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One-step Synthesis of a Pentacyclic Structure. Novel Crown Compounds Incorporating 3,7-Diazabicyclo[3.3.1]nonane Moieties

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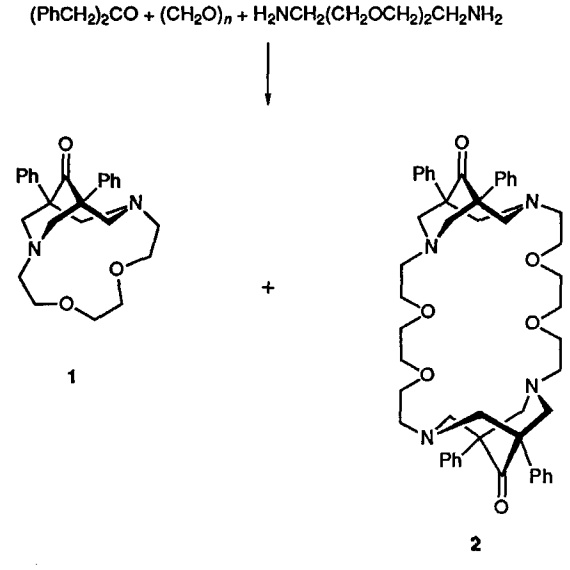
Mannich condensation of 1,8-diamino-3,6-dioxaoctane, dibenzylketone and paraformaldehyde leads to the formation of two novel crown compounds **1** and **2** containing 3,7-diazabicyclo[3.3.1]nonane moieties.

3,7-Diazabicyclo[3.3.1]nonanes (and their natural derivatives) have been widely investigated during the last decade as models in conformational studies.[1] They are also known to form 1:1 and 2:1 complexes with Cu^{II} and Ni^{II} salts[2–4] and with some other compounds (the complexes of sparteines with Grignard reagents should be mentioned[5]). The conformation of 3,7-dialkyl-3,7-diazabicyclo[3.3.1]nonan-9-ones changes from a chair–boat to a chair–chair one during complex formation[1,4–9] (*e.g.* compounds **3** and **4**). Thus, fragments of this kind are expected to be interesting for the design of novel macrocyclic ligands. Nonetheless, no synthesis of crown compounds incorporating the 3,7-diazabicyclo[3.3.1]nonane moiety has been reported until recently, except one publication[10] which appeared when the present work was finished.

We report here the synthesis of compounds **1** and **2** of this type (Scheme 1) in one step by a Mannich condensation (similarly to the synthesis of 3,7-dialkyl-3,7-diazabicyclo[3.3.1]nonan-9-ones[11]). Dibenzylketone (2.1 g), 1,8-diamino-3,6-dioxaoctane (0.25 ml) and paraformaldehyde (2.4 g) in 500 ml of absolute ethanol were refluxed for 50 h. The solvent was evaporated and the residue was chromatographed on a silica column, eluting with ethanol, to yield pure **1**† (0.6 g, 15%) and **2**† (0.3 g, 7%). The structure of **1** has been confirmed by X-ray crystallography, and it has been shown that the bicyclo[3.3.1]nonane fragment in **1** has a chair–boat conformation.[12] This conformation is typical for 3,7-dialkyl-3,7-

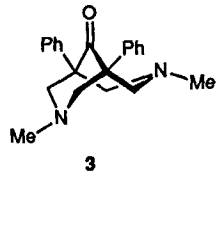


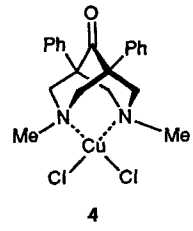
Scheme 1

† Satisfactory elemental analyses were obtained for compounds **1** and **2**.

For **1**: m.p. 158 °C (from ethanol); ^{1}H NMR (250 MHz, $CDCl_3$) δ 2.94 (t, 4H, *J* 4.8 Hz, $NCH_2^aCH_2O$), 3.26 (d, 4H, *J* 11 Hz, $PhCCH_2^a$), 3.67–3.74 (m, 8H, $CH_2OCH_2CH_2OCH_2$), 3.94 (d, 4H, *J* 11 Hz, $PhCCH_2^b$), 7.2–7.35 (m, 10H, Ph); *m/z* 406 (M^+).

2: m.p. 229 °C (from acetone); ^{1}H NMR (360 MHz, $CDCl_3$) δ 2.67 (t, 8H, *J* 5 Hz, $NCH_2^aCH_2O$), 3.10 (d, 8H, *J* 10 Hz, $PhCCH_2^a$), 3.53 (d, 8H, *J* 10 Hz, $PhCCH_2^b$), 3.58–3.60 (m, 16H, $CH_2OCH_2CH_2OCH_2$), 7.17–7.30 (m, 20H, Ph); *m/z* 812 (M^+).





diazabicyclo[3.3.1]nonan-9-ones,[1] but it was hardly expected for compound **1**, having an 8-atom chain connecting the nitrogen atoms. On the basis of above-mentioned data a chair–boat conformation for the bicyclo[3.3.1]nonane fragments in compound **2** could also be expected.

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