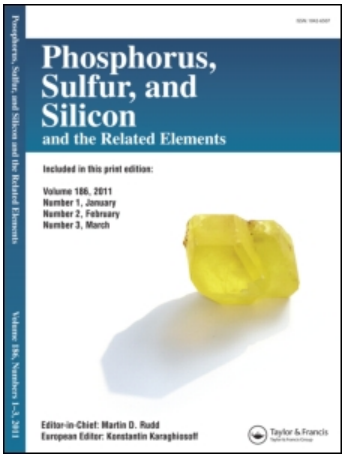


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Reactions of Trialkylamines with the Cyclocarbaphosphazene $Cl_2PN(ClCN)_2$: Selectivity in the Cleavage of Alkyl Groups

Anil J. Elias[a]; P. K. Mishra[a]; M. Senthil Kumar[a]; N. Behera[a]; N. D. Reddy[b]
[a] Department of Chemistry, Indian Institute of Technology, Delhi, Hauz Khas, New Delhi, India [b] Department of Chemistry, Pondicherry University, Pondicherry, India

To cite this Article Elias, Anil J. , Mishra, P. K. , Kumar, M. Senthil , Behera, N. and Reddy, N. D.(2005) 'Reactions of Trialkylamines with the Cyclocarbaphosphazene $Cl_2PN(ClCN)_2$: Selectivity in the Cleavage of Alkyl Groups', Phosphorus, Sulfur, and Silicon and the Related Elements, 180: 8, 1785 — 1794
To link to this Article: DOI: 10.1080/104265090888414
URL: http://dx.doi.org/10.1080/104265090888414

Phosphorus, Sulfur, and Silicon, 180:1785–1794, 2005

ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/104265090888414

Taylor & Francis
Taylor & Francis Group

Reactions of Trialkylamines with the Cyclocarbaphosphazene $Cl_2PN(ClCN)_2$: Selectivity in the Cleavage of Alkyl Groups

Anil J. Elias
P. K. Mishra
M. Senthil Kumar
N. Behera
Department of Chemistry, Indian Institute of Technology, Delhi, Hauz Khas, New Delhi, India

N. D. Reddy
Department of Chemistry, Pondicherry University, Pondicherry, India

Reactions of unsymmetrically substituted trialkylamines $MeNEt_2$, $MeN(allyl)_2$, $MeN(Benzyl)_2$, $Me_2N(Benzyl)$, $EtNPr^i_2$, $MeNPr^i_2$, $MeN(c\text{-}C_6H_{11})_2$, and $Me_2N(c\text{-}C_6H_{11})$ with the carbaphosphazene $(ClCN)_2(Cl_2PN)$ were carried out to understand the preference for the cleavage of various alkyl groups on the amino nitrogen. All the trialkylamines underwent dealkylation and the generated dialkylamino groups substituted regiospecifically on the carbon atoms of the cyclocarbaphosphazene. When $MeNEt_2$ was reacted with $(ClCN)_2(Cl_2PN)$, one of its ethyl groups was preferentially cleaved. Deallylation was favored over the cleavage of methyl group in the reaction of $MeN(allyl)_2$ with $(ClCN)_2(Cl_2PN)$. Benzyl and cyclohexyl groups were more readily cleaved than the methyl group when $MeN(Benzyl)_2$, $Me_2N(Benzyl)$, $MeN(c\text{-}C_6H_{11})_2$, and $Me_2N(c\text{-}C_6H_{11})$ were reacted with $(ClCN)_2(Cl_2PN)$. The isopropyl group was found to be cleaved preferentially over ethyl and methyl groups in the reactions of $EtNPr^i_2$ and $MeNPr^i_2$ with $(ClCN)_2(Cl_2PN)$. Sterically hindered trialkylamines also underwent dealkylation with monosubstitution of the carbaphosphazene. The results show that the ease of cleavage of the alkyl groups depends primarily on the stability of the alkyl carbocation of the cleaved group.

Keywords Cyclocarbaphosphazene; dealkylation; selectivity; trialkylamines

Received July 8, 2004; accepted September 7, 2004.

A. J. E. thanks the Department of Science and Technology (DST), India, for financial assistance in the form of a research grant.

Address correspondence to Anil J. Elias, Department of Chemistry, Indian Institute of Technology, Delhi, Hauz Khas, New Delhi, 110016, India. E-mail: elias@chemistry.iitd.ac.in

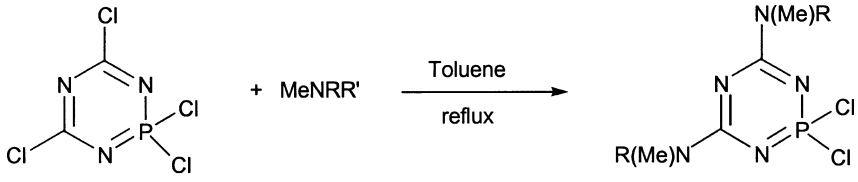
INTRODUCTION

Cyclocarbaphosphazenes can be considered the linking heterocycles between cyclophosphazenes and *s*-triazines as they contain both P-N and C-N moieties as part of their ring framework.[1] A variety of cyclocarbaphosphazenes have been prepared with ring sizes varying from 6 to 16 and better synthetic routes for the same have been reported recently.[2] Quite recently, Chandrasekhar and colleagues have prepared the first examples of pendant cyclodicarbaphosphazatriene-containing monomers and polymers and the perchlorinated carbaphosphazenes have also been found to undergo ring-opening polymerization reactions leading to the formation of novel carbaphosphazene-based polymers.[3] Carbaphosphazenes also show interesting regiospecificity in their chlorine substitution reactions. Roesky and Mainz, as well as others, have demonstrated from selected reactions the regiospecificity in substitution reactions of carbaphosphazenes, which stems from the difference in the reactivities of C—Cl and P—Cl bonds of these heterocycles.[4,5] One of the unique reactions of perchlorinated carbaphosphazenes and carbathiazenes is that they initiate C—N bond cleavage of trialkylamines resulting in the regiospecific substitution of the dialkylamino group on the ring carbon atom of the heterocycles.[6–9] Alkyl cleavage reactions of amines, although in low yields, have also been observed in selected cases of cyclophosphazenes as well.[1] However, it is of interest to note that there are no reports on the comparative preference for the cleavage of a specific alkyl group of a tertiary amine in these reactions. The present work has been designed so as to understand the preference for the cleavage of alkyl groups of trialkyl amines in their dealkylation reactions with cyclocarbaphosphazenes. Herein we report the results of dealkylation reactions of a variety of unsymmetrically substituted trialkylamines: $MeNEt_2$, $MeN(allyl)_2$, $MeN(Benzyl)_2$, $Me_2N(Benzyl)$, $EtNPr^i_2$, $MeNPr^i_2$, $MeN(c\text{-}C_6H_{11})_2$, and $Me_2N(c\text{-}C_6H_{11})$ with the carbaphosphazene $(ClCN)_2(Cl_2PN)$.

RESULTS AND DISCUSSION

The reactions of $(ClCN)_2(Cl_2PN)$ (I) with unsymmetrical trialkylamines were carried in toluene at refluxing temperature for 24 h. In all cases, dealkylation of the amine was found to occur and preference for the cleavage of a specific alkyl group was observed (Schemes 1 and 2).

$(ClCN)_2(Cl_2PN)$ (I) reacted with diethylmethylamine and cleaved one of the ethyl groups showing preference for the cleavage of ethyl group over methyl. When one of the substituents of the unsymmetrical amine was isopropyl, its cleavage was favored over methyl or ethyl groups. This

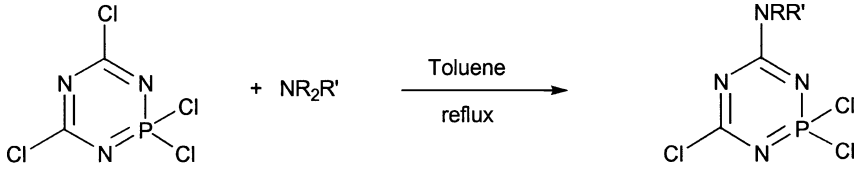


I **a - e** **1 - 4**

a R = R' = Et, **1**
b R = R' = Allyl, **2**
c R = R' = Benzyl, **3**
d R = Me, R' = Benzyl **4**
e R = Me, R' = *c*-C_6H_{11} **4**

SCHEME 1

was observed in the reactions of I with $MeNPr^i_2$ and $EtNPr^i_2$ where the formation of 5 and 6 was preferred. The reactions of I with dibenzylmethylamine and dimethylbenzylamine revealed that the cleavage of the benzyl group was favored over the cleavage of the methyl group. The fact that the cyclohexyl group was preferentially cleaved when dicyclohexylmethylamine or dimethylcyclohexylamine was reacted with I showed that the cleavage of cyclohexyl was favored over the methyl group. Similarly the cleavage of the allyl group was favored over the methyl group as observed in the reaction of I with $MeN(allyl)_2$. Thus, in all cases examined, the alkyl over the methyl group cleavage was observed. The details of the study are given in Table I.



I **f - h** **5 - 7**

f R = Pr^i, R' = Me, **5**
g R = Pr^i, R' = Et, **6**
h R = *c*-C_6H_{11}, R' = Me **7**

SCHEME 2

TABLE I Nature of Obtained Products in Dealkylation Reactions with Yields

S. no	Amine used	Alkyl group cleaved	Product obtained	Yield %	^{31}P NMR δ
1	$MeNEt_2$	Et	$[Me(Et)NCN]_2(Cl_2PN)$ (1)	80	56.5
2	$MeN(allyl)_2$	Allyl	$[allyl(Me)NCN]_2(Cl_2PN)$ (2)	70	56.9
3	$MeN(Benzyl)_2$	Benzyl	$[(Benzyl)(Me)NCN]_2(Cl_2PN)$ (3)	28	56.6
4	$Me_2N(Benzyl)$	Benzyl	$(Me_2NCN)_2(Cl_2PN)$ (4)	80	56.6
5	$MeNPr^i_2$	Pr^i	$[Pr^i(Me)NCN](ClCN)(Cl_2PN)$ (5)	71	52.5
6	$EtNPr^i_2$	Pr^i	$[Pr^i(Et)NCN](ClCN)(Cl_2PN)$ (6)	65	52.8
7	$MeN(c\text{-}C_6H_{11})_2$	$c\text{-}C_6H_{11}$	$[(c\text{-}C_6H_{11})(Me)NCN](ClCN)\ (Cl_2PN)$ (7)	35	52.8
8	$Me_2N(c\text{-}C_6H_{11})$	$c\text{-}C_6H_{11}$	$(Me_2NCN)_2(Cl_2PN)$ (4)	91	56.6

Quite interestingly, the sterically hindered and nonnucleophilic base, $EtNPr^i_2$, as well as its methyl analogue, $MeNPr^i_2$, and dicyclohexylmethylamine gave only the monosubstituted carbaphosphazene derivatives 5, 6, and 7 respectively (Scheme 2).

The evidence for cleavage of a particular alkyl group was obtained from the characterization of the corresponding carbaphosphazene derivative. The carbaphosphazene derivatives 1–7 were purified either by recrystallization or by flash chromatography. They have been characterized using IR, NMR (^{1}H, ^{13}C, ^{31}P), mass spectral data, and elemental analysis. ^{1}H NMR spectra of the carbaphosphazene derivatives shows that in comparison to the starting amine, α protons of alkyl groups of corresponding carbaphosphazene derivative are highly deshielded. This deshielding nature of α protons is similar to dialkylamino-substituted *s*-triazines, where it has been attributed to the high electron withdrawing effect of triazine ring.[9,10] Therefore, a partial double-bond character for the exocyclic C–N bond can be envisaged (Figure 1) and X-ray structural studies of dialkylamino substituted carbaphosphazenes show shorter exocyclic C—N bonds.[5,6,11]

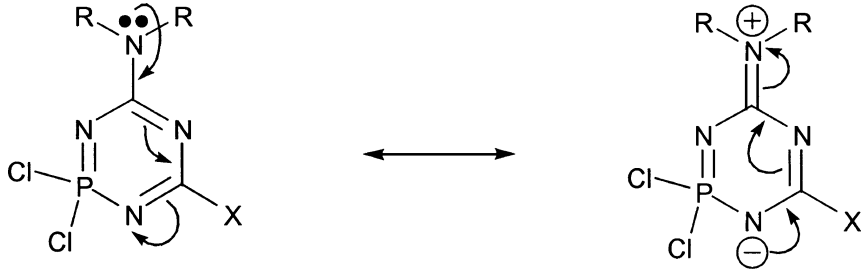
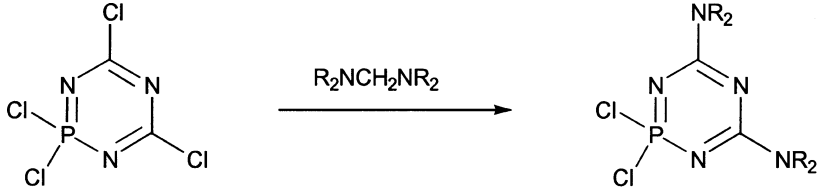


FIGURE 1

^{31}P NMR is helpful in characterizing the derivatives of I, especially to differentiate mono- and disubstituted carbaphosphazenes (Table I). The ^{31}P chemical shifts of monosubstituted carbaphosphazenes, 5, 6, and 7 are observed around 52 ppm, whereas ^{31}P chemical shifts of disubstituted carbaphosphazenes, 1, 2, 3 and 4, are observed around 56 ppm. This feature is useful in differentiating mono- and disubstituted carbaphosphazenes. In comparison with $(ClCN)_2(Cl_2PN)$ (I) (54.85),[1] phosphorus is shielded by around 2 ppm in case of monosubstituted carbaphosphazenes and deshielded by around 2 ppm in case of disubstituted carbaphosphazenes.

The formation of 1 does not agree with the observation that in von Braun cyanogen bromide reaction of unsymmetrically substituted tertiary amines of low molecular weight, the cleavage occurs predominantly in the direction involving displacement of the smallest group.[12] However the results of this study show that the cleavage, even in the case of amines of low molecular weights, depends more on the relative stability of the carbocation of the cleaved alkyl group which is formed during dealkylation. As ethyl, isopropyl, allyl, benzyl, and cyclohexyl carbocations are more stable than methyl carbocation, their cleavage seems to dominate over demethylation in these reactions. To further confirm this view, reactions of bis(dimethylamino)methane and bis(morpholino)methane were carried out with I (Scheme 3). In these reactions it was found that the bridging methylene group was preferentially cleaved over the terminal methyl groups or the morpholino ring. This can be attributed to the formation of highly stable carbocation, $R_2NCH_2^+$ ($R_2N = Me_2N$, OC_4H_8N), which is stabilized by the adjacent hetero-atom.[13]



4 R = Me
8 NR_2 = Morpholino

SCHEME 3

Yields of the substituted carbaphosphazenes suggest that the amine containing readily displaceable groups does not necessarily give a good

yield of the product. For example, dibenzylmethylamine forms only 28% of the product whereas dimethylethylamine yields 80% of the product in spite of the greater lability of benzyl over the ethyl group. Poor yields in the case of dibenzylmethylamine may be attributed to the steric hindrance of the benzyl group.

Reactions of $(ClCN)_2(Cl_2PN)$ were also carried out with a few secondary amines to see if there will be any preference for dealkylation over the expected dehydrohalogenation reaction. Preliminary reactions of diethylamine, dibenzylamine, dicylcohexylamine, and N-methylcyclohexylamine with $(ClCN)_2(Cl_2PN)$ indicates that the major product isolated in these reactions is the expected bisdialkylamino-substituted carbaphosphazene $[(RR'N)CN]_2(Cl_2PN)$, which suggests the preference of dehydrohalogenation over dealkylation in the reactions of secondary amines with chlorocarabphosphazenes.

In conclusion, a systematic study on dealkylation reactions of unsymmetrically substituted trialkylamines with the carbaphosphazene $(ClCN)_2(Cl_2PN)$ (I) has been carried out. The study indicates that the ease of removal of alkyl groups depends primarily on the relative stability of the carbocation of the cleaved group. Sterically hindered trialkylamines also underwent the reaction, however, with poor yields and monosubstitution of the heterocycle.

EXPERIMENTAL

Materials

Bis(dimethylamino)methane, bis(morpholino)methane, *N*,*N*-diisopropylmethylamine, *N*,*N*-dimethylbenzylamine, *N*,*N*-dibenzylmethylamine, and *N*,*N*-dimethylcyclohexylamine were also prepared by literature method.[14] *N*,*N*-Dicyclohexylmethylamine (Fluka), *N*,*N*-diethylmethylamine, and *N*,*N*-diisopropylethylamine (Lancaster) had been procured and distilled prior to use. Hexane, toluene, chloroform, and light petroleum (bp 60–80) were dried and distilled by standard procedures.

General Procedures

A conventional vacuum line equipped with a dry nitrogen facility and Schlenk glassware was used for all reactions. Reactions were carried out and worked up under an atmosphere of dry nitrogen. Separation of solids from reaction mixtures was performed by slow filtration using a frit. Infrared spectra were recorded on a Perkin-Elmer 1320 spectrometer, ^{1}H, ^{13}C, and ^{31}P NMR spectra using a Bruker WM-400 or a JEOL

JNM-LA400 FT-NMR spectrometer or a JEOL JNM-PMX60SI spectrometer with $CDCl_3$ as solvent and TMS and H_3PO_4 as references and mass spectra on a JEOL D-300 (EI/CI) spectrometer in the EI mode. Analysis were carried out on a Carlo Erba CHNS-O 1108 elemental analyzer.

Reactions of $(ClCN)_2(Cl_2PN)$ (I)

With N,N-*diethylmethylamine*. In a nitrogen-filled 50 mL round bottomed flask I (1.20 g, 5.03 mmol) was taken and dissolved in toluene (20 mL). *N*,*N*-diethylmethylamine (1.75 g, 20.11 mmol) was added dropwise to this solution while stirring. The resultant mixture was refluxed for 24 h under nitrogen and cooled to room temperature. The solid formed, which was identified as the amine hydrochloride, was filtered using a frit. The filtrate was concentrated to 2 mL and kept at 0°C overnight to yield $[Me(Et)NCN]_2(Cl_2PN)$ (1) (1.14 g, 80%) as a microcrystalline solid. mp: 35–37°C; IR: (nujol) (cm^{-1}) 1250 s, 1220 m, 1170 w, 1090 s, 1020 s, 910 s, 880 m, 845 m, 790 s, 750 w, 710 w, 660 w; NMR: ^1H, δ 1.2 (t, 6H, NCH_2CH_3), 3.1 (s, 6H, NCH_3), 3.6 (m, 4H, NCH_2CH_3); ^{13}C, δ 13.4 (N CH_2CH_3), 34.0 (NCH_2CH_3), 43.2, 43.8 (NCH_3), 163.5 (NCN); ^{31}P, δ 56.5; MS (EI) [m/e (species) intensity]: 283 ($M^{\oplus}$) 84, 268 ($M^{\oplus}$-CH_3) 100, 254 ($M^{\oplus}$-C_2H_5) 48, 248 ($M^{\oplus}$—Cl) 58.

With N,N-*diallylmethylamine*. The reaction between I (1.52 g, 6.37 mmol) and *N*,*N*-diallylmethylamine (2.85 g, 25.68 mmol) in toluene (20 mL) was carried out and worked up as described for the synthesis of 1. The residue that was obtained after the evaporation of toluene was purified on a silica gel column using light petroleum–chloroform (50:50) to yield a semisolid. This was dissolved in a minimum amount of hexane and cooled to −50°C to get a crystalline solid, $[allyl(Me)NCN]_2(Cl_2PN)$ (2) (1.39 g, 70%). mp: 62–63°C; NMR: ^1H, δ 3.0 (s, 6H, NCH_3), 4.1 (d, 4H, $CH_2CH=CH_2$), 5.1 (m, 4H, $NCH_2CH=CH_2$), 5.8 (m, 2H, $NCH_2CH=CH_2$); ^{13}C, δ 34.2 (NCH_3), 51.6 ($NCH_2CH=CH_2$), 116.7 ($NCH_2CH=CH_2$), 133.4 ($NCH_2CH=CH_2$), 163.9 (NCN); ^{31}P, δ 56.9; MS (EI) [m/e (species) intensity]: 307 ($M^{\oplus}$) 25; 292 ($M^{\oplus}$-CH_3) 100, 272 ($M^{\oplus}$-Cl) 41, 257 ($M^{\oplus}$-CH_3Cl) 11. Anal. Calcd. for $C_{10}H_{16}N_5Cl_2P$: C, 39.0; H, 5.2; N, 22.7. Found: C, 38.2; H, 4.6; N, 23.0.

With N,N-*dibenzylmethylamine*. The reaction between I (1.43 g, 5.95 mmol) and *N*,*N*-dibenzylmethylamine (5.10 g, 24.17 mmol) in toluene (20 mL) was carried out and worked up as described for the synthesis of 1. After removing the unreacted amine from the toluene part, the residue was purified on a silica gel column using a mixture of light petroleum and chloroform (30:70) to get a crystalline solid,

[(Benzyl)(Me)NCN]$_2$(Cl_2PN) (3) (0.68 g, 28%). Physical and spectral data of this compound were found to agree with the reported values.[11]

With N,N-*dimethylbenzylamine*. I (1.27 g, 5.32 mmol) was reacted with *N*,*N*-dimethylbenzylamine (3.00 g, 22.22 mmol) in toluene (20 mL) and worked up as described for the synthesis of 1. After evaporating toluene, the unreacted amine was removed under reduced pressure. The residue was redissolved in minimum amount of toluene and kept at 0°C overnight to yield crystals of ($Me_2NCN)_2$ (Cl_2PN) (4) (2.56 g, 80%). Physical and spectral data of 4 were found to agree with the reported values.[11]

With N,N-*diisopropylmethylamine*. I (0.95 g, 3.98 mmol) in toluene (20 mL) was reacted with *N*,*N*-diisopropylmethylamine (1.85 g, 16.09 mmol) and worked up as described for the synthesis of 1. Toluene was evaporated and hexane (10 mL) was added. The clear solution was decanted and concentrated to 2 mL and cooled to −50°C to get a microcrystalline solid, [Pr^i(Me)NCN](ClCN)(Cl_2PN) (5) (0.78 g, 71%). mp: 50–52°C; IR: (nujol) (cm^{-1}) 1250 s, 1230 s, 1200 s, 1175 m, 1135 s, 1090 m, 1070 m, 1050 m, 1020 s, 950 s, 870 s, 840 w, 750 s, 660 w; NMR:^{1}H, δ 1.2 [d, 6H, NCH(CH_3)$_2$], 3.0 (d, 3H, NCH_3), 5.0 [m, 1H, NCH(CH_3)$_2$]; ^{13}C, δ 19.5 [NCH(CH_3)$_2$], 28.3 [NCH(CH_3)$_2$], 49.1 (NCH_3), 156.8, 168.5 (NCN); ^{31}P, δ 52.5; MS (EI) [m/e (species) intensity]: 274 ($M^{\oplus}$) 51, 258 ($M^{\oplus}$-CH_4) 87, 196 [$M^{\oplus}$-(Pr^i+Cl)] 35, 72 [(Me)(Pr^i)N] 100.

With N,N-*diisopropylethylamine*. The reaction between I (1.02 g, 4.27 mmol) and *N*,*N*-diisopropylethylamine (2.21 g, 17.13 mmol) was carried out in toluene (20 mL) and worked up as described for the synthesis of 1. To the residue, which was obtained from toluene, hexane (10 mL) was added and the clear solution was decanted. The solution was concentrated to 2 mL and kept at 0°C to get a solid mass, [Pr^i(Et)NCN](ClCN)(Cl_2PN) (6) (0.8 g, 65%). mp: 77–78°C; NMR: ^{1}H, δ 1.2 [m, 9H, NCH(CH_3)$_2$, 3H, NCH_2CH_3], 3.4 (m, 2H, N$CH_2$$CH_3$), 5.0 [m, 1H, N$CH$($CH_3$)$_2$]; ^{13}C, δ 14.7 (NCH_2CH_3), 20.4 [NCH(CH_3)$_2$], 38.0 [NCH(CH_3)$_2$], 47.8 (NCH_3), 161.6, 168.4 (NCN); ^{31}P, δ 52.8; MS (EI) [m/e (species) intensity]: 289 ($M^{\oplus}$ + 1) 11, 288 ($M^{\oplus}$) 7, 274 ($M^{\oplus}$-CH_2) 21, 258 ($M^{\oplus}$-2CH_3) 59, 244 ($M^{\oplus}$-3CH_3) 20, 72 (EtNHCHCH_3) 80. Anal. Calcd. for $C_7H_{12}N_4Cl_3P$: C, 29.0; H, 4.2; N, 19.4. Found: C, 29.1; H, 4.4; N, 19.2.

With N,N-*dicyclohexylmethylamine*. I (1.35 g, 5.66 mmol) was reacted with *N*,*N*-dicyclohexylmethylamine (4.50 g, 23.07 mmol) in toluene (20 mL) and worked up as described for the synthesis of 1. To the residue that was obtained in the toluene part, hexane (10 mL) was added and the clear solution was decanted. After evaporating

hexane, the unreacted amine was removed under reduced pressure using a kugelrohr unit. The residue was purified on a silica gel column using light petroleum/chloroform (70:30) to get a powder, [(*c*-C_6H_{11})(Me)NCN](ClCN)(Cl_2PN) (7) (0.78 g, 35%). mp: 75–77°C; IR: (nujol) (cm^{-1}) 1250 s, 1220 s, 1150 w, 1100 s, 1070 s, 1025 m, 1000 s, 950 s, 930 m, 880 m, 860 m, 835 w, 810 w, 740 s, 650 s; NMR: ^{1}H, δ 1.3 (m, 20H, CH_2), 2.9 (s, 6H, NCH_3), 4.5 (s, br, 2H, NCH); ^{13}C, δ 25.4, 29.5 (set of singlets, CH_2), 30.1 (NCH_3), 55.3 (d, CH), 162.4, 168.7 (NCN); ^{31}P, δ 52.8; MS (EI) [m/e (species) intensity]: 314 ($M^{\oplus}$) 19, 299 ($M^{\oplus}$-Me) 21, 279 ($M^{\oplus}$-Cl) 10, 232 ($M^{\oplus}$-C_6H_{10}) 47, 196 [$M^{\oplus}$-(C_6H_{11}+Cl)] 100. Anal. Calcd. for $C_9H_{14}N_4Cl_3P$: C, 34.3; H, 4.5; N, 17.8. Found: C, 34.1; H, 4.4; N, 17.5.

With N,N-*dimethylcyclohexylamine.* The reaction between I (1.22 g, 5.11 mmol) and *N*,*N*-dimethylcyclohexylamine (3.00 g, 23.62 mmol) was carried out in toluene (20 mL) and worked up as described for the synthesis of 1. The unreacted amine was removed under reduced pressure from the toluene part and redissolved in a minimum amount of toluene. This on standing at 0°C overnight gave colorless crystals of ($Me_2NCN)_2$ (Cl_2PN) (4) (1.19 g, 91%).

With bis(dimethylamino)methane. The reaction between I (1.43 g, 5.99 mmol) and bis(dimethylamino)methane (2.45 g, 24.02 mmol) was carried out in toluene (20 mL) and worked up as described for the synthesis of 1. The toluene part was concentrated and kept at 0°C overnight to get colorless diamond-like crystals of ($Me_2NCN)_2$ (Cl_2PN) (4) (1.43 g, 97%).

With bis(morpholino)methane. I (1.02 g, 4.28 mmol) was reacted with bis(dimethylamino)methane (3.20 g, 17.58 mmol) in toluene (20 mL) and worked up as described for 1. The toluene part was concentrated untill a small amount of microcrystals were obtained and kept at 0°C overnight to get colorless prismatic crystals of [(OC_4H_8N)CN]$_2$(Cl_2PN) (8) (1.34 g, 92%). mp: 222–223°C; NMR:^{1}H, δ 3.7 (m, NCH_2 and OCH_2): ^{31}P, δ 57.8 (s). MS (EI) [m/e (species) intensity]: 339 ($M^{\oplus}$) 100, 309 ($M^{\oplus}$-CH_2O) 65, 253 [$M^{\oplus}$-N(CH_2CH_2)$_2$O] 24, 274 [$M^{\oplus}$-(CH_2O+Cl)] 43, 86 [N(CH_2CH_2)$_2$O] 80. The spectral data agreed with the reported values for the same in a mixture.[5]

REFERENCES

[1] A. J. Elias, M. Jain, and N. D. Reddy, *Phosphorus, Sulfur, Silicon Relat. Elem.*, **140,** 203 (1998).

[2] E. Rivard, A. J. Lough, and I. Manners, *Inorg. Chem.*, **43,** 2765 (2004)

[3] V. Chandrasekhar, A. Athimoolam, N. D. Reddy, S. Nagendran, A. Steiner, S. Zacchini, and R. Butcher, *Inorg. Chem.*, **42,** 51 (2003) and references therein.
[4] H. W. Roesky and B. Mainz, *Z. Anorg. Allg. Chem.*, **540/541,** 212 (1986).
[5] P. P. Kornuta, N. V. Kolotilov, and L. N. Markowskii, *Zh. Obshch. Khim.*, **48,** 2218 (1978).
[6] A. Vij, A. J. Elias, R. L. Kirchmeier, and J. M. Shreeve, *Inorg. Chem.*, **36,** 2730 (1997).
[7] N. D. Reddy, A. J. Elias, and A.Vij, *J. Chem. Soc., Dalton Trans.*, 1515 (1999).
[8] N. D. Reddy, A. J. Elias, and A. Vij, *J. Chem. Res. (S),* 1998, 504.
[9] T. V. V. Ramakrishna, A. J. Elias, and A. Vij, *Inorg. Chem.*, **38,** 3022 (1999).
[10] A. R. Katritzky, D. C. Oniciu, I. Ghiviriga, and R. A. Barcock, *J. Chem. Soc. Perkin. Trans.*, **2,** 785 (1995).
[11] M. L. Glowka and I. Iwanicka, *Acta Crystallogr. Sect. C.*, **47,** 616 (1991)*; ibid* 1036.
[12] J. March, *Advanced Organic Chemistry, Reactions, Mechanisms and Structure*; New York: Wiley-Interscience, (1992).
[13] G. A. Olah and P. Schleyer, *Carbonium Ions*, **4,** (1985).
[14] H. E. Baumgarten, *Org. Synth. Coll. Vol. 5*, New York: John Wiley, 434 (1973).