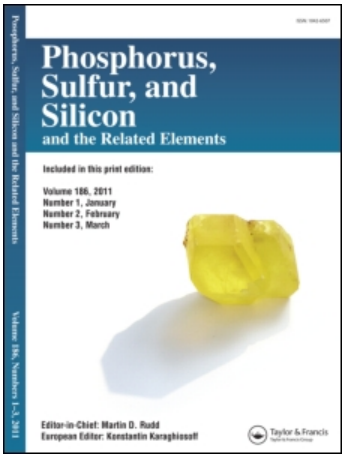

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The Chemistry of Cyclic Carbaphosphazenes: The First Observation of $(R_2PN)(ClCN)_2$ (*R*Cl, Ph) as a Reagent for the Conversion of Alcohols to Aldehydes, Ketones, and Alkyl Chlorides

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The Chemistry of Cyclic Carbaphosphazenes: The First Observation of $(R_2PN)(ClCN)_2$ (R=Cl, Ph) as a Reagent for the Conversion of Alcohols to Aldehydes, Ketones, and Alkyl Chlorides

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*The oxidation of nine primary and secondary alcohols to the corresponding aldehydes and ketones has been carried out under mild conditions and in good yields using the cyclocarbaphosphazenes (R_2 PN)$(ClCN)_2$ [$R_2P = Cl_2P$(**1**), Ph_2P(**2**)] along with dimethylsulfoxide. While both the P—Cl and C—Cl bonds of the carbaphosphazene can in principle bring about the reaction, we observed an increased preference for the C—Cl bonds over the P—Cl bonds in the oxidation of alcohol. Blocking the reactive P site on the heterocyclic ring with the phenyl groups was found to reduce the yields of the oxidized products, while blocking the C- sites with diethylamino groups resulted in no reaction. In addition, along with DMF, the same cyclocarbaphosphazene has been found to be useful for the conversion of alcohols to alkyl chlorides.*

Keywords Aldehydes; alkyl chlorides; cyclocarbaphosphazene; dimethylformamide; dimethyl sulfoxide; oxidation

INTRODUCTION

The impact of inorganic and hybrid inorganic-organic heterocycles, such as halogenated cyclophosphazenes and cyclocarbaphosphazenes, has not only been in use as precursors for inorganic polymers but also in finding the unique heterocyclic framework useful for novel reactions and applications. For example, cyclophosphazenes are found to be useful as stable cores for dendrimer synthesis,[1] as scaffolds for multicenter ligand synthesis,[2] in the design of unique supramolecular networks,[3] and

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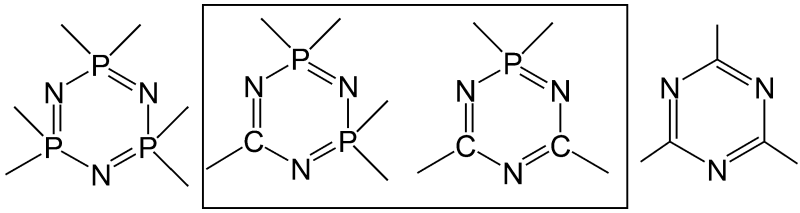
as supramolecular hosts,[4] all of which result from their unique structural framework, reactivity of the P-halogen bonds, and orientation of substituents around the heterocycle. $N_3P_3Cl_6$ has also been used as a reagent for the conversion of carboxylic acids to acid anhydrides[5] and aldoximes as well as acid halides to nitriles.[6,7] Related cyclic carbaphosphazenes having both PCl_2 and C—Cl moieties in their ring framework has revealed a chemistry that differs in many ways when compared to cyclophosphazenes (Scheme 1).



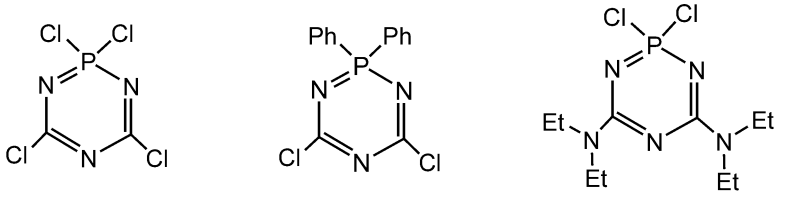
SCHEME 1

Reactions such as dealkylation[8] and ring opening of tertiary amines[9] and those showing regioselectivity in nucleophilic substitution[10] have been unique for carbaphosphazenes. The difference in the reactivities of C—Cl and P—Cl bonds of carbaphosphazenes accounts for these unique reactions. Quite recently, Chandrasekhar and coworkers have prepared the first examples of pendant carbaphosphazene containing monomers and polymers making use of the unique reactivity of carbaphosphazenes.[11] New examples of carbaphosphazenes and better methods for their synthesis have also been reported recently.[12] In this article we report the first observation of the use of chlorinated carbaphosphazenes as a reagent along with dimethylsulfoxide for the mild oxidation of alcohols to aldehydes and ketones. We also report herein the conversion of alcohols to alkyl chlorides when DMF is used instead of DMSO along with the carbaphosphazene.

RESULTS AND DISCUSSION

The oxidation of alcohols using activated DMSO has been first observed by Mancuso and Swern, who used oxalyl chloride along with DMSO.[13] Although routinely used, the Swern oxidation still has some disadvantages as the reaction is violent, oxalyl chloride is sensitive to hydrolysis, and its vapors toxic. The use of reactive halides has since been reported for the same reaction with DMSO, and some of them, such as hypervalent phosphorus[14] as well as iodine compounds[15] and cyanuric chloride,[16] are highly reactive compounds that are relatively difficult

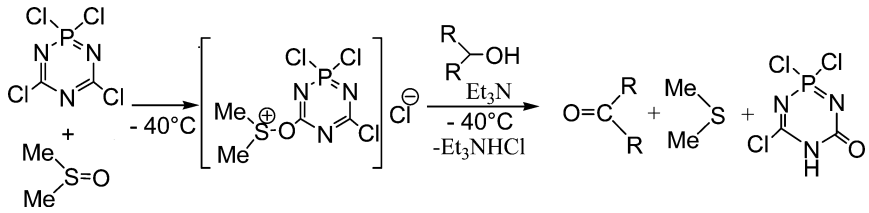
to handle. Our interest in using $(Cl_2PN)(ClCN)_2$ for this reaction stems from the fact that this carbaphosphazene, which is easily prepared by a one-step method, is easier to handle and is more stable than some of the highly reactive DMSO activators. In addition, since P—Cl, C—Cl, or both bonds can in principle bring about such an activation, the unique structure of the hybrid heterocycle also provides an opportunity to determine the relative reactivity of the P—Cl and C—Cl bonds in such mild oxidation reactions. We have chosen three different carbaphosphazenes in the present study with one having both reactive P—Cl and C—Cl bonds(**1**), one with only reactive C—Cl bonds(**2**), and one with only reactive P—Cl bonds(**3**) (Scheme 2).



1 **2** **3**

SCHEME 2

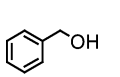
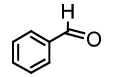
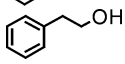
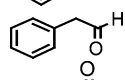
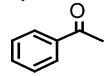
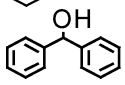
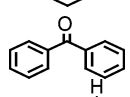
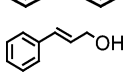
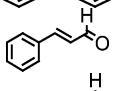
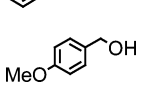
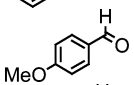
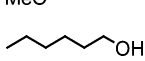
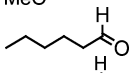
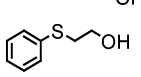
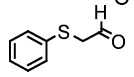
Reactions of cyclocarbaphosphazene **1** were carried out with a variety of alcohols. It was observed that $(Cl_2PN)(ClCN)_2$/DMSO efficiently brings about the oxidation of the alcohols in the presence of triethylamine (Scheme 3). Nine different alcohols were tried that were found to undergo the reaction resulting in oxidized products with yields varying from 31 to 87%. The results are given in Table I.



SCHEME 3

The oxidation of the alcohols were conveniently carried out using CH_2Cl_2 or THF as a solvent. The relatively better procedure with higher yields involved the treatment of cyclocarbaphosphazene with five equivalents of DMSO in CH_2Cl_2 at $-40^\circ C$ for 1 h followed by the addition of alcohol. After an additional 30 min, triethylamine was added, and the reaction was allowed to run for 2.5 h. Bringing the reaction to r.t.

TABLE I The Conversion of Alcohols Into the Corresponding Carbonyl Compounds

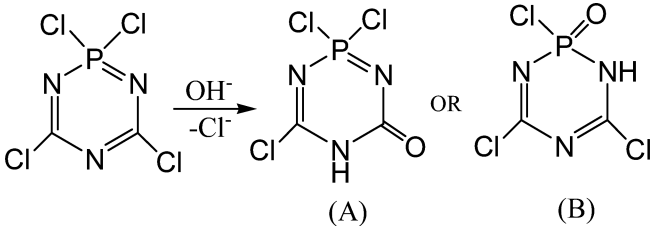
ROH	R′CHO/R_1R_2CO	Percentage yield
		87
		53
		70
		72
		87
		85
		75
		57
		31

and working up yields the carbonyl compound. The reactions were carried out at -40°C to prevent the eventual formation of undesirable byproducts, such as chloro derivatives and thiomethyl ethers. The desired product along with unreacted alcohol, if any, was obtained, from which yields of the products were determined by NMR analysis. Pure aldehydes and ketones were isolated in all cases, and their identity was confirmed by standard spectroscopic methods and comparison with authentic samples.

Taking benzhydrol as a standard, the ideal conditions were worked out so as to maximize yields. It was observed that after the addition of a base, the more the time given for reaction the more was the yield. In order to see the effect of the temperature on yields, reactions were also carried out at -20°C and 0°C. In both cases, the yields were relatively poor, i.e., 32% and 21%, respectively. But when attempted at -60°C, the reaction was complete, and the yield was almost quantitative (>96%). By changing the solvent (THF instead of CH_2Cl_2), the reaction can be carried out, but with a decrease in yields of the products. The oxidation of 2-phenylthioethanol was slow, resulting in a lesser yield, which was

also been observed in a previously reported oxidation reaction of this alcohol.[16]

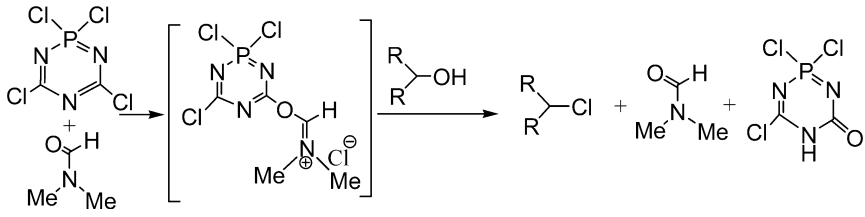
The substitution of Cl by OH groups on chlorinated phosphazenes and cyanuric chloride has been shown to result in the partial ring saturation and formation of an exocylic P=O or C=O bond, respectively, with the adjacent ring nitrogen getting protonated.[8,17] The formation of P=O and C=O bonds of relatively higher stability in comparison to P=N and C=N bonds is the driving force for this reaction in such ring systems. The carbaphosphazene used in the present study has both Cl_2P=N and ClC=N moieties in its framework, and it can in principle get converted to (A) or (B) during the oxidation and chlorination of the alcohols (Scheme 4). To verify this aspect, compounds **2** and **3** having partially blocked phosphorus and carbon sites were prepared and reacted with an alcohol.



SCHEME 4

The reaction of compound **3** having only reactive P—Cl bonds was carried out with benzyl alcohol along with DMSO under conditions that yielded maximum oxidized products in the reaction of alcohols with **1**. However, there was no desired product, and the unreacted alcohol was isolated from the reaction mixture. On the other hand, in a reaction of compound **2** having only reactive C—Cl bonds, the same alcohol was found to react, and benzaldehyde was obtained in 17% yield. This study clearly indicates that C—Cl bonds of the carbaphosphazene are more reactive in comparision to the P—Cl bonds in the previously discussed transformation. A decrease of yield in the oxidized product may be attributed to steric and electronic effects induced by the phenyl groups present on the phosphorus site on the reactivity of the C—Cl bonds.

Reactions of the carbaphosphazene $(Cl_2PN)(ClCN)_2$ with the coreagent DMF brings about an efficient conversion of alcohols to the corresponding alkyl chlorides in CH_2Cl_2 at r.t. (Scheme 5). Among the secondary alcohols used, only 1-phenylethanol gives a better yield than benzhydrol. It is noteworthy that benzyl alcohol, cinnamyl alcohol, and 4-methoxybenzyl alcohol give yields that are almost quantitative. The



SCHEME 5

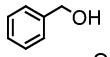
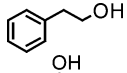
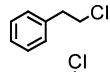
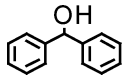
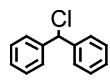
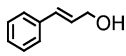
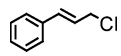
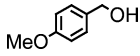
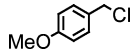
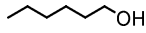
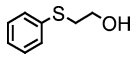
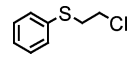
reaction of *n*-hexanol resulted in a mixture of 1- and 2-chlorohexane, and NMR analysis of the mixture revealed that the latter is the major product in the chlorination reaction.

Details of the alcohols used and chlorinated products obtained are given in Table II.

As shown in Schemes 3 and 5, oxidation and chlorination reactions proceed possibly through the formation of alkoxysulfonium and imidinium salts of carbaphosphazene as intermediates. It is important to note that while DMSO gets converted to Me_2S in an oxidation reaction, the role of DMF is more or less catalytic in nature in the conversion of alcohols to alkyl chlorides (Scheme 5).

In conclusion, we report herein the first use of a chlorinated carbaphosphazene as a reagent for the mild oxidation of alcohols as well

TABLE II The Conversion of Alcohols to Alkyl Chlorides

ROH	RCl	Percentage yield
		94
		68
		72
		50
		95
		81
	Mixture of isomers	71
		66

as the conversion of alcohols to alkyl chlorides in good yields in the presence of DMSO and DMF as coreagents.

EXPERIMENTAL

All solvents and alcohols used were obtained from commercial sources and were distilled and dried prior to use by standard procedures. Cyclocarbaphosphazene, $(Cl_2PN)(ClCN)_2$,[18] $(Ph_2PN)(ClCN)_2$,[19] and $(Cl_2PN)(Et_2NCN)_2$[8] were prepared according to literature procedures. All products obtained from the reactions of alcohols were separated, purified, and characterized by ^1H and ^{13}C NMR and IR spectroscopy, and wherever possible, their spectra were compared with authentic samples of aldehydes, ketones, and alkyl chlorides from the literature.

The General Procedure for the Oxidation of Alcohols

DMSO (1.25 mL, 17.6 mmol) was added to a solution of $(Cl_2PN)(ClCN)_2$ (0.86 g, 3.6 mmol) in CH_2Cl_2 (20.0 mL) and was stirred and maintained at -40°C under a nitrogen atmosphere.[20] After 1 h, alcohol (3.0 mmol) in CH_2Cl_2 (10.0 mL) was added slowly at -40°C with stirring, followed by triethyl amine (2.0 mL, 14.3 mmol) after an additional 30 min. After 2.5 h, the reaction mixture was brought to r.t., and the solvent evaporated under vacuum. Diethyl ether (50.0 mL) was then added to the viscous solid formed. The mixture was then quenched with 1N HCl. It was observed that the organic phase selectively dissolved the aldehyde/ketone along with any unreacted alcohol present, and the oxidized carbaphosphazene remained in the aqueous layer. The organic phase was washed with 15 mL of a saturated solution of $NaHCO_3$ followed by brine. After that, it was dried with anhydrous Na_2SO_4, and the solvent evaporated off to get the product. Impure products were purified by column chromatography over silicagel using hexane/ethyl acetate. All products were characterized by spectral data and compared with authentic samples.

The General Procedure for the Conversion of Alcohols to Alkyl Chlorides

$(Cl_2PN)(ClCN)_2$ (1.2 g, 5.0 mmol) was slowly added to DMF (1.0 mL) under a nitrogen atmosphere and maintained at 25°C.[21] A reddish brown colored mass formed, which was stirred for 30 min, and then CH_2Cl_2 (25.0 mL) was added, followed by alcohol (4.5 mmol). After the addition, the mixture was stirred at r.t. for 2 h. Water was added, and the organic phase was then washed with 15 mL of a saturated solution of

Na_2CO_3, followed by 1N HCl and brine. The organic layers were dried with anhydrous Na_2SO_4, and the solvent evaporated off to yield the chlorides. Compounds were purified by column chromatography over silicagel using hexane/ethyl acetate as an eluant.

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