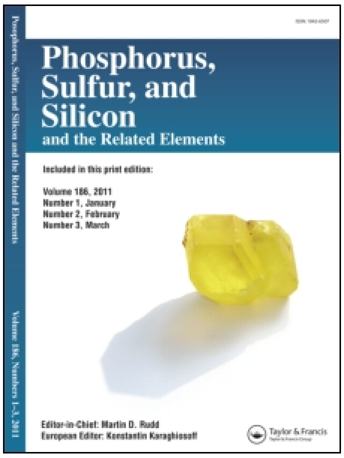

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Thermal Behaviour of Some Organ0 Phosphorus Compounds

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To cite this Article Diallo, O. S. , Lopez, L. and Barrans, J.(1990) 'Thermal Behaviour of Some Organ0 Phosphorus Compounds', Phosphorus, Sulfur, and Silicon and the Related Elements, 49: 1, 363 — 366
To link to this Article: DOI: 10.1080/10426509008038980
URL: http://dx.doi.org/10.1080/10426509008038980

Phosphorus, Sulfur, and Silicon, 1990, Vols. 49/50, pp. 363-366
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THERMAL BEHAVIOUR OF SOME ORGANO PHOSPHORUS COMPOUNDS

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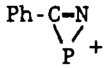
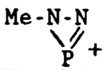
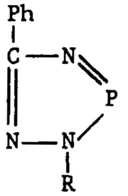
So far organophosphorus chemists have been interested in synthesizing low coordinated phosphorus compounds and in studying them in solution at temperatures rarely above 300 °C. As a matter of fact there are few reports on the behaviour of dicoordinated phosphorus molecules at temperatures above 500 °C under low pressure. Another interesting point is that such a study would allow to assess the correlation between mass spectral processes and thermal ones.

This prompted us to study the flash thermolysis of cyclic organophosphorus compounds such as diaza and triazaphospholes and cyclopolyphosphine $(PhP)_5$.

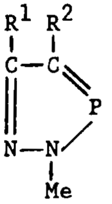
Triazaphospholes mass spectra showed peaks which could be attributed to ions of small rings. The main point is their high relative abondances.

Table I : from 1 mass spectrum

m/e	ion	rel. ab.
177	M^+	50
134		40
107	$PhCH_2NH_2$	23
103	$Ph-C\equiv N$	10
77	Ph^+	10
74		100



R=Me 1
R=Ph 2



R^1=Me R^2=H 3
R^1=Ph R^2=H 4
R^1=Ph R^2=Me 5

It is obvious that synthesizing an unsaturated three membered ring containing 2 or 3 heteroelements should be of great interest.

Thermolysis of 1 at temperatures above 600 °C under pressures lower than 10^{-3} mmHg gives several products including polymers. Some of them are readily identified as :

$PhC{\equiv}N$, MePH, Me-P(H)-P(H)Me, Me_2P-P-Me_2 , P_4 etc..

Thermolysis of 2 under the same conditions as for 1, results in the formation of $PhC{\equiv}N$, $PhPH_2$, Ph_2PH, Ph-P(H)-P(H)-Ph and polymers.

A reaction pathway which can explain the formation of these molecules should take into account transient species such as Me-P: and PhP: .

In fact Grützmacher (1) showed that thermolysis of pentaphenyl cyclopentaphosphine $(PhP)_5$ could yield phenyl phosphinidene and other products such as Ph_2PH, $PhPH_2$ and P_2. A mass spectrometer was used to identify the products.

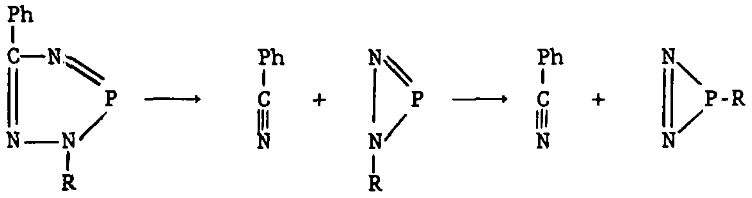
To give an NMR confirmation of their findings and explain some of ours, we thermolysed $(PhP)_5$ under the same conditions as for 1 and 2. $PhPH_2$ and Ph_2PH and P_4 were identified as major products. Attempt to trap phosphinidene with dimethylbutadiene failed.

These facts point out that if phosphinidene is formed in a vapor phase it is likely to abstract hydrogen and yield RPH_2, R_2PH,etc.

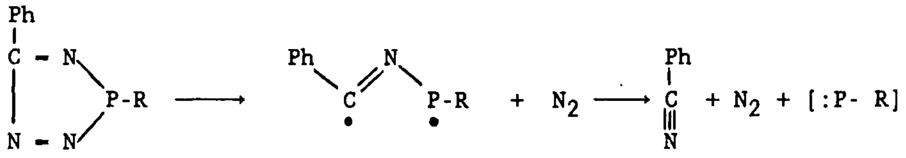
The formation of phosphinidenes MeP: or PhP: can be accounted for by two splitting processes of 1 (scheme 1). The first one involves in its first step, the elimination of benzonitrile and the formation of a three membered ring. The second process starts with the migration of the methyl group followed by the loss of molecular nitrogen.

Scheme 1

R = Me 1 R = Ph 2



5 6



7 8

Because the phosphorus atom in 6 is bonded to two electronegative atoms, its lone pair orbital should be contracted so far it could be involved in conjugation with the Π bond. Therefore 5 and 6 are antiaromatic and at high temperatures their decomposition activation barriers should be readily overcome after they are formed. Thus 6 should decompose at high temperature to yield the more thermodynamically stable product which should be molecular nitrogen. Therefore it is not surprising that $R\text{-}PH_2$, R_2PH be obtained as phosphidene R-P: is formed. It should be noticed that 5 and 6 are no longer antiaromatic when they bear a positive charge. That could explain why they are more stable and therefore more abundant in mass spectral process.

Another point is that diradical 8 could cyclise to yield an aza-phosphirene, whatever this possibility, attempt to prepare in mild conditions stabilized aza-phosphirene has failed (2).

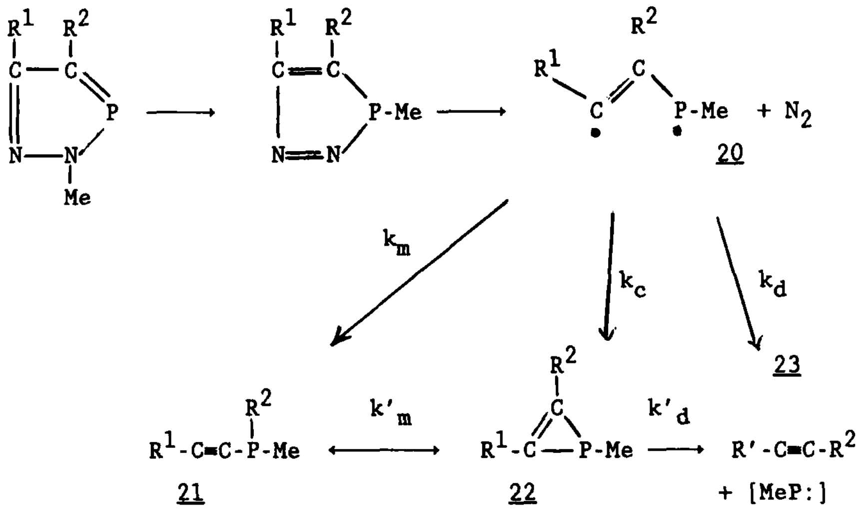
These experiments show that a ring containing two nitrogen atoms doubly bonded is likely to lose them as molecular nitrogen at high temperature.

That prompted us to undertake the thermolysis of diazaphospholes such as 3 and 4 and 5 despite the low abundance of three membered rings on their mass spectra.

All the results obtained can be accounted for by a preliminary loss of molecular nitrogen and formation of a diradical (scheme 2).

The relative yields of the products depend on the substituent effects of R^1 and R^2. e.g. their ability to stabilise the lone electrons.

Scheme 2



In all cases the phosphirene 22 is not obtained despite its stability (3). That means that the rate constant k_c is too smaller than either k_m and k_d or k'_m and k'_d.

Diazaphospholes 3 and 5 mass spectra do not show peaks corresponding to three membered rings. On the over hand ions corresponding to thermal process products have low relative abundances in mass spectral process..

Under experimental conditions so far used, thermolysis of diazaphospholes and triazaphospholes parallels poorly mass process.

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Acknowledgment : The authors are greatly indebted and grateful to Dr. Hélène GERMA for her help and suggestions.