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

Synthesis of Interlocked Diazacoronand System

Piotr Tarnowski[a]; Piotr Piatek[a]; Rafał R. Siciński[a]; Janusz Jurczak[ab]
[a] Department of Chemistry, University of Warsaw, Warsaw, Poland [b] Institute of Organic Chemistry, Polish Academy of Sciences, Warsaw, Poland

To cite this Article Tarnowski, Piotr , Piatek, Piotr , Siciński, Rafał R. and Jurczak, Janusz(2000) 'Synthesis of Interlocked Diazacoronand System', Supramolecular Chemistry, 12: 2, 217 — 219

To link to this Article: DOI: 10.1080/10610270008027454

URL: http://dx.doi.org/10.1080/10610270008027454

SUPRAMOLECULAR CHEMISTRY, Vol. 12, pp. 217-219
Reprints available directly from the publisher
Photocopying permitted by license only

Published by license under
the Harwood Academic Publishers imprint,
part of the Gordon and Breach Publishing Group.
Printed in Malaysia

Synthesis of Interlocked Diazacoronand System

PIOTR TARNOWSKI[a], PIOTR PIĄTEK[a], RAFAŁ R. SICIŃSKI[a] and JANUSZ JURCZAK[ab]*

[a]*Department of Chemistry, University of Warsaw, Pasteura 1, 02–093 Warsaw, Poland and* [b]*Institute of Organic Chemistry, Polish Academy of Sciences, Kasprzaka 44, 01–224 Warsaw, Poland*

(In final form March 31, 2000)

New 2,9-disubstituted 1,10-phenanthroline derivatives have been obtained, retaining the ability to form stable complexes with transition metals. Due to special, pseudotetrahedral topography of the copper(I) complexes the subsequent ring formation reaction can lead to copper(I) catenates. Thus, the known 2,9-bis(*p*-hydroxyphenyl)-1,10-phenanthroline ligand, was elongated by the reaction with *tert*-butyl bromoacetate, forming a diester capable of undergoing a double amidation reaction. Such synthetic strategy can provide the corresponding diazacoronands as well as amide-containing interlocked catenane systems, when a three-dimensional template effect of copper atom is employed.

The strong tendency of 1,10-phenanthroline as well as its simple alkyl-substituted analogs to interact with transition metals have long been recognized and their coordination chemistry has been a subject of numerous studies [1, 2]. Particularly interesting studies have been recently performed by Sauvage and his coworkers. They elaborated an efficient method for the synthesis of 2,9-disubstituted 1,10-phenanthrolines [3] and showed that such ligands form very stable copper(I) pseudotetrahedral complexes [4] which can serve as precursors of interlocked macrocycles – catenanes [5, 6].

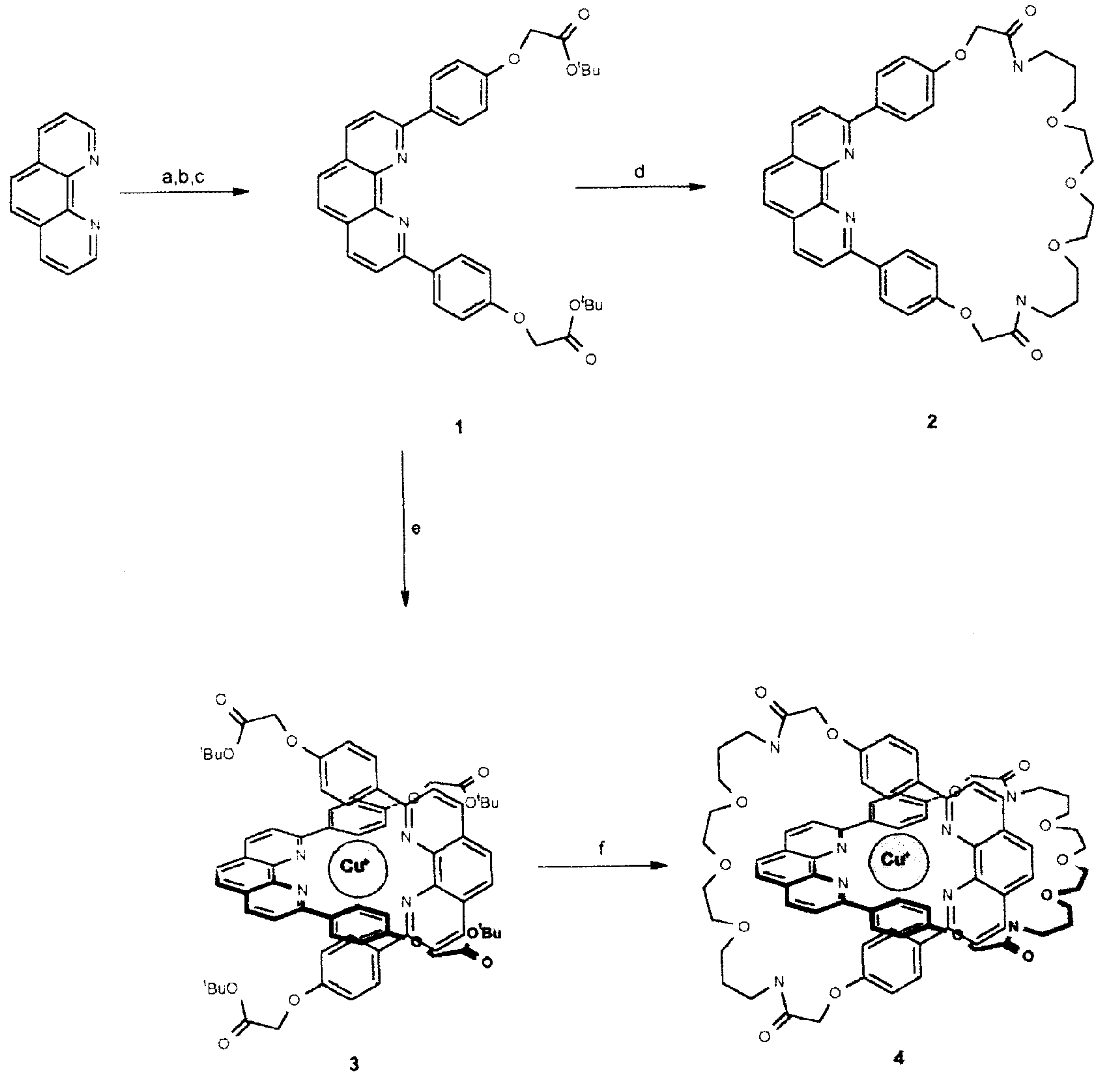
Our first objective was to obtain the prototypic diazacoronand with 1,10-phenanthroline unit, using our double-amidation procedure [7]. Then, we wanted to test the possibility of extending this approach for the synthesis of catenanes. It was also of interest to establish whether additional nitrogen atoms in the synthesized macrocycle influence the interaction of phenanthroline moiety with *transition* metals.

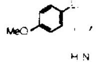
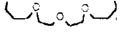
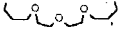
At first, we attempted a macrocyclization of the analog of diester **1**, possessing two carboxymethyl groups. However, its exceptionally low solubility in methanol (preferred reaction medium) forced us to use the *tert*-butyl ester **1**, that was much better soluble in alcohols. The compound **1** proved to be a convenient substrate for attempted ICHOPAN-2 reaction [8], because in the presence of DBU it underwent slow transesterification to the methyl ester which, in turn, reacted with 1,13-diamino-4,7,10-trioxatridecane. Thus by carrying out the cyclization reaction of diester **1** for 7 days we could isolate the diazacoronand **2** in 55% yield. The structure of this 35-membered macrocyclic diamide has been supported by its spectral data (^{1}H and ^{13}C NMR, MS) and elemental analysis.

Elaboration of macrocyclization of the diester **1** allowed us to explore the possibility of using it as a substrate for the catenate **4** preparation. We have applied two strategies of the three-dimen-

---

* Author for correspondence.



(a) (*i*) , toluene, 25°C, 48h, (*ii*) H_2O, (*iii*) MnO_2; (**b**) Py, HCl, 200 °C, 3h; (**c**) $BrCH_2COO^tBu$, DHF, K_2CO_3, reflux, 0.5h; (**d**)  MeOH, DBU, 7 days, rt; (**e**) $Cu(CH_3CN)_4{}^+BF_4{}^-$, CH_2Cl_2; (**f**) 2 mol  MeOH, DBU, 7 days, rt

sional template synthesis of interlocked rings, suggested by Sauvage [5, 6], i.e., the one-pot procedure using copper(I) complex of diester **1** (compound **3**), and a method requiring an intermediate copper(I) complex of diester **1** and macrocycle **2**, which was ineffective in our hands. TLC control of the one-pot reaction of the complex **3** showed disappearance of its red-colored spot and simultaneous formation of a few polar products shortly after the addition of the aliphatic diamine. This observation, as well as a appearance of the corresponding spots of uncomplexed diester **1** and macrocycle **2** in the examined reaction mixture, indicate that the aliphatic amine with poly(oxyethylene) chain strongly interacts with the copper(I) ion, destroying the existing phenanthroline complex **3**. However, the catenate **4**, made of two interlocked 35-membered rings and a central copper(I) atom, was also formed and chromatographically isolated from the fraction containing polar products. The catenane structure of this compound has been determined by its mass spectrum showing molecular ion peak at m/z 1391.5 (48,8%), in addition to the isotope peaks 1392.5 (46.4%), 1393.5 (47.2%), 1394.5 (23.6%), and the parent peak of the monomeric macrocycle at m/z 727.2 (35,2%).

We have also established that alternative synthetic strategy involving a complex of copper(I) with different ligands, i.e., diester **1** and macrocycle **2**, failed to give the catenate structure. During additional experiments an explanation of this fact has been found: the macrocyclic compound **2** has relatively low tendency to form a complex with copper atom, even in the presence of large excess of $Cu(CH_3CN)_4^{-} \cdot BF_4^{-}$ reagent. Therefore, only copper(I) complexes of the structure **3** can be considered as suitable precursors for the templated synthesis of interlocked diazacoronands. Further work in this area is in progress in our laboratory.

Acknowledgements

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

References

[1] Dwyer, F.P.; Mellor, D.P.; *Chelating Agents and Metal Chelate*. Academic Press, New York **1964**.

[2] McKenzie, E.D.; *Coord. Chem. Rev.*, **1971**, *6*, 187.

[3] Dietrich-Buchecker, C.O.; Marnot. P.A.; Sauvage, J.P.; *Tetrahedron Letters* **1982**, *23*, 5291.

[4] Dietrich-Buchecker, C.O.; Marnot. P.A.; Sauvage, J.P.; Kintzinger, J.P.; Maltese, P. A.; Sauvage. *J.* P.; Kintzinger. J. P.; Maltese. P. *Nouv. J. Chim.*, **1984**, *8*, 573.

[5] Dietrich-Buchecker C.O.; Sauvage, J.P.; *Chem. Rev.*, **1987**, *87*, 795.

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

[7] Jurczak, J.; Stankiewicz, T.; Salański, P.; Kasprzyk, S.; Lipkowski, P.; *Tetrahedron*, **1993**, *49*, 1478.

[8] (a) Gryko. D. T.: Piątek, P.; Sałański, P.; Jurczak, J.; *Tetrahedron Asymmetry*, **1998**, *9*, 1771.
(b) Gryko, D. T.; Piątek. P.; Jurczak, J.; *Synthesis*, **1999**, 336.