

## Letters to the Editor

### Synthesis of nitrobenzoazacrown compounds by ring transformations of nitrobenzocrown ethers

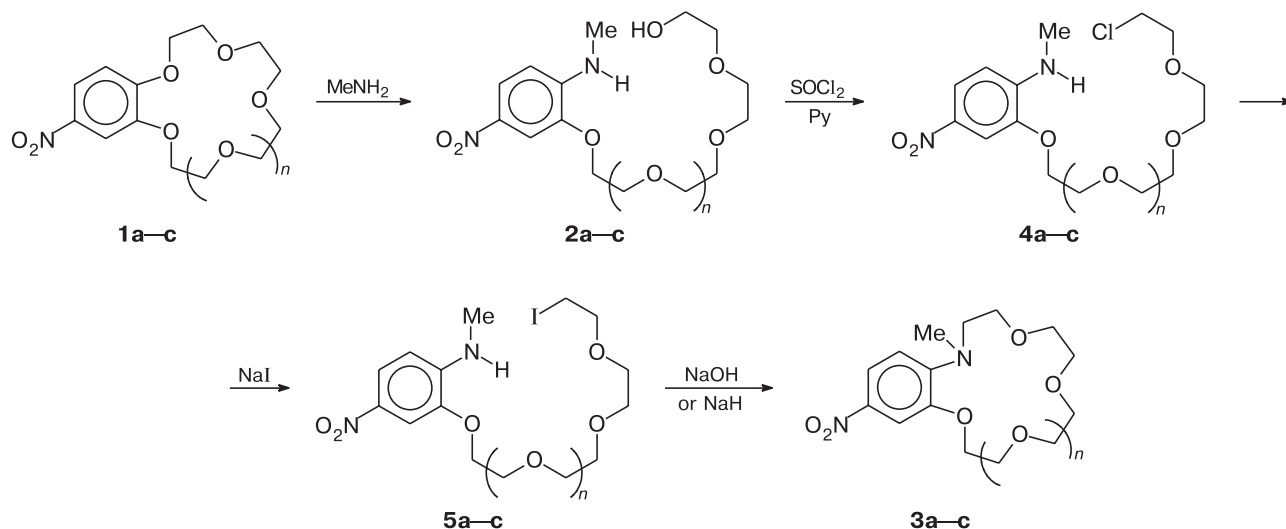
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The main approach to ring construction in the modern chemistry of crown compounds is based on the condensation of two acyclic derivatives (so-called 1 + 1 condensation).<sup>1–3</sup> At the same time, it has been shown that many three- to seven-membered heterocycles can be not only constructed from several fragments, but also ob-

tained by ring transformations including the ring opening and subsequent closure of a new heterocycle involving intermediate acyclic compounds.<sup>4,5</sup>

There are only few examples of the opening of crown ethers.<sup>6,7</sup> Nevertheless, we believe that the macrocycle opening in accessible crown ethers and the synthesis of



new crown compounds from podands formed is a promising alternative to the current synthetic methods in the chemistry of macroheterocyclic compounds.

Earlier, we have found that the opening of nitrobenzocrown ethers **1a–c** on heating them with MeNH<sub>2</sub> gives nitrogen-containing podands **2a–c** in 92–98% yields.<sup>8,9</sup>

We developed a method for the cyclization of podands **2a–c** into previously unknown nitro derivatives of *N*-methylbenzoazacrown compounds **3a–c**. The reactions of the podands with SOCl<sub>2</sub> in the presence of pyridine affords chloro derivatives **4a–c** in 94–96% yields. The Cl atom in compounds **4a–c** is replaced by an I atom in the reactions with NaI to give iodides **5a–c** in 88–98% yields. When heated with NaOH or NaH, iodides **5a–c** undergo intramolecular cyclization into nitrobenzoazacrown compounds **3a–c** in 36–80% yields.

The structures of all the compounds obtained were determined using <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy, including two-dimensional NOESY spectra, and confirmed by high-resolution mass spectra.

The proposed approach based on stepwise transformation of the macroheterocycle makes it possible to synthesize previously unknown nitrobenzoazacrown compounds from accessible benzocrown ethers. The nitro group can be reduced to an amino group and further modified by the known methods to give a family of benzoazacrown derivatives, which are promising for use as ion-selective dyes and extracting agents of metal ions.

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