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Novel reactions of cyclocarbaphosphazenes and cyclocarbathiazenes

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Abstract. The hybrid inorganic-organic heterocycles, pentachlorocyclocarba phosphazene, $(ClCN)_2(Cl_2PN)$ and triachlorocyclocarbathiazene, $(ClCN)_2(ClSN)$ were synthesized and their reaction chemistry explored with emphasis on dealkylation reactions of the heterocycles with tertiary amines. Reactions of $(ClCN)_2(Cl_2PN)$ were carried out with bicyclic, unsymmetric and sterically hindered tertiary amines as well as aminomethyl ferrocenes. In all cases, the C–Cl bonds of the carbaphosphazene were found to react with the tertiary amines resulting in the cleavage of an alkyl group and regiospecific substitution of the dialkylamino group on the ring carbon atoms of the heterocycle. While bicyclic amines were found to undergo ring opening, the preference of the cleaved group in the case of unsymmetrical amines were found to depend on the stability of the carbocations formed. Similar dealkylation was observed in the reactions of the carbathiazene $(ClCN)_2(ClCN)$ with tertiary amines.

Keywords. Cyclocarbaphosphazene; cyclocarbathiazene; dealkylation; regio-specificity.

1. Introduction

Cyclophosphazenes and *s*-triazines form two entirely different classes of heterocyclic compounds – the former as inorganic heterocycles which are easily polymerized to yield the well-known phosphazene polymers[1] while the latter is organic and aromatic and forms the basic skeletal framework for a wide variety of heterocycles[2]. Cyclocarba-phosphazenes and cyclocarbathiazenes can be considered as the linking heterocycles between *s*-triazines and cyclophosphazenes or cyclothiazenes as they contain carbon as a third hetero element of the ring framework. Cyclocarbaphosphazenes show properties of phosphazenes being easily polymerized to carbaphosphazene polymers[3] and also show antioxidant and anticorrosive properties similar to *s*-triazines[4]. A variety of these unsaturated cyclic compounds having alternate single and double bonds with ring sizes varying from six to twelve and showing variance in the number and position of the ring phosphorus and carbon atoms have been prepared and characterized[5].

The major difference in the chemistry of cyclocarbathiazenes in comparison with binary sulfur nitrides is the observation that unlike the latter, many examples of the former undergo redox reactions to afford remarkably stable radical and/or antiaromatic species[6]. Among the various types of substituted carbathiazenes, those having a reactive S(IV)–Cl bond have shown the promise of generating stable radicals which are potential candidates in the design of one dimensional molecular conductors[7].

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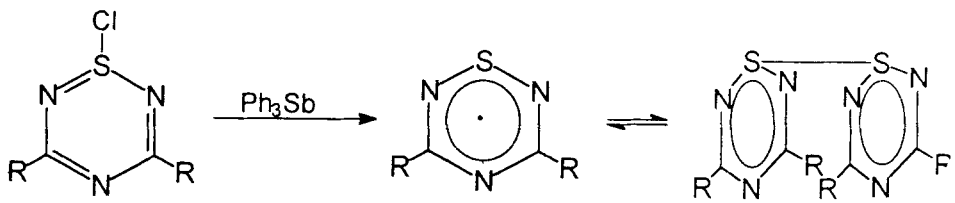
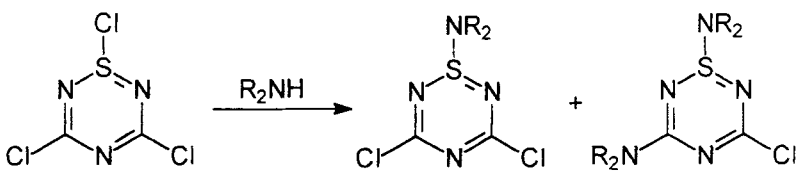


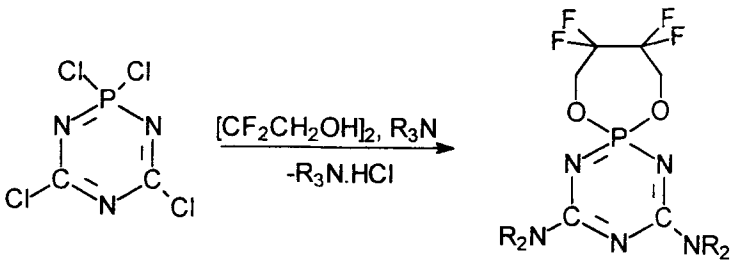
The compounds used so far for preparing such radicals have been restricted mainly to those having an alkyl, aryl or perfluoroalkyl group on the ring carbon atoms. Stable 1,2,4,6-thiatriazenyl radicals are generated by the homolytic cleavage of the S–Cl bonds of the heterocycles and these in turn can be envisaged to form a stack of heterocycles held together with S–S interactions which can be conducting in nature. However, C-amino substituted carbathiazenes have so far not been used for such studies. The main reason for the same seems to result from the fact that C-amino S-chloro substituted cyclothiatriazines cannot be obtained by simple primary or secondary amino substitution of the trichlorothiatriazene heterocycle. In all the reactions of primary and secondary amines with trichlorothiatriazene known so far, replacement of the S–Cl bond by the amino group has been observed as the initial step followed by further reaction of the amine with one of the C–Cl bonds [8].



Attempts to make heterocycles with dialkylamino groups substituted on the ring carbon atoms by direct reactions involving NSCl and dialkylcyanamides or by the reaction of $S_3N_2Cl_2$ and dimethylguanidine hydrochloride have resulted in the formation of $(R_2NCN)(NSCl)_2$ and larger ring systems [9].

N-dealkylations and more specifically *N*-demethylations of tertiary amines are important in organic syntheses and structural determinations of complex organic molecules. C–N bond cleavage of tertiary amines also plays a vital role in cytochrome *P*-450 specific reactions [10] as well as hydrodenitrogenation (HDN) reactions of crude oil [11]. The unusual dealkylations of tertiary amines with heteroaromatic halides were first reported by Kober *et al* [12]. Recently, Matsumoto and coworkers have shown that aromatic and heteroaromatic monohalides can also dealkylate aliphatic tertiary amines however at a pressure of 8 kbar (0·8 GPa) at 100°C over a period of four days [13]. Roesky and coworkers in their studies on chlorocarbaphosphazenes have shown that C–Cl bonds of the PNC heterocycles react preferentially with silylated amines while metal alkoxides favour reaction at the P–Cl bonds [14].

The main impetus for our work is the recent unusual observation that tertiary amines used as HCl scavengers in the reactions of carbaphosphazenes were found to undergo dealkylation. The tertiary amines react with the C–Cl bonds of carbaphosphazenes with the cleavage of an alkyl group and the substitution of NR_2 groups on the ring carbon atoms of the heterocycle [15].



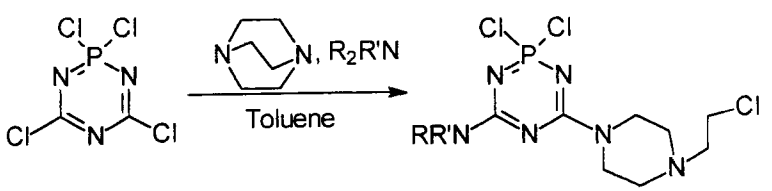
2. Experimental

The cyclocarbaphosphazene, $(ClCN)_2(Cl_2PN)$ and the cyclocarbathiazene, $(ClCN)_2$ (ClSN) were prepared by the reaction of sodium dicyanoamide with PCl_5 and $SOCl_2$ respectively [11,16]. The heterocycles were purified by recrystallization or by kugelrohr distillation. The aminomethyl ferrocenes as well as methylenebis amines used in the study were prepared by literature methods [17]. A typical reaction of the heterocycle was carried out in toluene under reflux conditions for a period of 24 h or in diethyl ether at room temperature. Products were separated by column chromatography over silicagel or by recrystallization. Details of the various experiments have been reported by us elsewhere [18–20].

3. Results and discussion

3.1 *Dealkylation reactions of DABCO*

Unlike simple trialkylamines, reactions of tertiary diamines such as DABCO, TMEDA and 1,4-dimethyl piperazine with chlorocarbaphosphazenes have been observed to result in the formation of large amounts of insoluble solids. For example, an equimolar reaction of DABCO and $(ClCN)_2(Cl_2PN)$ has been observed to give 75% w/w of a white solid which was insoluble in common organic solvents. However, the reaction of $(ClCN)_2(Cl_2PN)$ with one mole of an acyclic tertiary amine followed by one mole of DABCO was found to result in the formation of soluble products wherein both the dealkylated acyclic amine and ring cleaved DABCO were found to substitute regiospecifically on the ring carbon atoms of the heterocycle. The cleaved alkyl part of DABCO was found to remain as a CH_2CH_2Cl group on the piperazino ring.



R = Et(1), n-Pr(2),i-Pr (3), Me(4)
R' = Et(1), n-Pr(2), Et(3), Me(4)

The isolation and characterization of compounds resulting from the ring opening reactions of DABCO with $(ClCN)_2(Cl_2PN)$ unambiguously proves that the cleaved alkyl group in dealkylation reactions of trialkylamines with chlorocarbaphosphazene remains initially as

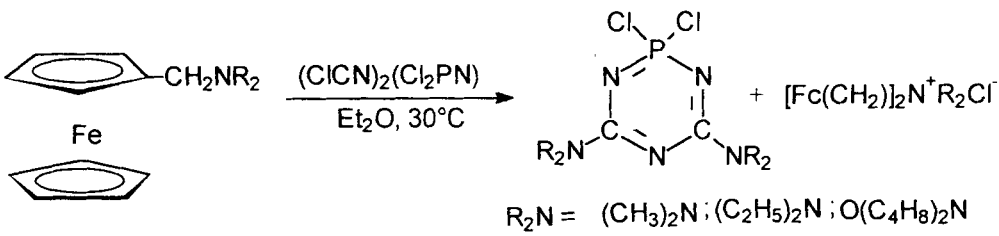
an alkyl chloride [19]. The isolation of amine hydrochloride from reactions of trialkylamines with carbaphosphazenes [15] as well as the proposed formation of tetraalkylammonium chloride [13] can be envisaged as an outcome of further reaction of the cleaved alkyl halide as has been observed in the case of von Braun cyanogen bromide reaction [21]. Dealkylation reactions reported of *N*-methylmorpholine and *N*-methylpiperidine with chlorocarbaphosphazenes did not show any evidence of ring cleaved products [15]. However our reactions show that bicyclic tertiary amines can be made to undergo ring cleavage with chlorocarbaphosphazenes and by careful control of the reaction parameters, one can obtain stable ring cleaved products of the bicyclic amines.

3.2 *Reactions of unsymmetrical tertiary amines with $(ClCN)_2(Cl_2PN)$*

Kapnang and Charles have reported the dealkylation of unsymmetrical tertiary amines with carbonochloridate reagents [22]. From their studies it was observed that the stability of the formed carbocation plays a role in deciding the nature of the group which gets cleaved during a dealkylation reaction in case of an unsymmetrical trialkylamine. Our studies on dealkylation reactions of unsymmetrical tertiary amines with cyanuric chloride [19] and carbaphosphazenes were found to be in agreement with these observations. In the dealkylation reactions of $(c\text{-}C_6H_{11})_2MeN$, $(allyl)_2MeN$ and $(PhCH_2)_2MeN$ we have observed that the groups which get cleaved are cyclohexyl, allyl and benzyl respectively. Reaction of Et_2MeN with $(ClCN)_2(Cl_2PN)$ however was found to give a mixture of products namely $(Et_2NCN)_2(Cl_2PN)$ and $(EtMeCN)_2(Cl_2PN)$. A unique observation was that even sterically hindered non-nucleophilic amines like Hunig's base could be made to undergo dealkylation with the chlorocarbaphosphazene. The group which cleaved in the reaction of $(i\text{-}Pr)_2EtN$ with $(ClCN)_2(Cl_2PN)$ was preferentially the isopropyl group. However the steric effects seem to dominate in deciding the number of C–Cl bonds which can be made to react with the tertiary amines. Unlike other reactions, the reaction of Hunigs base with $(ClCN)_2(Cl_2PN)$ resulted only in the substitution of one C–Cl moiety of the carbaphosphazene under similar reaction conditions.

3.3 *Reactions of $(ClCN)_2(Cl_2PN)$ with aminomethyl ferrocenes*

Reactions of aminomethyl ferrocenes, $FcCH_2NR_2$ ($NR_2 = NMe_2$, NEt_2, $N(CH_2CH_2)_2O$) (Fc = ferrocenyl), were carried out with $(ClCN)_2(Cl_2PN)$ in diethyl ether at room temperature [23]. The amines were found to undergo a facile cleavage at the bridging methylene group and the cleaved dialkylamino groups were found to substitute on the carbaphosphazene heterocycle. The substitution was found to be regiospecific similar to the case of the other amines with only the C–Cl bonds of $(ClCN)_2(Cl_2PN)$ taking part in the reaction and the P–Cl bonds remaining inactive. The analysis of the reaction residue indicated that the cleaved ferrocenyl group had reacted with one more molecule of the amine to give a tetraalkylammonium halide.



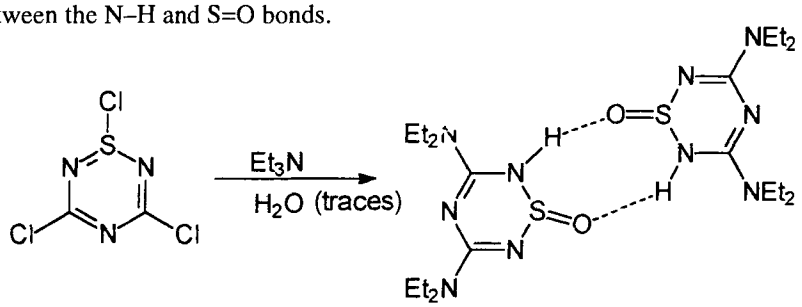
These reactions were found to proceed even at room temperature in diethylether medium. The reaction shows similarities to the von Braun cyanogen bromide reaction reported for dimethylaminomethyl ferrocene, in the mode of cleavage at the bridging methylene group as well as the formation of the tetraalkylammonium halide as the side product[24]. It is noteworthy that as the side product, possible formation of tetra-alkylammonium halide was predicted in S_N1Ar reactions of heteroaromatic halides with trialkylamines[13].

3.4 *Reactions of difunctional tertiary amines with cyanuric chloride and carbaphosphazene*

Reactions of the methylene bridged diamine $Me_2NCH_2NMe_2$ (TMMDA), with $(ClCN)_2(Cl_2PN)$ was found to give exclusively $(Me_2NCN)_2(Cl_2PN)$ indicating the cleavage of the diamine. However reactions of diamines TMEDA and 1,4-dimethyl piperazine when carried out with cyanuric chloride in presence of another tertiary amine yielded derivatives with two heterocycles bridged by the diamine. Unlike the case of TMMDA, in these reactions we did not observe the bridging ethylene group or the pipearazino heterocycle undergo any cleavage. Reactions are underway to explore the potential of this route to make bridged derivatives with carbaphosphazenes as well as those with different heterocycles bridged by the same diamine.

3.5 *Reactions of carbathiazenes with tertiary amines*

Reactions of the S(IV) carbathiazene, $(ClCN)_2(ClSN)$, were carried out with tertiary amines. The primary product of the reaction of $(ClCN)_2(ClSN)$ with triethylamine, $[(Et_2N)CN]_2(ClSN)$ was found to be quite sensitive and underwent hydrolysis of the S-Cl bond in presence of traces of moisture to give a partially saturated thiatriazine heterocycle, $[(Et_2N)CN]_2[S(O)NH]$. This observation was quite similar to the partial hydrolysis of C-diethylamino carbaphosphazene $[(Et_2N)CN]_2(Cl_2PN)$ in presence of traces of moisture where one of the P–Cl bonds is hydrolyzed with the formation of a P=O bond and protonation of one of the adjacent ring nitrogens[15]. The NH proton in the ^1H NMR spectrum of $[(Et_2N)CN]_2[S(O)NH]$ appears as a broad peak at 6·50 ppm Structural studies of the same showed it to be existing as a dimer with hydrogen bonding interactions between the N–H and S=O bonds.



However, reaction of $Me_2NCH_2NMe_2$ with $(ClCN)_2(ClSN)$ gave the compound $(Me_2NCN)_2(ClSN)$ with the S–Cl bond intact and the C–Cl bonds substituted with the dimethyl amino groups. This shows that by the reactions of tertiary amines with chlorocarbathiazines, one can realize dialkylamino substituted carbathiazenes which can undergo homolytic cleavage of the S–Cl bonds to generate stable radical species.

Table 1. Comparison of α hydrogen chemical shifts of dialkylamino carbaphosphazene derivatives prepared in this study with their parent tertiary amines.

Amine used	Fragment	δ in amine	δ in $(R_2NCN)_2(Cl_2PN)$ derivative	Difference in chemical shifts
$N(Et)(i\text{-}Pr)_2$	N–CH	3·03	5·02	1·99
	$N–CH_2$	2·48	3·38	0·90
$N(Me)(Cy)_2$	$B–CH_3$	2·22	2·90	0·68
	N–CH	2·46	4·50	2·04
$N(Et)_3$	$N–CH_2$	2·52	3·50	0·98
$N(Pr)_3$	$N–CH_2$	2·37	3·42	1·05
$Me_2NCH_2NMe_2$	$N–CH_3$	2·26	3·10	0·84
$Me_2NCH_2CH_2NMe_2$	$N–CH_3$	2·25	3·14	0·89
	$N–CH_2$	2·39	3·73	1·34
1,4-Dimethyl piperazine	$N–CH_2$ $N–CH_3$	2·49	3·85	1·36
N-methyl-piperazine	$N–CH_2$	2·49	3·80	1·31
N,N-methylene-bismorpholine	$N–CH_2$	2·40	3·70	1·30

3.6 *Spectral features of dialkylamino substituted carbaphosphazenes*

One of the very interesting features of the proton NMR spectra of the compounds prepared in this study was that in comparison to the starting tertiary amine, the α protons of the dialkylamino groups of the carbaphosphazene derivatives were found to be highly deshielded. This was in conformity with the observation of Katritzky *et al*[25] on methylene protons of similar compounds based on *s*-triazines[23] and has been attributed as a consequence of the high electron withdrawing effect of the carbaphosphazene ring. While N–CH groups are found to be deshielded in the range of 1·99–2·04 ppm, $N–CH_2$ groups are found to get deshielded around 0·90–1·36 ppm. The least observed shift is that for the $N–CH_3$ groups which is in the range of 0·68–0·89 ppm (table 1). This observation indicates a conjugation of the lone pair on the amino nitrogen with the highly electron deficient carbaphosphazene ring resulting in the electron withdrawal from the alkyl group attached to the exocyclic nitrogen. One could therefore envisage increased double bond character for the exocyclic C–N bond.

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