *J. Am. Chem. Soc.*, 1954, vol. 76, no. 18, pp. 4550–4552.
7. Karyakin, Yu.V. and Angelov, I.I., *Chistye khimicheskie reaktivy* (Pure Chemicals), Moscow: Khimiya, 1955.