Abstract Remarkably, although chiral cyclophosphazenes bearing biphenoxy or binaphtoxy groups are known, no particular attention was given to the stereochemical course of the reaction. We have therefore investigated in more detail the synthesis of some bis-spirocyclic phosphazenes obtained with racemic mixtures of the diols 2,2’-dioxybiphenyl and 2’, 2’’-dioxy-1’,1’’-bi-2-naphtyl (abbreviated as biphenoxy or binaphtoxy, respectively) and N₃P₃Cl₆.

INTRODUCTION

The diols 2,2’-dioxybiphenyl (biphenoxy) or 2’,2’’-dioxy-1’,1’’-bi-2-naphtyl (binaphtoxy) were already used for the synthesis of spirocyclic phosphazenes.¹⁶ Tris(biphenoxy)⁵ is stable at least up to 350°C and does not polymerize by ring-opening thermal polymerization. Hence, increased thermal stability may be expected for polymers in which these motifs are incorporated. Furthermore, binaphtoxy is commercially available in form of two atropisomers which do not interconvert at ambient temperature. Therefore a simple synthesis of enantiomerically pure spirocyclic phosphazenes and hence chiral polymers shall be possible. The latter may have interesting properties as supports for catalyst. We have therefore investigated in more detail the synthesis of bis-spirocyclic phosphazenes of the type (O,O)₂Cl₂P₃N₃ (where O,O stands for a cheleting diol) and report here the somewhat unexpected results which were obtained.
RESULTS AND DISCUSSION

Starting from hexachlorocyclotriphosphazene and two equivalents of biphenolate or binaphtholate, the bis-spirocyclic cyclotriphosphazenes 1 and 2, respectively, were obtained. Remarkably, exclusively the meso forms of the 1,1-P-dichlorosubstituted cyclotriphosphazenes 1-meso and 2-meso are formed.

The reaction of 1-meso with two equivalents of sodium 4-methoxyphenolate gives surprisingly a racemic mixture of 3(R,R) and 3(S,S) (Scheme 1). Under the reaction conditions, the configuration at one phosphorus of the educt 1-meso is changed from R to S (or vice versa) and products with R,R or S,S configurated phosphorus centers are obtained. This was confirmed by X-ray crystal structure analyses. In the case of 2-meso, the reaction with two equivalents of sodium 4-methoxyphenolate gives a mixture of the stereoisomers 4-meso, 5(R,R) and 5(S,S) (Scheme 1); 4-meso being the major product \( \text{ratio } 4\text{-meso} : [5(\text{R,R})+5(\text{S,S})] = 70 : 30 \).

We attempted to find a plausible mechanism for the change of the configuration at the phosphorus centers within one \( \text{P}_3\text{N}_3 \) unit. While one might speculate about penta-coordinated phosphorus centers undergoing Berry rotation when the biphenoxy substituted cyclotriphosphazene 1-meso is reacted with an anionic nucleophile, such a
possibility is highly unlikely for 2-meso. Instead, an intermolecular exchange of R- or S-configurated (O,O)P units must have taken place, and we propose a mechanism via the formation of a twelve-membered ring as a dimer of two P3N3 units to explain this observation (Scheme 2).

Nucleophilic attack on the electrophilic PCl2 group leads to ring opening and formation of intermediate A. This may act as a further nucleophile and attacks a second equivalent of a meso-configurated 1,1-dichlorocyclotriphosphazene. A dimer B containing a twelve-membered P6N6 ring may result but higher oligomers cannot be ruled out. The structures of cyclophosphazenes (R2PN)n have been thoroughly determined for n = 3-12. It is found, that in particular the P-N-P angles widen with ring size [i.e. 133° in (Me2PN)6]. This may increase the steric interactions between substituents on neighboring phosphorus centers and may be particularly unfavorable for R,S-configurated pairs. Finally the larger ring B collapses into the thermodynamically more stable six-membered chiral phosphazenes. While this mechanism is admittedly highly speculative, it explains why no 4-meso is obtained when 2(R,R) (obtained by reaction of hexachlorocyclotriphosphazene with two equivalents of enantiomerically pure binaphtolate(R)) is reacted with two equivalents of 4-methoxy phenolate. To our knowledge, equilibria between rings of different size as is here indirectly evidenced by exchange of stereochemical different (O,O)P groups have not been described in cyclophosphazene chemistry.

Phosphorus Research Bulletin Vol. 10 (1999), 722
REFERENCES


