A General Method for the Synthesis of Diazacoronands

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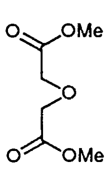
α,ω-Diamino aliphatic ethers react under ambient conditions with dimethyl α,ω-dicarboxylates, in methanol as a solvent, to give the cyclic diamides in good yields, and their subsequent reduction with lithium aluminium hydride affords the respective diazacoronands.

There is a continuing interest in the preparation of diazacoronands which have important uses as macrocyclic molecular receptors[1] as well as being valuable intermediates for the synthesis of cryptands and related compounds.[2] The methods for the formation of diazacoronands have been extensively reviewed[3,4] Among these methods, the high-dilution technique[5] is commonly used as the most versatile procedure. This process is, however, inconvenient as it requires a simultaneous addition of the diamine and diacid chloride to a large volume of solvent over an extended period of time. Recently, Morphy *et al.*[6] have reported that, consistent with the earlier findings of Tabushi,[7,8] no high-dilution technique was required for the reaction of dimethyl malonates with α,ω-diamines to form the cyclic diamides. This fact prompted us to apply a similar approach to the synthesis of diazacoronands and we now report the results of these studies.

We found that α,ω-diesters **1** and **2** reacted with 1 equiv. of α,ω-diamines **3** and **4** under ambient conditions (methanol as a solvent, 25 °C, 7 days, reagent concentrations 0.1 mol dm^{-3})



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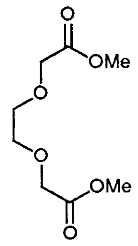

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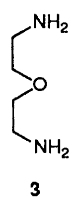

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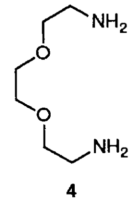

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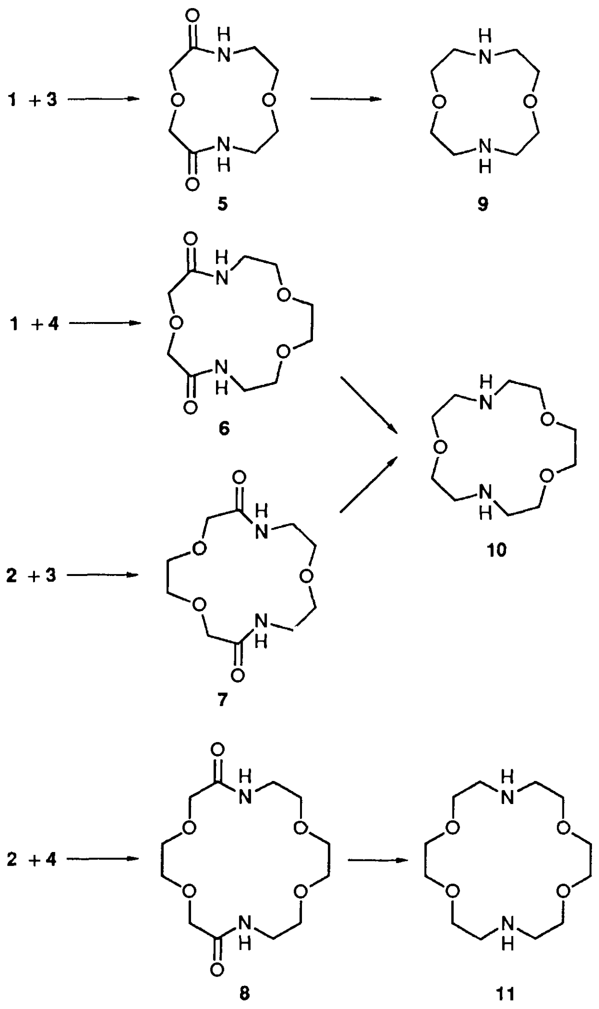


Scheme 1

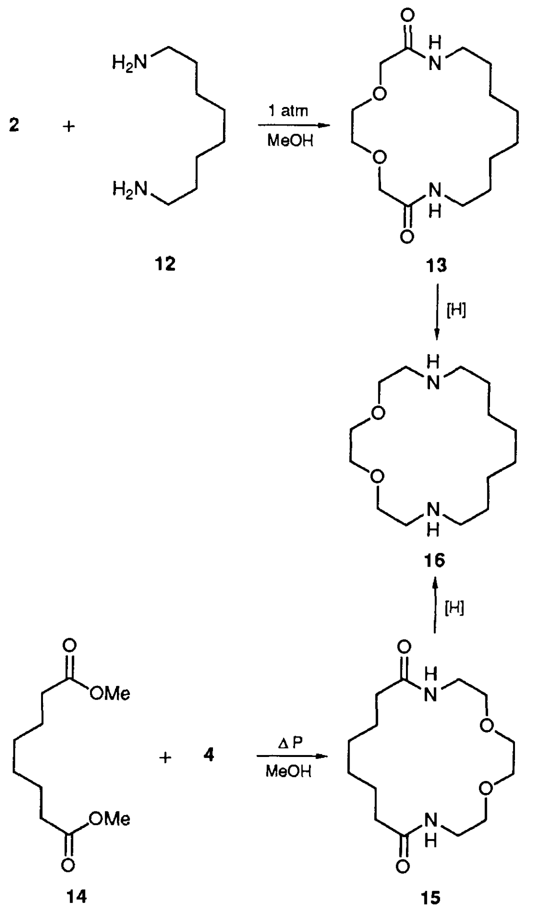
Table 1. Synthesis of diazacoronands

Diester	Diamine	Reaction conditions[a] P/bar	t/days	Diamide	Yield (%)	Diaza-coronand	Yield (%)
1	**3**	1	7	**5**	60	**9**	50
1	**4**	1	7	**6**	60	**10**	85
2	**3**	1	7	**7**	70	**10**	80
2	**4**	1	7	**8**	75	**11**	75
2	**12**	1	7	**13**	30	**16**	65
14	**4**	8000	2	**15**	25	**16**	70

[a] All reactions performed at 25 °C.

to give the respective diamides **5**, **6**, **7** and **8** as colourless solids (Scheme 1, Table 1).† Reduction followed by treatment with lithium aluminium hydride (LAH) (tetrahydrofuran, reflux, 24 h) afforded the respective diazacoronands **9**, **10** and **11**.

The reaction between diester **2** and 1,8-diaminooctane **12** furnished under the same conditions the diamide **13**. The reaction of diester **14** with 1,2-bis(2-aminoethoxy)ethane **4** failed, however, under ambient conditions.‡ In this case we



Scheme 2

successfully applied high-pressure conditions (8 kbar, methanol as solvent, 25 °C, 48 h, reagents, concentrations 0.1 mol dm^{-3}) affording the diamide **15**. LAH reduction of both diamides **13** and **15** led to the same diazacoronand **16** (Scheme 2, Table 1).

This simple and efficient method should be useful, particularly for preparations of more elaborate diazacoronands. This work was supported by the Polish Academy of Sciences, grant No. C.P.B.P. 01.13.

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† Satisfactory analyses and spectral data were obtained for all new compounds.

‡ For the high-pressure experiment we used the piston-cylinder type apparatus described earlier.[9]

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