Supramolecular Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713649759

The Use of Tripodal Reagents in the Effective Preparation of Highly Elaborated Azacoronands

Piotr Piatek[a]; Piotr Lipkowski[b]; Daniel T. Gryko[b]; Janusz Jurczak[ab]
[a] Department of Chemistry, Warsaw Uniwersity, Warsaw, Poland [b] Institute of Organic Chemistry, Polish Academy of Sciences, Warsaw, Poland

To cite this Article Piatek, Piotr , Lipkowski, Piotr , Gryko, Daniel T. and Jurczak, Janusz(2000) 'The Use of Tripodal Reagents in the Effective Preparation of Highly Elaborated Azacoronands', Supramolecular Chemistry, 12: 2, 209 — 211
To link to this Article: DOI: 10.1080/10610270008027452
URL: http://dx.doi.org/10.1080/10610270008027452

SUPRAMOLECULAR CHEMISTRY, Vol. 12, pp. 209-211
Reprints available directly from the publisher
Photocopying permitted by license only

The Use of Tripodal Reagents in the Effective Preparation of Highly Elaborated Azacoronands

PIOTR PIĄTEK[a], PIOTR LIPKOWSKI[b], DANIEL T. GRYKO[b] and JANUSZ JURCZAK[ab*]

[a]*Department of Chemistry, Warsaw Uniwersity, 02–093 Warsaw, Poland and* [b]*Institute of Organic Chemistry, Polish Academy of Sciences, 01–224 Warsaw, Poland*

(In final form March 31, 2000)

In one reaction step only, the self-assembly promoted synthetic pathways lead to various products like: pendant benzophanes, bis-macrocyclic compound and tricyclic cryptand. The self-assembly phenomena are probably stimulated by hydrogen bonds formed among substrates and molecules of the solvent.

Keywords: self-assembly, pendant benzophanes, bis-macrocyclic compound, tricyclic cryptand

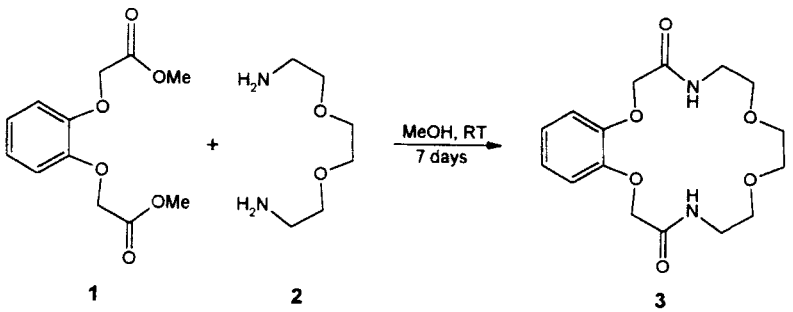
The self-assembly phenomena are used by nature to generate a variety of biochemical systems [1] e.g. membranes, duplex nucleic acid and viral coat proteins. In these self-assembly processes complex structures are prepared from small, relatively simple subunits *via* weak noncovalent bonds. Very precise recognition features present in each subunit allow a large degree of control in the construction process, thus natural self-assembly processes are efficient and self-checking.

In a laboratory chemists have tried to mimic self-assembly phenomena found in nature. Examples include hydrogen-bonded species [2], metal-bipirydyl [3], aryl-aryl charge transfer interaction [4]. The order of the substrates, which characterizes the unnatural assemblies, can lead to products new in form as well as in functions. The self-assembly synthetic pathway can replace or compete with conventional synthetic methodology of making compounds step-by-step. A good and illustrative example is the synthesis of tricyclic cryptands. Those compounds are usually synthesized *via* step-by-step protocol [5]. There are only few examples in the literature of the synthesis of tricyclic cryptand using self-assembly phenomena [6].

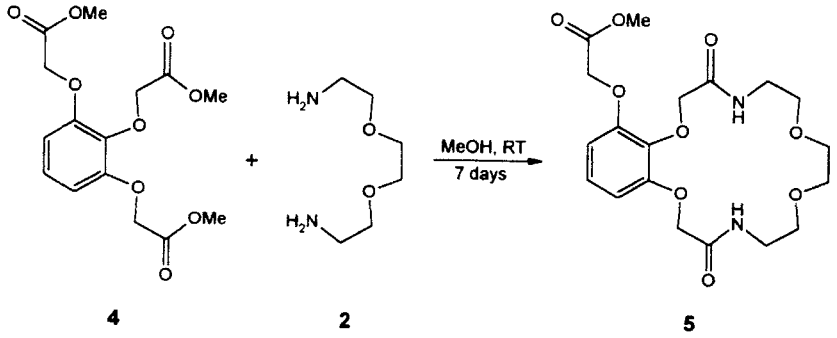
Our own studies on self-assembly promoted synthetic pathways of highly elaborated azacoronands are based on the macrocyclization procedure developed by us. We have reported that dimethyl α,ω-dicarboxylates (e.g. **1**) react under ambient conditions with α,ω-diamino aliphatic ethers (e.g. **2**) in methanol to afford the macrocyclic bisamides (e.g. **3**) in good yields (Scheme 1) [7].

Following the procedure adopted previously, we have decided to examine macrocyclization reaction of tripodal reagents. The tripodal trimethyl ester **4** (an armed analogue of **1**) was reacted with diamine **2** to give the pendant benzophanes **5** (Scheme 2) [8]. It is noteworthy that even if excess of diamine is present in the reaction mixture, bisamide is the only isolable product. Similar

* Author for correspondence.



SCHEME 1



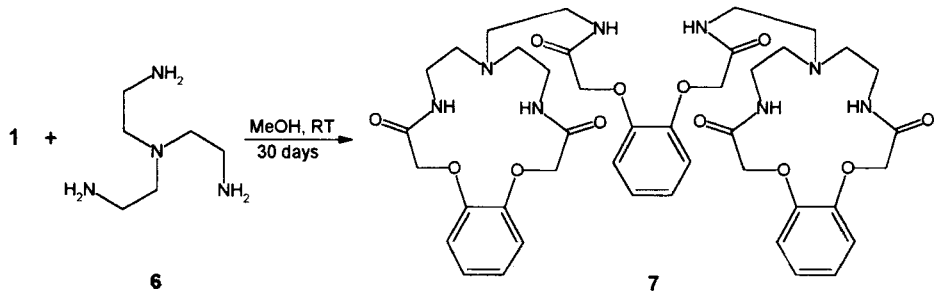
SCHEME 2

results were obtained for 1,2,4- and 1,3,5-trihydroxybenzenes. The one-step strategy used by us leads to diazacoronands possessing pendant arm attached to the phenyl ring in exactly defined position. This feature is unique among reactions leading to pendant benzophanes [9].

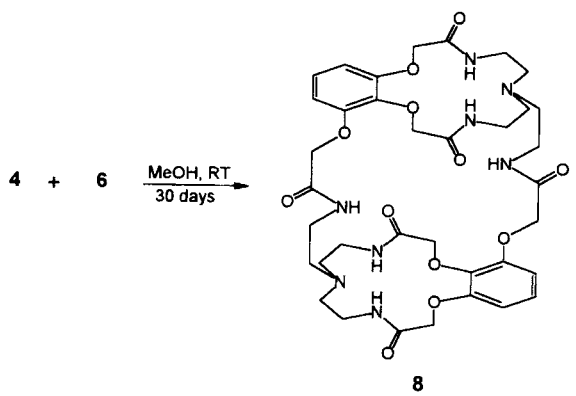
An alternate approach in preparation of pendant benzophanes can involve use of tripodal amine and dipodal methyl ester as substrates. This idea was tested by treatment of dimethyl ester **1** with tripodal tris(2-aminoethyl)amine **6** (Scheme 3). As a result, we have obtained crystalline bis-macrocycle **7** (34% yield) as the only product [10]. The compound **7** partly precipitated from the reaction mixture, and after several attempts, we managed to obtain well shaped crystals suitable for X-ray analysis, which justified the proposed structure [10].

In the next experiment the tripodal amine **6** was treated with tripodal trimethyl ester **4** to afford tricyclic cryptand **8** in a yield of 39% (Scheme 4) [10]. The structure of **8** was determined by ^{1}H, ^{13}C NMR and mass spectrometry. Unfortunately, all attempts to obtain crystals appropriate for X-ray crystallographic analysis were unsuccessful. The reaction, in which compound **8** is formed, is an example of a rare multi-centred reaction which leads to highly elaborated macrocyclic compounds.

It is noteworthy that all macrocyclization reactions were proceeded in methanol. The self-assembly phenomena are probably stimulated by hydrogen bonds formed among substrates and molecules of the solvent.



SCHEME 3



SCHEME 4

Acknowledgements

This work was supported by State Committee for Scientific Research (Project 3 T09A 127 15).

References

[1] Lindsey, J. S.; New J. *Chem.* **1991**, *15*, 153.

[2] Timmerman, P.; Vreekomp, R. H.; Hulst, R.; Verboom, W.; Reinhandt, D. N.; Rissanen, K.; Udachin, K.A.; Ripmeester, J.; *Chem. Eur. J* **1997**, *3*, 1823.

[3] Dietrich-Buchecker, C.; Sauvage, J-P.; *Tetrahedron* **1990**, *46*, 503.

[4] (a) Ashton, P. R.; Goodnow, T. T.; Kaifer, A. E.; Reddington, M. V.; Slawin, A. M. Z.; Spencer, N.; Stoddart, J. F.; Vincent, C.; Williams D. J.; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 1396.
(b) Ballardini, R.; Balzani, V; Gandolfi M. T.; Gillard, R. E.; Stoddart, J. F.; Tabellini, E.; *Chem. Eur. J.* **1998**, *4*, 449.

[5] (a) Kumar, A.; Mageswaran S.; Sutherland, I.O.; *Tetrahedron* **1986**, *42*, 3291.
(b) Nakano, A.; Li, Y.; Geoffroy, P.; Kim, M.; Atwood, J. L.; Bott, S.; Zhang. H.; Echegoyen, L.; Gokel, G. W.; *Tetrahedron Lett.* **1989**, *30*, 5099.
(c) Sholl, A. F.; Sutherland, I.O.; *J. Chem. Soc. Chem. Commun.* **1992**, *17*, 1252.
(d) Krakowiak, K. E.; Bradshaw, J.S.; Kou, X.; Dalley, N. K.; *J. Heterocycl. Chem.* **1995**, 32, 931.

[6] (a) Krakowiak, K. E.; Bradshaw, J.S.; Dalley, N. K.; Zhu, C.; Yi, G.; Curtis, J. C.; Li, D.; Izatt, R. M.; *J. Org. Chem.* **1992**, *57*, 3166.
(b) Clark, B. P.; Harris, J. R.; Timms, G. H.; Olkowski, J. L.; *Tetrahedron Lett.* **1995**, *36*, 3889.

[7] Gryko, D.T., Piatek, P., Jurczak, J.; *Tetrahedron* **1997**, *53*, 7957.

[8] Analytical data for **5**: ^{1}H NMR (200 MHz, $CDCl_3$, δ), 7.51 (bt, 1H, NH), 7.29 (bt, 1H, NH), 7.02 (t, J=8.5 Hz, 1H, Ph), 6.55 (ABq, 2H, Ph), 4.70 (s, 2H, OCH_2C=O), 4.59 (s, 2H, OCH_2C=O), 4.57 (s, 2H, OCH_2C=O), 3.79 (s, 3H, OCH_3), 3.79 – 3.56 (m., 12H); ^{13}C NMR (50 MHz, $CDCl_3$, δ), 169.0, 168.6, 167.8, 151.4, 151.0, 136.4, 124.6, 107.3, 107.2, 71.8, 70.1, 70.0, 69.5, 69.1, 68.3, 65.5, 52.3, 38.9, 38.8. HRMS m/z calculated for $C_{19}H_{26}N_2O_9$ $(M)^+$ 426.1638 found 426.1637. Anal. calculated for $C_{19}H_{26}O_9N_2$, C, 53.52%; H, 6.14%; N, 6.57%. Found C, 53.46%; H, 6.35%; N, 6.55%.

[9] (a) Stott, P. E.; Bradshaw, J.S.; Parish W. W.; Copper, J. W.; *J.* W.; J. *Org. Chem.* **1980**, *45*, 4716.
(b) Dietl, F.; Gierer, G.; Merz A.; *Synthesis* **1985**, *6/7*, 626.
(c) Percec, V.; Johansson, G.; Heck, J.; Ungar, G.; Batty S. V.; *J. Chem. Soc. Perkin Trans. I* **1993**, *13*, 1411.

[10] Lipkowski, P., Gryko D.T., Jurczak, J., Lipkowski J.; *Tetrahedron Lett.*, **1998**, 39, 3833.