SIMPLE SYNTHESIS OF UNSYMMETRICAL DIBENZO CROWN ETHERS

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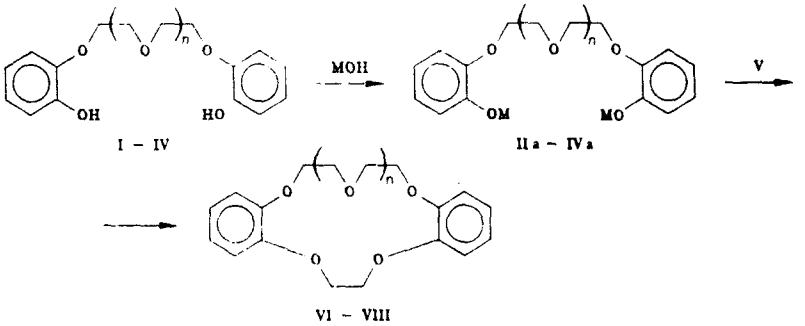
UDC 547.898.057

Until now the only starting compound for the synthesis of the unsymmetrical crown ethers dibenzo-15-crown-5 (VI) and [2,4]-dibenzo-18-crown-6 (VII) has been 1,2-bis-(2-hydroxyphenoxy)ethane (I) [1, 2]. But the complexity of the synthesis of (I) has made these crown ethers difficultly accessible.

We have developed a simple and convenient synthesis of crown ethers (VI-VIII); it is based on the reaction of bis-ethers of di-, tri-, and tetraethylene glycols (II-IV) [as the phenolates (IIa-IVa)] (which are more available than (I) [3]), with 1,2-dibromoethane.

In the presence of crown ethers in a two-phase system (organic solvent–aqueous alkali), when (V) or its homologs are used dehydrobromination is the predominant reaction [4]. When compounds (II-IV) were cyclized to crown ethers (VI-VIII) in the presence of aqueous alkali the results of [4] were confirmed. To avoid the elimination reaction, we carried out the synthesis of (IIa-IVa) and the cyclization with dibromide (V) in nonaqueous medium. In our opinion this route can be recommended for the synthesis of a wide variety of unsymmetrical dibenzocrown ethers. By this same method we obtained [2,5]-dibenzo-21-crown-7 (VIII) for the first time.



IIa M=Na, IIIa, IVa M=K; I $n=0$, II, VI $n=1$, III, VII $n=2$, IV, VIII $n=3$

Synthesis of Crown Ethers (VI-VIII). A mixture of 0.1 mole of (II-IV) and 0.2 mole of sodium (or potassium) hydroxide in 40% aqueous solution was boiled with stirring in 300 ml of isoamyl alcohol, using a water trap, until complete removal of water. Dibromide (V), 0.1 mole, was added, and the mixture was boiled for 10 h, cooled, and filtered. The filtrate was evaporated to dryness at reduced pressure. The residue was dissolved in 50 ml of 5 M sodium hydroxide, and the hot solution was extracted with 1:3 benzene–heptane (3 × 100 ml). The extractant was removed and the residue was recrystallized from heptane. **Dibenzo-15-crown-5 (VI).** Mp 113.5-114°C. PMR spectrum ($CDCl_3$): 3.6-4.1 (m, 8H, CH_2O), 4.38 (s, 4H, CH_2O), 6.93 ppm (s, 8H, C_6H_4). Yield 50%. **[2,4-Dibenzo-18-crown-6 (VII).** Mp 117-118°C. PMR spectrum ($CDCl_3$): 3.60-4.10 (m, 12H, CH_2O), 4.35 (s, 4H, CH_2O), 6.93 ppm (s, 8H, C_6H_4). Yield 42%. **[2,5]-Dibenzo-21-crown-7 (VIII).** Mp 50-51°C. PMR spectrum ($CDCl_3$): 3.60-4.10 (m, 16H, CH_2O), 4.38 (s, 4H, CH_2O), 6.93 ppm (s, 8H, C_6H_4). Yield 33%.

Elemental compositoin of (VI-VIII) agreed with the calculated values.

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Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 12, pp. 1697-1698, December, 1990. Original article submitted April 12, 1990.

0009-3122/90/2612-1414$12.50

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ALTERNATIVE REACTIVITY OF BENZIMIDAZOLIUM YLIDS

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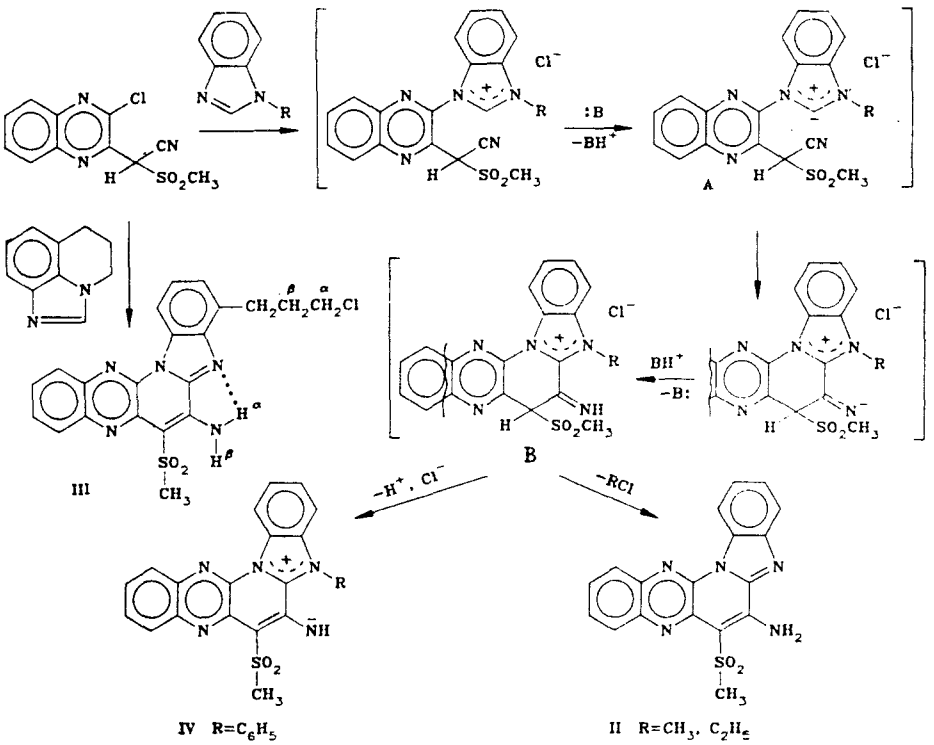
UDC 547.863.13:239.2.785.5

The reaction of α-sulfonyl[2-(3-chloro)quinoxalylacetonitrile (I) with benzimidazole leads ultimately to derivatives of 6-amino-7-sulfonylbenzimidazo[1',2':1,6]pyrido[2,3-b]quinoxaline [1]. A similar reaction with 1-substituted benzimidazoles has so far not been studied. We have found that the course of that reaction is determined by the nature of the substituent on the nitrogen of the benzimidazole nucleus.

In our opinion, the reaction proceeds by the following scheme:



Quaternization of the benzimidazole nucleus facilitates deprotonation of position 2 to a salt by the action of excess benzimidazole in the reaction medium to form ylid (A). Nucleophilic attack by the nitrile carbanion gives the cyclic intermediate B, the subsequent fate of which depends on the nature of the substituent on nitrogen. In the case of 1-alkylbenzimidazoles

T. G. Shevchenko State University, Kiev. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 12, pp. 1698-1699, December, 1990. Original article submitted April 3, 1990.