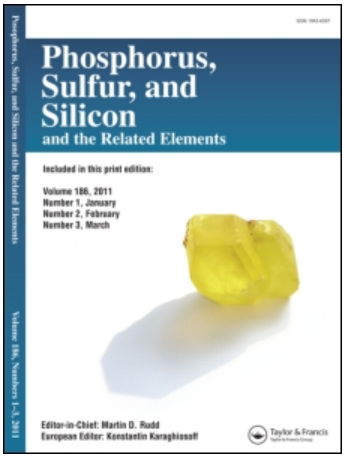

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NEW STRATEGIES IN PREPARING ORGANO-SUBSTITUTED CYCLOPHOSPHAZENES

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Abstract Nucleophilic addition of a copper-phosphazene anion $[(NPCl_2)_2NPR]_2Cu^-$ (R = alkyl) to an aldehyde or ketone, followed by acid hydrolysis, leads to the formation of geminal alkyl(hydroxy-alkyl) derivatives in reasonable to high yields.
Isocyanato cyclophosphazenes provide another entrance to organo-substituted derivatives, in which $(NPCl_2)_2NPNH_2NCO$ appears to be a versatile starting material. Interesting differences are observed between the reactions of $(NPCl_2)_3$ with alkali cyanates and silver cyanate in the presence of an alcohol, using acetonitrile as a solvent.

INTRODUCTION

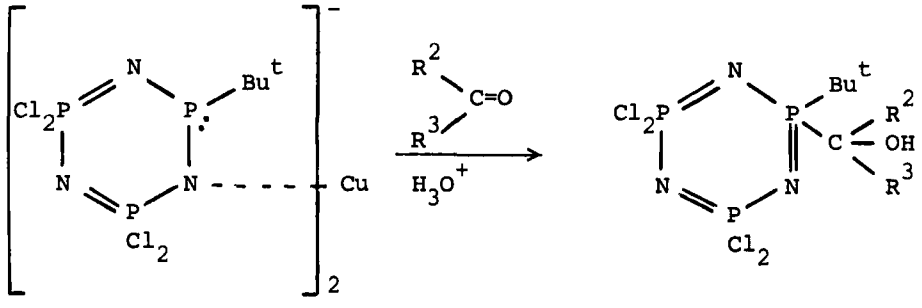
Many examples are known where cyclic or linear phosphazene systems act as carriers for (re)active ligands, which may vary from bioactive substrates to catalysts. One of the most striking examples is formed by the class of 1-aziridinyl substituted cyclophosphazenes, members of which show a pronounced cytostatic activity.[1-3] Catalytic activity has been found for transition metal derivatives.[4] Cyclophosphazenes bearing an organic ligand with an unsaturated site are versatile precursors for the preparation of polymeric systems with a carbon-carbon backbone and pendent inorganic groups.[5] Usually, the chlorine replacement reactions on

cyclo(thia)phosphazene systems lead to complicated reaction mixtures, thus hampering the isolation and lowering the yield of the products desired.

In the present study we describe two regio-specific routes for the preparation of organo-substituted cyclo(thia)phosphazenes, in general leading to a well-defined product formation, a. via a $[(NPCl_2)_2NPR]_2Cu^-$ [6] anion (R = alkyl) and b. via isocyanato derivatives. Both methods provide compounds still possessing PCl_2 moieties as an entrance for further reactions. Moreover, the organic group introduced may offer the opportunity for side-group reactions, i.e. functional group transformation or polymerization.

RESULTS AND DISCUSSION

a. According to the procedure of Allcock et al.[6] hexachlorocyclotriphosphazene $(NPCl_2)_3$ is allowed to react with Bu^tMgCl in the presence of $[Bu^n_3PCuI]_4$. Treatment of the reaction mixture thus obtained by an aldehyde or ketone and subsequent hydrolysis in acid medium leads to the formation of the corresponding alcohols linked to the phosphazene ring by a P-C bond.

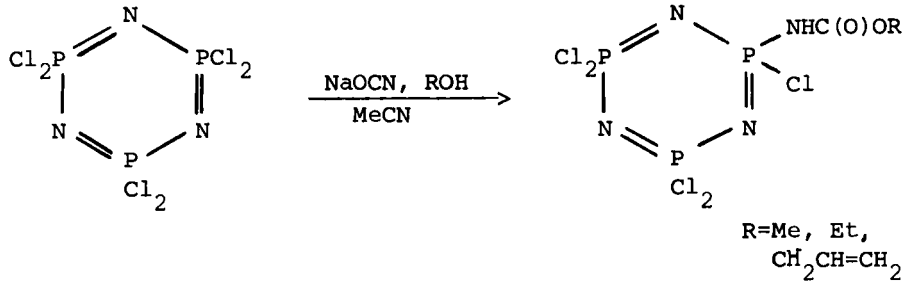


In this straightforward way several new compounds $(NPCl_2)_2NPBu^t[C(R^2R^3)OH]$ are prepared e.g. with R^2 = H, R^3 = Ph; R^2 = H, R^3 = C_6H_4-p-NO_2; R^2 = R^3 = Me; R^2 = Me, R^3 = CH_2Cl. Generalization of this method using MeMgCl or Pr^iMgCl leads to an

additional number of compounds. As an example $(NPCl_2)_2NPPr^i[CHPh(OH)]$ can be prepared in a 70% yield. Both the PCl_2 moieties and the reactive sites on the $C(R^2R^3)OH$-group (OH, Cl, NO_2) make the compounds $(NPCl_2)_2NPR^1[C(R^2R^3)OH]$ to versatile precursors in further reactions.

b. A modification of the procedure of Hofmann[7] and Tesi et al.[8] offers the possibility to prepare $(NPCl_2)_2NPNH_2NCO$ in an excellent yield starting from $(NPCl_2)_2NP(NH_2)_2$. The amino-isocyanato derivative can react with a reagent, carrying an active proton. Reactions with amines and alcohols in an 1:1 molar ratio show an almost quantitative conversion into the corresponding urea or carbamate derivatives. The absence of any reaction at the PCl_2 moieties emphasizes the specificity of this route.

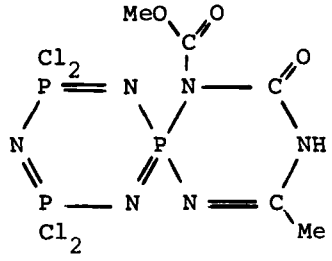
Carbamate derivatives can also be obtained in high yields when $(NPCl_2)_3$ is allowed to react with alkali cyanate salts in the presence of aliphatic alcohols [molar ratio $(NPCl_2)_3$: Na(K)OCN: ROH = 1:1:5]. Some examples are given below



A sluggish process involving the initial formation of $(NPCl_2)NPClNCO$ and a subsequent degradation of this product is observed when the alcohol is omitted. ^{31}P NMR spectra of crude reaction mixtures with two equivalents of the cyanate salt [molar ratio $(NPCl_2)_3$: Na(K)OCN: ROH = 1:2:5] reveal that the second substitution follows a predominantly non-geminal pathway.

A completely different picture is obtained when using AgNCO in

stead of alkali cyanates in the presence of ROH. In acetonitrile generally three products are formed viz. the geminal compounds $(NPCl_2)_2NP[NHC(O)OR]OR$ and $(NPCl_2)_2NP[NHC(O)OR]_2$ (R = Me, Et) and a spirocyclic compound, the structure of which (R = Me) being established by an X-ray structure determination



A geminal attack by an acetonitrile molecule underlies the formation of the spiro compound. The relative yields of the three products are strongly dependent on the molar ratio of the reactants.

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