SIMPLE METHOD OF INTRODUCING AZOLES INTO THE SIDE CHAIN OF AZACROWN ETHERS

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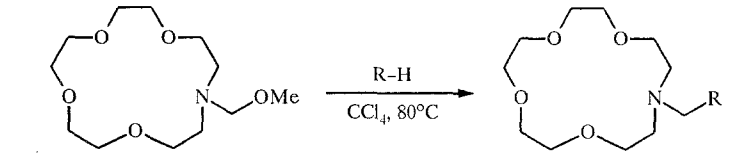
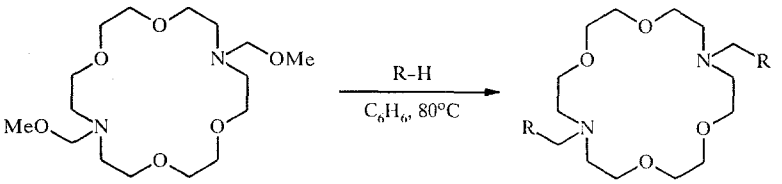
We have previously reported an efficient method for synthesizing azacrown ether derivatives containing phenol, nitro, amide, and sulfamide groups [1-3]. The method is based on C- and N-aminomethylation of nucleophilic substrates by N-methoxymethylazacrown ethers. In the present communication, we demonstrate a simple method for preparing azacrown ethers with azoles in the side chain.

The reaction of 3,5-dimethylpyrazole and benzotriazole with equimolar amounts of N-methoxymethylaza-15-crown-5 (I) in boiling CCl_4 produced the previously unknown crown ethers II and III. Analogously, the reaction of N,N'-bis(methoxymethyl)diaza-18-crown-6 (IV) with imidazole derivatives produced crown ethers V-VII.

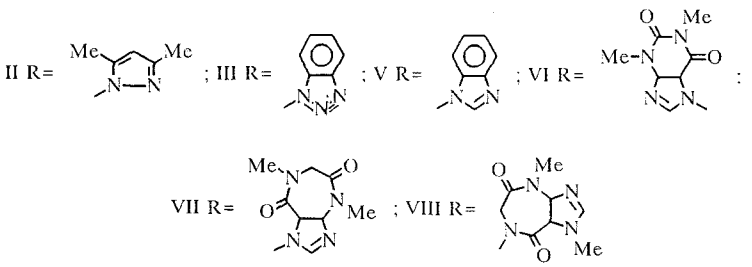
As previously reported, 2-pyrrolidone, in contrast with acyclic secondary amides, smoothly reacts with macrocyclic N-methoxymethylamines [1, 4]. The synthesis of VIII provides an example that 7-membered cyclic amides also easily react through aminomethylation at the secondary amide.



I II, III



IV V-VIII



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Compound II ($C_{16}H_{29}N_3O_4$). Oil. PMR* spectrum: 2.13 (3H, s, 5-CH_3), 2.21 (3H, s, 3-CH_3), 2.83 (4H, t, J = 5.4 Hz, NCH_2), 3.62 (16H, m, OCH_2), 4.75 (2H, s, NCH_2N), 5.68 ppm (1H, s, C=CH). M^+ 327. Yield 97%.

Compound III ($C_{17}H_{26}N_4O_4$). Oil. PMR spectrum: 2.92 (4H, t, J = 5.5 Hz, NCH_2), 3.66 (16H, m, OCH_2), 5.53 (2H, s, NCH_2N), 7.57 ppm (4H, m, ArH). M^+ 350. Yield 98%.

Compound V ($C_{28}H_{38}N_6O_4$). mp 95-96°C. PMR spectrum: 2.95 (8H, t, J = 5.1 Hz, NCH_2), 3.65 (16H, m, OCH_3), 5.25 (4H, s, NCH_2N), 7.60 ppm (9H, m, ArH, HCHN). M^+ 522. Yield 98%.

Compound VI ($C_{28}H_{46}N_{10}O_8$). mp 194-195°C. PMR spectrum: 2.99 (8H, t, J = 5.1 Hz, NCH_2), 3.41 (6H, s, CH_3), 3.68-3.60 (22H, m, OCH_2, CH_3), 5.41 (4H, s, NCH_2N), 7.98 ppm (2H, s, NCHN). M^+ 646. Yield 68%.

Compound VII ($C_{30}H_{50}N_{10}O_8$). mp 150-151°C. PMR spectrum: 2.92 (8H, t, J = 5.2 Hz, NCH_2), 3.17 (6H, s, CH_3), 3.46 (6H, s, CH_3), 3.62-3.56 (16H, m, OCH_2), 3.99 (4H, s, CH_2CO), 5.31 (4H, s, NCH_2N), 7.81 ppm (2H, s, NCHN). M^+ 660. Yield 64%.

Compound VIII ($C_{30}H_{50}N_{10}O_8$). mp 145-146°C. PMR spectrum: 2.89 (8H, J = 5.4 Hz, NCH_2), 3.43 (6H, s, CH_3), 3.63-3.58 (16H, m, OCH_2), 3.88 (6H, s, CH_3), 4.07 (4H, s, CH_2CO), 4.40 (4H, s, NCH_2N), 7.40 ppm (2H, s, NCHN). M^+ 660. Yield 72%.

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*Here and henceforth the spectra are recorded in $CDCl_3$ with an internal standard of HMDS on a 250 MHz instrument.