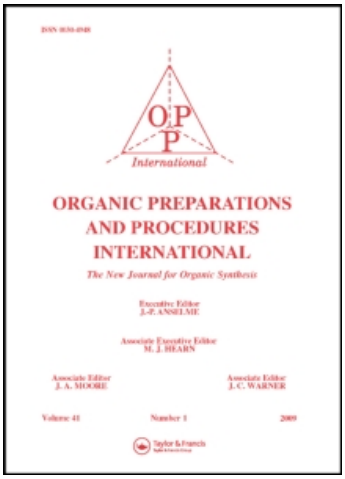

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AN IMPROVED SYNTHESIS OF 4',5'-DIAMINOBENZO-15-CROWN-5

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AN IMPROVED SYNTHESIS OF 4',5'-DIAMINOBENZO-15-CROWN-5

Submitted by (10/16/89) Yasar Gök

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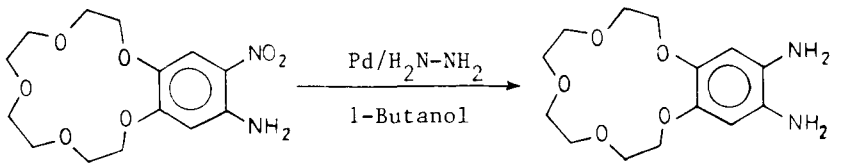
Crown ether compounds first synthesized by Pedersen,[1] have been the focus of great deal of interest for the past twenty-five years because of the chemical and biological applications of their ion-binding capability, solvation and transport effects.[2] The molecular structure of the complexes has been studied by infrared, ^{1}H and ^{13}C NMR spectroscopy and X-ray crystallography.[3] Recently, crown ethers have also been employed to construct new compounds with extraordinary properties; ion channels were formed by the superposition of crown ether macrocycles in tetrakis(crown ether) substituted phthalocyanines;[4] bis(crown ether) Schiff-base,[5] quinoxaline,[6] and 2',2'-azobis(15-

crown-5)-eno[g]quinoxaline[7] ligands containing recognition sites for alkali and transition metal guest cations have been reported.

Although 4',5'-diaminobenzo(15-crown-5) is briefly mentioned in the literature,[8] no procedure nor physical properties were reported. We now describe its synthesis by reduction of 5'-amino-4'-nitrobenzo(15-crown-5) in hydrazine.[8]



ANB DAB

EXPERIMENTAL SECTION

^{1}H NMR and IR spectra were recorded on a Bruker 200 MHz spectrophotometer and on a Perkin-Elmer 177 spectrophotometer, respectively. The UV-visible spectra were measured on a GBC 911 spectrophotometer (1 cm quartz cells). Elemental analyses were performed on a Perkin-Elmer 240C elemental analyzer.

Preparation of 4',5'-Diaminobenzo(15-crown-5).- To a solution of aminonitrobenzo(15-crown-5) (3.6 g, 11.07 mmol)[8] in 1-butanol (50 ml) heated to 120°, was added 0.750 g of Pd/C (10%); then 20 ml of 100% hydrazine hydrate was added dropwise. The mixture was stirred and refluxed for 50 min. After having been cooled to room temperature, the mixture was filtered and then the filtrate cooled at -5° for 4 hrs. The crude white crystalline solid was collected, washed with cold 1-butanol and dry diethyl ether. Then, the crude product was recrystallized from 1-butanol (30 ml) and dried in vacuo to yield 2.2 g (90%) of platelets, mp. 128°. IR (KBr pellets): 3350-3280 (NH_2), 1640 (NH_2), 3020, 2880, 1250-1230, 1150-1120 cm^{-1}; UV-vis ($CHCl_3$): λ max (ε): 340 nm (447), 285 nm (1490), 256 nm (31200), 215 nm (1266); NMR ($CDCl_3$): δ 3.10-3.45 (s, broad, 4H), 3.60-4.05 (m, 16H), 6.70 (s, 2H).

Anal. Calcd for $C_{14}H_{22}N_2O_5$: C, 56.37; H, 7.38; N, 9.39. Found: C, 56,16; H, 7.18; N, 9.13

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PREPARATION OF AN o-SUBSTITUTED BENZAMIDINE BY THE PINNER METHOD. A LITERATURE CLARIFICATION

Submitted by (02/05/90)

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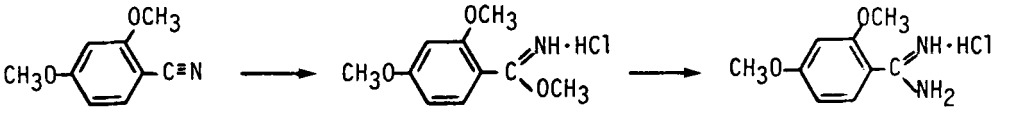
The Pinner amidine synthesis[1] consisting of formation of imino esters (imidates) by the addition of anhydrous hydrogen chloride to a solution of the appropriate nitriles in an alcohol and followed by treatment with ammonia (or primary or secondary amines), is the most practical and widely used method for the preparation of a variety of amidines. However, it has been repeatedly stated[2] that o-substituted benzamidines cannot be prepared by this method and they can only be obtained[3] by O-alkylation of their imidate salts. Nevertheless, reports on the synthesis of 2-hydroxy- and 2,4-dihydroxybenzamidines in low yields by the Pinner process have been reported.[4]



1 2 3

2,4-Dimethoxybenzamidinium chloride (3) which was required as an intermediate for another study,[5] has not been reported although the free amidine was mentioned in a biological study, albeit without any information of its synthesis.[6] In spite of the fact that other approaches were suggested for the synthesis of o-substituted benzamidines,[2,3,7] it was decided to study the feasibility of using