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LETTERS TO THE EDITOR

AN ORIGINAL APPROACH TO THE AMINATION OF CROWN ETHERS

A. S. Lyakhovnenko[1], A. V. Aksenov[1]*, and M. M. Kugutov[1]

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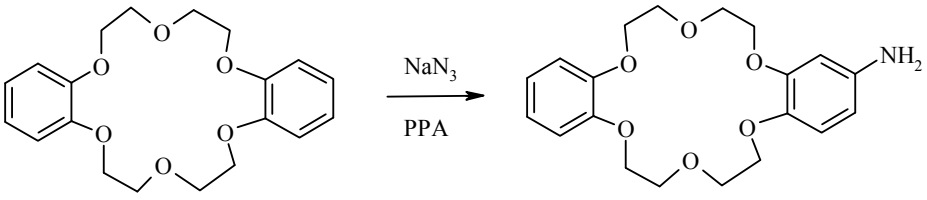
Crown ethers hold considerable importance in the study of supramolecular chemistry. Special interest is found in methods to functionalize these compounds, for example, the techniques described by Jeong and Cho [1]. Early we have developed a method for the direct amination of perimidines in PPA [2, 3]. In the present work, we report the electrophilic amination of dibenzo[18]crown-6 ether **1** by this reagent system. Heating ether **1** (0.36 g, 1 mmol) and sodium azide (0.072 g, 1.1 mmol) in PPA (2-3 g) at 90-100°C for 3 h with monitoring by thin-layer chromatography leads to 4'-aminodibenzo[18]crown-6 (**2**) in 61% yield. The sample of PPA containing 87% P_2O_5 was prepared according to Uhlig [4].



1 **2**

Diamination products, which could not be isolated as pure products, are probably formed as side products.

The ^1H and ^{13}C NMR spectra were taken on a JNM-ECX400 spectrometer at 400 and 100 MHz, respectively, in $CDCl_3$ with TMS as the internal standard. The reaction course and purity of the products were monitored on Silufol UV-254 plates using 1:1 ethyl acetate–ethanol as the eluent.

The reaction mixture was treated with 50 ml water and brought to pH 8-9 by adding ammonium hydroxide. The precipitate formed was filtered off. The mother liquor was extracted with three 50-ml portions of methylene chloride. The solvent was evaporated and the residue was combined with the precipitate. The crude product was recrystallized from butanol to give 0.226 g (61%) ether **2**; mp 158-163°C (butanol)

* To whom correspondence should be addressed, e-mail: k-biochem-org@stavsu.ru.

[1]Stavropol State University, Stavropol 355009, Russia.

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(mp 159-163°C [1]). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 3.42 (2H, br. s, NH_2), 4.02 (8H, m, OCH_2); 4.10 (4H, m, OCH_2); 4.16 (4H, m, OCH_2); 6.21 (1H, dd, *J* = 8.4, *J* = 2.6, ArH); 6.29 (1H, d, *J* = 2.6, ArH); 6.88 (4H, m, ArH); 6.70 (1H, d, *J* = 8.4, ArH). ^{13}C NMR spectrum, δ, ppm: 68.8, 69.1, 70.1, 70.2, 70.5, 102.7, 107.5, 113.6, 113.8, 121.5, 121.6, 148.8. Found, %: C 64.14; H 6.67; N 3.69. $C_{20}H_{25}NO_6$. Calculated, %: C 63.99; H 6.71; N 3.73.

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