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Synthesis of aza macrocycles (lariats): Splitting of geminal protons

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ABSTRACT

Aza crown were prepared from the reaction of diester and diamine in refluxing methanol. Aza crowns bearing side arms were prepared from the reaction of halides in nucleophilic conditions. The ¹H NMR spectra in methylene region of crowns show the coupling of germinal protons. The rigidity from aza crown to aza crown bearing some side arms was increased. © 2013 Trade Science Inc. - INDIA

KEYWORDS

Larits; Aza crown; ¹H NMR; Germinal protons; Synthesis; Macrocycle; SEM image.

INTRODUCTION

The first crown ethers were prepared by Pedersen in 1967 and their host-guest properties were identified^[1]. The supramolecular properties of crown ethers were improved by the use of several structural modifications such as, the use of other donor atoms, especially nitrogen and sulfur^[2], and insertion of side chains (lariats)^[3] in their structures and the synthesis of three dimensional macrocycles^[4].

Macrocyclic chemistry has been developed into a field of major scientific and technological importance due to the mentioned changes^[5]. So a wealth of applications have been discovered for the vast range of macrocyclic structures. They have also played a pivotal role in the synthesis and study of challenging molecular architectures^[6]. self-assembly of macrocycles is an important tool for the construction of supramolecular arrays such as nanostructures.

In continuation of our research group for the syn-

thesis of aza crowns and their derivatives^[7], in this research work aza macrocycles (lariats) of dinaphtho sulfides were prepared and their derivatives with side arms were synthesized. ¹H NMR spectroscopy in methylene region for macrocycles with side arm showed the splitting of geminal hydrogens.

RESULTS AND DISCUSSION

In this research work (1) was prepared from the reaction of 2-naphthol and sulfur dichloride (SCl₂) according to the reported procedure^[8]. Diester (2) was prepared from the reaction of (1) and methylchloroacetate in acetonitrile and dimethylformamide (DMF) in the presence of K₂CO₃ at room temperature (Scheme 1) based on the reported procedure^[9]. Aza crown (3) was synthesized from the reaction of (2) and diethylenetriamine in refluxing methanol for 24h^[9]. lariats were prepared from the reaction of (3) and aniline chloroamide (4) and benzyl chloride (5), to afford (6)^[10] and (7) respectively (Scheme 2).

¹H NMR spectroscopy shows the difference between methylene region of (3), (6) and (7). Methylene region of (3) shows no splitting an as a result the macrocycle is flexible but in (6) and (7) splitting show more rigid of these macrocycles in comparison with (3). The introduction of aniline amide and benzyl in the structure of macrocycle lead to the rigid structure and the germinal hydrogens in methylene regions splits.

EXPERIMENTAL

The reactions were carried out in an efficient hood. All the materials were purchased from Merck, Fluka and Aldrich chemical companies. The melting points (uncorrected) were measured with an Electrothermal en-







Scheme 2 : Synthesis of lariats (6) and (7).

gineering LTD 9100 apparatus. Elemental analysis was performed by a CHN-O- Rapid Heraeus elemental analyzer. IR spectra were measured on a Perkin-Elmer model 543, the ¹H NMR and ¹³C NMR spectra were obtained using BRUKER AVANCE DRX 500 and BRUKER AVANCE DPX 300 MHz apparatus and mass spectra were obtained with Shimadzu GC-MS-QP 1100 EX model. Scanning electron micrograph (SEM) images were obtained using JXA-840 (JEOL) and XL30 (Philips) models.

Synthesis of (7), (10), 13-triaza-1-thia-16,4-dioxa-10-phenylmethyl - 6,14-dioxo -2,3;17,18dinaphtho-cyclooctadecane- (7)

To macrocycle (3) (1 mmol, 0.50 g) in acetonitrile (100 ml) were added benzyl chloride (5) (1 mmol), sodium carbonate (1 mmol, 0.14g) and catalytic amounts of sodium iodide. The resulting mixture was

stirred at room temperature for 24h. After completion of the reaction (monitored by TLC), water (50 ml) was added, extracted with chloroform (3×50 ml) and washed with HCl (10%, 2×50 ml). The combined chloroform layers were dried (Na₂SO₄) and evaporated to afford crude product which was purified by recrystallization in Ethanol to afford 7 in 84% yield and melting point of 259-260 °C; IR (KBr): 3405, 3061, 2961, 2938, 1676, 1663, 1589, 1531, 1504, 1460, 1271, 1226, 1150, 1090, 1050, 814, 805 cm⁻¹; ¹H NMR (DMSOd₆, 300 MHz) δ: 3.28-3.38 (broad, 4H), 3.49 (broad, 4H and water of solvent), 3.59-3.64 (broad, 2H), 4.36-4.52 (two triplets, 4H), 7.30-7.54 (m, 11H), 7.91 (t, J=6, 9 Hz, 4H), 8.12 (t, 2H), 8.34 (d, J=9 Hz, 2H) ppm; ¹³C NMR (DMSO-d₆, 75 MHz) δ: 169.72, 155.81, 133.87, 131.52, 129.90, 129.77, 129.42, 129.17, 128.98, 128.66, 127.33, 124.05, 116.76,

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Organic CHEMISTRY An Indian Journal

338



Figure 3 : 300 MHz $^1\!H$ NMR spectrum of (7) (methylene region) in DMSO-d_6 and the proposed structure.



Figure 4 : SEM images of (6).



Figure 5 : SEM images of (7).





Full Paper

114.73, 67.41, 57.55, 51.95, 33.97 ppm; MS (EI) m/z: 501 [M - Bn]⁺ (7%), 500 [M - [Bn + H]]⁺ (12%), 359 (4%), 318 (3%), 300 (8%), 216 (35%), 187 (32%), 144 (100%), 115 (66%), 91 (Bn, 78%), 63 (18%), 42 (23%); Anal. Calcd. for $C_{35}H_{33}N_3O_4S$: C, 71.04; H, 5.62; N, 7.10. Found C, 71.12; H, 5.55; N, 7.18.

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