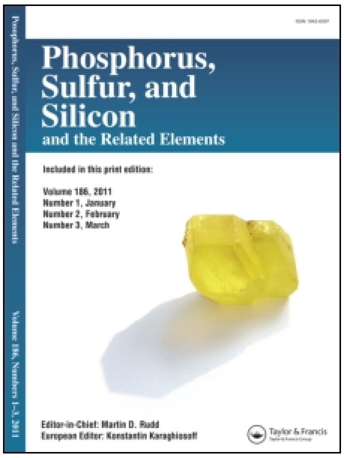

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Phosphenium Cations in Heterocyclic Chemistry

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Phosphenium Cations in Heterocyclic Chemistry

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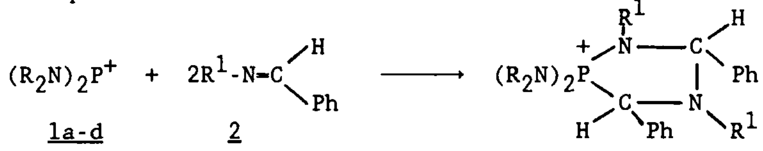
In the singlet state phosphenium cations feature both a vacant orbital and a lone pair at the phosphorus center (1). The anticipated amphoterism property of these species can be used for the synthesis of unusual heterocyclic derivatives. Our interest (2) in this type of chemistry bring us to report the reactions of stable phosphenium ions with unsaturated organic reactives i.e imines, α diimines, amidines and isocyanides.

1 - Reactions with imines and α diimines :

Phosphenium cations 1a-d were treated with aldimines 2 at -30 °C in CH_2Cl_2 solution ; to be complete the reaction necessitated addition of two equivalents of aldimines :

(1) 

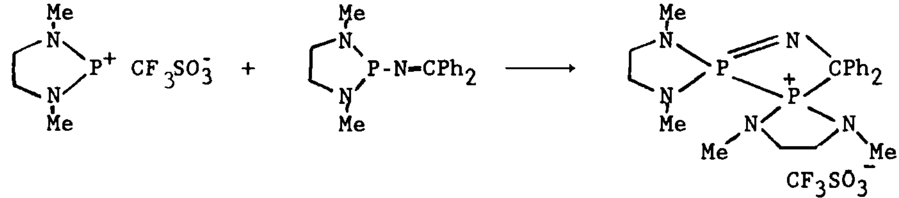
1a-d 2 3a-h

R = Me, Et, iPr R^1 = Me, CH_2Ph

NR_2 = Me-N N-Me anion : $AlCl_4^-$ or $CF_3SO_3^-$

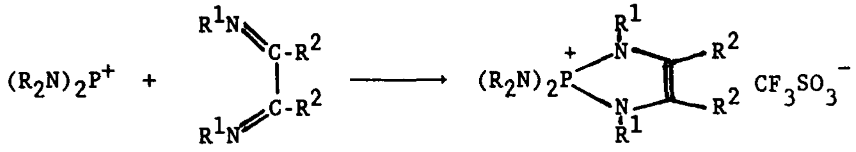
The eight (3a-h) 1,4,2 diazaphospholanium salts are prepared in a one step synthesis in quantitative yields. They are white solids forming a mixture of two diastereoisomers dueto the presence of two chiral carbon atoms (table 1).

When the R^1 group of imine is a bis(dialkylamino)phosphane 4, the phosphenium ion 1d acts as a dienophile, affording by a 1-3 dipolar cycloaddition (3) the new 1 aza,2,3 diphosphetine cation 5.

(2) 

1d 4 5

Lastly with α diimines, the electrophilic phosphenium cations react in a [2+4] cycloaddition giving a 1,3 diaza 2 phospholenium cations. The same type of reaction was reported by Baxter (4), Cowley et al. (5) with the 1-3 dienes.



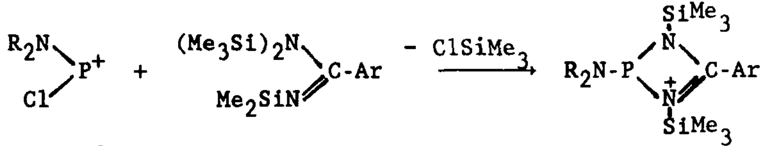
1a-d   6

R^1 = Pr R^2 = Me
R^1 = tBu R^2 = H

The X ray crystal structure of cation 6 (R = Et, R^1 = Pr, R^2=Me) will be reported.

2 - Reactions with amidines

It is well known that amidines are useful reagents (6) in the heterocyclic phosphorus chemistry. We have found a convenient access to the 1-3 diaza 2 σ^3 phosphetine cations 7 by reacting chlorophosphenium salts 1e-f with NNN' tris trimethyl silyl amidines :

(4)


1e-f   Ar = C_6H_5 , pMe-C_6H_4 7

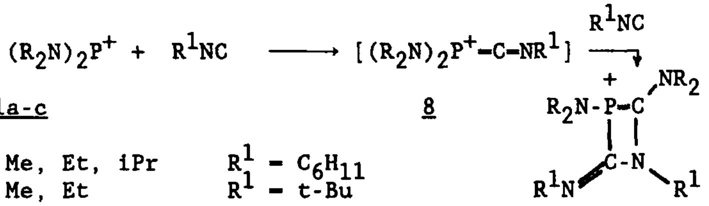
1e : R = Et
1f : R = iPr   anion : $AlCl_4^-$, $CF_3SO_3^-$

One of these stabilized cyclic carbenium species (R=iPr, Ar=C_6H_5) has been characterized by X ray structure analysis.

The more interesting features which will discussed are the charge delocalization on the N-C-N fragment, the large difference between the P-N bonds lenghts : 1.64 Å for the exocyclic P-N and 1.79, 1.80 Å for the two endocyclic P-N bonds and the small N-P-N cyclic angle : 73.2°.

3 - Reactions with isocyanides :

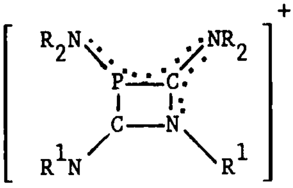
Phosphenium cations react with isocyanide as carbenes, according to equation(5). The reaction presumably proceeds through transient cationic phosphacumulenes 8 which immediatly react with a second equivalent of isocyanide to give the stable 1 aza, 3 $\sigma^3\lambda^4$ phosphetine cations 9.

(5)


1a-c   8   9a-e

R = Me, Et, iPr R^1 = C_6H_{11}
R = Me, Et R^1 = t-Bu

The structures of 9a-e were fully characterized by ^{31}P, ^{13}C, ^{1}H NMR data. The stability of 9 is a result of the charge delocalization



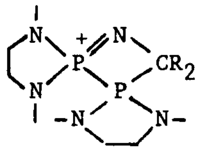
Surprisingly addition of t-Butyl isocyanide to the phosphenium cation 1c did not lead to the corresponding cyclic ion 9, but to the dicyano diisopropylamino phosphane 10 (equation 6).

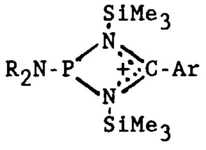
$$(6)\quad \underset{1c}{(iPr_2N)_2P^+\ CF_3SO_3^-} + 2\ t\text{-}BuNC \longrightarrow \underset{10}{iPr_2NP(CN)_2} + 2CH_2CMe_2 + iPr_2NH_2\ CF_3SO_3^-$$

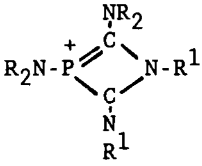
The multisteps of this reaction have been established and corroborated by two experiments which evidence the formation of two intermediates $[(iPr_2N)_2PCN]$ and $[iPr_2NP^+CN]$.

Table 1 gives the most important spectroscopic NMR data of one compound of each familly.

In conclusion the electrophilic phosphenium cations $(R_2N)_2P^+$ and $Cl\text{-}P^+\text{-}NR_2$ exhibit a great diversity in their reactions with >C=N insaturated organic reactives. The more interesting fact is the access at new small insaturated phosphorus heterocycles :







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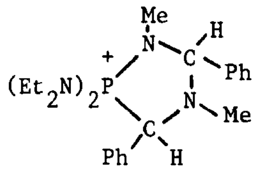
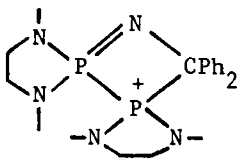
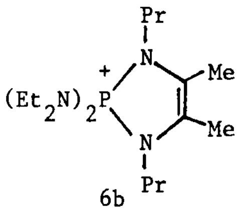
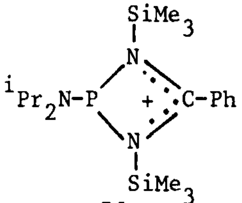
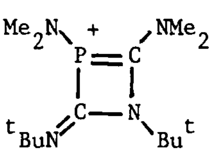
	$\delta^{31}P$	^{13}C $\delta(J)$	^{1}H $\delta(J)$
 3b	a) δ_1=52.8 δ_2= 51.8	δC_3 61.22 ; 70.4 ($^1J_{CP}$ = 110) δC_3 82.9 ; 83.4 $^3J_{CP}$ = 13.5	P-N-Me : δ_1 2.57 δ_2: 2.45 $^3J_{HP}$=8.4 P-C-H : δ_1= 4.72 (10) δ_2= 4.66 (6.5)
 5	δ_1= 50.0 δ_2= 59.2 J_{PP}=180	δCPh_2 = 53.8 ΣJPC = 15 δCH_2=42.3 (15.5) =40.6 (15.5)	
 6b	δ = 39	=C-CH_3 δ = 24.6 =C- δ = 116.2 (14.7) N-CH_2(Et):40 (3.20) N-CH_2(Pr)43.8 (2.8)	=C-Me δ = 2.0 N-CH_2(cycle) δ= 3.25(7) NCH_2 (Et) δ= 3.14(7)
 7f	δ=111	δCH(iPr) 47.5(29.9) 48.0 (7.9) δC-Ph = 179.5 (^{2}JCP = 15.6)	CH_3(iPr) δ=1.23 -1.42 (6) $CH_3(Me_3Si)$ δ=0.17
 9d	δ=130	P-C-N 160.4 (20.3) P-C=N- 159.8 (2.1)	Me(t.Bu) δ 1.35 1.59 P-N-Me_2 δ: 2.51 (2) δ : 2.82(13.2) C-N-Me_2 δ = 2.67 3.53

Table 1 : Pertinent NMR data of one compound bearing to each heterocycle types (a) two diastereoisomers % = 80/20