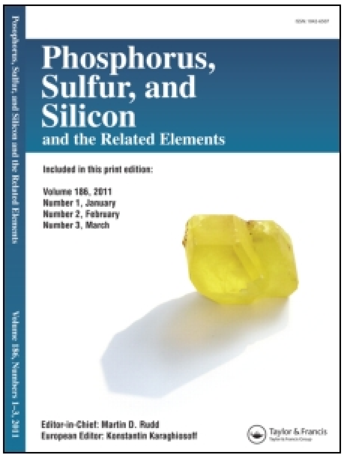

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CYCLOCARBOPHOSPHAZENES: SYNTHESES, REACTIONS AND PROPERTIES

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CYCLOCARBOPHOSPHAZENES: SYNTHESES, REACTIONS AND PROPERTIES

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The syntheses, reactions, properties and uses of cyclocarbophosphazenes have been described. The specific synthetic methodologies adopted for the syntheses of the six, eight and twelve membered heterocycles with varying ring substituents from fully halogenated to fully aliphatic or aromatic substituted have been discussed. The different types of reactions of these heterocycles have been classified under nucleophilic substitution, partial ring saturation and ring degradation and polymerization reactions. The physical and spectral properties with emphasis on IR, NMR and X ray structural investigations as well as important applications of these compounds have also been presented.

Keywords: syntheses; reactions; cyclocarbophosphazene; cyclodicarbophosphatriazene; cyclocarbodiphosphatriazene; heterocycles; properties

1. INTRODUCTION

Cyclophosphazenes (**Ia**)[1] and *s*-triazines (**Id**)[2] form two entirely different class of well studied heterocyclic compounds – the former as inorganic heterocycles which are easily polymerized to yield the well known phosphazene polymers[3] while the latter is organic and aromatic and forms the basic skeletal framework for a wide variety of heterocycles which include melamines and cyanuric halides whose uses range from herbicides in agriculture to optical brighteners in textile and plastic industry.[4]

Cyclocarbophosphazenes (**Ib**, **Ic**) can be considered as the linking heterocycles between *s*-triazines and cyclophosphazenes as they contain both C-N and P-N moieties as part of their ring framework. They show properties of phosphazenes being easily polymerized to carbophosphazene poly-

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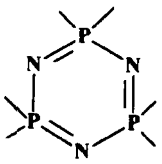
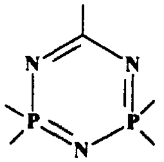
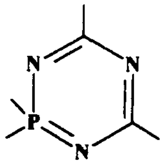
* Corresponding Author.



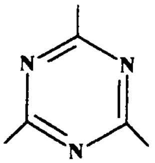
Ia



Ib



Ic



Id

mers[5] and also show antioxidant and anticorrosive properties similar to s-triazines.[6,7,8] 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. The substituents on the ring vary from halogens to alkyl, aryl, amino, alkoxy, aryloxy, arylthio and perfluoroalkoxy groups. Highlights in the chemistry of carbophosphazenes have been reviewed along with cyclophosphazenes annually.[9] In this review we have attempted to cover the literature on these compounds in detail till to date with emphasis on the synthetic and structural characteristics as well as their reactions, properties and potential applications.

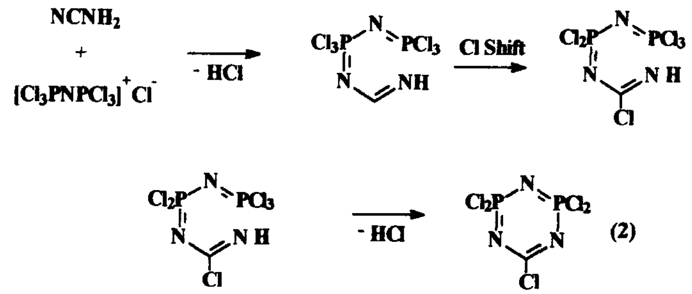
Generally two different approaches have been used for the preparation of cyclocarbophosphazenes. The former involves synthesis of fully or partially halogenated cyclocarbophosphazenes followed by substitution reactions on the rings. The latter method involves the direct synthesis of partial or fully alkyl or aryl substituted heterocycles by the reaction of pentavalent phosphorus halides or substituted halides with amidines or by the cyclocondensation reaction of amidines or ammonium salts with acyclic phosphazenium or carbophosphazenium halides.

2. SYNTHESIS OF SIX MEMBERED CYCLOCARBODIPHOSPHATRIAZENES

Substituted carbodiphosphatriazenes except those having three halogens and two alkyl / aryl groups on the ring skeleton have been synthesized. The halogen atoms on the ring have been restricted to chlorines only. The direct synthesis of these compounds have been carried out by a variety of synthetic routes.

a) With five halogen atoms as substituents($N_3P_2CX_5$)

The only example of this type, $N_3P_2CCl_5$ (**2**) was prepared by Fluck and coworkers in 1975 by the reaction of cyanamide with the halophosphazenium salts $[Cl_3PNPCl_3]^+ PCl_6^-$ or $[Cl_3PNPCl_3]^+ Cl^-$. The yields varied from 13 – 61 % depending on the nature of the solvent as well as the nature of the halophosphazene salt used.[10] A plausible mechanism for the formation of these species has been proposed as follows.

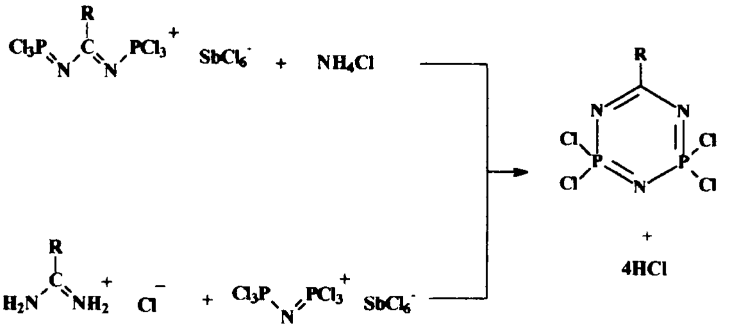


(2)

A modified procedure of this method was recently used by Allcock and coworkers to prepare the heterocycle in 20 – 40 % yield. This was used to make the first carbophosphazene polymer by ring opening polymerization at 120 °C.[5,11]

b) With four halogens and one alkyl/aryl substituent ($N_3P_2CX_4R$) (3)

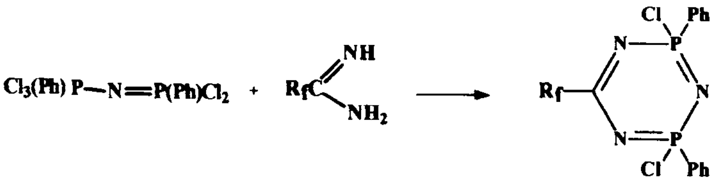
Schmidpeter and coworkers have prepared these compounds using two main synthetic strategies. A [5+1] cyclocondensation of N,N-(trichlorophosphoranylidene) amidinium hexachloroantimonate with ammonium chloride or a [3+3] thermal cyclocondensation of $[RC(NH_2)_2]Cl$ (R= Ph, Me_2N) with $[N(PCl_3)_2]SbCl_6$ gave the ring compounds in good yields.[12] Another variety of this compound with R = CCl_3 and CF_3 were prepared by Glemser et al. as a side product in the reaction of $Cl_3C{:}CCl_2N{:}PCl_3$ or $CF_3{:}CCl_2N{:}PCl_3$ with NH_4Cl while preparing dicarbomonophosphatriazenes.[13]



(3)

c) With two halogens and three alkyl/aryl substituents ($N_3P_2CX_2RR_2'$)

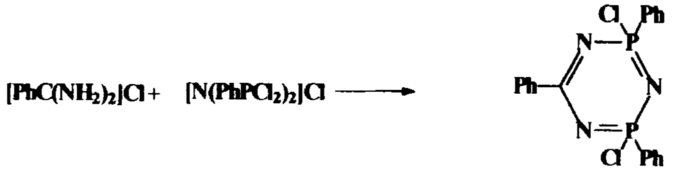
Compounds having one chlorine atom on each phosphorus and a perfluoroalkyl substituent on the carbon atom (**4a**) were prepared by Pacioreck and coworkers by the direct reaction of perfluorinated octanoyl amidines and linear phosphazenes of the type $PhPCl_2{:}NPPhCl_3$.[14,15]



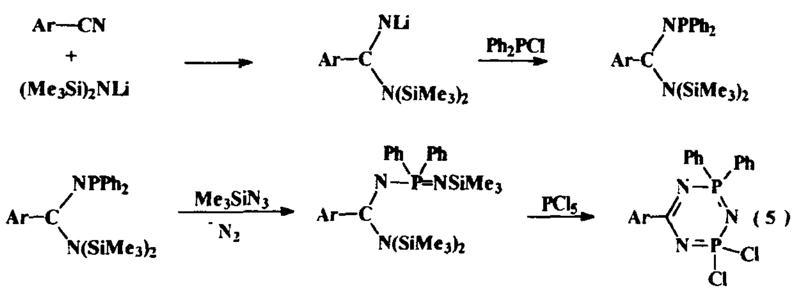
(4a)

R_f = n C_7F_{15}; $C_3F_7OCF(CF_3)CF_2OCF(CF_3)$

Schmidpeter and coworkers have shown that cyclocondensation of $[Ph(CNH_2)_2]Cl$ with $[N(PhPCl_2)_2]_2$ gives the cis and trans isomers of the compound $PhC(NPPhCl)_2N$ (**4b**).[12] The geminal isomer having both halogens on the same phosphorus (**5**) was also prepared by a different route starting with a substituted aromatic nitrile.[16]

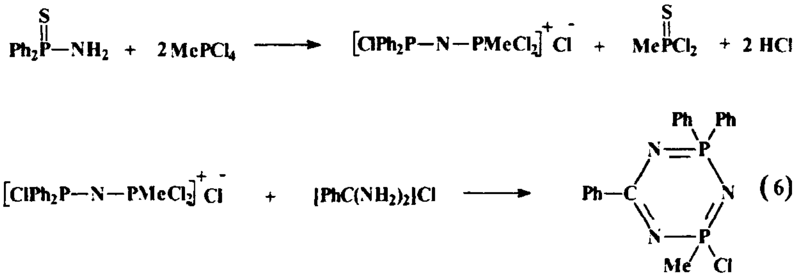


(4b)



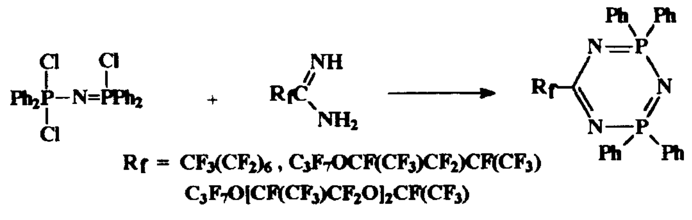
d) With one halogen and four alkyl/aryl substituents ($N_3P_2CXRR_3'$)

The only example of this type of heterocycle prepared by direct synthesis, PhC[$NPPh_2$][NPMeCl]N (**6**), was obtained in 88 % yield from the cyclocondensation of [$Ph(CNH_2)_2$]Cl with [$Ph_2PCl{:}NPMeCl_2$]Cl.[14]



e) With five alkyl/aryl groups as substituents (7,8)

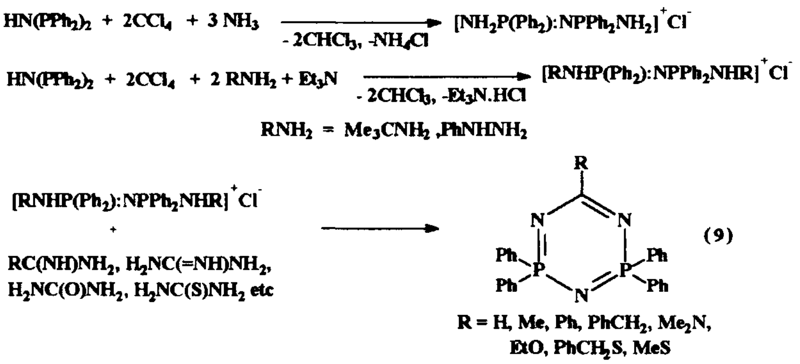
Carbodiphosphatriazene having five phenyl substituents, $N_3CP_2Ph_5$ (**7**) was prepared by Chandrasekhar et al. as a side product in the reaction of Ph_2PCl_3 and Li[$CPh(NSiMe_3)_2$].[17] The compounds having two different R groups (**8**)[18] as well as three different R groups[19] were prepared by Pacioreck and coworkers by varying the substituents on the amidines and the linear phosphazenium compounds.



$R_f = CF_3(CF_2)_6$, $C_3F_7OCF(CF_3)CF_2)CF(CF_3)$
$C_3F_7O[CF(CF_3)CF_2O]_2CF(CF_3)$

(8)

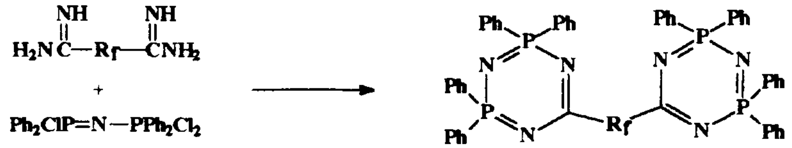
Another route to prepare a variety of carbodiphosphatriazenes including those having a hydrogen attached to the ring carbon atom (**9**) was reported by Appel and coworkers. Bis(diphenyl phosphino)amine on reaction with CCl_4 along with ammonia, t-butylamine or phenyl hydrazine forms the ionic compound $[RNHP(Ph_2):NPPh_2NHR]^+Cl^-$. Cyclocondensation of this compound with amidines, guanidines, isoureas and isothioureas gave the corresponding carbodiphosophatriazenes.[20]



R = H, Me, Ph, $PhCH_2$, Me_2N, EtO, $PhCH_2S$, MeS

(9)

A different variety of this class of compounds having two of the carbodiphosphazene rings coupled together by a perfluoroalkyl group through the carbon atoms (**10**) were prepared by the reaction of bridged amidines with $Ph_2ClP:NPPh_2Cl_2$.[21]



(10)

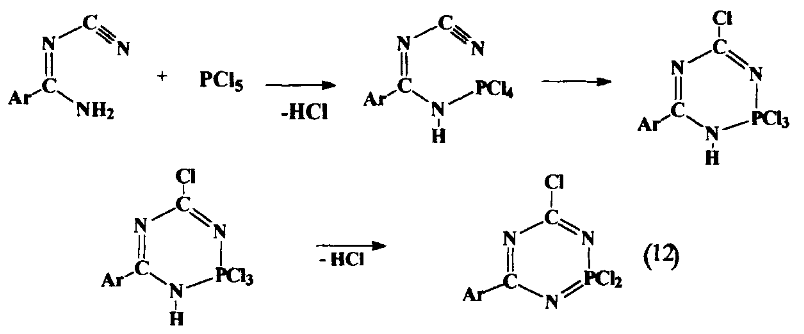
3. SYNTHESIS OF SIX MEMBERED CYCLODICARBOPHOSPHATRIAZENES

a) With four halogens as ring substituents ($N_3PC_2X_4$)

The example of this kind with four chlorine atoms on the ring $(ClCN)_2(Cl_2PN)$ (**11**) was prepared by M. Becke Goehring and coworker in 71% yield by the reaction of $NaN(CN)_2$ with PCl_5 in 1,2-dichloroethane.[22] The same compound was prepared by Kornuta et al. by a different route using PCl_5 and $NCN{:}CCl{:}NH_2$ in 84 % yields.[23] The partially fluorinated heterocycle $(ClCN)_2(F_2PN)$ has been reported to form when (**11**) is reacted with SbF_3.[24]

b) With three halogens and one alkyl/aryl/amido substituent. $(RCN)(N_2CPCl_3)$

Examples with aryl substituents on one of the carbon atoms (**12**) were prepared by Kornuta et al. by the reaction of p-$YC_6H_4C({:}NCN)NH_2$ and PCl_5 (Y = H, Cl, Me, MeO) in 72–92 % yields.[25] Similar compounds with R = CCl_3, Me_3C, Me, Et were prepared by the reaction of cyanamidines $NCN{:}CRNH_2$ with PCl_5.[24] Reaction of dicyandiamide and PCl_5 in 1:2 molar ratio gave a compound with both the carbons having chlorine substituents and one of the substituents on the phosphorus as $Cl_3P{=}N$-, a phosphinimino group.[22]

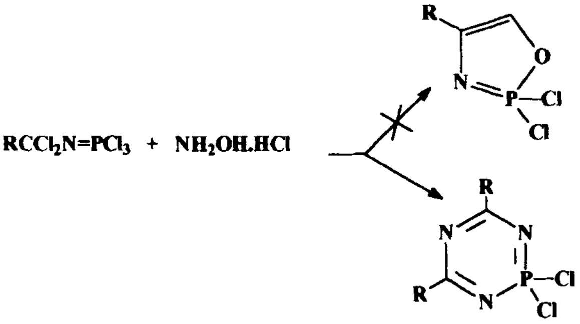


(12)

c) With two halogens and two alkyl/aryl substituents $(RCN)_2(NPX_2)$ (13)

Reactions of $Cl_3C{:}CCl_2N{:}PCl_3$ or $CF_3{:}CCl_2N{:}PCl_3$ with NH_4Cl in the presence of $AlCl_3$ gave heterocycles with CCl_3 and CF_3 groups substituted on the ring carbon atoms in 35–38% yields.[13] Compounds with X = Cl or Br and perfluoroalkyl or perfluoroalkyl ether groups on the carbon atoms were prepared by the reaction of PCl_5 and perfluoroalkyl or perfluoroalkyl ether imidoylamidines ($H_2NCR{:}NCR{:}NH$) in an inert atmosphere in presence of Et_3N.[26] The difluoro analogues of (**13**) [R = CCl_3, CF_3] were obtained only by reactions of (**13**) with SbF_3.[27]

The reaction of 1,1-dichloroalkylphosphorimidic trichlorides with hydroxylamine hydrochloride, instead of yielding the five membered oxodiazaphospholes gave the 2,2-dichloro, 1,3,5,2,-triazaphosphorine.[28]



(13)

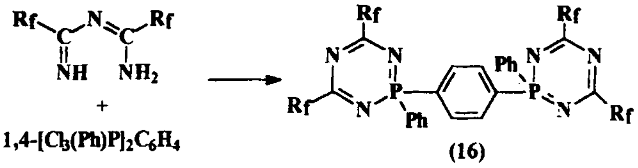
d) With one halogen and three alkyl/aryl substituents$(N_3PC_2R_3X)$ (14)

Examples of these type of compounds have been prepared only by substitution reactions on phosphadihaloheterocycles of the type (**13**) with alkali metal amides or metal alkoxides.[29]

e) With four alkyl/aryl/amino substituents

The reaction of Ph_2PCl_3 with amidines of the type $HN{:}CRN{:}CRNH_2$ gave the heterocycles having two phenyl groups on the phosphorus atom and a perfluoroalkyl or perfluoroalkyl ether group on the carbon atoms of the formula $(Ph_2PN)(R_fCN)_2$ (**15**).[30] Amino substitution on the partially halogenated rings gave compounds having both alkyl/aryl and amino groups as substituents on the ring.

Reactions of Ph_2PCl_3 with $H_2NCR{:}NC({:}NH)]_2Z$, $[Z{=}CF_2)_8$, R= perfluoroalkyl, perfluoroalkyl ether] gave polymeric systems having more than one dicarbophosphazene rings coupled together through the carbon atoms.[31] A similar compound having two dicarbophosphazene units coupled through the phosphorus atoms on the 1,4- positions of a phenyl ring was obtained from the reaction of $1,4\text{-}(PhCl_3P)_2C_6H_4$ with imidoylamidines of the type $RC({:}NH)N{:}CRNH_2$ [$R = F_3C(CF_2)_6$ (**16a**), $F_3CCF_2CF_2OCF(CF_3)CF_2OCF(CF_3)$ (**16b**)].[32] Roesky and coworkers reported the synthesis of a similar ring but bridged by two PPh units which was obtained from a reaction of Me_2NCN with $LiN(SiMe_3)_2$ and $PhPCl_2$(**17**).[33]

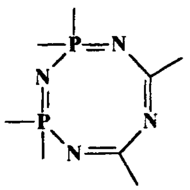


(16)

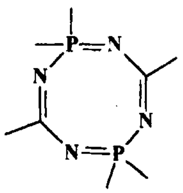
$Rf = CF_3(CF_2)_6\text{-}, C_3F_7OCF(CF_3)CF_2OCF(CF_3)\text{-}$

4. SYNTHESIS OF EIGHT MEMBERED CARBOPHOSPHAZENES

A series of isomeric diphosphatetraazacyclooctatetraenes having the 1,3 as well as the 1,5 phosphorus arrangements have been reported. All the reported examples have aryl, perfluoroalkyl or perfluoroalkyl ether substituents on the phosphorus and carbon atoms.

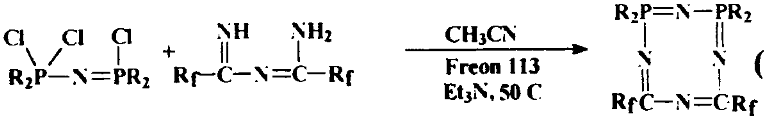


1,3 - isomer



1,5 - isomer

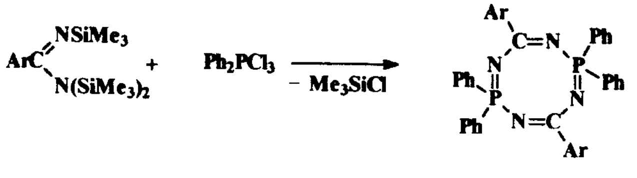
The 1,3 isomers, e.g. (**18**), were prepared exclusively by the reaction of perfluoroalkylimidoyl amidines and imido-tetraphenyl-diphosphinic acid trichloride in 80–98 % yield using acetonitrile and freon −113 as solvents in the presence of triethylamine at 50 °C.[34]



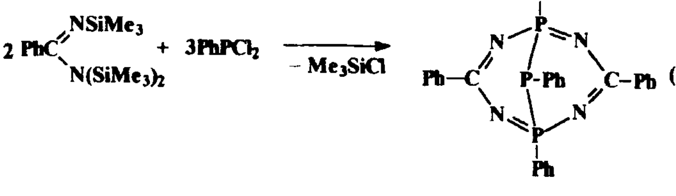
(**18**)

Performing the reaction in the absence of a solvent or in s-tetrachloroethane always resulted in the formation of the six membered cyclocarbophosphazenes with poor yields of the cyclotetrazenes.

The first report on the synthesis of the 1,5- isomer involved the reaction of aryl phosphites with aryl amidines.[35] The heterocycle obtained underwent the oxophosphazane rearrangement in presence of hydroxyl ions leading to partial ring saturation. The 1,5 isomer having perfluoroalkyl groups on the carbon atom was best synthesized by the reaction of $R_fC(:NH)NH_2$ with Ph_2PCl_3 under similar reaction conditions.[34] However the yields varied from 11 to 32 % and quite often the product was formed along with the mono and diphospha s-triazines. Reaction of Ph_2PCl_3 with $Li[PhC(NSiMe_3)_2]$ or $ArCN_2(SiMe_3)_3$ ($Ar = C_6H_4CH_3$-4, $C_6H_4CF_3$-4) gave the eight membered 1,5-$Ph_4P_2N_4C_2Ar_2$ (**19**).[17] A 2:3 reaction of $PhC(:NSiMe_3)N(SiMe_3)_2$ with $PhPCl_2$ gave an eight membered heterocycle having an intramolecular P-P bridging with a PPh unit (**20**).[33]



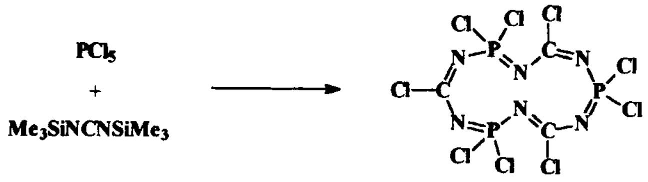
(19)



(20)

5. SYNTHESIS OF TWELVE MEMBERED CYCLOCARBOPHOSPHAZENE

The only example of a twelve membered cyclocarbophosphazene, $[Cl_2PN_2CCl]_3$,**(21)** was prepared by the reaction of PCl_5 and Me_3Si-NCN-$SiMe_3$ in a reaction performed in toluene in equimolar ratio. The compound which was obtained in 80 % yield was air sensitive decomposing on storage to an insoluble polymer.[36]



(21)

6. REACTIONS OF CYCLOCARBOPHOSPHAZENES

A variety of reactions have been carried out on the cyclocarbophosphazene heterocycles. The most prominent among these were the nucleophilic substitution reactions on the fully or partially halogenated heterocycles. In addition, reactions leading to partial saturation of the double bonds, ring opening leading to degradation as well as polymerization have been carried out especially on the six membered cyclocarbodiphosphatriazenes and cyclodicarbophosphatriazenes.

6.1 Nucleophilic substitution reactions

These involves the major type of reactions so far carried out on both monocarbo and dicarbo phosphatriazenes. Complete substitution of the five chlorine atoms by secondary amino (diethylamino, aziridino)[37] groups as well as by a variety of alkoxy (CH_3O, CF_3CH_2O)[11] and aryloxy (C_6H_5O, p-$Bu^tC_6H_4O$-, p-BrC_6H_4O-, p-$[PhC(CH_3)C_6H_4O$-, p-$CH_3OC_6H_4O$-, p-PhC_6H_4O-, p-$CH_3OC(O)C_6H_4O$-, p-$CF_3C_6H_4O$- and o-$CF_3C_6H_4O$-)[5] groups have been carried out on **(2)** . It is interesting to note that reactions of $N_3P_2CCl_5$ with two moles of diethylamine led to monosubstitution on the ring carbon atom only.[37] In contrast to alkoxy and polyfluoroalkoxy derivatives of cyclophosphatriazenes, similar derivatives of $N_3P_2CCl_5$ were found to be hydrolytically sensitive. However, pentasubstitution by arylamino and aryloxy groups was found to provide additional stability to the ring frame work.

Schmidpeter and coworkers have carried out substitution reactions on tetrachloro ($RCN_3P_2Cl_4$, R = Ph, Me, NMe_2) (**3**) and vicinal dichloro ($R_3CN_3P_2Cl_2$, R = Ph) (**4b**) carbodiphosphatriazenes. Secondary amines like pyrrolidine, piperidine, morpholine, aziridine, dimethylamine as well as ammonia and tert- butyl amine were effectively substituted on the phosphorus atoms of (**3**).[38] Substitution with amines like aziridine, imidazole, dimethylamine and diethylamine were carried out on (**4b**). Controlled vicinal and geminal disubstitution on these heterocycles were demonstrated by reactions with t- butyl amine and piperidine.[39] Alkoxy derivatives of (**3**) (R = Me and Ph) and (**4b**) have been prepared by their reactions with alcohols in presence of pyridine as HCl scavenger. However in case of (**3**) (R = Me) the yields were poor due to ring cleavage and formation of $(RO)_3P{=}N{-}P(O)(OR)_2$ and $[MeC(NH_2)_2]Cl$. Proton transfer from the pyridine hydrochloride to the ring nitrogen and further attack of a molecule of alcohol on the adjacent phosphorus atom has been proposed as the initiation step for this ring cleavage. Higher yields are obtained in these reactions when sodium salt of the alkoxide is used instead of alcohol and pyridine, supporting this contention. Reactions of (**3**) (R = Me, Ph , NMe_2) when performed with sodium alkoxides (RONa ; R = Me, n- Bu, p-MeC_6H_4, C_2H_5) gave a mixture of two products, one with tetrasubstitution and the other with trisubstitution at the phosphorus sites which were easily identifiable by phosphorus NMR data.[40]

An interesting aspect of nucleophilic substitution on dicarbophosphatriazenes was the regioselectivity observed in the substitution pattern on these heterocycles. Certain nucleophiles, especially amines have an increased tendency to preferentially substitute on the carbon atoms. Roesky et al. have demonstrated this regioselectivity on $N_3PC_2Cl_4$ (**11**) by comparing reactivity of $Et_2NSiMe_3$and CF_3CH_2OLi in controlled stoichiometric conditions. While Et_2NSiMe_3 reacted preferentially on the two carbon atoms, CF_3CH_2OLi reacted only at the phosphorus site.[41] However, on reacting with a large excess of secondary amines (aziridine[42], dimethylamine[43]) tetraamino substitution on the ring was observed.

Kornuta and coworkers have also observed that the order in which the chlorine atoms were replaced on 6-Phenyl, 2,2,4-trichloro- 1,3,5,2 λ^5

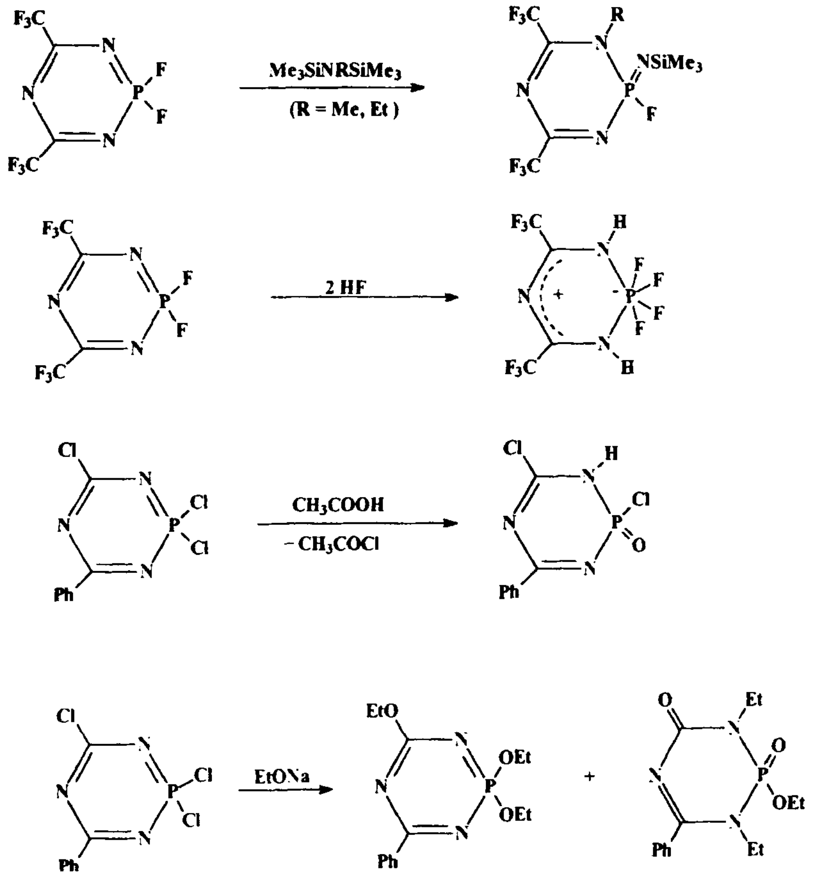
dicarbophosphatriazenes (**12**) depends on the nature of the nucleophile. While weak nucleophiles like butyl alcohol, acetic acid, water attacked the phosphorus site,[23,25a] strong nucleophiles like amines,[44,45] and sodium benzene thiolate[46] preferred to react initially at the carbon site. With sodium methoxide and sodium phenoxide both carbon and phosphorus centers were found to substitute simultaneously.[46] However a contrasting observation was reported by Fisher et al. who observed that C-Cl bond remains unreacted and disubstitution at the phosphorus occurs when $[NCPh][N_2PCCl_3]$ is reacted with Me_2NH in diethylether at –60 ° C.[47]

Reactions of difunctional reagents of the type $HX(CH_2)_nXH$ [$X = NCH_3$, n = 2[48] ; $= NC_6H_5$, n = 2 ; X = O, n = 3; X = S, n = 3][49] with dichlorodicarbophosphatriazenes of the type (**13**) were found to give spirocyclic derivatives when performed in presence of Et_3N. However catechol reacted with (**13**) forming a spirocycle which in the course of the reaction formed clathrates with solvent molecules like C_6H_6, $C_6H_5CH_3$, C_6H_5Cl, $C_6H_5CF_3$, CH_2Cl_2 and $CHCl_3$. Novel spirocyclic compounds where the spirocyclic group itself is a P-N moiety was obtained from the reaction of dichlorocarbophosphatriazene (**13**) ($R = CF_3$) with ammonia or primary amines followed by reaction with PCl_5 to yield phosphinimino groups and finally closing of the ring with silylated amines.[48]

An unusual type of reaction was observed when $N_3P_2CCl_5$ (**2**) as well as $N_3PC_2Cl_4$ (**11**) were reacted with polyfluorinated diols, $(CF_2)_n(CH_2OH)_2$ (n = 2,3) in presence of tertiary amines. The tertiary amines were found to undergo a facile C-N bond cleavage and the generated secondary amino groups were found to substitute regioselectevely on the ring carbon atoms. The polyfluorodiols were found to substitute preferentially as a spirocycle on the phosphorus site.[50] It was also observed that when aliphatic tertiary amines were reacted alone with (**2**) and (**11**), selective substitution by dialkylamino groups on the ring carbon atoms occured.[50] This kind of dealkylation was also found to happen with $(ClCN)_3$.[51] Reactions of (**2**) and (**11**) with $(CF_2)_n(CH_2OLi)_2$ (n = 2,3) gave exclusive spirocyclic substitution on the phosphorus sites.

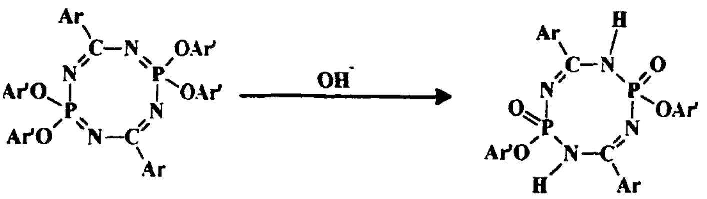
6.2 Reactions leading to partial ring saturation

Unlike cyclophosphazenes, cyclocarbophosphazenes show an increased tendency to undergo partial saturation of the ring double bonds. This phenomenon was quite pronounced at the phosphorus site and especially with alkoxy substituents, the phosphorus site undergoes a rearrangement akin to the alkoxyphosphazene – oxophosphazane rearrangement shown by cyclophosphazenes.



In a few cases of alkoxy substitution, the carbon center also underwent conversion to a carbonyl group, which is quite a common feature in the chemistry of cyanuric acids and their derivatives. In general, reagents like silylated amines,[26] HF,[52,53] acetic acid, butanol,[25a] sodium ethoxide[44] and water[50] were found to bring about these reactions.

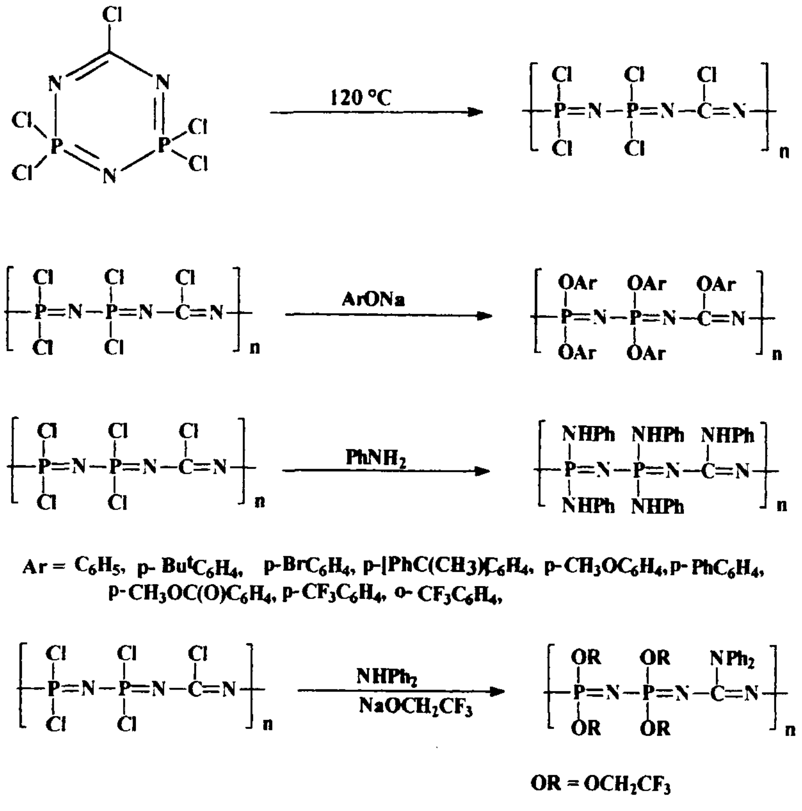
The eight membered heterocycle was also found to undergo partial ring saturation in presence of hydroxyl ions.[35]



6.3 Ring degradation and Polymerization reactions

Hydrolysis of trichlorinated dicarbophosphatriazenes, (**12**) lead to ring cleavage and formation of acyclic species. N alkyl, N cyano N'(dialkoxyphosphinyl)ureas which were viscous high boiling liquids were obtained when perchlorinated dicarbophosphatriazene [(**12**) R = CCl_3] was treated with sodium alkoxides in presence of alcohols.[44,48] The aryl analogue of the same yielded N- cyano benzamidines when treated with water along with phosphoric acid and HCl.[25b] Alkoxy substituted carbodiphosphatriazenes also underwent ring cleavage in presence of amine hydrochloride[38]

The thermal ring opening polymerization of $N_3P_2CCl_5$ (**2**) in evacuated sealed glass ampoules yielded the polycarbophosphazene polymer, $[N_3P_2CCl_5]_n$.[54,55] The temperature of polymerization 120 °C, which was much below the normal polymerization temperature of $N_3P_3Cl_6$ was very crucial in this reaction as above this temperature a complex mixture of products and cross linked polymeric mixtures resulted. The polymer was a hydrolytically sensitive, adhesive elastomeric material. The glass transition temperature of this polymer (-21°C) was significantly higher than that observed for $[NPCl_2]_n$ (-63°C) which indicated that the backbone bonds of this polymer have significantly less torsional flexibility than $[NPCl_2]_n$. A variety of aryloxy and anilino groups have been substituted on the P-Cl and C-Cl bonds yielding polymers which were hydrolytically quite stable.[5a] Regioselective addition of Ph_2N group to the carbon atoms have also been achieved with the phosphorus substituted with trifluoroethoxy groups. However substitution with alkylamines led to formation of polymers which were sensitive to hydrolysis.[5b]



Ar = C_6H_5, p-$Bu^tC_6H_4$, p-BrC_6H_4, p-[$PhC(CH_3)$]C_6H_4, p-$CH_3OC_6H_4$, p-PhC_6H_4, p-$CH_3OC(O)C_6H_4$, p-$CF_3C_6H_4$, o-$CF_3C_6H_4$,

OR = OCH_2CF_3

7 PROPERTIES AND USES OF CARBOPHOSPHAZENES

7.1 Physical Properties

Similar to the reaction behavior, physical and spectral properties of carbophosphazenes show similarity to both s- triazines and cyclophosphatriazenes. The halogenated heterocycles were quite sensitive towards moisture while the substituted heterocycles, especially perfluoroalkyl and aryloxy derivatives were quite stable against decomposition in presence of moisture.[5] However compared to alkoxy and polyfluoroalkoxy derivatives of cyclophosphazenes which were quite stable, similar derivatives of carbophosphazenes were hydrolytically sensitive.[11] The thermal stability and antioxidant property of perfluoralkyl group containing carbophosphazenes have made them excellent candidates as additives in various high temperature fluids and lubricants. Pacioreck and coworkers have carried out extensive studies on the decomposition and antioxidant properties of these compounds.[25,30,31,32,56,57,58]

Theoretical studies (Pariser-Parr-Pople,[59] SCF-LCAO-MO within CNDO/2 approximation[60]) on carbophosphazenes have been carried out to predict their electronic structures and ring stabilities. Similar to triaziridinyl triazines (TEM) and hexaaziridinyl phosphatriazenes (MYKO63) which show potential antitumor activity, quantum calculations predict that the aziridino derivatives of cyclocarbodiphosphatriazenes and cyclodicarbophosphatriazenes may have good or even better antitumor properties. Basicity studies on $[NPR_2]_2[NCR]$ indicate that in these compounds protonation is preferred at the P-N-C rather than the P-N-P segments.[61]

Dipole moments of a series of dicarbophosphatriazenes have been determined to study the polarisability and decreased stability of carbophosphazenes compared to s- triazines and cyclophosphatriazenes.[62,63] The variation in the dipole moments were found to depend upon the substituents on the ring.

7.2 Spectral characteristics of Carbophosphazenes

The vibrational analysis of six membered ring systems $[NPCl_2]_2[NCCl]$ (**2**) and $[NPCl_2][NCCl]_2$ (**11**) have been carried out and compared with $[NPCl_2]_3$ and $[NCCl]_3$.[64,65] Strong IR bands at 1462 cm^{-1} (**2**) and 1521 cm^{-1} (**11**) have been assigned to ν_{as} NCN. The other important ring stretching frequencies ν_s NPN, ν_s NCN and ν_s CPN were observed in the range of 1271–1357 cm^{-1} for (**2**) and 1182–1350 cm^{-1} for (**11**). ν_{as} NCN of $[Cl_2PN_2CCl]_3$,(**20**) was observed at 1584 cm^{-1}.

^{31}P NMR chemicals shifts of carbophosphazenes have been found to be quite sensitive to both the ring structure as well as the ring substituents and assists extensively in the characterization of these compounds. The ^{31}P chemical shifts of $N_3P_3Cl_6$, $N_3P_2CCl_5$ (**2**) and $N_3PC_2Cl_4$ (**11**) are observed at 20.0, 36.9 and 54.8 ppm respectively.(in $CDCl_3$)[50,66] However upon ring substitution on the phosphorus atom, ^{31}P chemical shifts of carbophosphazenes generally are found to get shielded. In carbodiphosphatriazenes, when only the carbon atom is substituted, the ^{31}P chemical shifts of the chlorinated phosphorus atom is found to get deshielded slightly (2-4 ppm). Similar observation is reported for dicarbophosphatriazenes. Generally $N_3P_2C(OAr)_5$ (Ar = aryl) compounds show ^{31}P chemical shifts in the range of 19–22 ppm while the representative examples of

$N_3P_2C(OR)_5$ ($R = CH_3$ and CF_3CH_2) show chemical shifts at 30.7 and 27.8 ppm respectively. Similar spectral behavior is observed in case of alkoxy, aryloxy and amino derivatives of carbophosphazenes having an alkyl, aryl or amino substituent on the carbon atoms.[11] ^{31}P NMR chemical shift for $[Cl_2PN_2CCl]_3$,(**20**), was observed as a singlet at 9.35 ppm.[36] The available data on fully aryl substituted 1,5 -isomer of eight membered heterocycles show the phosphorus chemical shifts in the range −0.6 to + 1.8 ppm.[17]

^{13}C NMR spectal data also was found to assist, but to a lesser extent in the identification and characterization of carbophosphazenes. Upon amino substitution, the ^{13}C chemical shifts of dicarbophosphatriazenes were found to get shielded from 172 to 164 ppm[41,61]. ^{35}Cl NQR studies on $N_3PC_2Cl_4$ have also been reported.[67,68] Mass spectral analysis of a variety of dicarbophosphatriazenes having pefluoroalkyl and perfluoroalkyl ether substituents have also been carried out.[69]

7.3 X Ray structural studies on carbophosphazenes

The detailed crystal structure analysis of $N_3P_2CCl_5$ (**2**) and $N_3PC_2Cl_4$(**11**) have been reported recently.[11,50,70] From the crystal structures of the compounds $(ClCN)_n(Cl_2PN)_{3-n}$ ($n = 0,1,2,3$), a general comparison of the bond distances indicated that on going from $n = 1$ to $n = 3$, the C-Cl bond distances decreased while on going from $n = 0$ to $n = 2$, the P-Cl bonds distances decreased and the P-N bond distances increased.[70] Single crystal X ray structural studies for cyclocarbophosphazene derivatives generally show the expected differences in the P-N and C-N bond distances . Except for a few, all of them have distorted ring skeletal structure. Table (I) lists the important bond parameters of these compounds. In the case of (**2**) , the distortion caused by the replacement of a phosphorus atom by a much smaller carbon atom appears to generate a significant amount of ring strain and this increased ring strain has been attributed as one of the reasons for the observed decrease in the temperature of ring opening polymerization of (**2**) (120°C) in comparison with $N_3P_3Cl_6$ (250°C).[11] According to the X ray diffraction data, dicarbophosphatriazenes having groups like CF_3 or CCl_3 on the carbon atoms and amino/phosphinimino substituents on the phosphorus site have the endocyclic P-N bond distances much longer than the exocyclic P-N bond distances.[81] However in the case of tetrakisdimethylamino dicarbophosphatriazene,[75] the endocyclic P-N bonds were shorter than the exocyclic bonds as expected. According to quantum mechanical calculations, this was due to the increasing difference in the multiplicity of these bonds as a result of π donor effect.[72]

TABLE I X Ray structural data of cyclocarbophosphazenes

SNo	*Compound*	*Endocyclic Bond Distances (Å)*		*Endocyclic Bond Angles (°)*				*Planarity (mean deviation in Å)*	*Ref.*
		P-N	*C-N*	*NPN*	*PNP/CNC*	*NCN*	*CNP*		
1	$N_3P_2CCl_5$	1.58–1.62	1.31–1.33	117.1–117.8	115.6–116.0	133.6–134.0	117.0–118.0	Nonplanar	11
		1.566–1.603	1.309–1.316	116.5–117.4	116.1–116.4	133.1–134.6	117.0–118.7	Nonplanar	70
		1.587–1.613	1.320–1.327	116.6–117.4	115.6–116.4	133.1–133.2	117.8–118.4	Nonplanar	50^+
2	$N_3P_2C(OPh)_5$	1.576–1.614	1.305–1.331	114.8–115.2	118.2	132.3	118.0–119.0	Puckered	11
3	$N_3PC_2Cl_4$	1.611	1.338	111.8	115.3	131.4	115.1	NA	70
4	$[(CF_2CH_2O)_2PN][(Et_2N)CN]_2$	1.585–1.586	1.352–1.362	115.6	118.9	127.6–127.7	114.9–115.0	Nonplanar (0.023)	50
5	$[(CF_2CH_2O)_2PN][(Pr_2N)CN]_2$	1.579–1.583	1.346–1.364	115.6	118.8	128.0	114.5–114.7	Nonplanar (0.021)	50
6	$[(CF_2CH_2O)_2PN]_2[(Et_2N)CN]$	1.572–1.584	1.365	118.8	114.4	125.4	121.1	Nonplanar (0.024)	50
7	$[(Et_2N)CN](Cl_2PN)_2$	1,594–1.602	1.364	118.6–118.9	113.8	127.6	120.0–120.6	Nonplanar (0.022)	50
8	$[(Pr_2N)CN](Cl_2PN)_2$	1.573–1.591	1.356 – 1.358	118.5–119.3	113.7	127.3	120.0–120.9	Nonplanar (0.026)	50
9	$(ClCN)_2[(CF_2CH_2O)_2PN]$	1.595–1.598	1.299–1.333	112.2	115.0	131.4–131.7	114.7–115.0	Planar	50
10	$(ClCN)_2[CF_2(CF_2CH_2O)_2PN]$	1.609–1.611	1.305–1.344	111.7	114.9	131.5–131.8	114.7–115.3	NA	50
11	$(ClCN)(Cl_2PN)[(CF_2CH_2O)_2PN]$	1.561–1.609	1.303–1.334	116.6–117.2	116.3	133.3	117.3	Puckered	50
12	$[(CF_2CH_2O)_2PN][(4\text{-}FC_6H_4O)\ CN]_2$	1.585–1.590	1.326–1.336	114.2	116.4	130.1–130,4	114.0–114.1	Nonplanar (0,039)	50
13	$[(CF_2CH_2O)_2PN][(4\text{-}FC_6H_4S)\ CN]_2$	1.591 – 1.592	1.322–1.338	112.8	115.9	129.9–130.9	115.1–115.3	Nonplanar	50

SNo	*Compound*	*Endocyclic Bond Distances (Å)*		*Endocyclic Bond Angles (°)*				*Planarity (mean deviation in Å)*	*Ref.*
		P-N	*C-N*	*NPN*	*PNP/CNC*	*NCN*	*CNP*		
14	$[(CF_2CH_2O)_2PN][(Me_2N)CN]_2$	1.571–1.579	1.341–1.357	114.8–115.2	119.0–120.1	127.0–127.6	115.4	Planar	50
15	$[CF_2(CF_2CH_2O)_2PN][(Et_2N)CN]_2$	1.575–1.580	1.346–1.371	116.6	119.6	127.5–128.0	113.9–114.3	Nonplanar (0,016)	50
16	$N_3P_2CPh_5$	1.601–1.626	1.334	116.4	116.4	130.1	120.1	Nonplanar (0.067)	71
17	$N_3P_2Ph_4CMe$	1.597–1.620	1.335	116.5	115.4	129.1	119.9	Puckered	72
18	$N_3P_2Ph_4C(NMe_2)$	1.597–1.608	1.336	117.1	115.4	128.6	120.9	Puckered	73
19	$N_3P_2Me_4C(NMe_2)^*$	NA	NA	NA	NA	NA	NA	NA	74
20	$N_3PC_2(NMe_2)_4$	1.583–1.618	1.335–1.354	111.3–113.2	117.6–118.2	128.2–128.5	116.5–116.9	Nonplanar (0.032)	75
21	$N_3PCl_2C_2(CF_3)_2$	1.616	1.308–1.339	111.6	115.3	131.4	115.2	NA	76
22	$N_3PF_2C_2(CF_3)_2^{\#}$	1.58	1.30	109.2	119.6	127.5	118.1	NA	77
23	$N_3P[N(CH_2)_2]_2C_2(CF_3)_2$	1.635	1.295–1.338	109.3	115.5	131.1	116.3	Nonplanar (0.020)	78
24	$N_3P[NPPh_3]_2C_2[CCl_3]_2$	1.657–1.659	1.295–1.337	107.1	115.1	131.5–131.7	116.9	NA	79
25	$N_3P[N(CH_3)_2]_2C_2[CCl_3]_2$	1.640	1.330–1.530	109.0	116.0	114.0	105.0	NA	80
26	$[NP(C_6H_5)_2]_2[NC(C_6H_4CH_3\text{-}4)]_2$	1.592–1.615	1.293–1.328	124.9–127.9		129.8–131.3	124.7–139.8	Puckered	17
27	$N_6P_3C_3Cl_9$	1.582–1.613	1.300–1.318	112.3–117.8		126.6–127.7	118.7–135.4	Puckered	36

[*] Only partial structural data is available in literature.

[+] Data collected at 193 K.

[#] Gas Electron difraction study.

8. USES OF CARBOPHOSPHAZENES

The most interesting application of carbodiphosphatriazenes came from the finding that the pentachloro analogue can be effectively polymerized at 120 °C leading to carbophosphazene polymers which can be considered as polymers having both inorganic and organic moieties in the basic polymer chain. A variety of these stable polymers have been prepared and properties studied.[5,11,54,55,82] The dicarbophosphatriazenes, especially those having a perfluoro or perfluoro ether group attached to the carbon atoms were found to be excellent additives for drastic reduction of oxidation of perfluoroalkyl ether fluids. Degradation studies carried out on both six and eight membered ring systems indicate their stability even up to 316 °C. Both were found to be extremely effective in arresting degradation of polyfluoroalkyl ether fluids (eg. Krytox, Fomblin Z) in oxidizing atmospheres and in the presence of metal alloys.[6,7,8] Table II gives a representative example on the details of such a study using $Ar[(R_fCN)_2(PhPN)]_2$ [$Ar = C_6H_4$, $R_f = C_3F_7OCF(CF_3)CF_2OCF(CF_3)$](**16b**).

TABLE II Effect of 1,4-bis [1-phenylphospha-3,5-bis(perfluoroalkyl ether)-2,4,6-triazino] benzene (**16b**) on perfluoroalkyl ether fluids in presence of M 50 alloy at elevated temperatures in oxygen over a period of 24 hours.[32]

*Fluid**	*grams*	*Additive*	*Temp °C*	*Oxygen Consumed*		*Products Formed*	
Krytox	12.13	None	316	24.6 %	5.8 mg/g	576.7 mg	47.5 mg/g
Krytox	4.83	1 % **16b**	316	0.0 %	0.0 mg/g	6.3 mg	1.3 mg/g
Fomblin Z	3.34	None	288	13.6 %	12.1 mg/g	1117.1 mg	421.6 mg/g
Fomblin Z	4.14	1 % **16b**	288	0.0 %	0.0 mg/g	7.9 mg	1.9 mg/g

*Krytox ($F\text{-}[CF(CF_3)\text{-}CF_2O]_n\text{-}C_2F_5$; Dupont) and Fomblin Z (Montedison trade name) are linear polyfluoroalkyl ethers.

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