A Versatile Synthesis of Chiral Crown Amino-ethers

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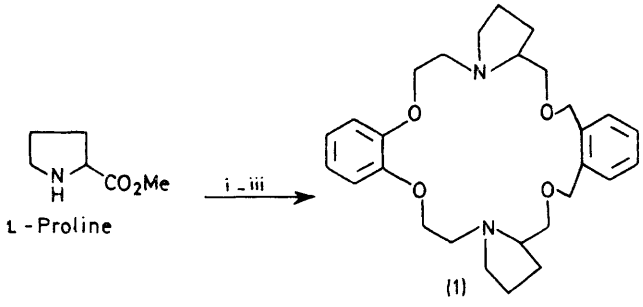
Summary A three-step synthesis of chiral macrocyclic amino-ethers in good yield is described.

THE remarkable properties of macrocyclic (crown) ethers[1] and macrobicyclic (cryptates) aminoethers[2] were reported recently. We present herein a preliminary report of the first versatile synthesis of chiral macrocyclic aminoethers.

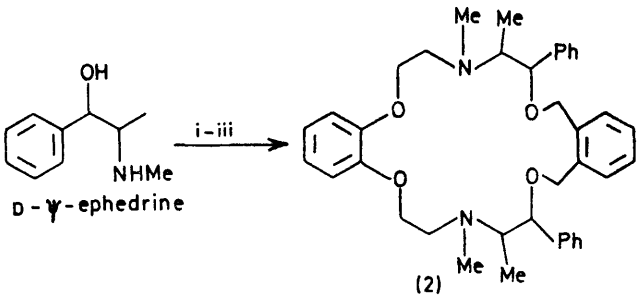
The synthesis is depicted in the Schemes. All steps gave products in good yield; for example, the overall yield in Scheme 2 was 40%.

Correct elemental analyses were obtained for the products (**1**) (a white crystalline solid, m.p. 98—99°) and (**2**) (also a crystalline solid, m.p. 94—95°). Both compounds were characterised spectroscopically.



SCHEME 1

Reagents: i, *o*-phenylenedioxydiacetyl chloride; ii, $LiAlH_4$; iii, αα′-dibromo-*o*-xylene–NaH–dimethyl sulphoxide.



SCHEME 2

Reagents: i, di-*p*-nitrophenyl *o*-phenylenedioxydiacetate; ii, $LiAlH_4$; αα′-dibromo-*o*-xylene–NaH–dimethyl sulphoxide.

Both the amino-ethers (**1**) and (**2**) form complexes with alkali and alkaline-earth cations in neutral media. They also (of course) form salts with halogen acids. We are currently determining the cationic and anionic selectivity of these and other systems made according to the above schemes.

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[2] J. M. Lehn and J. P. Sauvage, *Chem. Comm.*, 1971, **440**.