

This article was downloaded by:

On: 28 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713618290>

Unusual Regioselectivity in the Reactions of Chlorocyclophosphazene-Containing Crown Ethers with Dinucleophiles

Krystyna Brandt^a; Iwana Porwolik^a; K. Placha^a; T. Kupka^a; A. Olejnik^a; Robert. A. Shaw^b; David B. Davies^b

^a Institute of Polymer Chemistry, Polish Academy of Sciences, Zabrze, M.Curie Sldodowskiej 34 ^b Department of Chemistry, Birkbeck College London University, London, U.K.

To cite this Article Brandt, Krystyna , Porwolik, Iwana , Placha, K. , Kupka, T. , Olejnik, A. , Shaw, Robert. A. and Davies, David B.(1996) 'Unusual Regioselectivity in the Reactions of Chlorocyclophosphazene-Containing Crown Ethers with Dinucleophiles', *Phosphorus, Sulfur, and Silicon and the Related Elements*, 111: 1, 30

To link to this Article: DOI: 10.1080/10426509608054659

URL: <http://dx.doi.org/10.1080/10426509608054659>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

UNUSUAL REGIOSELECTIVITY IN THE REACTIONS OF CHLOROCYCLOPHOSPHAZENE-CONTAINING CROWN ETHERS WITH DINUCLEOPHILES

Krystyna Brandt, Iwona Porwolik, K. Placha, T. Kupka, A. Olejnik, Robert. A. Shaw*, David. B. Davies*

Institute of Polymer Chemistry, Polish Academy of Sciences, 41-800 Zabrze, M. Curie Skłodowskiej 34

* Department of Chemistry, Birkbeck College (London University), London WC1H 0PP, U.K.

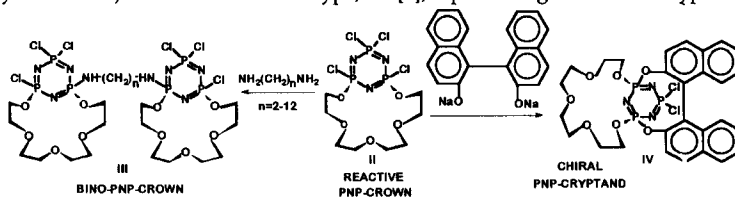
Abstract: New macrocyclic ligands with cyclophosphazene sub-units, representing geminally diamino-bridged derivatives of BINO-crown type (III), and bisansa-cyclosubstituted ones of chiral PNP cryptand type (IV) have been obtained by the regioselective substitution reactions of mono-ansa(oxytetraethylenoxy) reactive PNP-crown, $\text{N}_3\text{P}_3\text{Cl}_4[\text{O}(\text{CH}_2\text{CH}_2\text{O})_4]$ (II) with the dinucleophiles, like alkylenediamines or sodium diarylates. The supramolecular control of these processes is discussed.

Key Words: regioselective substitution, cyclophosphazenes, crown ethers, bis-crowns, cryptands

Only a few phosphorus cryptands and bmacrocycles are reported [1]. Therefore there is a need to develop synthetic routes to these systems which might present interesting complexation properties.

A new class of functional macrocyclic ligands with cyclophosphazene sub-units has been obtained in our laboratory by cyclosubstitution reactions of hexachlorocyclophosphazatriene, $\text{N}_3\text{P}_3\text{Cl}_6$ (I), with tetraethylene glycol in the presence of NaH, the resp. mono-ansa(oxytetraethylenoxy) derivative, $\text{N}_3\text{P}_3\text{Cl}_4[\text{O}(\text{CH}_2\text{CH}_2\text{O})_4]$, (II) being a major product of this reaction [2]. Owing to the incorporation of a 3-membered $-\text{P}=\text{N}-\text{P}-$ fragment of the N_3P_3 ring into the macrocyclic polyether skeleton, the crown II is capable of forming coordination complexes both with alkali and transition metal cations.

The presence in PNP-macrocyclic II of 4 reactive chloride functions enables the condensation of this compound with dinucleophiles, like alkylenediamines, or sodium diarylates, leading to the formation of the respective geminally diamino-bridged derivatives of BINO-crown type, III, or geminally cyclobis(dioxysubstituted) ones of the bis-ansa type, IV [3], representing chiral PNP cryptand:



Unusual regioselectivity of geminal substitution of chlorine atoms in II with the aforementioned dinucleophiles has been ascribed by us to the formation of the intermediate complexes of II with the resp. reagents; in the case of diamines a "sandwich"-type complex structure has been assumed. Without the supramolecular control the course of the given dinucleophilic substitution reactions would be determined by the respective steric and/or thermodynamic factors, that should yield structures different than III or IV: non-geminally bridged BINO-PNP-crowns (when reacting II with longer-chain diamines, $n > 4$), or spiro-substituted PNP-ansa-macrocycles (in the reactions of II with shorter-chain diamines ($n = 2, 3$) and bis- β -naphthol). The formation of spiro structures in the reaction of I with bis- β -naphthol has been previously reported [4]. Studies on elucidating the phenomenon of supramolecular control in dinucleophilic substitution reactions of II are under way.

This work has been supported by the European Commission (grant CIPA-CT93-0019) and the Polish State Research Council (grant 2 P303 068 06).

REFERENCES

1. A.-M. Caminade, and J.-P. Majoral, *Chem. Rev.*, **94**, 1183 (1994) and references therein.
2. K. Brandt, J. Drozd, T. Kupka, T., J.C. Van de Grampel and A. Meetsma, *Inorg. Chim. Acta*, **228**, 187 (1995).
3. K. Brandt, I. Porwolik, T. Kupka, A. Olejnik, R. A. Shaw and D. B. Davies (submitted for publication).
4. K. Brandt and Z. Jedlinski, *J. Org. Chem.*, **45**, 1672 (1980).