FOUR-MEMBERED HETEROCYCLES CONTAINING ONE PHOSPHORUS AND ONE OTHER HETEROATOM

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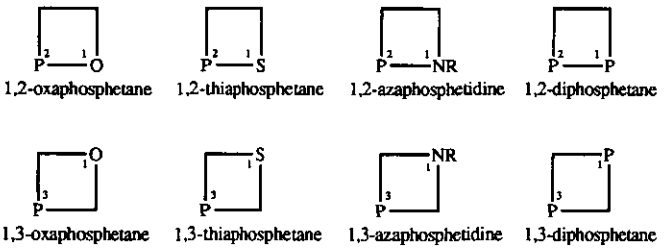
Abstract- Syntheses and properties of oxaphosphetanes, thiaphosphetanes, azaphosphetidines and diphosphetanes are reviewed.

Although in general four-membered saturated phosphorus heterocycles are not sparse, few containing one phosphorus and only one other heteroatom are known. This review addresses the chemistry of the eight ring systems in which phosphorus shares the ring with two carbon atoms and one of the following : nitrogen, sulfur, oxygen or another phosphorus.



As a class of compounds, the above ring systems raise intriguing questions regarding their modes of formation, stability and ring conformation. How much about these properties may be concluded from those of the corresponding saturated carbocycles or heterocycles containing only one heteroatom? What effect, if any, does the proximity of the heteroatoms have on the stability of the ring and how can this be extrapolated to other heteroatom-rich cycles?

This review is not able to answer these questions yet. Instead it brings together what is known of these ring systems so that trends and contrasts can be found. Of course, some individual ring systems are of interest on their own. For instance, the 1,2-azaphosphetidine ring system is structurally analogous to the azetidinone (β-lactam) ring system, while the 1,2-oxaphosphetanes are the intermediates in the synthetically important Wittig and related reactions. This aspect is deliberately played down to concentrate attention on the synthetic approaches.

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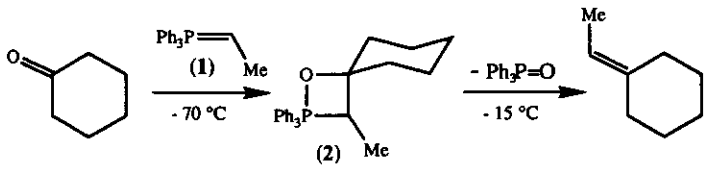
1. Synthesis

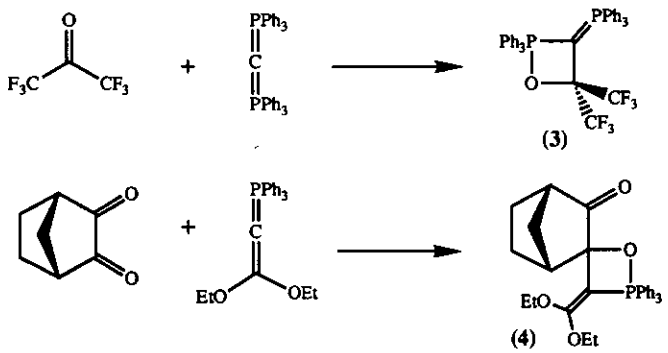
1.1. *Oxaphosphetanes*

As was mentioned above, 1,2-oxaphosphetanes are best known for their intermediacy in Wittig and Wadsworth-Emmons reactions. Usually, in these reactions, 1,2-oxaphosphetane intermediates are not isolable at room temperatures, although a good deal of evidence in support of their presence during reactions has been presented.[1-3] For instance, Vedejs reported that when ylide (**1**) was treated with cyclohexanone at -70 °C, an initial adduct (**2**) resulted, which upon warming to -15 °C broke down to the expected Wittig reaction products, triphenylphosphine oxide and an olefin.[1] Intermediate (**2**) was identified by its signal in the ^{31}P nmr spectrum.



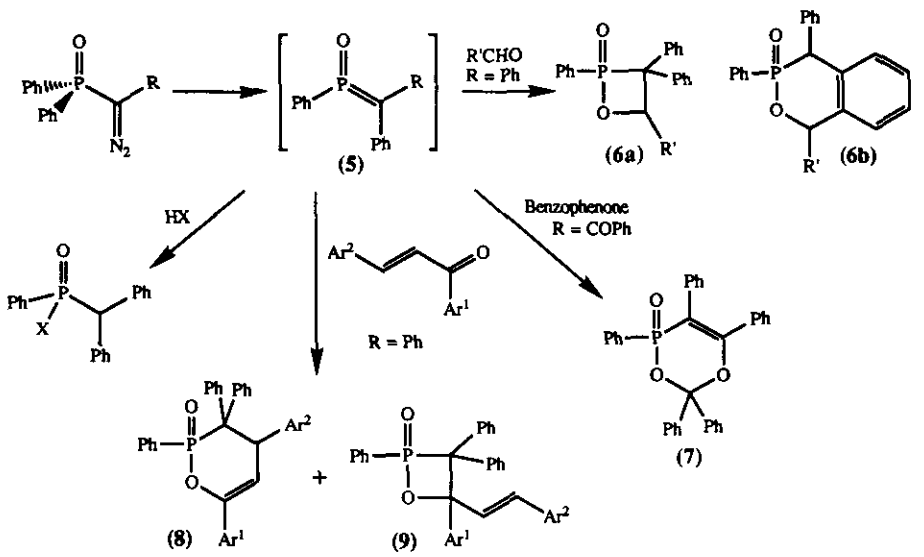
Scheme 1

In some cases, however, the intermediates do not decompose until much higher temperatures. For example, the two 1,2-oxaphosphetanes (**3**)[4] and (**4**)[5] are isolable as solids at room temperature.



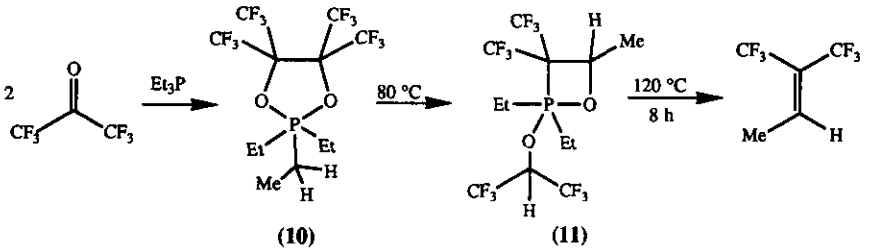
Scheme 2

Also, Regitz has reported the isolation of the 1,2-oxaphosphetanes (**6a**) and (**9**) by [2+2] addition of reactive intermediate (**5**, R=Ph), generated from a diazo precursor, to aldehydes and to ketones.[6] However, Kawashima has concluded, based on further nmr studies, that compound (**6**) is incorrectly assigned a 1,2-oxaphosphetane structure (**6a**) and that it is in fact a benzoxaphosphorin (**6b**).[7] Products (**7**) and (**8**) resulting



Scheme 3

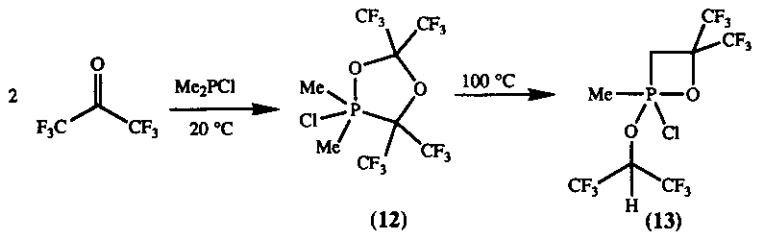
from [2+4] addition reaction were also obtained when intermediate (**5**) was trapped with α,β-unsaturated carbonyl compounds or when (**5**, R=COPh) was trapped with benzophenone (Scheme 3).



Scheme 4

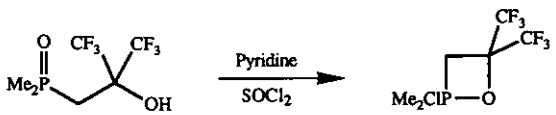
[2+2] Additions do not represent the only route for the synthesis of stable 1,2-oxaphosphetanes. Ramirez reported a ring contraction from a 1,3,2-dioxaphospholane (**10**) to an 2-alkoxy-1,2-oxaphosphetane (**11**) (Scheme 4)[8] (See section 1.2 for an analogous ring contraction of 1,3-dithiaphospholidines to 2-thio-1,2-thiaphosphetanes) and Gibson reported a similar reaction through a different proposed intermediate (**12**) (Scheme 5).[9] In both cases, the *gem*-trifluoromethyl substituents appear to contribute strongly to the stability of the ring. Presumably, the effect of two strongly electron withdrawing groups is to prevent decomposition of the ring through a non-concerted retro [2+2] reaction by destablising the developing carbocation character at

C-3 and C-4. In each case the retro [2+2] reaction, the normal mode of decomposition as we have already seen, requires much higher temperatures.



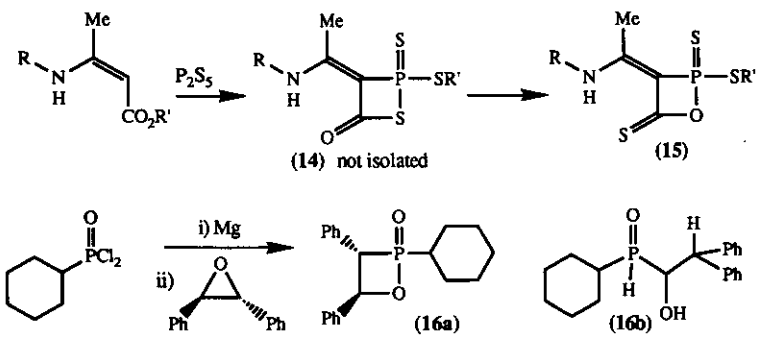
Scheme 5

The following example,[10] Scheme 6, is remarkable since it extends the ring closures utilising the oxygen of P=O as a nucleophile, which is more applicable to five and six membered rather than to four membered ring formation.

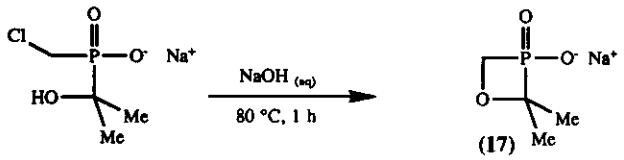


Scheme 6

1,2-Oxaphosphetanes (**15**)[11] and (**16a**)[12a] were also reported to be the products of the following two reactions although neither structures were rigorously proven. Further studies have shown that the the product from the latter reaction is not a 1,2-oxaphosphetane (**16a**) but rather an α-hydroxy phosphinate (**16b**).[12b]



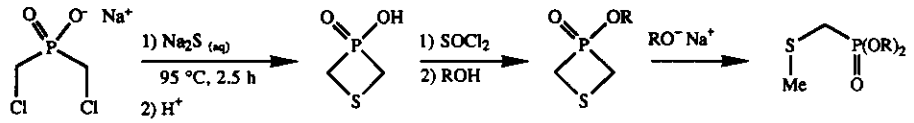
Scheme 7



Scheme 8

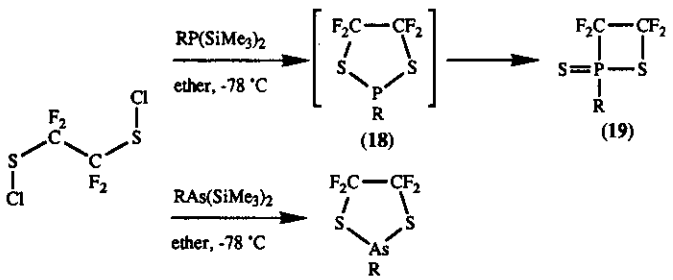
Only a single example of 1,3-oxaphosphetanes is known, namely (**17**).[13] It can be synthesised (Scheme 8) only as a salt since the free acid is unstable. Attempts to prepare the methyl ester by a similar route, or to manipulate the phosphorus functionality failed.

1.2. *Thiaphosphetanes*



Scheme 9

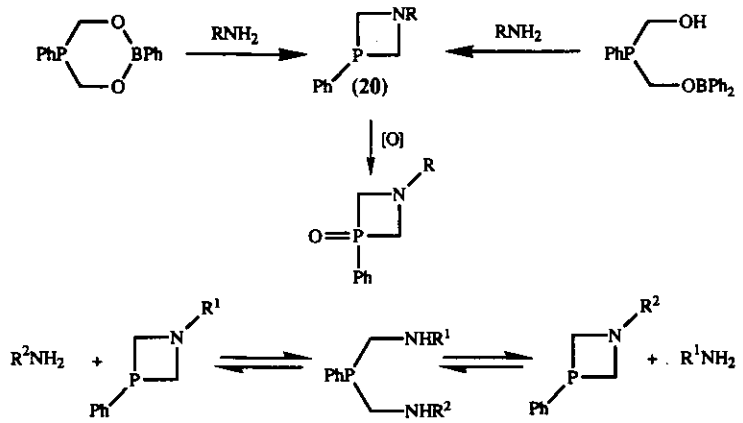
In contrast to oxaphosphetanes, 1,3-thiaphosphetanes, a synthesis of which is outlined above (Scheme 9),[14] are better known and studied[15] than the isomeric ring system. Until recently, the transient intermediate (**14**) (Scheme 7) was the only example of a 1,2-thiaphosphetane. However, in agreement with the observations made by Ramirez (see Scheme 4), Roesky reports the synthesis of 2-thio-1,2-thiaphosphetanes (**19**) *via* ring contraction of 1,3-dithiaphospholidines (**18**). Although no 1,3-dithiaphospholidine was isolated, their intermediacy is implied by the observation that the reaction of the arsenic analogue affords the five membered ring only (Scheme 10).[16]



Scheme 10

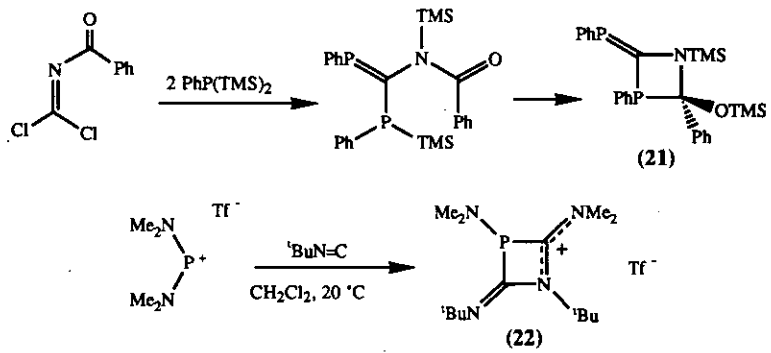
1.3. *Azaphosphetidines*

1,3-Azaphosphetidines (**20**) were first synthesised by Arbuzov and co-workers. Four membered ring closure was achieved *via* nucleophilic displacement. Arbuzov has shown that the 1,3-azaphosphetidine ring is labile allowing one to be made from another (Scheme 11).[17]



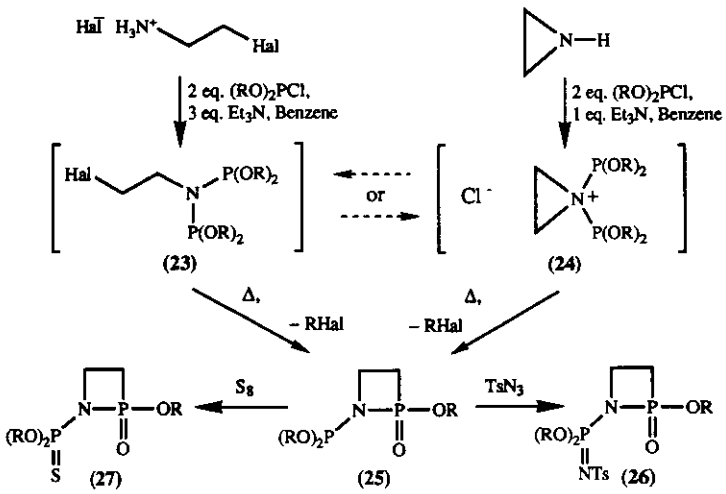
Scheme 11

The other two examples of this ring system are (**21**), the structure of which was confirmed by X-ray crystallography,[18] and (**22**) (Scheme 12).[19]



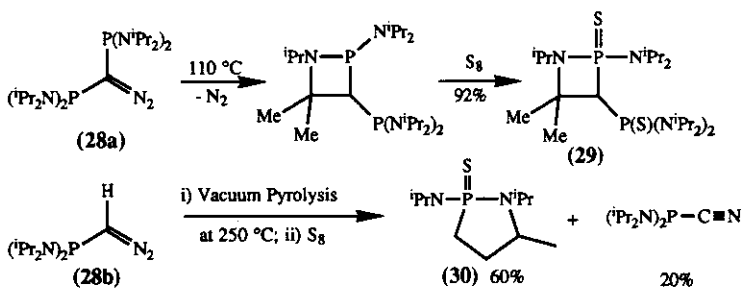
Scheme 12

Gubnitskaya and co-workers were the first to prepare 1,2-azaphosphetidines, namely compounds (**26**) and (**27**). The reaction appears to be an intermolecular Michaelis-Arbuzov reaction, though it may also proceed *via* a nucleophilic displacement affording an aziridinium cation which then undergoes ring expansion. Indeed, the presumed cyclisation precursors (**23**) and (**24**) can be prepared from β-haloethylamines[20] or aziridines (Scheme 13).[21]



Scheme 13

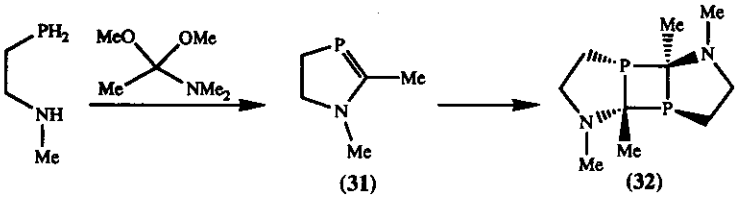
Bertrand reports a single example of the synthesis of 1,2-azaphosphetidine (**29**) by a CH insertion reaction of the carbene generated from diazo compound (**28a**) (Scheme 14).[22] Interestingly, the corresponding azaphospholidines (**30**) was obtained from a closely related system, (**28b**).



Scheme 14

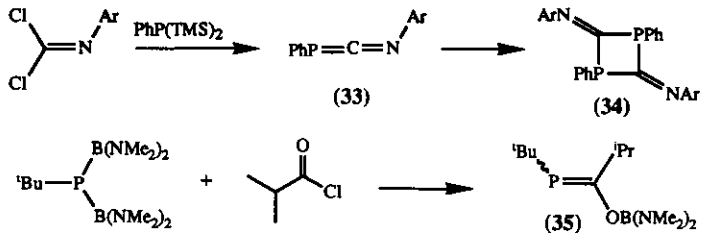
1.4. *Diphosphetanes*

To date, all diphosphetanes reported in the literature have been synthesised by dimerisation of phosphaalkene compounds. With the exception of four examples, each with bulky groups on phosphorus, which yield 1,2-diphosphetanes, all such [2+2] additions result in 1,3-diphosphetanes. For instance, Issleib serendipitously prepared tricyclic compound (**32**) when attempting to crystallise (**31**) after the following reaction sequence (Scheme 15).[23]



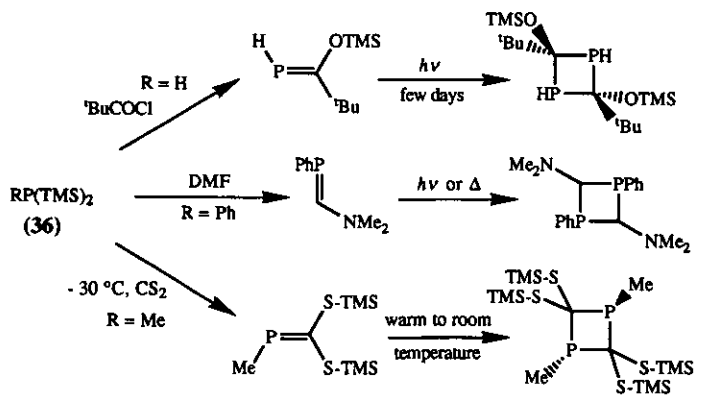
Scheme 15

Addition is not always spontaneous and monomers can be isolated. At least in one case, (**33**), addition is shown to be reversible and in another compound, (**35**), no dimerisation is reported (Scheme16, see also Scheme 19).[24]



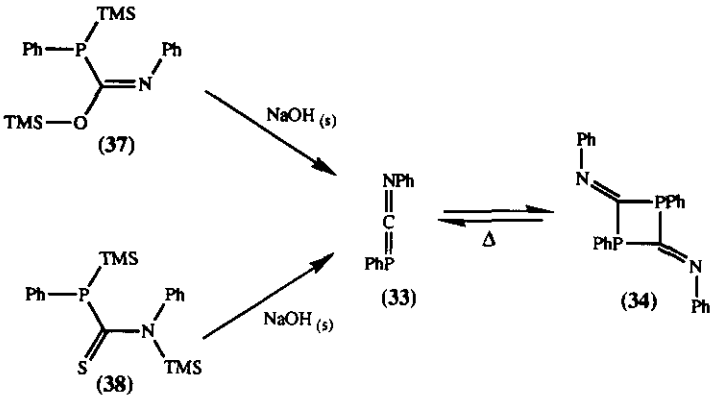
Scheme 16

In an extension of Appel's synthesis of (**34**) (Scheme 16),[25] Becker has prepared a range of heterocumulenes from bis(trimethylsilyl)phosphines (**36**) (Scheme 17) and other $\delta^3\lambda^3$ phosphorus precursors and has shown that some spontaneously dimerise to 1,3-diphosphetanes while the others require heat or light for this transformation.[26a,b,c]



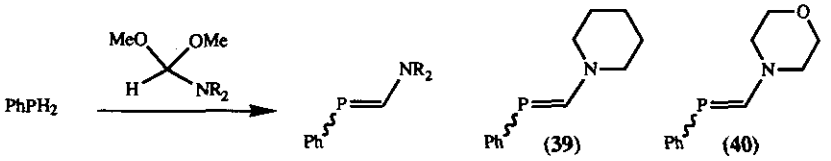
Scheme 17

Becker has further shown that Appel's 1,3-diphosphetane (**34**) can be prepared from phenyl(bistrimethylsilyl)phosphine (**36**, R= Ph) by treatment with aromatic isocyanates and isothiocyanates, to afford **37** and **38** respectively, followed by heating in the presence of a small amount of sodium hydroxide. It was also shown that **34** is in equilibrium with its monomer and that heat drives the equilibrium in favour of monomer (**33**).[27]



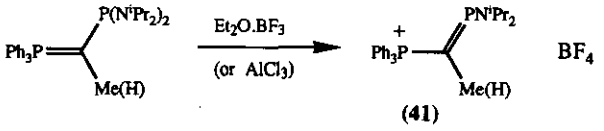
Scheme 18

It is also reported that the extent of dimerisation of aminophosphaalkenes depends on the amine substituents. It is not clear if this effect can be attributed to steric factors alone since compound (**39**) is monomeric in solution whereas the structurally analogous **40** is reported to be 50% dimer (Scheme 19, also see Scheme 16).[28]



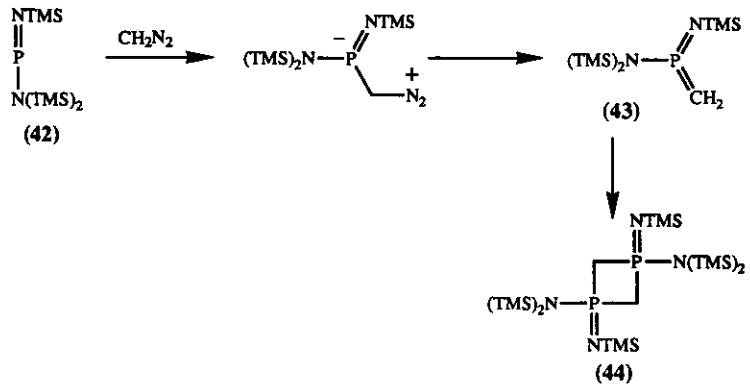
Scheme 19

In a recent report, compound (**41**) was prepared and reported to undergo dimerisation, though it could also be trapped by dienes.[29]



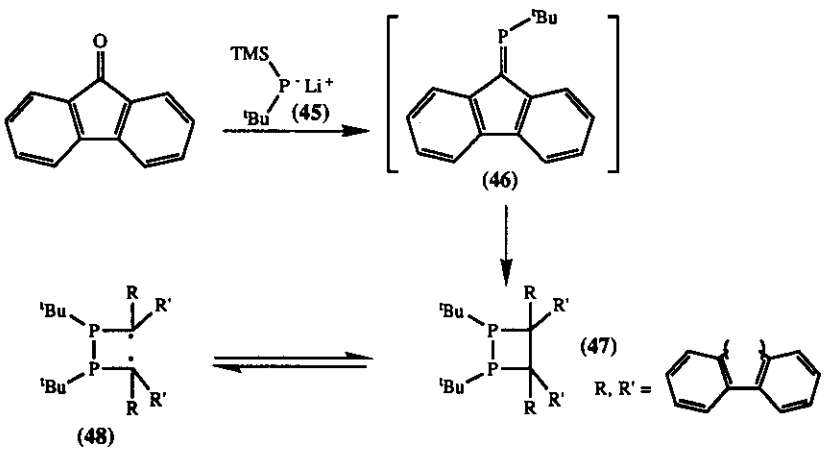
Scheme 20

Precursors to diphosphetanes do not necessarily contain $\sigma^3\lambda^3$ phosphorus. For example, when iminomethylenephosphorane **(42)** was treated with diazomethane, 1,3-diphosphetane **(44)** was obtained, presumably through monomer **(43)**, a $\sigma^3\lambda^5$ phosphorus compound.[30]



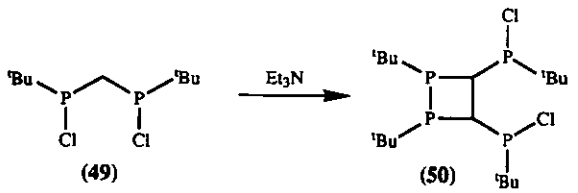
Scheme 21

As was mentioned earlier, in all known examples of 1,2-diphosphetanes, phosphorus atoms bear bulky substituents. For example, treatment of lithium phosphide **(45)** with 9-fluorenone gave, through monomer **(46)**, compound **(47)**. In benzene solution, this compound was in equilibrium with the diradical form **(48)** (ESR).[31]



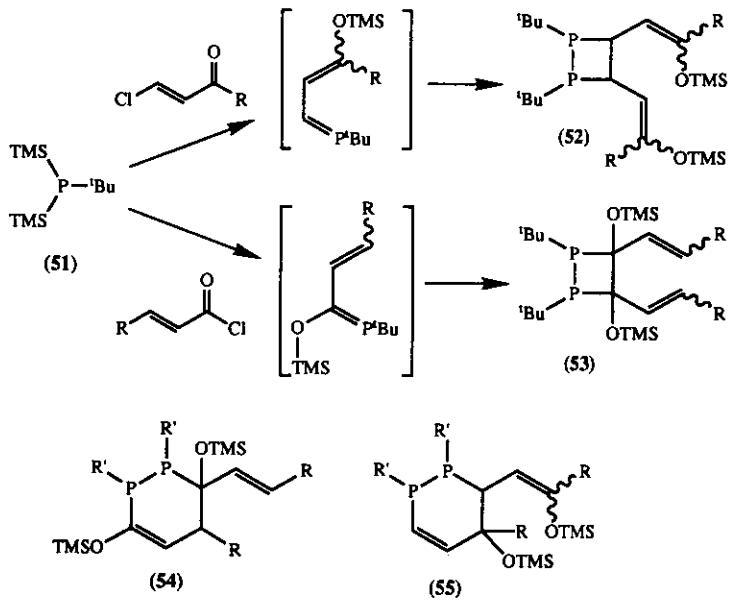
Scheme 22

When compound **(49)** was treated with triethylamine a 1,2-diphosphetane **(50)** was obtained.[32]



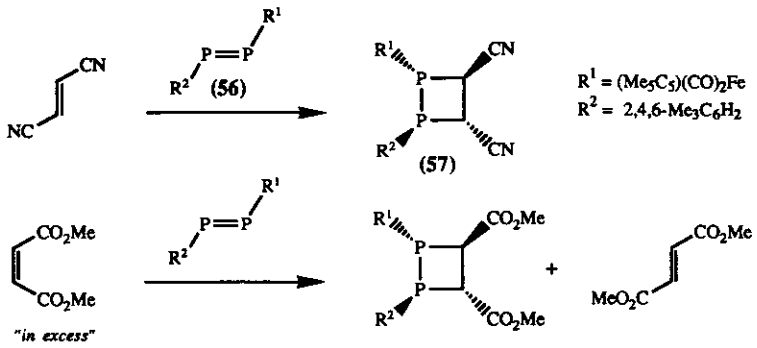
Scheme 23

Appel obtained 1,2-diphosphetanes **(52)** and **(53)** by the route outlined below (Scheme 24). When the tbutyl substituent in starting material **(51)** was replaced with other groups a [4+2] addition occurred instead, to give compounds **(54)** and **(55)**.[33]



Scheme 24

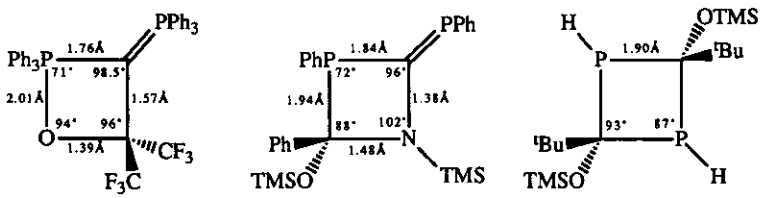
Lastly, diphosphene **(56)** undergoes formal [2+2] cycloaddition with fumaronitrile to afford **57** the structure of which is confirmed by X-ray crystallography. The reaction proceeds *via* a bis radical (*cf* compounds **(47)/(48)**) since in the reaction of **56** with excess of dimethyl maleate, unreacted olefin is recovered as the isomer, dimethyl fumarate.[34]



Scheme 25

2. Structure and Properties

From the available crystal structures (a representative selection is shown in Scheme 26),[4,18,26a] it appears that in oxaphosphetanes and azaphosphetidines, the phosphorus within the ring makes an angle of about 70° with adjacent ring atoms, whereas in the 1,3-diphosphetanes, a wider angle of 84-87° is observed. Since all rings that have been studied by X-ray crystallography are shown to be essentially planar, it appears that the ring distortion from a square to a "kite-like" tetragon is predominantly to allow for longer bonds between phosphorus and adjacent atoms. In 1,3-diphosphetanes where the bond lengths within the ring are more or less similar, allowing for unsymmetrical substitutions, such a distortion is unnecessary and is not observed. This distortion also means that the four membered ring can accommodate wider bond angles, and ring strain is somewhat reduced. Another way in which the ring strain may be relieved is with the ring phosphorus atom having a near trigonal bipyramidal coordination sphere. This is observed, for instance, for compounds (**11**) and (**13**) (see Schemes 4 and 5).



Scheme 26

1,3-Thiaphosphetanes have not yet been subject to crystallographic study although extensive spectroscopic studies, infrared and dipole moment measurements in particular, have been conducted to determine the ring geometry.[15]

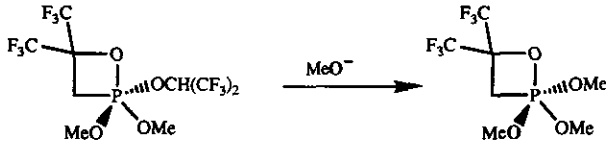
3. Stability of The Rings

As already mentioned, the principal mode of decomposition is that of fragmentation in the sense of affording an olefin and a P=X bonded species. Different ring systems have different tendencies for this reaction and, as we have seen, ring substituents also play a role.

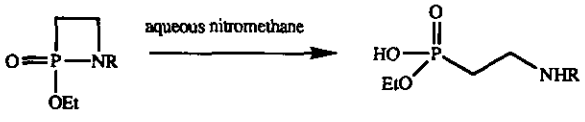
Although X-ray crystallography has confirmed the existence of covalently bonded rings in the solid phase, ^{31}P nmr analysis on the same compounds has revealed that many 1,3-diphosphetanes in solution exist as wholly non-cyclised monomers or in equilibrium with the monomer. This suggests that for these compounds the energy required for fragmentation of the ring is small, and the interatomic forces in the crystalline lattice are enough to overcome the energy barrier for cyclisation.

The 1,2-azaphosphetidines and 1,2-oxaphosphetanes are more robust ring systems, though still susceptible to similar decomposition. As we have seen, the presence of electron withdrawing groups such as CF_3, contributes to the kinetic stability of the ring.

A second, less facile, mode of decomposition is that of ring opening resulting from nucleophilic attack on phosphorus and subsequent P-X (X= O, NR, S) bond scission. An example has already been encountered in the chemistry of thiaphosphetanes (Scheme 9). Again, depending on ring substituents, ring opening occurs with differing degrees of ease as the following examples show. Oxaphosphetane **(58)** was robust enough to withstand sodium methoxide,[35] whereas 1,2-azaphosphetidine **(59)** opens readily when dissolved in wet solvents.[20]



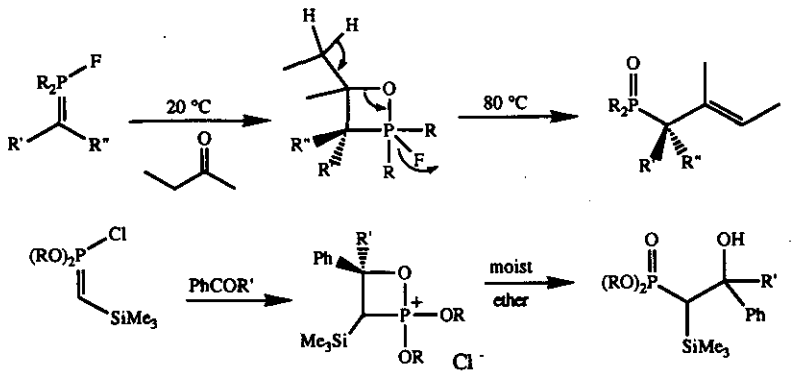
(58)



(59)

Scheme 27

Decomposition modes of those compounds bearing a halogen ligand on phosphorus is different, as the following two examples show.[36a,b] For these compounds the ring cleavage is dictated by the leaving group ability of the halogen.



Scheme 28

Conclusions

A decade ago, four-membered heterocycles containing one phosphorus and one other heteroatom were rare and were considered exotic species which did not fall within the realm of rational synthesis. Today this interesting class of heterocycles is out of the shadows. Although not all is known about their modes of formation and many syntheses of these ring systems still remain novel, or indeed unproven, trends are emerging. Intramolecular nucleophilic displacement, cycloaddition and ring contraction can all be used for their synthesis. Retero-cycloadditions and nucleophilic displacement can also account for their modes of decomposition. As with other carbocycles and heterocycles of their size, stability of the rings varies greatly and depends on substituents, although it can be said that many such heterocycles are robust enough to withstand chemical manipulation. Hence, many interesting questions can now be posed, not only regarding their synthesis but also their chemical transformations.

Acknowledgment

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