

Cycloaddition Reactions of Heterophospholes

Raj K. Bansal, Neelima Gupta, and Nidhi Gupta

Department of Chemistry, University of Rajasthan, Jaipur 302 004, India

Received 27 November 2003; revised 19 January 2004

ABSTRACT: *The cycloaddition reactions namely, [2 + 4], [4 + 2], [2 + 3] and [1 + 4] given by the heterophospholes, which are five-membered 6π aromatic heterocycles containing at least one σ^2 , λ^3 phosphorus, are reviewed in the present article. Different aspects of these reactions such as stereoselectivity, regioselectivity, relative reactivities and theoretical correlations thereof are included. The literature has been surveyed up to December 2003. © 2004 Wiley Periodicals, Inc. Heteroatom Chem 15:271–287, 2004; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20002*

INTRODUCTION

Heterophospholes are five-membered 6π aromatic systems having a two-coordinate, trivalent (σ^2 , λ^3) phosphorus which contributes one electron to the aromatic sextet [1–4]. In the neutral heterophosphole ring, besides sp^2 -phosphorus, there must be at least one heteroatom like NR, O, or S(Se,Te) contributing two π -electrons. In view of the close resemblance between carbon and phosphorus [5–8], heterophosphole ring may be thought as derived from the classical heteroles such as pyrrole, furan, or thiophene by substituting one ring $=CH-$ by $=P-$. Furthermore, as in diazoles, oxazoles, thiazoles, or triazoles, the heterophosphole ring may contain one or more two-coordinate nitrogen atoms or even more than one two-coordinate phosphorus atom. Likewise, the anellated heterophospholes [9,10] may be

perceived as phosphorus analogues of the classical fused systems such as indole, indolizine, benzofuran, benzothiazole, benzimidazole, benzoxazole, or azapentalenes.

In heterophospholes, two functionalities: $>C=P-$ or $-N=P-$ and lone pair on phosphorus, give a variety of cycloaddition reactions. 1,2-Addition on $C=P$ leads to [2 + 4], [2 + 3], or [2 + 2] cycloadditions whereas 1,1-addition on phosphorus results in cheletropic [1 + 4] cycloaddition. In some cases, the heterophosphole ring reacts as the diene component with acetylene and phosphaacetylene derivatives to form [4 + 2] cycloadducts. The mode of cycloaddition (1,2- or 1,1-addition) depends on the HOMO/LUMO combination of the heterophosphole available to the reagent [11,12]; however, no sufficient theoretical calculations appear to have been carried out so far to make a definite prediction in this regard. The results reported indicate that normally electron-rich dienes such as butadienes, cyclopentadiene, etc. give [4 + 2] cycloadducts, whereas electron-deficient heterodienes including *o*-quinones form [4 + 1] cycloadducts. There are, however, exceptions, particularly in the cycloadditions with heterodienes.

Sometimes two of the above mentioned cycloadditions occur successively, e.g. a [2 + 4] addition on $>C=P-$ is followed by [1 + 4] addition on phosphorus leading to the product having a five-coordinate phosphorus [13,14]. In some other cases, particularly if the $>C=P-$ unit is not sufficiently activated, [2 + 4] cycloaddition is preceded by a [1 + 4] addition on phosphorus [15–20]. An initial [1 + 4] addition on phosphorus may be followed by dimerization across the $-N=P-$ moiety [21,22]. In a limited number of cases, particularly in those heterophospholes which have a strong electron-donating centre at the

Correspondence to: Raj K. Bansal; e-mail: rajbns@yahoo.com.
Contract grant sponsor: Department of Science & Technology, Government of India, New Delhi.
© 2004 Wiley Periodicals, Inc.

β -position (e.g. NR), cheletropic [1 + 4] cycloaddition on phosphorus occurs successively twice giving a zwitterionic product having a six-coordinate (σ^6, λ^5) phosphorus [23,24, Bansal, R. K.; Gupta, N.; Surana, A. (unpublished results)].

Different modes of cycloadditions of the heterophospholes have been outlined in Scheme 1.

The cycloaddition reactions given by the heterophospholes will therefore be described under the following five categories:

1. [2 + 4] Cycloadditions
2. [4 + 2] Cycloadditions
3. [2 + 3] Cycloadditions
4. [2 + 2] Cycloadditions
5. [1 + 4] Cycloadditions

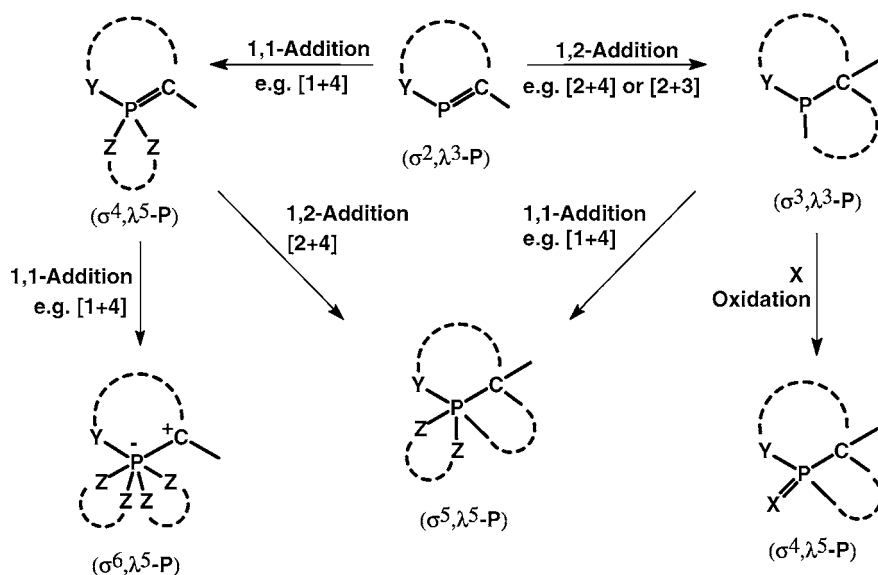
An earlier review on "cycloadditions on λ^3, σ^2 -phosphorus multiple bonds" includes cycloaddition reactions of heterophospholes [25]. Other later reviews [1–4,9,10] also cover these reactions, though in a limited manner.

In the present review it is intended to highlight different aspects, namely stereoselectivity, regioselectivity, relative reactivities, theoretical calculations, etc., of the cycloaddition reactions of the heterophospholes. Although greater emphasis has been placed on the results reported during the last 5–6 years, earlier results have also been described wherever necessary. The literature has been covered up to December 2003.

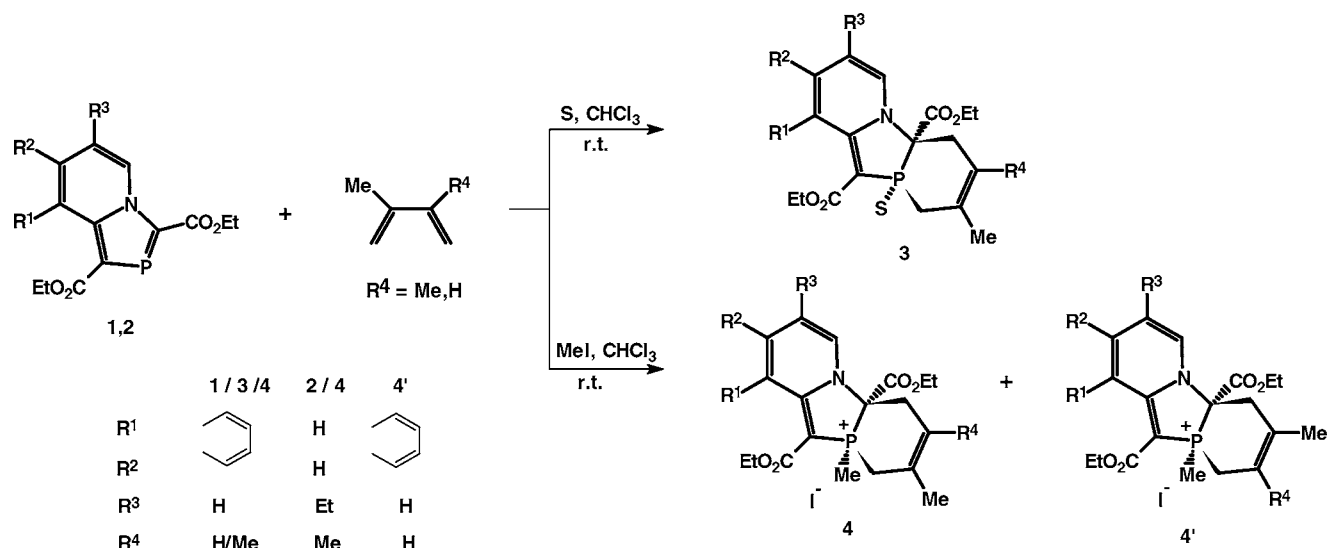
[2 + 4] Cycloadditions

The $>C=P-$ moiety in the heterophospholes, as in acyclic phosphalkenes [26–29], acts as dienophile and undergoes [2 + 4] cycloaddition with a variety of 1,3-dienes, such as 2,3-dimethylbutadiene, 1,4-diphenylbutadiene, isoprene, cyclopentadiene, 1,4-diphenylazabutadiene and *o*-quinones [13,30–39]. The reaction with unsymmetrical diene such as isoprene or 1,4-diphenylazabutadiene proceeds regioselectively, the regioselectivity in many cases being 100%. In the reaction with a cyclic diene, like cyclopentadiene, the kinetically preferred endo-isomer is formed at low temperature.

1,3-Bis(ethoxycarbonyl)-1,3-azaphospholo[5,1-*a*]isoquinoline **1** reacts with 2,3-dimethylbutadiene in the presence of sulfur or methyl iodide at room temperature to give [2 + 4] cycloadducts **3** and **4** respectively [37,38]. The reaction with isoprene in presence of sulfur proceeds regiospecifically to give **3** only, but in presence of methyl iodide the regioselectivity is lowered and two regioisomers **4** (62%) and **4'** (38%) are formed (Scheme 2). The structure of **3** ($R^4 = H$) has been confirmed by X-ray crystal studies [38]. Although 3-ethoxycarbonyl-1,3-azaphospholo[1,5-*a*]pyridine was found to be unreactive towards 2,3-dimethylbutadiene [Bansal, R. K.; Gupta, N. (unpublished results)], 1,3-bis(ethoxycarbonyl) derivative **2** reacted with 2,3-dimethylbutadiene and methyl iodide smoothly at room temperature to give **4** [38]. This difference in the reactivities was correlated qualitatively with FMO energies calculated by semiempirical



SCHEME 1



SCHEME 2

PM3 method [37]. The reaction of **1** with 2,3-dimethylbutadiene alone was found to be sluggish at room temperature and could be completed ($\delta^{31}\text{P} = 14.1$) only on refluxing in chloroform for 4 days [38]. The role of sulfur or methyl iodide therefore appears to push a reversible reaction between the 1,3-azaphosphole ring and diene in the forward direction by oxidizing σ^3 P atom of the initially formed [2 + 4] cycloadduct.

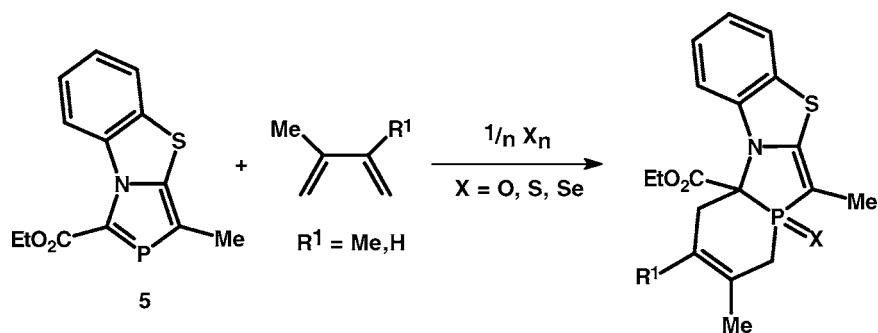
The [2 + 4] cycloadditions of 1,3-bis(ethoxycarbonyl)-1,3-azaphospholo[5,1-*a*]isoquinoline with 2,3-dimethylbutadiene and with isoprene in presence of sulfur could be accomplished under microwave irradiation in much shorter times (10–22 min) without affecting the yields. The reaction with isoprene occurs regiospecifically under these conditions as well [39].

Similar pattern of regioselectivity has been observed in several other cases. 1,3-Azaphospholo[5,1-*b*]benzothiazole **5** undergoes [2 + 4] cycloaddition with 1,3-dienes, only in the presence of oxygen, sulfur, or selenium, the reaction with isoprene oc-

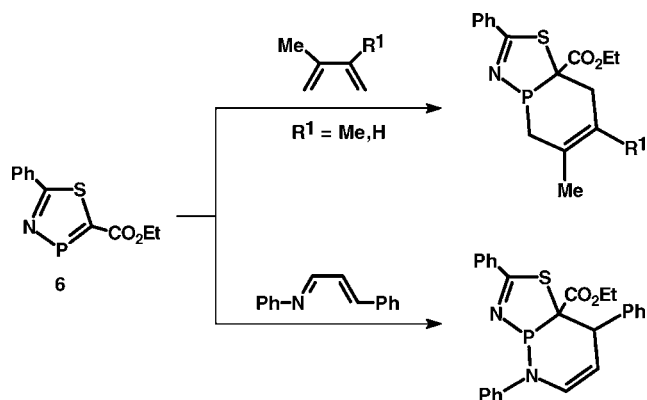
curing with 100% regioselectivity (Scheme 3) [40, Bansal R. K.; Karaghiosoff, K.; Mahnot, R.; Gupta, N. (unpublished results)].

5-Ethoxycarbonyl-2-phenyl-1,3,4-thiazaphosphole **6** forms [2 + 4] cycloadducts with 1,3-butadienes [2, Bansal, R. K.; Gupta, S. (unpublished results)] and 1,4-diphenyl-1-azabutadiene [2], 100% regioselectivity being observed in the reaction with isoprene and 1,4-diphenyl-1-azabutadiene (Scheme 4).

Diazaphospholes have been found to react with 1,3-dienes without the aid of an oxidizing agent. 1,4,2-Diazaphospholo[4,5-*a*]pyridines ($\text{R} = \text{H}$, CO_2Et) **7**, -[5,4-*b*]benzothiazole ($\text{R} = \text{CO}_2\text{Et}$) **8**, and -[5,4-*b*]thiazolines ($\text{R} = \text{CO}_2\text{Et}$) **9** form [2 + 4] cycloadducts with 1,3-butadienes ($\text{R}^1 = \text{Me}$, H). The initially formed cycloadducts are, however, oxidized during workup and hence the reactions have been carried out in the presence of sulfur or selenium. The cycloaddition with isoprene in all these cases proceeds regioselectively, as indicated by ^{31}P NMR (Scheme 5) [9,32, Bansal R. K.; Karaghiosoff, K.;



SCHEME 3



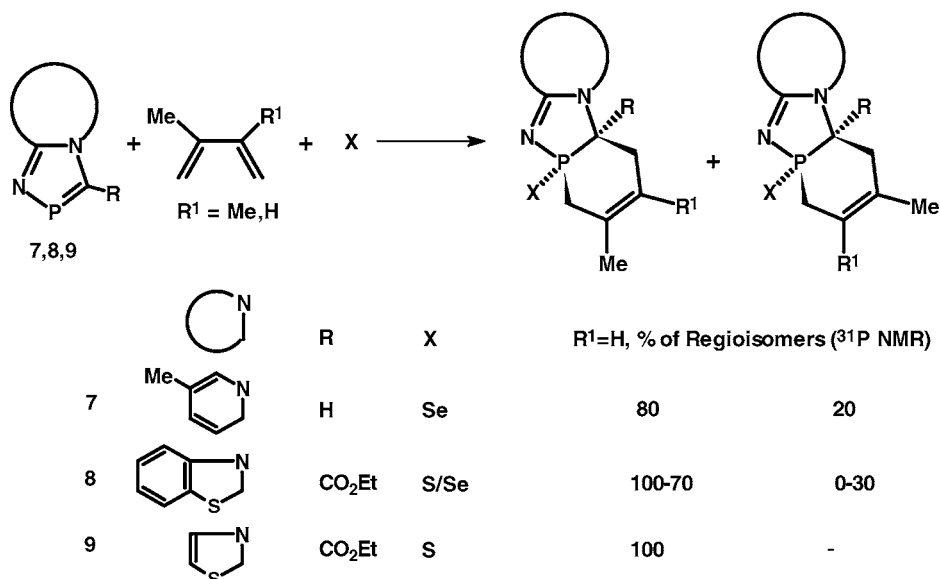
SCHEME 4

Gupta, N.; Mahnot, R.; Sharma, D. C.; Gandhi, N. (unpublished results)]. The reaction of **7** with isoprene in presence of methyl iodide also leads to the corresponding two regioisomers in 70:30 ratio [Bansal R. K.; Karaghiosoff, K.; Gupta, N.; Mahnot, R.; Sharma, D. C.; Gandhi, N. (unpublished results)].

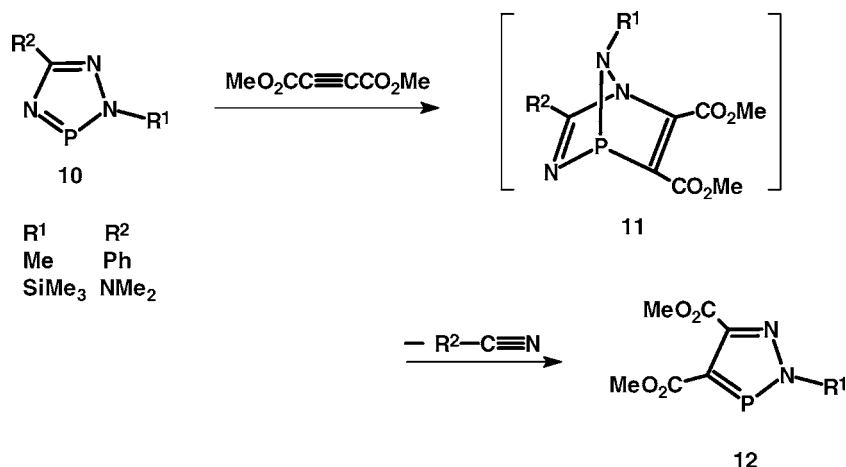
Similarly, complete regioselectivity has been reported in the reaction of 2-acetyl-1,2,3-diazaphosphole with isoprene [33]. The reaction of 2-acetyl-1,2,3-diazaphosphole with cyclopentadiene gave an endo-product immediately (15 min, 15°C) which, after 3 days in solution at room temperature, changed to the thermodynamically more stable exo-product through cycloreversion [34]. 2-*tert*-Butyl-1-ethyl-1,3-benzodiphosphole [30,31] and 1*H*-1,2,3-benzazadiphosphole [41] have been reported to form [2 + 4] cycloadducts with 1,4-diphenylbutadiene and 2,3-dimethylbutadiene re-

spectively. 1,3-Benzoxaphospholes behave likewise and yield [2 + 4] cycloadducts with 2,3-dimethylbutadiene and with tetrachloro-*o*-benzoquinone (TCQ) [13]. Structure of the cycloadduct of 2-methyl-1,3-benzoxaphosphole with TCQ has been confirmed by X-ray crystal structure [14]. The [2 + 4] cycloadduct of 2-*tert*-butyl-1,3-benzoxaphosphole with TCQ on reacting with more TCQ undergoes cheletropic 1,1-addition on phosphorus to give a product with a five-coordinate phosphorus [13].

An attempt has been made to explain reactivities and regio- and stereoselectivities observed in these reactions on the basis of the theoretical calculations of the model [2 + 4] cycloadditions of phosphaphethene with 1,3-butadiene and isoprene [42]. The DFT(B3LYP/6-311+G**) activation energies of these reactions, 12–14 kcal/mol, are much lower than that of the parent ethene-butadiene reaction, 28 kcal/mol, even though the exothermicities of all lie in the same range, –29 to –33 kcal/mol. Thus introduction of σ^2 P in the dienophile, as in the diene [43,44], lowers the activation energy relative to that of the hydrocarbon systems due to the weakness of the C=P π bond compared to the C=C π bond. Moreover, it is indicated that the approach of the reactants with endo P–H group is kinetically more favorable than the attack with an exo P–H [42,44]. However, computed activation barriers and exothermicities of the reactions (endo and exo) of phosphaphethene with isoprene suggest that the experimentally observed regioselectivities of the products (having phosphorus and methyl group in meta position) cannot be accounted for by the closed shell pericyclic mechanism, i.e. concerted [2 + 4] cycloaddition. Instead, alternative



SCHEME 5



SCHEME 6

radical cation mechanism involving stepwise addition of the isoprene radical cation with phosphathene could explain high regioselectivities [42].

[4 + 2] Cycloadditions

The [4 + 2] cycloadditions in which heterophosphole acts as the diene component are described in this category.

It has been found that the hetero-1,3-diene system present in those heterophospholes and heterodiphospholes which have a heteroatom (N, O, S, Se) adjacent to the two-coordinate phosphorus react with an electron deficient dienophile such as alkene, acetylene, or phosphaacetylene to yield a [4 + 2] cycloadduct. The cycloadduct formed with acetylene usually undergoes cycloreversion accompanied by the loss of a nitrile or similar molecule to furnish a new heterophosphole (Scheme 6). The initially formed cycloadduct with phosphaacetylene, however, undergoes further [2 + 2 + 2] cycloaddition, i.e., homo Diels-Alder reaction by reacting with more phosphaacetylene to give interesting cage compounds.

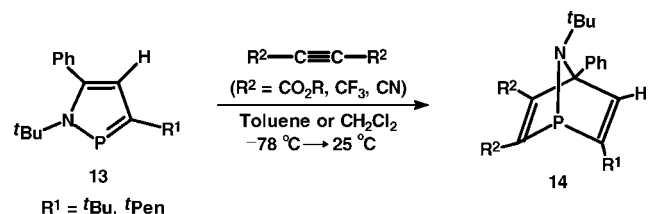
The hetero-1,3-diene behavior was first observed for 1,2,4,3-triazaphospholes **10** which reacted with dimethyl acetylenedicarboxylate to give 1,2,3-diazaphosphole derivatives **12**. Monoalkyl esters of acetylenedicarboxylic acid formed both regioisomers. The reaction involves the initial formation of a [4 + 2] cycloadduct **11** which undergoes cycloreversion accompanied by the loss of a nitrile molecule to yield the final product (Scheme 6) [45].

1,3,2-Diazaphosphole-4,5-dicarbonitriles exhibit similar behavior which on reacting with electron deficient acetylene derivatives afford 1*H*-

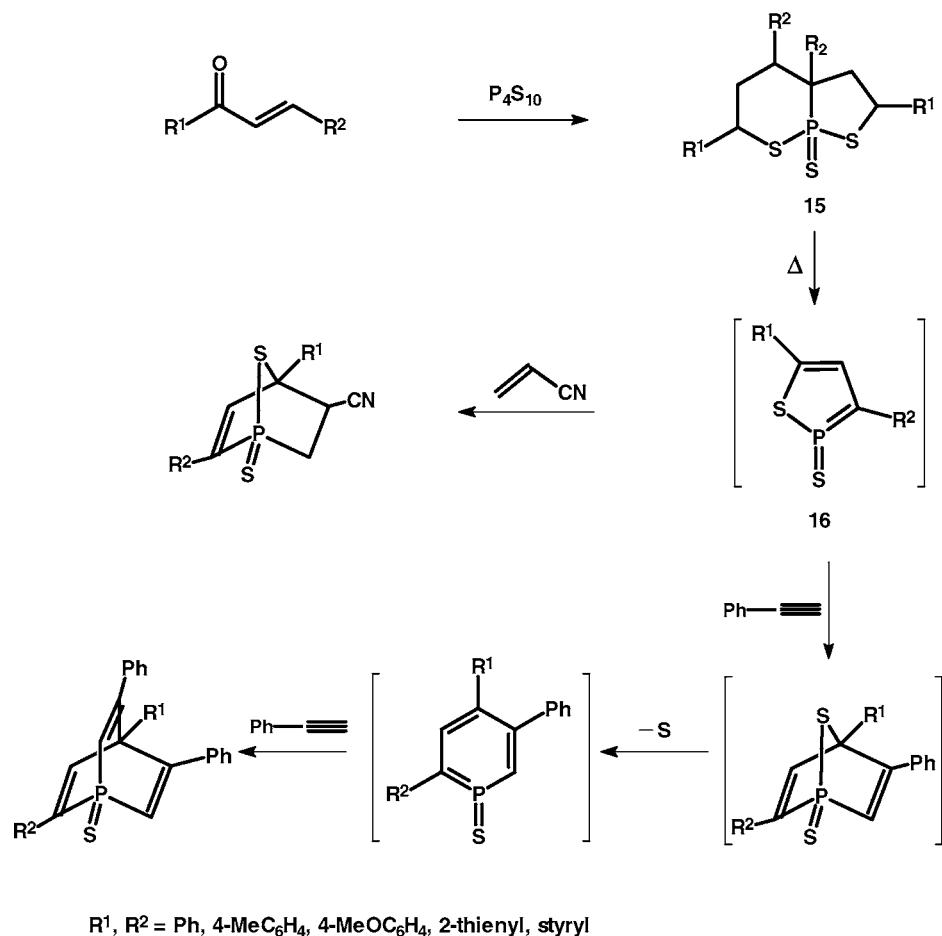
1,2-azaphosphole-5-carbonitriles through [4 + 2] cycloaddition/reversion [46]. An analogous reaction has been reported for 1,3,2-diaza- and 1,2-azaphosphinines [47]. 1*H*-1,2-Azaphospholes **13**, however, form stable [4 + 2] cycloadducts with electron-deficient acetylenes (Scheme 7) [48]. The structure has been confirmed by X-ray crystal structure determination of a representative (**14**, $\text{R}^1 = t\text{Bu}$, $\text{R}^2 = \text{CF}_3$) [48].

1,2-Thiaphosphole-2-sulfides **16**, generated in situ from thermolysis of 2,9-dithia-1-phospha-bicyclo[4.3.0]nona-3,7-diene-1-sulfides **15** [49] in absence of a phosphine, form stable [4 + 2] cycloadducts with a variety of dienophiles such as acrylonitrile, norbornene, norbornadiene, phenylethyne, and dimethyl acetylenedicarboxylate [50,51]. In many cases, double Diels-Alder cycloadducts are produced, or the initially formed [4 + 2] cycloadduct undergoes secondary reactions like ring expansion or Michael addition [52]. Reaction with acrylonitrile [50] and phenylethyne [51], occurring regiospecifically are shown in Scheme 8.

1,2-Thiaphosphole, acting as heterodiene, shows interesting reactivity towards cyclopentadiene [53] and cyclooctyne [54]. With cyclopentadiene no reaction occurs at 20–80°C, but at 120°C in a sealed tube, 3,5-diphenyl-1,2-thiaphosphole **19** combines



SCHEME 7



SCHEME 8

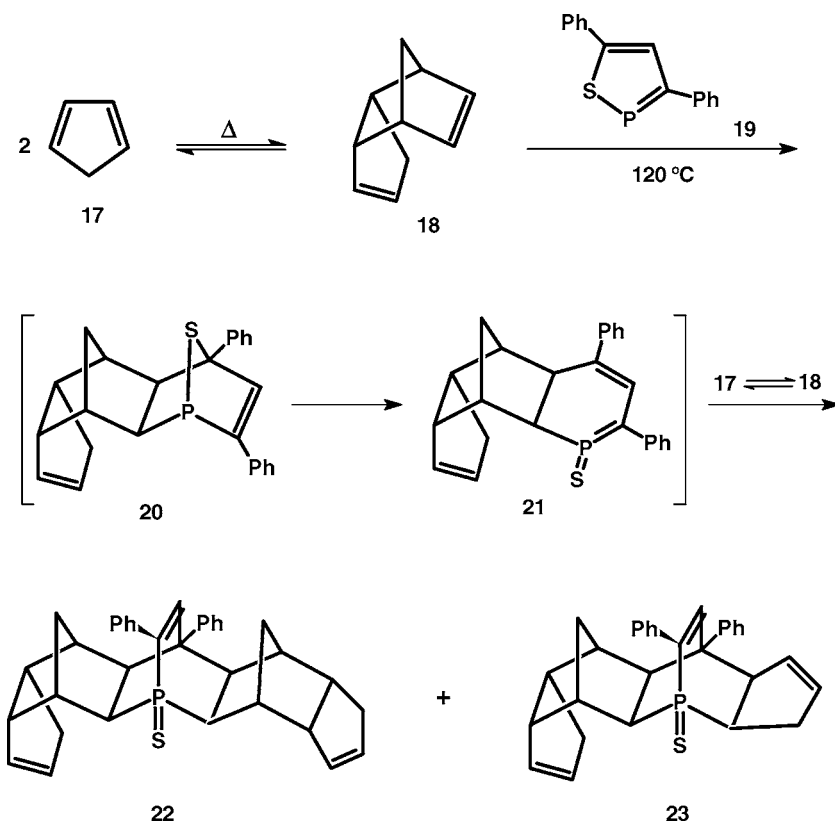
with dicyclopentadiene (dienophile) to form a [4 + 2] cycloadduct. The latter undergoes subsequently successive ring expansion and further [4 + 2] cycloaddition either with dicyclopentadiene to form **22** or with cyclopentadiene to produce **23**. The structure of **22** was confirmed by X-ray crystal studies [53] (Scheme 9).

1,2-Thiaphosphole **24** ($R = t\text{Bu}$) reacts with twofold excess of cyclooctyne **25** to give polycyclic compounds **28** and **31** through successive [4 + 2] cycloaddition, cycloexpansion, and again [4 + 2] cycloaddition. ^{31}P NMR although indicated the formation of **30** also in the reaction mixture, it could not be isolated, however [54] (Scheme 10). The reaction of other 1,2-thiaphosphole derivatives **24** ($R = \text{CMe}_2\text{Et}$, Me^cPen , Me^cHex) under similar conditions generated the corresponding **28** in much smaller extents which, however, could not be isolated in pure form [54].

The [4 + 2] cycloaddition of 1,2,4-thiadiphospholes **32** ($X = \text{S}$) [55] and of 1,2,4-oxadiphosphole **32** ($X = \text{O}$) [56] are followed by retro Diels-Alder reaction accompanied by the loss of phosphaacety-

lene to give 1,2-thiaphosphole **33** ($X = \text{S}$) and 1,2-oxaphosphole **33** ($X = \text{O}$), respectively (Scheme 11). In the case of 1,2,4-thiadiphosphole (**32**, $X = \text{S}$; $R = t\text{Bu}$) side products **35** are also formed as a result of the [2 + 4] cycloaddition of the phosphaacetylene, liberated in the reaction, with 1,2,4-thiadiphosphole, followed by [2 + 2 + 2] cycloaddition of **34** with acetylene derivative [55].

Unlike 1,2,4-thiadiphospholes, 3,4-bis(trifluoromethyl)-1,2,5-thiadiphosphole forms stable [4 + 2] cycloadducts with bis(trifluoromethyl)acetylene and with maleic anhydride [57]. Phosphaacetylenes have also been used as dienophiles in the [4 + 2] cycloadditions of 1,2,4-oxadiphosphole **32** ($X = \text{O}$) [56], 1,2,4-thiadiphosphole **32** ($X = \text{S}$) [55,58], and 1,2,4-selenadiphosphole **32** ($X = \text{Se}$) [59,60]; the initially formed [4 + 2] cycloadduct **36** in these cases undergoes homo Diels-Alder reaction with second molecule of phosphaacetylene to afford the hetero-tetraphospha cage compounds **37** (Scheme 12). In the case of 1,2,4-thiadiphosphole [55,58], the homo Diels-Alder reaction of the intermediate bicyclodiene **36** with phosphaacetylene



SCHEME 9

occurs regiospecifically, but 1,2,4-selenadiphosphole [59,60] and 1,2,4-oxadiphosphole [56] give both regioisomers **37** and **37'**.

The X-ray crystal structures of the final products produced by 1,2,4-thiadiphosphole [55,58] and 1,2,4-selenadiphosphole [59] have been determined. It may be mentioned in this connection that the intermediate **36** could not be detected by ^{31}P NMR. However, a structurally related molecule, 1,3,5-triphospha-Dewar-benzene, has been found to undergo homo Diels-Alder reaction, i.e., $[2 + 2 + 2]$ cycloaddition with acetylene in similar manner [61].

1-Triphenylstannyl-1,2,4-triphosphole **38** also undergoes successive $[4 + 2]$ and $[2 + 2 + 2]$ cycloadditions with two molecules of *tert*-butylphosphaacetylene (Scheme 13). Both cycloadditions occur regiospecifically [62].

The structure of **39** has been confirmed by X-ray crystal studies [62].

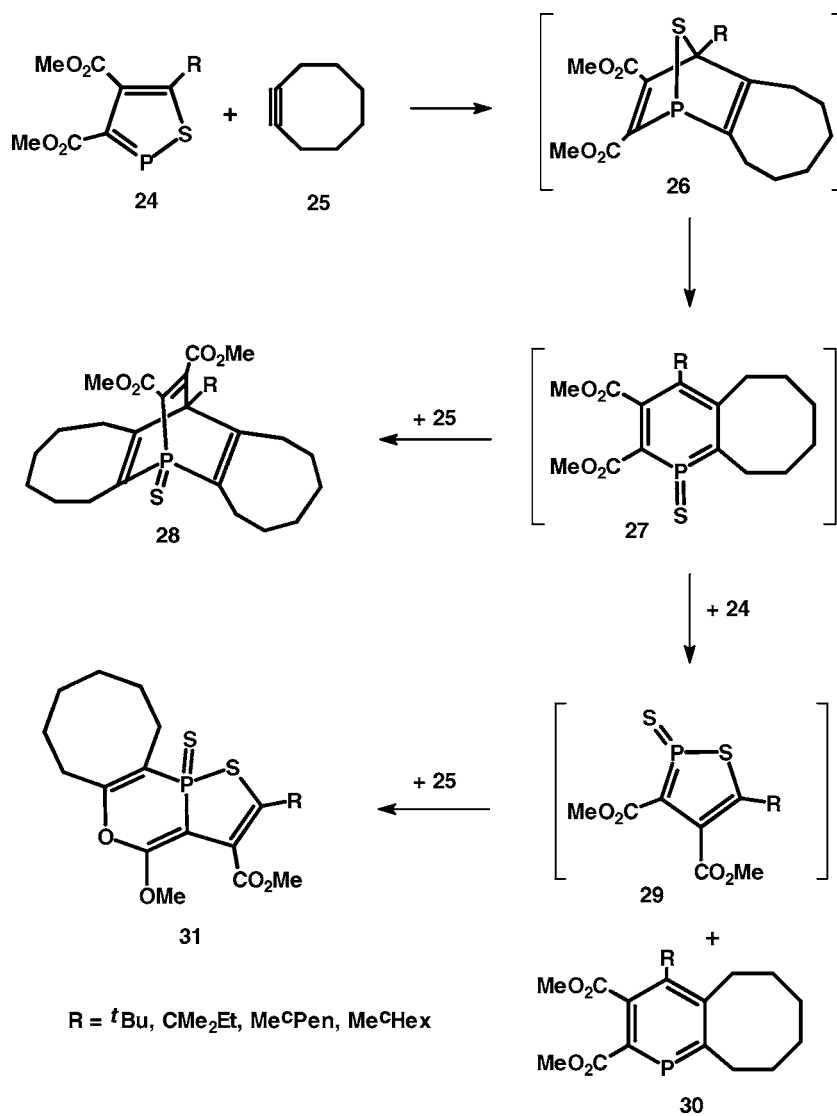
$[2 + 3]$ Cycloadditions

The $[2 + 3]$ cycloadditions of heterophospholes have been carried out with a variety of 1,3-dipoles. The reactions with nitrilimines, nitrile oxides, and

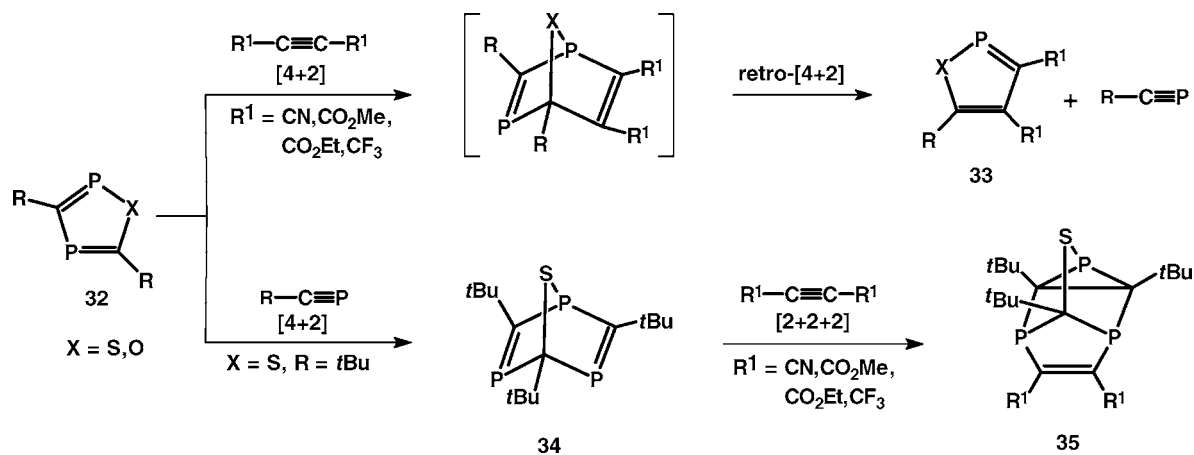
nitrile ylides proceed regiospecifically, carbon of the 1,3-dipole being bonded to the phosphorus of the heterophosphole. Addition of the diazoalkanes, $\text{R}^1\text{R}^2\text{CN}_2$, to the $\text{C}=\text{P}$ unit of the heterophosphole may, however, lead to both products having $\text{C}-\text{N}$ or $\text{P}-\text{N}$ bonding, the actual course depending upon the substituents R^1 and R^2 . The cycloadducts resulting from addition of diazoalkanes and azides are usually stabilized by proton shift or loss of nitrogen. 1,2,4-Oxazaphospholes **40** and 2*H*-1,2,3-diazaphospholes **42** undergo $[2 + 3]$ cycloaddition with nitrile oxides regiospecifically to give cycloadducts **41** [63,64] and **43** [65,66], respectively (Scheme 14).

2*H*-1,2,3-Diazaphospholes **42** form $[2 + 3]$ cycloadducts regiospecifically with nitrilimines [67] and nitrile ylides [68] also. The cycloadduct **45** formed with nitrilimine on heating eliminates benzonitrile and the resulting 4-anilindiazaphosphole **46** undergoes $[2 + 3]$ cycloaddition with one more equivalent of nitrilimine to give the final product **47** [67] (Scheme 15).

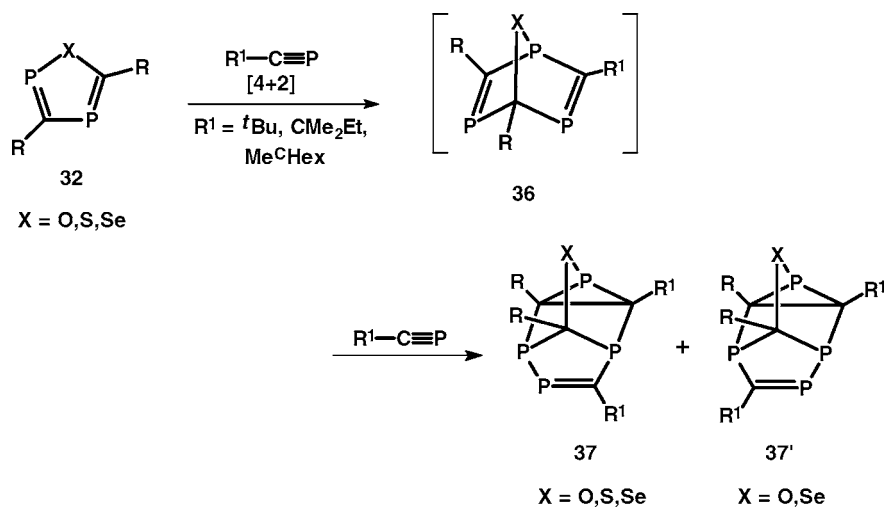
The regio-orientation of the diazoalkane ($\text{R}^3\text{R}^4\text{CN}_2$) in its cycloaddition to 2*H*-1,2,3-diazaphosphole depends on the nature of the substituent groups, R^3 , R^4 [25]. In the case, $\text{CR}^3\text{R}^4 = \text{CH}_2$



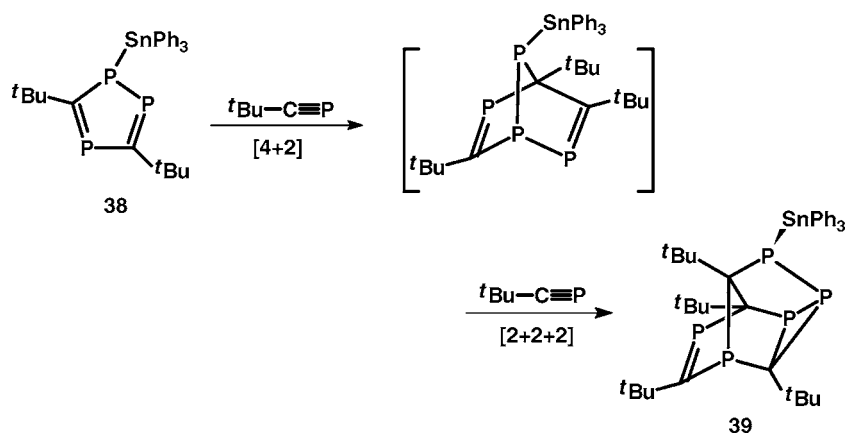
SCHEME 10



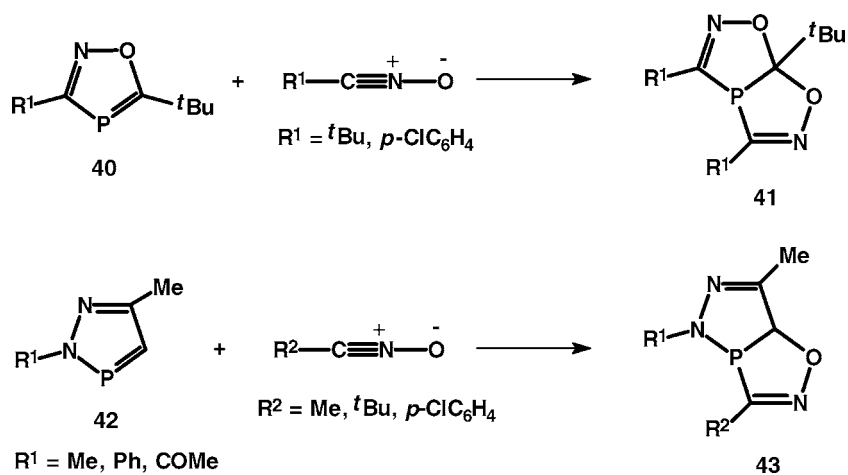
SCHEME 11



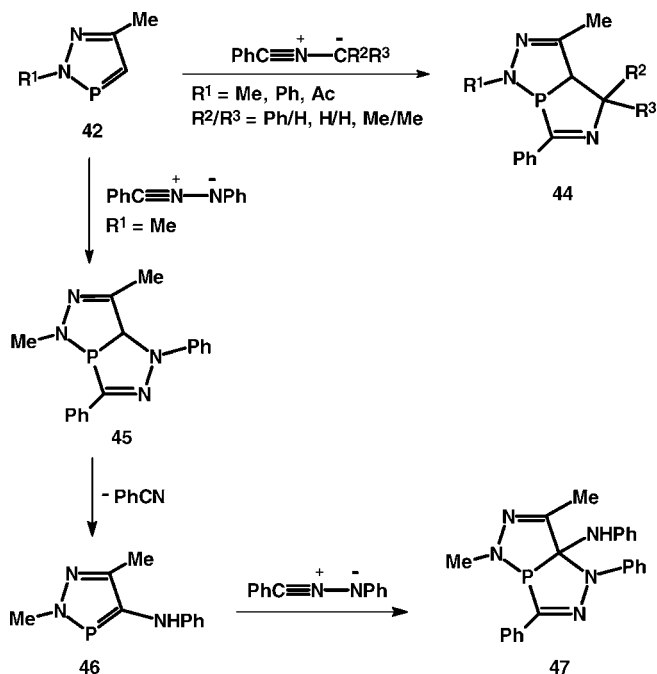
SCHEME 12



SCHEME 13



SCHEME 14



SCHEME 15

[69], CMe₂ [70–72], CMePh [73], CPh₂ [74], fluorenyl [69], and CHPO(OEt)₂ [75], nitrogen of the diazoalkane is bonded to the carbon of the C=P functionality of **42** to form the product **48**. But, if CR³R⁴ = CHiPr [74], CHtBu, CHCOMe [76], and CHCO₂Et [77], the regio-orientation of the diazoalkane is reversed resulting in the formation of **49**. The cycloadduct with CR³R⁴ = CHPO(OEt)₂, CHCOMe, and CHCO₂Et undergo two successive

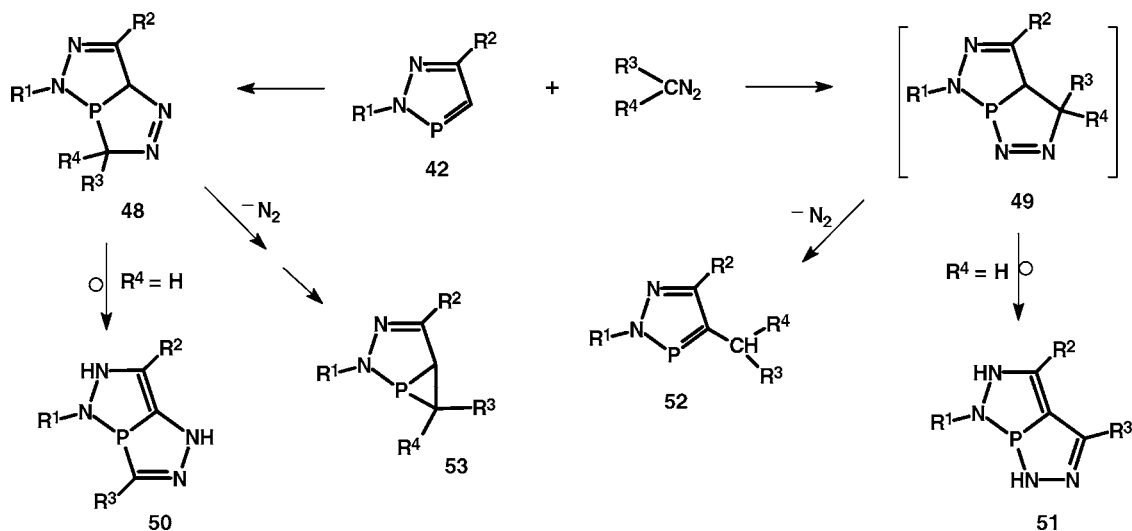
1,3-prototypic shifts to give **50** and **51**, whereas in other cases elimination of nitrogen occurs leading to 4-alkyldiazaphosphole **52** or bicyclic phosphirane **53** [74] and other products (Scheme 16).

The [3 + 2] cycloadditions of diphenyldiazomethane with 1,3,4-thiazaphosphole **6** [74] and 1,2-thiaphosphole **19** [78] also lead to bicyclic phosphiranes **54** and **55** respectively (Scheme 17). The latter readily formed the pentacarbonyltungsten complex **56**, which was characterized by single crystal X-ray diffraction studies [78].

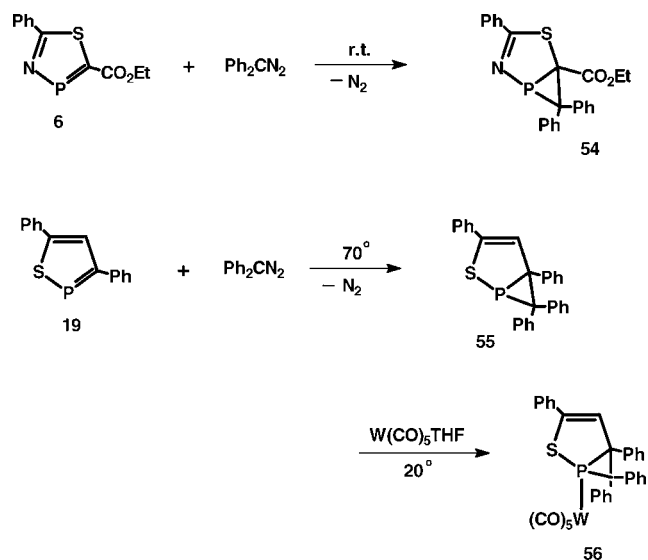
The [2 + 3] cycloadduct **57** formed by 2-methyl-5-phenyl-1,2,4,3-triazaphosphole **10** with diphenyldiazomethane yields after hydrolysis, 3,4-dihydrotriazaphosphole-3-oxide **60** presumably via the P-ylide **58** produced as an intermediate by loss of nitrogen from **57** [25] (Scheme 18).

Cyclohexane-anellated 1,2,3-diazaphosphole forms unstable cycloadducts with diazoalkanes which eliminate nitrogen to form mixtures of acyclic bis(hydrazones) and σ³P compounds [79]. The cycloadduct of 1,2,3-diazaphospholes with phenyl azide splits off nitrogen to generate phosphinimine which trimerizes [80].

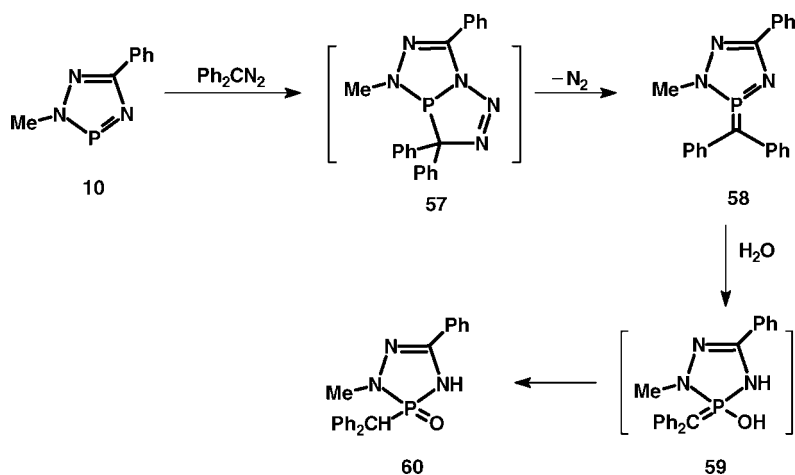
Recently [3 + 2] cycloadditions of (1-diazo-2-oxoalkyl)silanes have been investigated with 2*H*-1,2,3-diazaphospholes [81], 3*H*-1,2,3,4-triazaphospholes [82], and 1,2-thiaphospholes [53]. The silanes **61** are in equilibrium with minor amounts of diazocumulenes **62** which are much more reactive 1,3-dipoles than the former [83]. Their reaction with 2*H*-1,2,3-diazaphospholes **63** affords the [3 + 2] cycloadducts **64**. The latter on thermolysis change into the tricyclic heterocycles **65** through loss of nitrogen



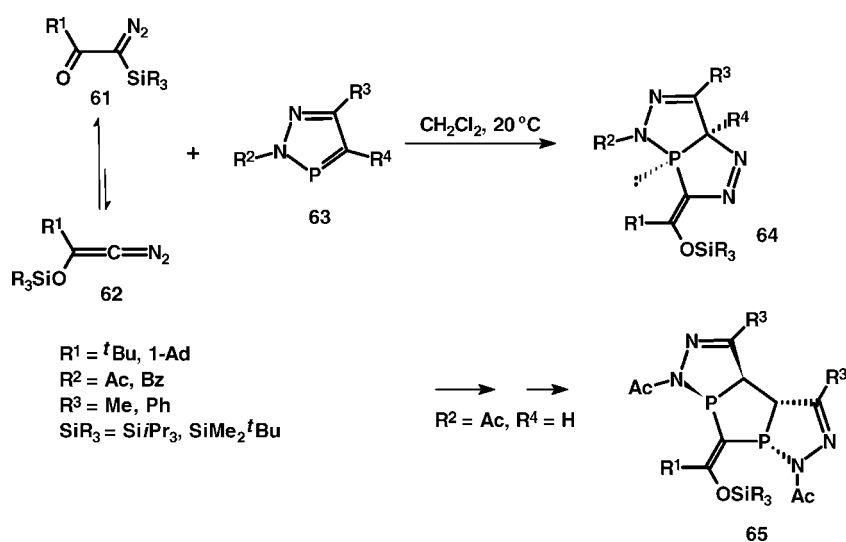
SCHEME 16



SCHEME 17



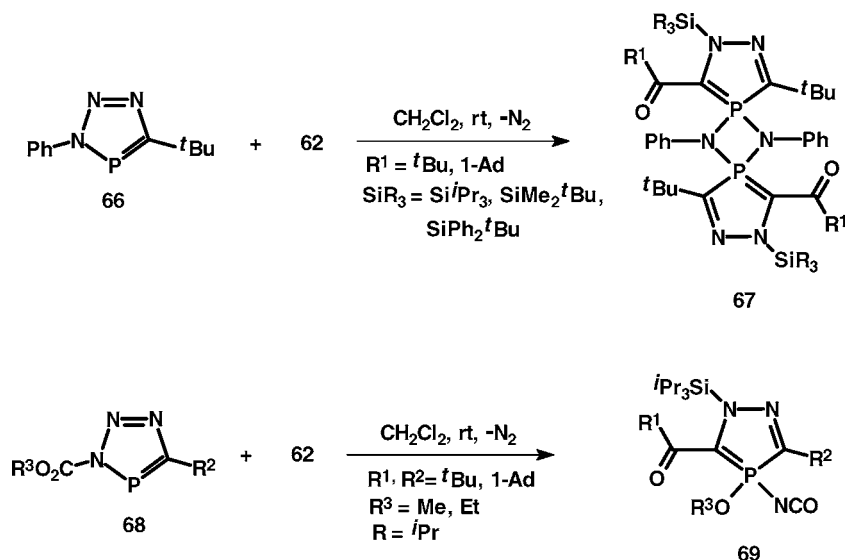
SCHEME 18



SCHEME 19

and $[3 + 2]$ cycloreversion followed by a $[3_{4\pi} + 2_{2\pi}]$ cycloaddition [81] (Scheme 19).

The reaction of **62** with 5-*tert*-butyl-3-phenyl-3*H*-1,2,3,4-triazaphospholes **66** leads to dispiroannulated 1,3-diaza-2,4-diphosphetidines **67**, the structure of the latter being confirmed by single crystal X-ray studies of a representative ($\text{R}^1 = t\text{Bu}$, $\text{SiR}_3 = \text{Si}i\text{Pr}_3$). However, 3-alkoxycarbonyl-3*H*-1,2,3,4-triazaphospholes **68** afford 4-alkoxy-4-isocyanato-1,2,4 λ^5 -diazaphospholes **69** under these conditions [82] (Scheme 20). The suggested mechanism involves loss of nitrogen from the initially formed $[3 + 2]$ cycloadduct to generate the intermediate 4-imino-1,2,4 λ^5 -diazaphosphole which, depending on the nature of the imino substituent, undergoes dimerization across $\text{P}=\text{N}$ (imino substituent Ph) to yield **67** or a 1,3($\text{C} \rightarrow \text{P}$) OR migration (iminosubstituent COOR) to generate **69** [82].



SCHEME 20

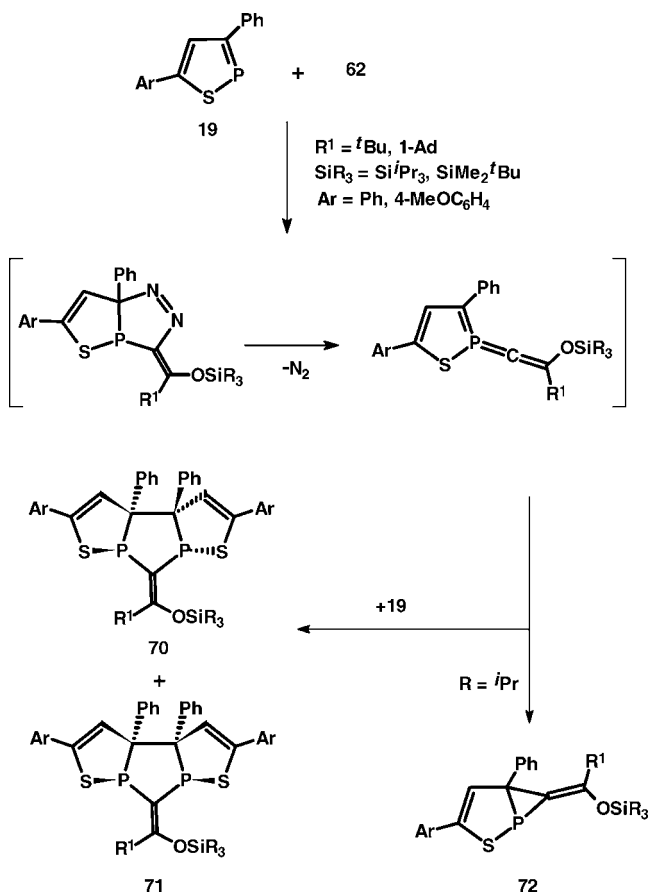
The reaction of diazocumulenes **62** with 1,2-thiaphospholes **19** furnishes the tricyclic compound **70** as the major product (36–83%). In the case of **62** ($\text{R}_3\text{Si} = ^i\text{Pr}_3\text{Si}$), the bicyclic alkylidenephosphi-

ranes **72** were also isolated in low yields (4–8%). The structure of **70** ($\text{R}^1 = t\text{Bu}$, $\text{R}_3\text{Si} = ^i\text{Pr}_3\text{Si}$, $\text{Ar} = \text{Ph}$) was confirmed by X-ray crystal studies [53]. In the reaction of **62** ($\text{R}^1 = t\text{Bu}$, $\text{R}_3\text{Si} = ^i\text{Pr}_3\text{Si}$) with **19** ($\text{Ar} = \text{Ph}$), trace amount of **71** was also isolated [53] (Scheme 21).

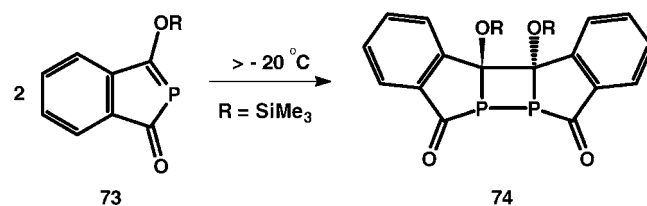
A simple FMO (frontier molecular orbital) analysis of 1,3-dipolar cycloaddition of diazo compounds with various classes of heterophospholes suggests in most cases HOMO(dipole)–LUMO(dienophile) control of the reactivity. But exceptions may be expected in the reaction of heterophospholes of higher HOMO energy with more electrophilic diazo dipoles such as diazocarbonyl compounds [84].

[2 + 2] Cycloadditions

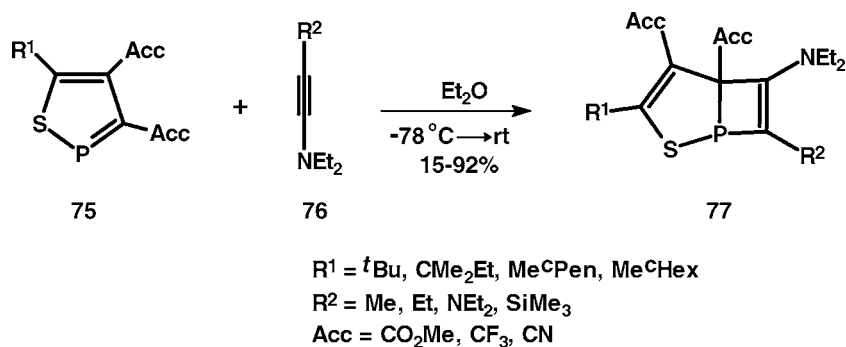
There are not many reports concerning [2 + 2] cycloadditions of the heterophospholes. It has been reported that isophosphindole derivative **73** dimerizes at $> -20^\circ\text{C}$ in head to head mode across $>\text{C}=\text{P}-$ to give **74** (Scheme 22). Structure of the latter was confirmed by X-ray studies [85], which revealed trans orientation of the two OSiMe_3 groups and



SCHEME 21



SCHEME 22



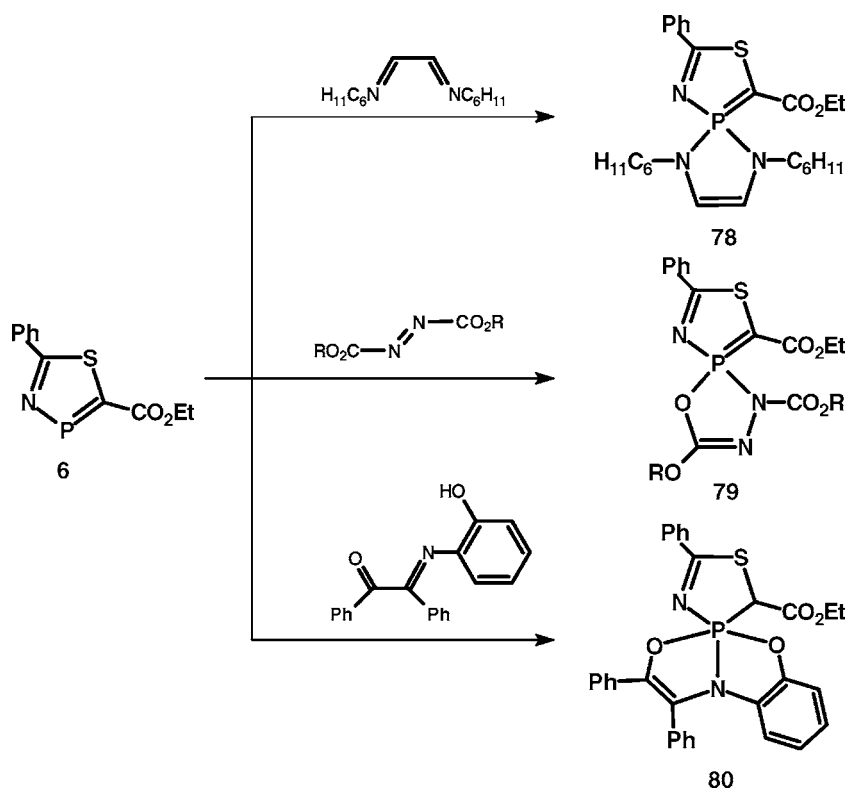
SCHEME 23

corrected an earlier report [86] suggesting head to tail dimerization.

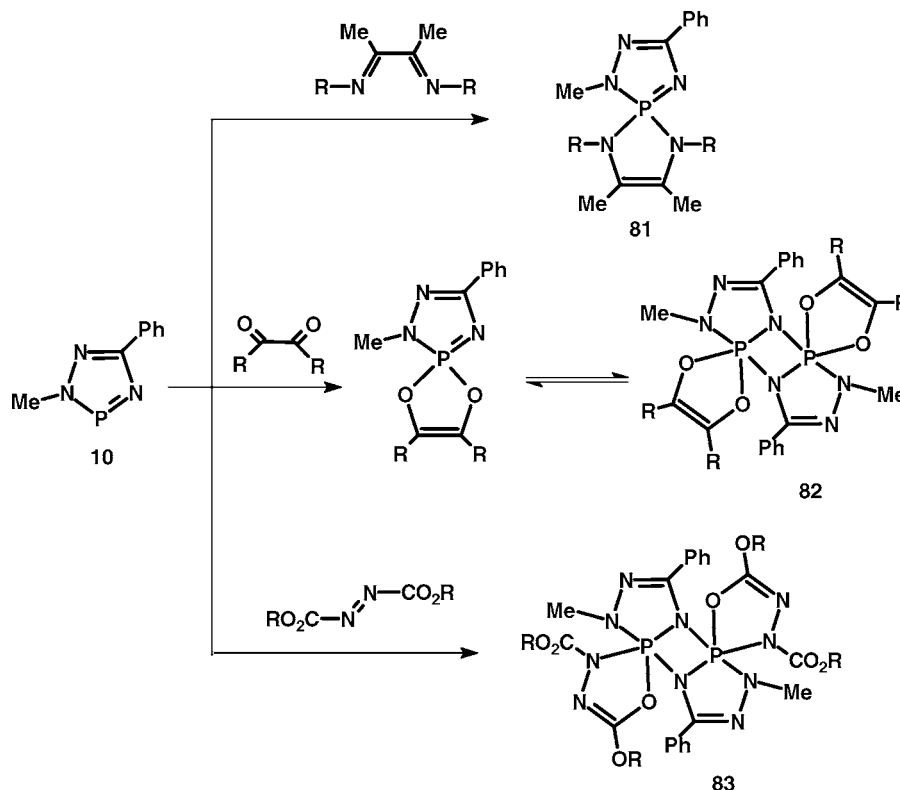
Acceptor substituted 1,2-thiaphospholes **75** undergo [2 + 2] cycloaddition with electron-rich acetylenes **76**, exclusively across the P=C bond, the reaction occurring regioselectively to give **77** [54] (Scheme 23). The structure of the product is confirmed by the X-ray crystal studies of **77** ($\text{R}^1 = t\text{Bu}$, $\text{R}^2 = \text{NEt}_2$, $\text{Acc} = \text{CO}_2\text{Me}$). Acceptor substitution of the P=C bond appears to be essential, as 3,5-diphenyl-1,2-thiaphosphole fails to react with **76** ($\text{R}^2 = \text{NEt}_2$) [54]. The cycloadducts form metallocarbonyl complexes [54].

[1 + 4] Cycloadditions

Heterophospholes undergo oxidative cheletropic [1 + 4] cycloadditions with electron-deficient heterodienes such as *o*-quinones, α -diketones, α -diimines, and azodicarboxylic esters to give spirocyclic products. The latter dimerize across --N=P-- bond or it may again undergo [1 + 4] cycloaddition with one more equivalent of the heterodiene giving zwitterionic products having a six-coordinate phosphorus. The latter course is observed, particularly in those cases, where a nitrogen lone pair is conjugated to the $>\text{C=P--}$ bond.



SCHEME 24



SCHEME 25

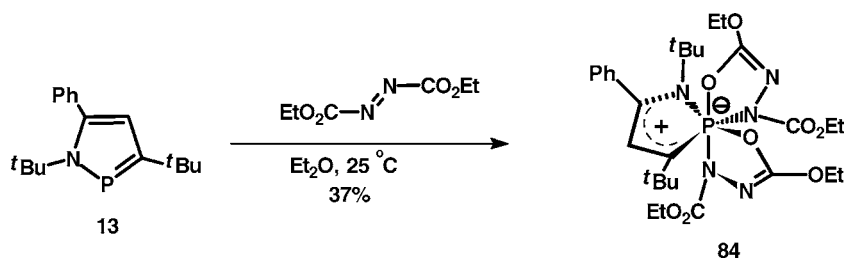
5-Ethoxycarbonyl-2-phenyl-1,3,4-thiazaphosphole **6** reacts with glyoxal bis(cyclohexylimine) and azodicarboxylic esters to form 1:1 spirocyclic [1 + 4] cycloadducts **78** and **79** respectively. The reaction with phenol having a heterodiene moiety in the *ortho*-position leads to tricyclic phosphorane **80** through [1 + 4] cycloaddition of the heterodiene on phosphorus and 1,2-addition of the phenolic group on $>C=P-$ bond [2] (Scheme 24).

2-Acetyl-5-methyl-1,2,3-diazaphosphole reacts with *N,N'*-dipropyldiacetyldiimine in similar manner [18].

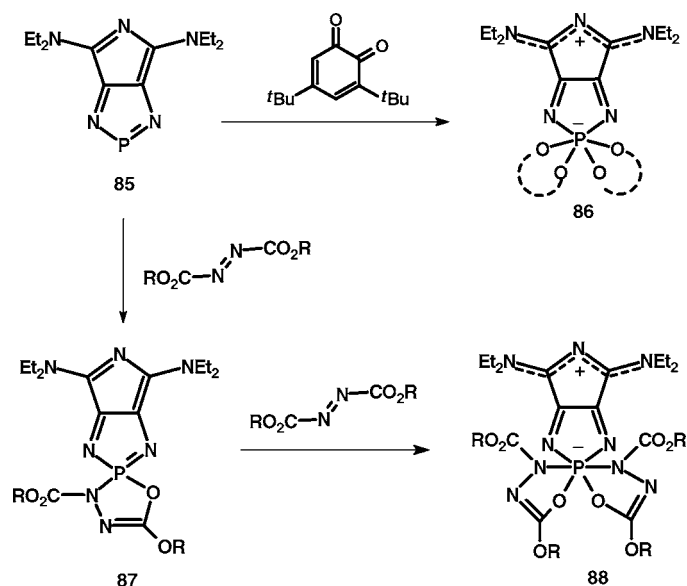
1,3,2-Benzodiazaphospholes, generated in situ by heating their tetramers, form 1:1 [1 + 4] cy-

cloadducts with α -diimines [18] and benzil [21]. Similar reactions are given by $AlCl_3$ -complexed 1-phenyl-1,3,2-benzodiazaphosphole [87] and 1,3,2-benzoxazaphosphole [18] with α -diimines. A cyclohexane anellated 1,2,3-diazaphosphole reacts analogously [79].

2-Methyl-5-phenyl-1,2,4,3-triazaphosphole **10** forms a stable [1 + 4] cycloadduct **81** with α -diimines [18,88,89], but the [1 + 4] cycloadduct produced with α -diketone dimerizes to give a diazadiphosphetidine derivative **82** having five-coordinate phosphorus [21]. Likewise, reaction with azodicarboxylic esters leads to **83** via [1 + 4] cycloaddition followed by dimerization [22] (Scheme 25).



SCHEME 26



SCHEME 27

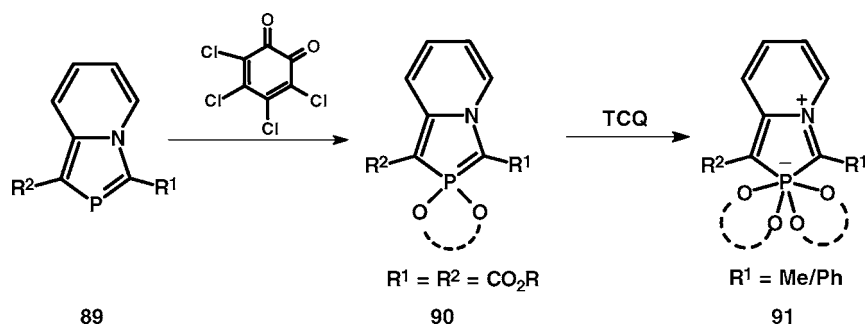
1,2-Azaphosphole **13** is, however, reported to undergo double [1 + 4] cycloaddition with diethyl azodicarboxylate to give a zwitterionic product **84** that has a six-coordinate phosphorus (Scheme 26), as confirmed by ^{31}P NMR ($\delta = -41.0$) and other spectral data [48].

4,6-Bis(diethylamino)-1,3,5-triaza-2-phosphapentalene **85** gives the zwitterionic 1:2 adducts **86** and **88** with 3,5-di-*tert*-butyl-*o*-benzoquinone (TBO) and azodicarboxylic esters respectively; in the latter case the monoadduct **87** could also be observed (Scheme 27). The ^{31}P NMR studies reveal each product to be a mixture of three stereoisomers [23,24].

2-Phosphaindolizines **89** ($\text{R}^1 = \text{Me}$ or Ph) exhibit similar behavior and react with two equivalents of tetrachloro-*o*-benzoquinone (TCQ) to give the zwitterionic products **91** that have a six-coordinate phosphorus,

as revealed by ^{31}P NMR ($\delta = -134$ to -141). The reaction cannot be stopped at the stage of 1:1 addition even if one equivalent of TCQ is used. But 1,3-bis(alkoxycarbonyl)-2-phosphaindolizine **89** ($\text{R}^1 = \text{R}^2 = \text{CO}_2\text{Et/Me}$) form only the 1:1 adducts **90** ($\delta^{31}\text{P} = 45\text{--}46$) even if excess of TCQ is used (Scheme 28). The $-\text{M}$ effect of the 1-alkoxycarbonyl group in the latter appears to nullify the electron-donating effect of nitrogen and thus prevents the formation of the 1:2 adduct [23, Bansal, R. K.; Gupta, N.; Surana, A. (unpublished results)].

2-Methyl-5-phenyl-1,2,4,3-triazaphosphole [21] and 1,3-benzazaphosphole [89] behave analogously and give zwitterionic 1:2 adducts. The reaction cannot be stopped at the 1:1 stage, even if the reactants are used in lesser molar ratios. In the reaction of 1,3-benzazaphosphole, excess TCQ leads to degradation. X-ray crystal investigation of an intermediate



SCHEME 28

1:3 adduct revealed cleavage of the P–C-2 bond accompanied by addition of a third equivalent of TCQ to C-2 [13, Heinicke, J. (Personal Communication)].

ACKNOWLEDGMENT

We are thankful to Dr. K. Karaghiosoff, Munich for his help in completing this review.

REFERENCES

- [1] Schmidpeter, A.; Karaghiosoff, K. In *Rings, Clusters and Polymers of Main Group and Transition Elements*; Roesky, H. W. (Ed.); Elsevier: Amsterdam, 1989; p. 307.
- [2] Schmidpeter, A.; Karaghiosoff, K. In *Multiple Bonds and Low Coordination in Phosphorus Chemistry*; Regitz, M.; Scherer, O. J. (Eds.); Thieme: Stuttgart, 1990; p. 258.
- [3] Schmidpeter, A. In *Comprehensive Heterocyclic Chemistry II*; Katritzky, A. R.; Rees, C. W.; Scriven, E. F. V. (Eds.); Pergamon: Oxford, 1996; Vol. 3, p. 709, 715; Vol. 4, p. 771.
- [4] Schmidpeter, A. In *Phosphorus-Carbon Heterocyclic Chemistry: The Rise of a New Domain*; Mathey, F. (Ed.); Elsevier: Oxford, 2001; p. 363.
- [5] Mathey, F. *Acc Chem Res* 1992, 25, 90.
- [6] Dillon, K. B.; Mathey, F.; Nixon, J. F. *Phosphorus: The Carbon Copy*; Wiley: New York, 1998.
- [7] Nyulaszi, L.; Veszpremi, T.; Reffy, J. *J Phys Chem* 1993, 97, 4011.
- [8] Schmidpeter, A. *Heteroatom Chem* 1999, 10, 529.
- [9] Bansal, R. K.; Karaghiosoff, K.; Schmidpeter, A. *Tetrahedron* 1994, 50, 7675.
- [10] Bansal, R. K.; Heinicke, J. *Chem Rev* 2001, 101, 3549.
- [11] Schoeller, W. W.; Niecke, E. *J Chem Soc, Chem Commun* 1982, 569.
- [12] Houk, K. N.; Joyner, S.; Duke, R. E.; Strozier, R. W., Jr.; George, J. K. *J Am Chem Soc* 1973, 95, 7287.
- [13] Heinicke, J.; Tzschach, A. *Tetrahedron Lett* 1983, 24, 5481.
- [14] Hausen, H. D.; Weckler, G. *Z Naturforsch B* 1984, 39, 628.
- [15] Schmidpeter, A.; Luber, J.; Tautz, H. *Angew Chem Int Ed Engl* 1977, 16, 546.
- [16] Schmidpeter, A.; Tautz, H.; Schreiber, F. *Z Anorg Allg Chem* 1981, 475, 211.
- [17] Alcaraz, M.; Mathey, F. *J Chem Soc, Chem Commun* 1984, 508.
- [18] Diallo, O.; Boisdon, M. T.; Lopez, L.; Malavaud, C.; Barrans, J. *Tetrahedron Lett* 1986, 27, 2971.
- [19] Le Floch, P.; Carmichael, D.; Ricard, L. *Organometallics* 1991, 10, 2432.
- [20] Le Floch, P.; Carmichael, D.; Ricard, L. *Organometallics* 1992, 11, 2475.
- [21] Diallo, O.; Boisdon, M. T.; Malavaud, C.; Lopez, L.; Barrans, J. *Tetrahedron Lett* 1984, 25, 5521.
- [22] Tautz, H.; Schmidpeter, A. *Chem Ber* 1981, 114, 825.
- [23] Schmidpeter, A.; Bansal, R. K.; Karaghiosoff, K.; Steinmüller, F.; Spindler, C. *Phosphorus Sulfur Silicon* 1990, 49/50, 349.
- [24] Karaghiosoff, K.; Sheldrick, W. S.; Schmidpeter, A. *Phosphorus Sulfur* 1987, 30, 780.
- [25] Arbuzov, B. A.; Dianova, E. N. *Phosphorus Sulfur* 1986, 26, 203.
- [26] Appel, R.; Knoll, F.; Ruppert, I. *Angew Chem Int Ed Engl* 1981, 20, 731.
- [27] Appel, R. *Pure Appl Chem* 1987, 59, 977.
- [28] Appel, R. In *Multiple Bonds and Low Coordination in Phosphorus Chemistry*; Regitz, M.; Scherer, O. J. (Eds.); Thieme: Stuttgart, 1990; p. 157.
- [29] Markovskii, L. N.; Romanenko, V. D. *Tetrahedron* 1989, 45, 6019.
- [30] Issleib, K.; Schmidt, H.; Leissring, E. *J Organomet Chem* 1990, 382, 53.
- [31] Schmidt, H.; Issleib, K.; Leissring, E. *Phosphorus Sulfur Silicon* 1990, 49/50, 355.
- [32] Karaghiosoff, K.; Cleve, C.; Schmidpeter, A. *Phosphorus Sulfur* 1986, 28, 289.
- [33] Chen, R.; Cai, B.; Li, G. *Synthesis* 1991, 783.
- [34] Yeung Lam Ko, Y. Y. C.; Carrie, R.; Toupet, L.; de Sarlo, F. *Bull Soc Chim Fr* 1986, 115.
- [35] Arbuzov, B. A.; Dianova, E. N.; Samitov, Yu. Yu. *Dokl Akad Nauk SSSR*, 1979, 244, 1117.
- [36] (a) Khusainova, N. G.; Smirnova, L. V.; Irtuganova, E. A.; Zabolina, Ya. *Zh Obshch Khim* 1992, 62, 1505; (b) Khusainova, N. G.; Smirnova, L. V.; Irtuganova, E. A.; Zabolina, Ya. *J Gen Chem USSR* 1992, 62, 1234.
- [37] Bansal, R. K.; Hemrajani, L.; Gupta, N. *Heteroatom Chem* 1999, 10, 598.
- [38] Bansal, R. K.; Jain, V. K.; Gupta, N.; Gupta, N.; Hemrajani, L.; Baweja, M.; Jones, P. G. *Tetrahedron* 2002, 58, 1573.
- [39] Bansal, R. K.; Dandia, A.; Gupta, N.; Jain, D. *Heteroatom Chem* 2003, 14, 560.
- [40] Karaghiosoff, K.; Hackenbracht, G.; Schmidpeter, A.; Bansal, R. K.; Gupta, N.; Sharma, D. C.; Mahnot, R.; Kabra, V. *Phosphorus Sulfur Silicon* 1993, 77, 235.
- [41] Rauzy, K.; Mazieres, M. R.; Page, P.; Sanchez, M.; Bellan, J. *Tetrahedron Lett* 1990, 31, 4463.
- [42] Wannere, C. S.; Bansal, R. K.; Schleyer, P. von R. *J Org Chem* 2002, 67, 9162.
- [43] Salzner, U.; Bachrach, S. M.; Mulhearn, D. C. *J Comput Chem* 1997, 18, 198.
- [44] Bachrach, S. M.; Liu, M. *J Org Chem* 1992, 57, 6736.
- [45] Schmidpeter, A.; Klehr, H. *Z Naturforsch B* 1983, 38, 1484.
- [46] Karaghiosoff, K.; Klehr, H.; Schmidpeter, A. *Chem Ber* 1986, 119, 410.
- [47] Avarvari, N.; Ricard, L.; Mathey, F.; Le Floch, P.; Löber, O.; Regitz, M. *Eur J Org Chem* 1998, 2039.
- [48] Peters, C.; Tabellion, F.; Schröder, M.; Bergsträßer, U.; Preuss, F.; Regitz, M. *Synthesis* 2000, 417.
- [49] Yamaguchi, H.; Kametani, S.; Karakasa, T.; Saito, T.; Motoki, S. *Tetrahedron Lett* 1982, 23, 1263.
- [50] Tanaka, H.; Kametani, S.; Saito, T.; Motoki, S. *Bull Chem Soc Jpn* 1985, 58, 667.
- [51] Tanaka, H.; Motoki, S. *Bull Chem Soc Jpn* 1986, 59, 2047.
- [52] Shinoda, I.; Takahashi, A.; Saito, T.; Uchida, T. *Bull Chem Soc Jpn* 1994, 67, 2785.
- [53] Kerth, J.; Jikyo, T.; Maas, G. *Eur J Org Chem* 2003, 1894.
- [54] Dietz, J.; Renner, J.; Bergsträßer, U.; Binger, P.; Regitz, M. *Eur J Org Chem* 2003, 512.

- [55] Dietz, J.; Schmidt, T.; Renner, J.; Bergsträßer, U.; Tabellion, F.; Preuss, F.; Binger, P.; Heydt, H.; Regitz, M. *Eur J Org Chem* 2002, 1664.
- [56] Mack, A.; Bergsträßer, U.; Reiss, G. J.; Regitz, M. *Eur J Org Chem* 1999, 587.
- [57] Kobayashi, Y.; Fujino, S.; Kumadaki, I. *J Am Chem Soc* 1981, 103, 2465.
- [58] d'Arbellof-Wilson, S. E.; Hitchcock, P. B.; Nixon, J. F.; Nyulaszi, L. *J Organomet Chem* 2002, 655, 7.
- [59] Asmus, S. M. F.; Bergsträßer, U.; Regitz, M. *Synthesis* 1999, 1642.
- [60] Asmus, S. M. F.; Seeber, G.; Bergsträßer, U.; Regitz, M. *Heteroat Chem* 2001, 12, 406.
- [61] Binger, P.; Günther, K.; Regitz, M. *Synthesis* 1999, 1363.
- [62] Elvers, A.; Heinemann, F. W.; Wrackmeyer, B.; Zenneck, U. *Chem Eur J* 1999, 3143.
- [63] Yeung Lam Ko, Y. Y. C.; Carrie, R.; Muench, A.; Becker, G. *J Chem Soc, Chem Commun* 1984, 1634.
- [64] Rösch, W.; Regitz, M. *Synthesis*, 1987, 689.
- [65] Yeung Lam Ko, Y. Y. C.; Carrie, R.; de Sarlo, F.; Brandi, A. *J Chem Soc, Chem Commun* 1981, 1131.
- [66] Yeung Lam Ko, Y. Y. C.; Tonnard, F.; Carrie, R. *Tetrahedron* 1983, 39, 1507.
- [67] Högel, J.; Schmidpeter, A.; Sheldrick, W. S. *Chem Ber* 1983, 116, 549.
- [68] Yeung Lam Ko, Y. Y. C.; Carrie, R.; de Sarlo, F.; Brandi, A. *Can J Chem* 1983, 61, 1105.
- [69] Arbuzov, B. A.; Dianova, E. N.; Sharipova, S. M. *Izv Akad Nauk SSSR, Ser Khim* 1981, 1113.
- [70] Arbuzov, B. A.; Dianova, E. N.; Galeeva, I. Z. *Izv Akad Nauk SSSR, Ser Khim* 1982, 1196.
- [71] (a) Ilyasov, A. V.; Chernov, A. N.; Nafikova, A. A.; Galeeva, I. Z.; Dianova, E. N.; Arbuzov, B. A. *Zh Obshch Khim* 1984, 54, 1511; (b) Ilyasov, A. V.; Chernov, A. N.; Nafikova, A. A.; Galeeva, I. Z.; Dianova, E. N.; Arbuzov, B. A. *J Gen Chem USSR* 1984, 54, 1346.
- [72] (a) Arbuzov, B. A.; Dianova, E. N.; Galeeva, I. Z.; Litvinov Yu.; Struchkov, Yu. T.; Chernov, A. N.; Ilyasov, A. V. *Zh Obshch Khim* 1985, 55, 3; (b) Arbuzov, B. A.; Dianova, E. N.; Galeeva, I. Z.; Litvinov Yu.; Struchkov, Yu. T.; Chernov, A. N.; Ilyasov, A. V. *J Gen Chem USSR* 1985, 55, 1.
- [73] Arbuzov, B. A.; Dianova, E. N.; Zabolina, E. Ya. *Dokl Akad Nauk SSSR* 1983, 273, 613.
- [74] Arbuzov, B. A.; Dianova, E. N.; Galiaskarova, R. T.; Schmidpeter, A. *Chem Ber* 1987, 120, 597.
- [75] (a) Arbuzov, B. A.; Dianova, E. N.; Zabolina, E. Ya. *Zh Obshch Khim* 1985, 55, 1471; (b) Arbuzov, B. A.; Dianova, E. N.; Zabolina, E. Ya. *J Gen Chem USSR* 1985, 55, 1310.
- [76] (a) Arbuzov, B. A.; Dianova, E. N.; Zabolina, E. Ya. *Zh Obshch Khim* 1987, 57, 1699; (b) Arbuzov, B. A.; Dianova, E. N.; Zabolina, E. Ya. *J Gen Chem USSR* 1987, 57, 1515.
- [77] Arbuzov, B. A.; Lisin, A. F.; Dianova, E. N. *Izv Akad Nauk SSR, Ser Khim* 1983, 2395.
- [78] Jikyo, T.; Maas, G. *Chem Commun* 2003, 2794.
- [79] (a) Arbuzov, B. A.; Dianova, E. N.; Zabolina, E. Ya.; Akhmetkhanova, I. Z. *Zh Obshch Khim* 1990, 60, 35; (b) Arbuzov, B. A.; Dianova, E. N.; Zabolina, E. Ya.; Akhmetkhanova, I. Z. *J Gen Chem USSR* 1990, 60, 29.
- [80] Arbuzov, B. A.; Dianova, E. N.; Sharipova, S. M. *Izv Akad Nauk SSR, Ser Khim* 1981, 1600.
- [81] Kerth, J.; Maas, G. *Eur J Org Chem* 1999, 2633.
- [82] Kerth, J.; Werz, U.; Maas, G. *Tetrahedron* 2000, 56, 35.
- [83] Munschauer, R.; Maas, G. *Angew Chem Int Ed Engl* 1991, 30, 306.
- [84] Jikyo, T.; Schatz, J.; Maas, G. *J Phy Org Chem* 2003, 16, 504.
- [85] Appel, R.; Casser, C.; Knoch, F.; Niemann, B. *Chem Ber* 1986, 119, 2915.
- [86] (a) Markovskii, L. N.; Romanenko, V. D.; Ruban, A. V.; Iksanova, S. V. *Zh Obshch Khim* 1982, 52, 2796; (b) Markovskii, L. N.; Romanenko, V. D.; Ruban, A. V.; Iksanova, S. V. *J Gen Chem USSR*, 1982, 52, 2465.
- [87] Nitcheu, S. K.; Malavaud, C. *Tetrahedron* 1993, 49, 4651.
- [88] N'Gando M' Pondo, Th.; Malavaud, C.; Lopez, L.; Barrans, J. *Tetrahedron* 1987, 28, 6049.
- [89] Kandri Rodi, Y.; Lopez, L.; Malavaud, C.; Boisdon, M.-T. *Can J Chem* 1993, 71, 1200.