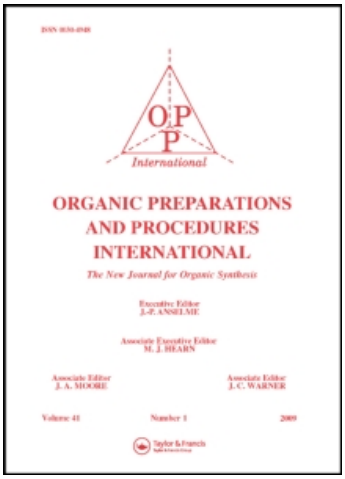

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SYNTHESIS OF REACTIVITY OF λ⁵-PHOSPHAZENES. USES AS SYNTHETIC INTERMEDIATES

José Barluenga[a]; Francisco Palacios[a]
[a] Departmento de Qulmica Organometálica, Facultad de Química, Universidad de Oviedo, Oviedo, Spain

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SYNTHESIS OF REACTIVITY OF λ^5-PHOSPHAZENES. USES AS SYNTHETIC INTERMEDIATES

José Barluenga* and Francisco Palacios*

Departmento de Química Organometálica, Facultad de Química
Universidad de Oviedo, 33071 Oviedo, SPAIN

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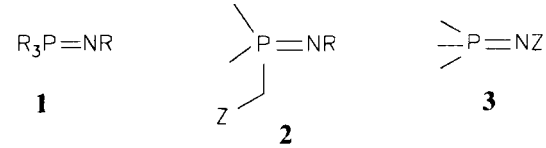
José Barluenga* and Francisco Palacios*

Departmento de Química Organometálica, Facultad de Química
Universidad de Oviedo, 33071 Oviedo, SPAIN

INTRODUCTION

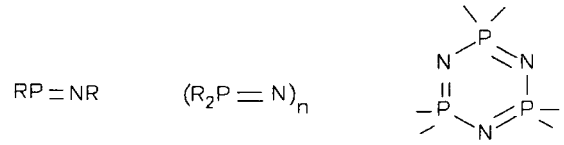
It is well known that λ5-phosphazenes were first synthesized as early as the beginning of this century.[1] However, although some phosphorus derivatives such as the phosphorus ylides have been widely used in preparative organic chemistry,[2-4] the isoelectronic λ5-phosphazenes have not been studied to the same extent. The purpose of this review is to focus on the posible uses of λ5-phosphazenes with alkyl and aryl groups at *P*-atom **1**. *C*α- and *N*-functionalized λ5-phosphazenes **2** and **3** will also be discussed here. Cyclic compounds containing phosphorus-nitrogen double bonds and organometallic λ5-phosphazenes are not included in this review since they have been covered in recent years.[5-9]



1 **2** **3**

The nomenclature used throughout this review is consistent with that found in most recent papers and enables 2-coordinate phosphorus compounds **4**,[10,11] and 4-coordinate phosphorus derivatives such as monomeric λ5-phosphazene **1** as well as poly- **5a** [5] and cyclophosphazenes **5b** [6] to be distinguished and compared. Although some aspects of phosphazene chemistry have been well reviewed,[8,9,12-19] dramatic advances have been made

in the last few years in the chemistry of λ^5-phosphazenes not only from the synthetic point of view but also with respect to their structural characteristics.[20]



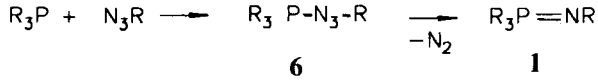
4 **5a** **5b**

I. *SYNTHESIS*

Althrough the early work on the synthesis of λ^5-phosphazenes is well covered in previous reviews,[8,9,12-19] we describe here a brief summary of the main methods of synthesis of λ^5-phosphazenes, as well as the most relevant contributions reported over the last decade.

1. Reaction of Phosphines and Azides. *Staudinger Reaction.*

The oldest method used and possibly the most widely used in the preparation of λ^5-phosphazenes [1,21] involves the reaction of phosphines with azides in diethylether or benzene. The reaction takes place with the formation of a 1:1 adduct **6** (Staudinger's adduct) which gives rise to the corresponding λ^5-phosphazenes **1** [18] by thermal elimination of nitrogen.



6 **1**

This reaction provides one of the best methods of preparation of λ^5-phosphazenes since it allows a wide range of variation of the substituents in both the phosphorus and nitrogen atoms. This method is limited by the accessibility of the corresponding azides. However, recently various methods of generation of azides in mild reaction condition[22] have been developed, the use of polymeric supports [23] or *"clayfen"* [24] increase its accesibility.

Although the most widely used phosphine in this process is triphenylphosphine, λ5-phosphazenes derived from diarylalkyl-, aryldialkyl-and trialkylphosphines, can likewise be prepared. Triphenylphosphine also can be replaced by a polymer-supported triarylphosphine, like polystyryldiphenyl phosphine.[25] Similarly λ5-phosphazenes substituted with alkyl [18,21] and aryl groups in the nitrogen atom [1,18] as well as heterocyclic derivatives such as pyridazine,[26] benzothiazol,[27] benzoxazole,[27] indole,[28] pyrazole,[29] triazole [29] and thiazole [29] **8a** can be obtained.

$$R^1R^2R^3P + N_3Z \xrightarrow[-N_2]{} R^1R^2R^3P{=}NZ$$

7 **8**

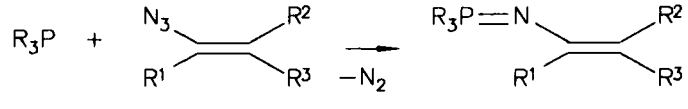
a, Z=Het c, Z=Tos

b, $Z=CH_2R$ d, Z=COR

e, $Z=CO_2R$

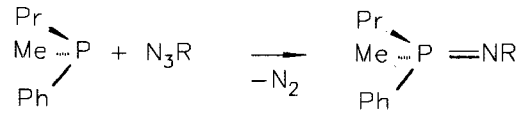
In this way, this reaction has been used over the last few years for the preparation of λ5-phosphazenes functionalized in the nitrogen atom **8b**, when silylated [30] and nitroxyl [31] azides as well as alkyl azides derived from heterocicles [32] and carbohydrates[33,34] are used. Azides substituted with electron-withdrawing groups such as tosyl (*p*-toluenesulphonyl),[19] carbonyl [19,35] and ethoxycarbonyl act similarly giving the corresponding *N*-functionalized λ5-phosphazenes **8c-e**.

Phosphines react with vinylic azides to give *N*-vinyl λ5-phosphazenes **9**, in which the double carbon-carbon bond can be monosubstituted ($R^1{=}R^2{=}R^3{=}H$),[36] disubstituted with aryl [37] ($R^1 = C_6H_5$) or ethoxycarbonyl groups [38] ($R^1 = CO_2Et$) and also tri[39-44] and tetrasubstituted derivatives.[45,46]



9

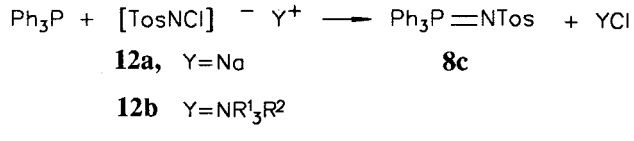
The use of chiral phosphines allows assessment of the stereochemical course of the process as well as the preparation of optically active λ^5-phosphazenes **11**. The reaction of (S)-(+)-methylpropylphenylphosphine **10** with aryl azides,[47] and with tosyl azides[48,49] occurs with retention of the configuration.



(S)-(+)-**10** (R)-(+)-**11**

2. Reaction of Phosphines with Haloamines and Derivatives

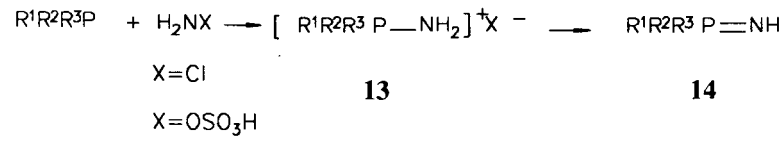
Chloramine-*T* (sodio *N*-chloro-*p*-toluenesulphonamide, **12a**) [50] and *N*-sulfinyl-sulfonamides [51] are reagents normally used for tosylimination. The reaction of the former with triarylphosphine lead to crystalline *N*-tosyl λ^5-phosphazenes **8c** in good yields. An alternative to the chloramine-*T* has recently been reported [52] which uses crystalline tetraalkylamonium salts derived from *N*-chlor-*p*-toluenesulfonamides **12b**. Phosphines react with chloramine-*T* with configurational inversion at the phosphorus atom, a fact that becames clear when chiral phosphines [48,49] are used.



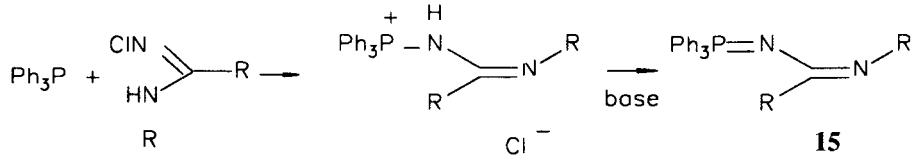
12a, Y=Na **8c**

12b Y=$NR^1_3R^2$

Likewise, dihalogenated amides prove to be satisfactory starting materials for the synthesis of λ^5-phosphazenes,[53,54] while the use of chloroamine [55,56] or sulfinic acids derived from hydroxylamine [57] produce the parent λ^5-phosphazenes **14**. These compounds are obtained by reaction of the latter amino derivatives with phosphines followed by treatment of the aminophosphonium salts **13** with base.

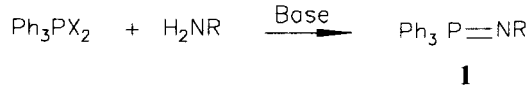


These reactions can also take place with *N*-cloroimino derivatives such as *N*-chloroimino carboxylic acid esters [58] while the reaction of triphenyl phosphine with *N*-chloro amidines followed by treatment with base gives *N*-imidoyl λ5-phosphazenes **15**.[59]

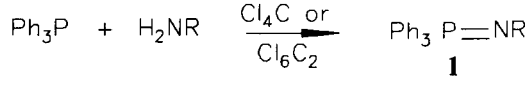


3. Reaction of Halogenated Phosphines with Amines and Derivatives

The Kirsanov reaction[60] represents a widely used method for the preparation of λ5-phosphazenes and involves the reaction of amine derivatives with dihalogenated triarylphosphines [61] in the presence of triethylamine as a base. This reaction leads to λ5-phosphazenes **1** derived from aromatic [61] and heterocyclic amines [62] as well as aliphatic amines, although in this last case the use of harder bases such as sodium amide [63] is required.

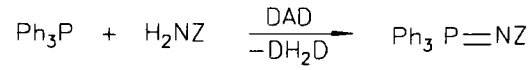


Appel's 3 component reaction [64] provides an interesting modification, which involves the use of phosphines, carbon tetrachloride or hexachloroethane and nitrogen derivatives such as ammonia, amines, sulfonamides and phosphorylated amides,[64] as well as a wide range of heterocyclic amines.[65,66]



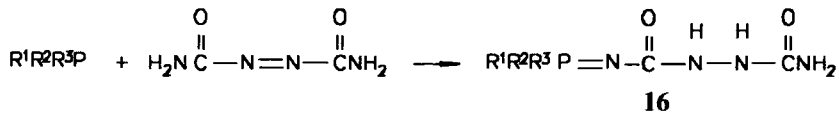
4. Coupling of Phosphines with Amide Derivatives Mediated by Azodicarboxilic Acid Compounds

The use of the redox system diethyl azodicarboxilate (DAD)-triphenyl phosphine in intermolecular and intramolecular dehydration reaction is well known[67-69] and has been applied to various acidic substrates. As carboxamides are not acidic enough, instead of dehydration, a redox condensation process occurs between the amide and the phosphine to produce *N*-acyl λ^5-phosphazenes. In this process the phosphorus (III) compound is oxidized to a phosphorus (V) derivative with racemization on phosphorus when a chiral phosphine is used,[49] while DAD is reduced to diethyl hydrazine dicarboxylate (DH_2D). This method is very satisfactory when aromatic amides, aliphatic amides with electron-withdrawing substituents bonded to the α-carbon atom, both aryl and alkylsulfonamides, ethyl carbamate, diphenylphosphinamide, cyanamide, urea, thiourea or sulfamide [70-72] are used.



The current procedure offers the advantages of the ease of product isolation and that the λ^5-phosphazene is formed directly from two partners - phosphine and amide - without the need of activated derivatives as in the classical methods, under mild, neutral, non polar conditions.

An elegant intramolecular version of this oxidation-reduction-condensation reaction has been reported [73] involving triaryl, diarylalkyl, aryldialkyl, and trialkylphosphines and instead of DAD an azodicarboxamide to give the corresponding *N*-acyl λ^5-phosphazenes **16**



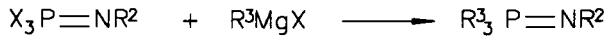
16

5. Reactions of λ5-Phosphazenes

These reactions will be dealt with briefly here, given that they will be covered in greater depth in section III about reactivity of λ5-phosphazenes.

a) Nucleophilic Substitution on the Phosphorus Atom

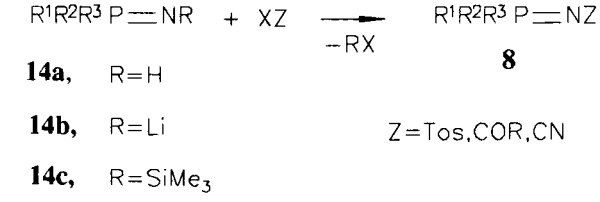
The nucleophilic attack of Grignard reagents upon λ5-phosphazenes halogenated on the phosphorus atom gives rise to the formation of carbon-phosphorus bonds, a process which has been applied to mono [74] and trihalogenated derivatives **17**.[75]



17 **1**

b) *N*-Functionalization of Simple λ5-Phosphazenes

The substitution on nitrogen in the parent λ5-phosphazene **14a** [76,77] is possible with a variety of acylating and tosylating agents, a process that when it is carried out with optically active λ5-phosphazenes occurs with retention of the configuration at the phosphorus atom.[48,49]



14a, R=H

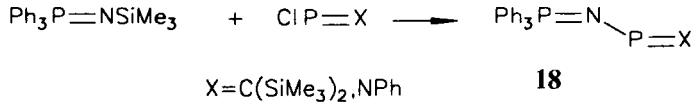
14b, R=Li

14c, R=SiMe3

8

Z=Tos,COR,CN

The preparation of organometallics derived from λ5-phosphazenes such as the *N*-lithiated derivatives **14b**, by direct metallation of compound **14a** with organo-lithium[78,79] and the *N*-silylated derivatives **14c** [80-83] has improved and widened the synthetic possibilities of this reaction. More recently, the reaction of compounds **14c** with *P*-halogenated dicoordinated phosphorus species has been described in an elegant synthesis of dienic systems containing phosphorus **18**.[84]



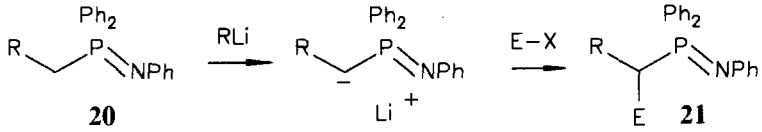
X=C(SiMe3)2,NPh

18

c) *C*α-functionalization of λ⁵-Phosphazenes

While *N*-metallated λ⁵-phosphazenes **14b** are easily obtained from the corresponding λ⁵-phosphazenes **14a** by way of their reaction with organolithium derivatives, the reaction of *N*-tosyl triaryl λ⁵-phosphazenes with aromatic organolithium compounds takes place with cleavage of the phosphorus-nitrogen bond producing the pentaarylphosphoranes.[85]

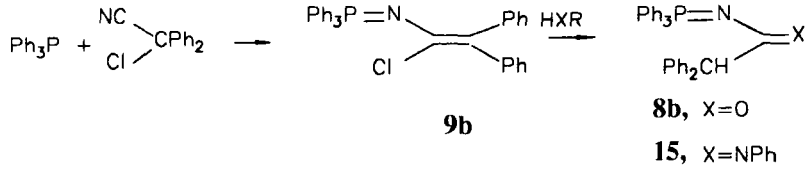
Nevertheless, when alkyldiaryl λ⁵-phosphazenes **20** are treated with organolithium compounds in a similar way to the metallationn of other phosphorylated derivatives, such as phosphine oxides[86] and sulfides[87], lithiation occurs in the α position. The *C*α-metallated λ⁵-phosphazenes thus produced react with a wide range of electrophilic reagents (E) giving rise to the formation of functionalized λ⁵-phosphazenes **21**.[88-91]



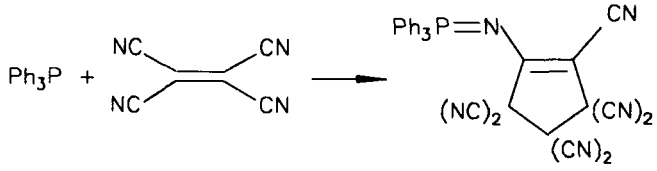
6. Miscellaneous Methods

a) Reaction of Phosphines with Nitriles

The reaction of chlorodiphenylacetonitrile with triphenylphosphine in the absence of protic solvent affords halovinyl λ⁵-phosphazenes **9b**, while in the presence of methanol or aniline *N*-acyl **8b** and *N*-imidoyl λ⁵-phosphazenes **15** [92,93] are obtained.



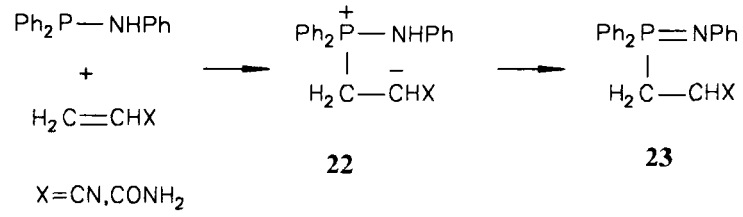
In this way, aromatic phosphines also react exothermically with tetracyano ethylene giving rise to the conjugated λ5-phosphazenes **9c**.[94,95]



9c

b) Reaction of Phosphines with Activated Olefins and Acetylenes.

Aminophosphines react with activated olefins such as acrylonitrile and acrylamide giving the stable λ5-phosphazenes **23**,[96] by proton transfer in the betainic intermediate or Michael adduct **22**.



22 **23**

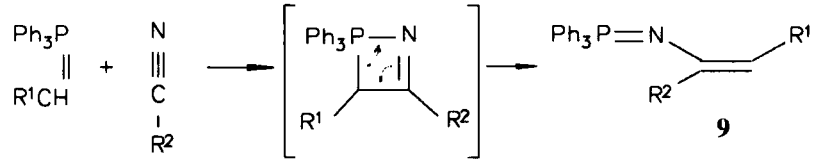
Iminophosphines [97] and isocyanatophosphines [98] show similar behaviour towards compounds which contain multiple carbon-carbon bonds, such as acrylic acid esters, acrylonitrile and acetylendicarboxylic acid esters affording cylic λ5-phosphazenes **24**.

24

c) Reaction of Phosphoranes with Schiff's Bases and Nitriles

Compounds containing double and triple carbon-nitrogen bonds are able to react with phosphoranes, thus an olefin is produced when Schiff's bases [15,99] are used. However,

the reaction of phosphorus ylides with nitriles leads to conjugated λ^5-phosphazenes **9**.[100,101]



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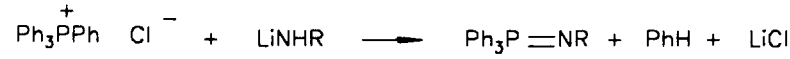
d) Reaction of Phosphonium Salts with Bases

Phosphonium salts such as tetraphenylphosphonium chloride undergo cleavage of a carbon-phosphorus bond [102] through reaction with lithium amides giving rise to the formation of *N*-alquil triphenyl λ^5-phosphazenes **1**. When triphenyl 4-pyridyl phosphonium triflate reacts with sodium azide in DMSO the insertion of a nitrogen atom between the carbon-phosphorus bond of the starting compound takes place leading to the formation of *N*-pyridyl λ^5-phosphazenes.[103]

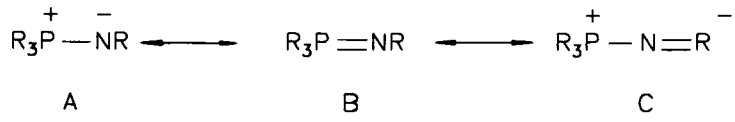


1

II. *STRUCTURE*

The two fundamental problems associated with the structure of λ^5-phosphazenes were the nature of the phosphorus-nitrogen bond and the determination of molecular geometries. Bond angle data from X-ray [104] of λ^5-phosphazenes reveal that the phosphorus atom is approximately tetrahedral (sp^3 hybridization) and are consistent with sp^2 hybridization at nitrogen, while the P-N bond lengths support a multiple phosphorus-nitrogen bond.

The structure of λ^5-phosphazenes can be represented by either a dipolar resonance form (A) or a multiple phosphorus-nitrogen bonded resonance form which involves a $p\pi$-$d\pi$ double bond (B) [105] in a similar way to the isoelectronic phosphoranes.



A B C

Physico-chemical properties of these compounds such as dipole moments [106] and P=N stretching frequency [107,108] are consistent with the polar nature of the phosphorus-nitrogen bond. This is supported also by theoretical studies.[109-112] However, the wide range of variation of the ν (P=N) between 1140 and 1500 cm^{-1} clearly shows an important variation of the bond order depending upon the substituents.

An analysis of the geometric and electronic factors by CNDO/2 [110] and *ab initio* molecular orbital calculations[111,112] reveals that the phosphorus-nitrogen multiple bond in H_3PNH shows similarities with that of the P-C bond in phosphorus ylides and involves a simple σ bond, together with a p transference of the phosphorus to the nitrogen atom. The latter is essentially reinforced by two reversal transferences $n_N \rightarrow d_p$, that is, which can be thought as a *pseudo* triple bond, which provides a P^+—N^- bond polarization in the λ^5-phosphazene derivatives.

Gas-phase photoelectron spectra of several *N*-hydrogen, *N*-alkyl and *N*-aryl λ^5-phosphazenes have been recorded [110] and compared to the corresponding phosphorus ylides and they show reduced oxidizability - higher Ionization Potentials-.

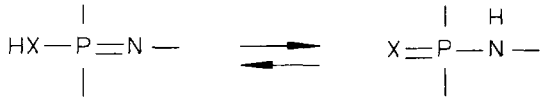
The electronic distributiom and conformation of λ^5-phosphazenes have been discussed in the context of their ^{13}C[110,113] and ^{31}P *-NMR* parameters.[113,114] In the case of *N*-aryl λ^5-phosphazenes it has been suggested that the *N*-aryl groups delocalize the nitrogen charge as demonstrated by characteristic ^{13}C*-NMR* chemical shifts and marked conjugative photoelectron splittings.[110] Recent studies in multinuclear *NMR* spectroscopy of *N*-aryl λ^5-phosphazenes [115,116] suggest the contribution of a new resonance form (C) to the resonance hybrid in λ^5-phosphazenes. The ^{31}P, ^{13}C, ^{15}N*-NMR* spectra, oxidation and reduction by cyclic voltammetry can be explained by inductive and resonance effects, a suggestion

reinforced by PRDDO molecular orbital calculations. The observed correlations between experimentally measured parameters and Hammet substituent constants of *N*-aryl- and *N*-tosyl λ^5-phosphazenes [117] suggest that the double bond in (B) is not necessarily completely of the $p\pi - d\pi$ type but could also involve overlap of a nitrogen electron pair with a σ^* orbital of the phosphorus-carbon bond ($p\pi - \sigma^*$).

A consequence of the polar nature of the P=N bond is the pronounced affinity towards protons, cations and other electrophiles. According to CNDO/2 [110] and *ab initio* calculations [111,112] for the proton adducts, a pyramidal nitrogen geometry is slightly favored over the planar form.

Acyclic λ^5-phosphazenes are strong bases [108.118,119] equivalent in many cases to tertiary amines and their basicity is significantly dependent on the substituents on phosphorus and nitrogen; *N*-phenyl λ^5-phosphazenes, for example, are far more basic than anilines and dimethylanilines.[18] Substituents on nitrogen have a greater influence on the basicity than substituents on phosphorus since the latter reduce the transmission of substituents effect.

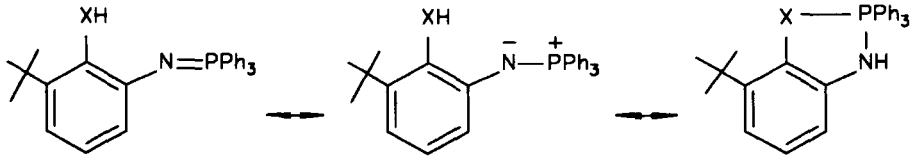
As a result of their basicity, functionalized λ^5-phosphazenes that contain acidic protons are often accompanied by prototropic rearrangements [18] and if the acidity of XH and NH is comparable the process is reversible.



In the case of allyl λ^5-phoaphazenes **20b** the proton shift undergoes an unusual double bond shift to form an isomeric vinylic structure **20c**. [120]

20b **20c**

Valence tautomerism of *N*-(hydroxyphenyl)- and *N*-(aminophenyl) λ5-phosphazenes **25** and the corresponding heterocyclic tautomeric forms **26** have been described as well as the equilibrium constants and the thermodynamic parameters obtained by quantitative NMR measurements.[121-123] The position of the equilibrium strongly depends on the substituents as well as on the solvent used.



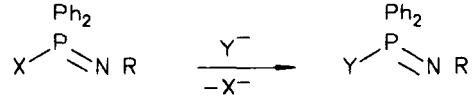
25 **26**

III. *REACTIONS*

1. Reactions without any Modification of the P=N Linkage

a) Nucleophilic Substitution on Phosphorus Atom

In section I.5.a it has been shown that *P*-halogenated λ5-phosphazene derivatives undergo nucleophilic reactions through organometallic compounds.[74,75] This reaction can be extended to other types of nucleophilic reagents (Y) such as azides, alkoxides or amines leading to a wide range of λ5-phosphazene derivatives **27**.[107,124]



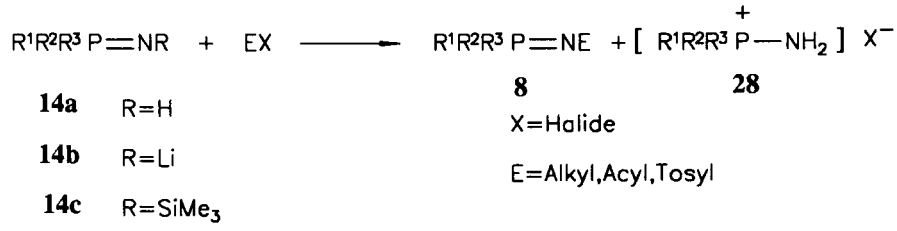
27

X=Cl R=Ph,Tos

Y=Ph,OR,NR_2,N_3

b) Substitution Reactions on Nitrogen Atom

Metallation of *N*-unsubstituted λ^5-phosphazene **14a** can be achieved by the treatment of this compound with methyl or buthyllithium.[78] The preparation of the lithiated azaylide **14b** has been recently improved.[79] Simple *N*-unsubstituted λ^5-phosphazene **14a** reacts *via* nucleophilic substitution with several electrophilic compounds [125] such as halogens, alkyl, acyl and tosyl halides and gives the corresponding *N*-substituted λ^5-phosphazenes **8** and the aminophosphonium salts **28**. The latter are formed after trapping the HX eliminated during the reactions by λ^5-phosphazene **14a**, acting as a base. This reaction proceeds with retention of the configuration at the phosphorus atom, a fact that has been shown when optically active λ^5-phosphazene are functionalised in the nitrogen atom.[48,49]

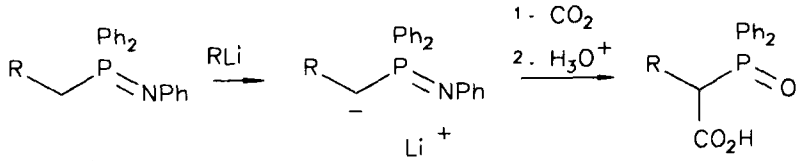


The formation of aminophosphonium salts **28** can be avoided by using organometallic λ^5-phosphazenes such as *N*-lithiated **14b** [79] and *N*-silylated derivatives **14c** [80-82] instead of **14a** in the previous reactions. Likewise, methylation of simple λ^5-phosphazene **14a** with diazometane has been recently reported. [56]

c) Reaction *via* Stabilized Carbanions Derived from λ^5-Phosphazene

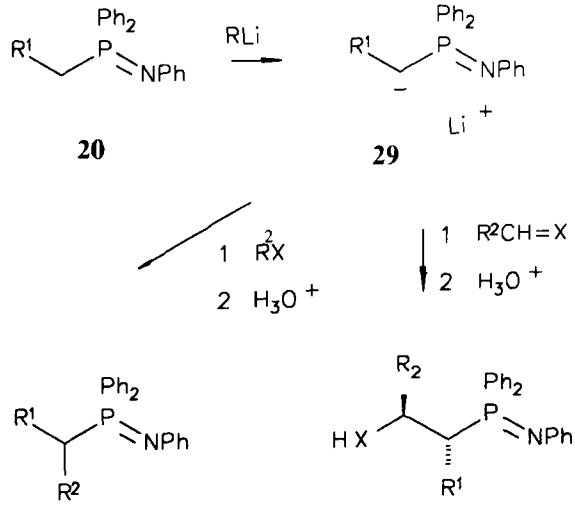
Many of the most useful procedures for the formation of carbon-carbon bonds involve carbanions and particularly significant are the metallated phosphorus compounds.[126] Thus, α-metallated λ^5-phosphazenes **29** are formed when *N*-phenyl *P,P,P*-alkyldiphenyl λ^5-phosphazenes **20** are treated with phenyl lithium [127] in a similar way to that reported for the

isoelectronic phosphine oxides [86] and sulfides.[87] These anions **29** are characterized by trapping with carbon dioxide. After acid work-up [127,128] (dilute HCl) the Cα-functionalized λ5-phosphazenes are not isolated, instead the corresponding acid hydrolysis products, the phosphine oxides **30** are obtained.



20 **29** **30**

Hydrolysis of λ5-phosphazene group can be avoided and hence Cα-functionalized λ5-phosphazene can be obtained in a regioselective fashion when the metallation of compounds **20** with lithium derivatives (Buli, LDA, ...) is carried out followed by addition of electrophilic reagents and quenching the reaction mixture with water.[88] The addition of alkyl halides to the α-metallated λ5-phosphazenes **29** leads to the formation of the new Cα-



20 **29**

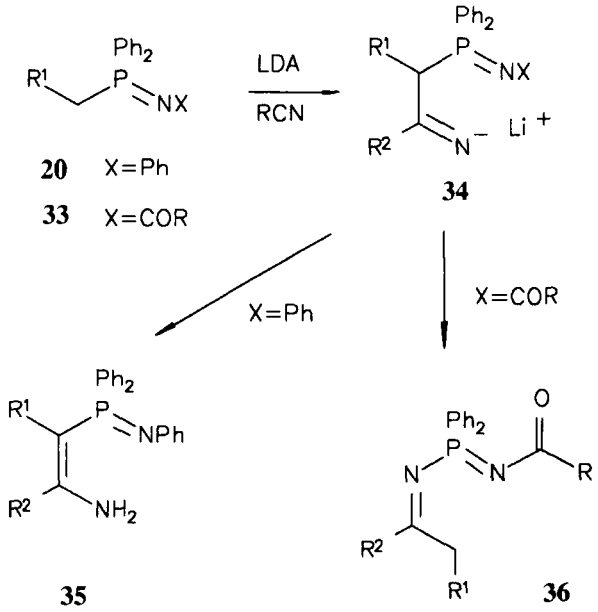
31a $R^1=R^2=$Alkyl **32a** X=O

31b $R^1=R^2=$SMe **32b** X=NPh

31c $R^2=$RCO

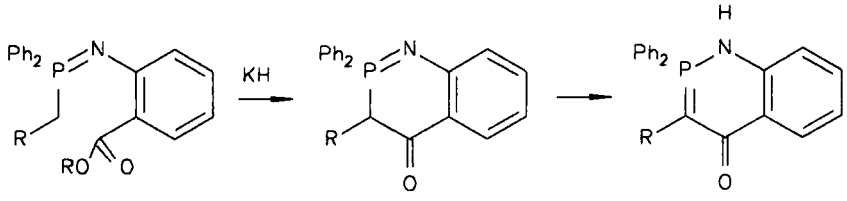
alkylated λ^5-phosphazenes **31a**, while when other electrophilic reagents such as dialkyl disulfides,[90] dimethylformamide [90] and carboxylic acid esters are used the process affords thioacetals **31b** or β-carbonyl derivatives **31c**. It is noteworthy that λ^5-phosphazenyl α-stabilized carbanions show higher diastereoselectivity than the corresponding phosphine oxide derivatives [130] towards aldehydes and *N*-phenylaldimines affording β-hydroxy- **32a**[90] and β-amino-alkyldiaryl λ^5-phosphazenes **32b** [91] in a diastereoselective fashion.

α-lithiated *N*-aryl λ^5-phosphazenes **29** shows similar behaviour when they react with reagents containing multiple bonds (such as nitriles) affording functionalized λ^5-phosphazenes **35**. These primary enamines are stable and useful synthetic reagents [131] owing to their ambident nuclophility.[88,89] Formation of **35** can be explained by prototropic tautomerism of the metallated compound **34,** which is initially formed.



However, λ5-phosphazenes with electron-withdrawing substituents at the *N*-atom **33** show different reactivity and when metallated *N*-acyl λ5-phosphazenes react with nitriles, imino λ5-phosphazenes **36** are obtained, in which nitrile insertion into the phosphorus-carbon bond of the *N*-functionalized λ5-phosphazene **33** has taken place.[35]

Cα-functionalisation of λ5-phosphazene by means of quenching the stabilized carbanionic compounds with electrophilic reagents is not limited, as was expected, to intermolecular reactions. The intramolecular version of this reaction is also known and observed when the phosphoryl-stabilized carbanoin is formed "*in situ*" from λ5-phosphazene derivatives containing an alkoxycarbonyl group **37a.** This process has been applied to the formation of heterocyclic compounds such as benzaza-phosphinones **39**,[132] reactions that probably proceed through cyclic λ5-phosphazenes **38a** followed by prototropic tautomerism. However, *N*-aryl λ5-phosphazenes derived from β-enamines **37b** lead to the stable cyclic λ5-phosphazene **38b**.[133] In this context, a λ5-phosphazene conjugated with a phosphorus ylide has been used in the preparation of boron heterocicles [134] by an annelation reaction of the stabilized carbanion and borohydride derivatives.



37a R=Alk-,Ph
37b R=RCNH$_2$ (‖)

38a,b

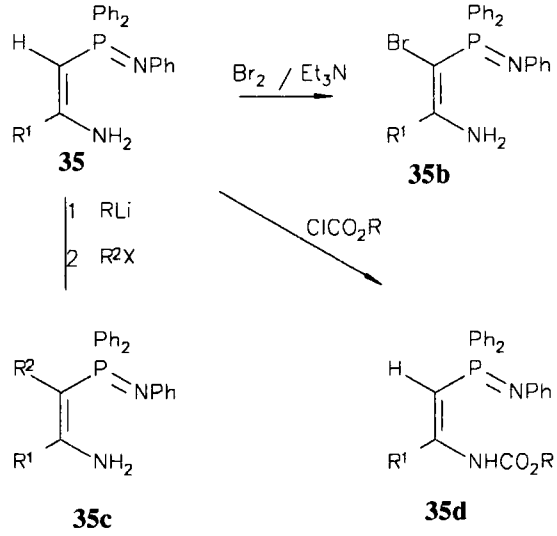
39

d) Reactivity of Polyfunctionalized λ5-Phosphazenes

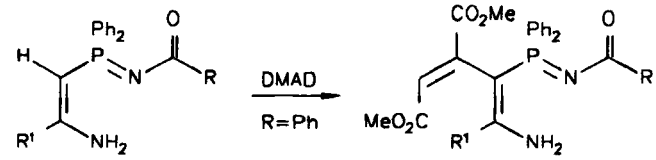
This section undertakes the selective reaction of other functional groups present in polyfunctionalized λ5-phosphazenes without the modification of the λ5-phosphazene group. Hence the latter can be considered, at least in some of these cases, as a protective group.

i. *P*-Functionalized λ^5-Phosphazenes

Primary β-enamino λ^5-phosphazenes **35** represent a class of bifunctionalized compounds (λ^5-phosphazene and enamine groups) which react with several electrophiles in a selective fashion without altering the λ^5-phosphazene linkage. They show typical enamine behaviour and lead to α-bromo β-enamino λ^5-phosphazenes **35b** as well as regioselective *C*-alkylation **35c** and *N*-acylation **35d** in their reactions with bromine in the presence of triethylamine, alkyl halides and chloroformates, respectively.[89]

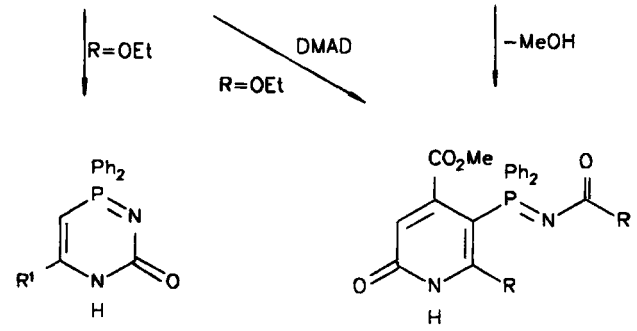


Likewise, primary enamines derived from *N*-aryl λ^5-phosphazenes **35e,f** can be used in the synthesis of phosphorus containing heterocycles. Thermal intramolecular cyclocondensation[135] of *N*-ethoxycarbonyl β-enamino λ^5-phosphazenes **35f** leads to 1,3,4-diaza-λ^5-phosphorin-2-ones **38c**. Functionalized β-enamines **35e,f** are also *synthons* in the preparation of nitrogen heterocycles when they are treated with acetylenedicarboxilic esters (DMAD). The conjugation of the λ^5-phosphazene group with electron-withdrawing substituents at the nitrogen atom, such as benzoyl **35e** or ethoxycarbonyl **35f** groups, supresses the addition of the P=N linkage to the acetylenic esters (see section III.2.f.2), but the CH emanino bond is involved, leading to phosphorylated 2-pyridones **40**.[136]



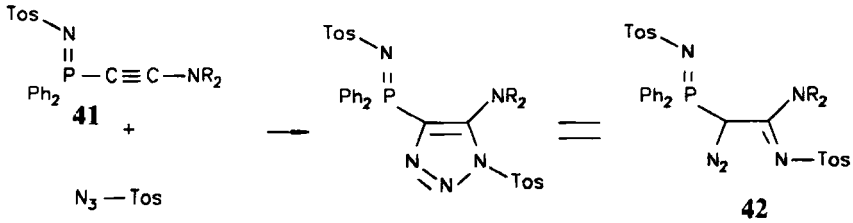
35e R=Ph

35f R=OEt



38c **40**

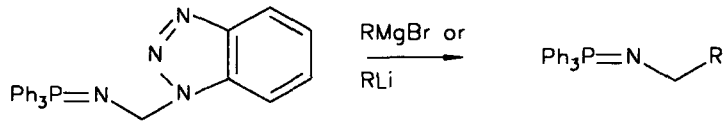
On the other hand, β-ynamines derived from λ5-phosphazenes [137] **41** can act as dipolarophile reagents in 1,3-dipolare cycloadditions towards tosyl azide leading to the formation of phosphorylated diazo compounds **42**, while the treatment of **41** with diphenyl ketene gives cyclic compounds.



ii. *N*-Functionalized λ5-Phosphazenes

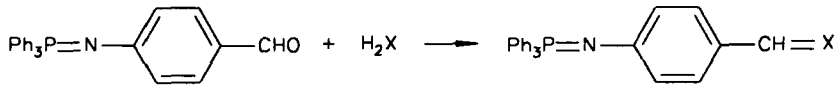
λ5-phosphazenes **7a** shows a very interesting reactivity affording a new and very efficient *synthon* for the preparation of primary amines.[32] The benzotriazole moiety of **7a**

can be replaced by Grignard or organolithium reagents leading to λ^5-phosphazenes **7**. Cleavage of the P=N double bond yields primary amines.



7a **7**

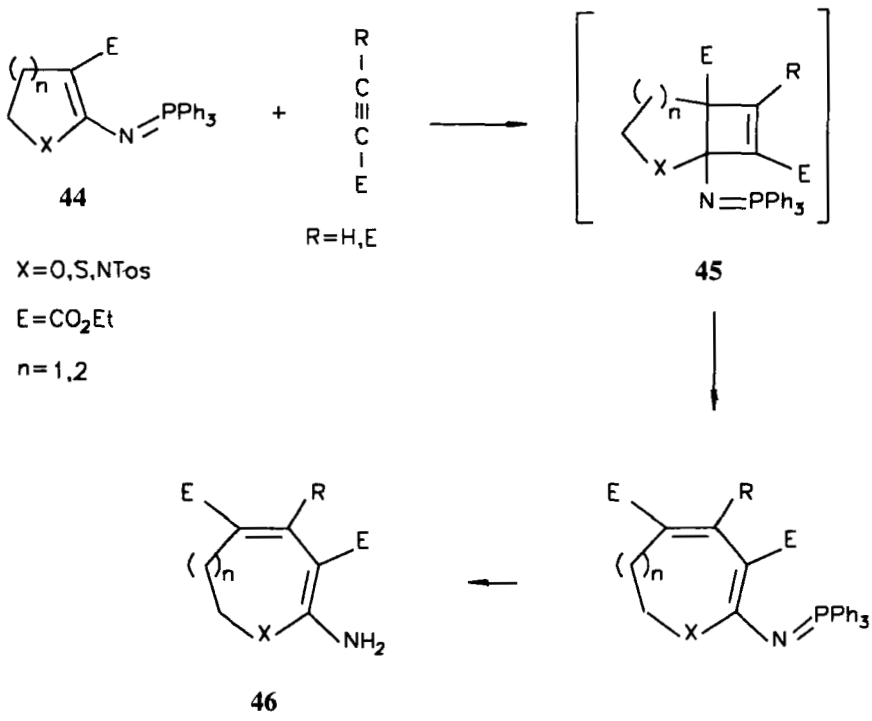
Aldehydic λ^5-phosphazenes can react in a selective fashion with active methylene compounds such as cyanoacetonitrile or ethyl cyanoacetate [138] affording α,β-unsaturated nitriles and esters **43a** without modification of the λ^5-phosphazene group. Similar behaviour was observed with amine derivatives such as anilines or hydroxylamine, giving rise to the formation of imine compounds **43b** through condensation reactions.[139]



43a X=C(CN)$_2$,C(CN)(CO$_2$Et)

43b X=NPh,NOH

N-Heterocyclic λ^5-phosphazenes derived from five and six membered heterocyclic β-enamino esters react with acetylenecarboxylic esters by means of a cycloaddition-ring expansion sequence and lead to an excellent two-carbon ring-enlargement procedure. Partially saturated *N*-heterocyclic triphenyl λ^5-phosphazenes **44** afford dihydrothiepin, -oxepins, -azepin and 2-H-thiocins **46**, [66,140] through the [2+2] cycloadduct **45**.



Other acetylenic derivatives such as cyanocetylene show different reactivity. In this case, the addition of two molecules of the acetylenic compound leads to the formation of benzo-condensed heterocycles.[141] On the other hand, the treatment of λ^5-phosphazenes derived from 1,3-dimethyluracils with dialkyl acetylene dicarboxilates in aprotic solvents affords zwitterionic pyridine derivatives. [142]

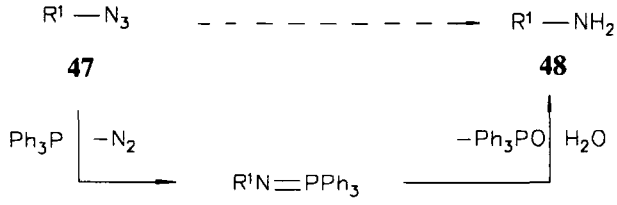
2. Reactivity of the P=N Linkage. Use of λ^5-Phosphazenes as Synthetic Intermediates

Reactions of λ^5-phosphazenes are often similar to those of the isoelectronic phosphoranes and their use as synthetic intermediates in the preparation of a broad range of acyclic and cyclic organic compounds has grown extraordinarily in recent years. The reactivity of this type of compound is a consequence of the polarity of the phosphorus-nitrogen bond as well as the high basicity of these systems, which is influenced by the substituents on the

phosphorus atom and, in particular, by those on the nitrogen. Electron-withdrawing groups on nitrogen which delocalize the negative charge increase the stability and decrease the reactivity of the corresponding λ^5-phosphazene.

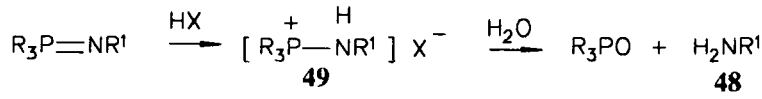
a) **Hydrolysis. Synthesis of Primary Amines**

The facility of hydrolysis depends on the basicity of the λ^5-phosphazenes derivatives in such a manner that *N*-unsubstituted (R^1=H) [55,56] and *N*-alkyl (R^1=alk.) λ^5-phosphazenes[1,63] are readily hydrolyzed in a humid atmosphere. However, the cleavage of stabilized λ^5-phosphazenes such as *N*-arylated, *N*-heterocyclic, *N*-tosylated and *N*-carbonyl derivatives normally requires the presence of dilute acids or bases.[9] The hydrolisis of *N*-substituted λ^5-phosphazenes leads to phosphine oxides and primary amines. Taking into account that the azide group is, in general, very easy to introduce in an organic molecule and in turn azides are precursors of λ^5-phosphazenes, this reaction, from a formal point of view, involves a reduction of azides to amines by means of λ^5-phosphazenes.



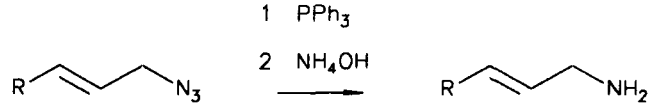
The mild reaction conditions, the non-contamination of secondary and tertiary amines as well as the experimental advances in the synthesis of azides in recent years, recommends this simple reaction as an excellent preparative method of primary amines. Acid hydrolysis of λ^5-phosphazenes involves initial protonation of the nitrogen atom **49** followed by nucleophilic attack of oxygen on the phosphorus atom [9,47] and has been used in the preparation of aliphatic, aromatic[143] and heterocyclic amines.[26] Likewise, this reaction has been used for the preparation of a wide range of functionalized amines [144,145] as well

aminoacid derivatives.[143,144] These reactions have the advantage, from a synthetic point of view, that the process can be carried out *"one pot"* without the isolation of the λ^5-phosphazene intermediates.[144,145]



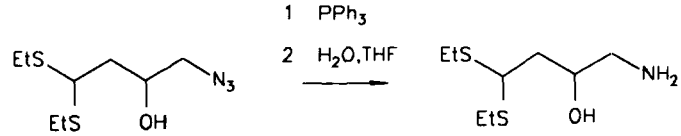
49 **48**

Base hydrolysis also leads to amines.[8] This reaction affords *"one pot"* preparation of primary amines,[32] making use of λ^5-phosphazenes as $^+CH_2NH_2$ equivalent synthons, as well as an elegant and high yield synthesis of primary allylamines[146] **48a** from azides in a selective fashion, without reduction of the carbon-carbon double bonds.



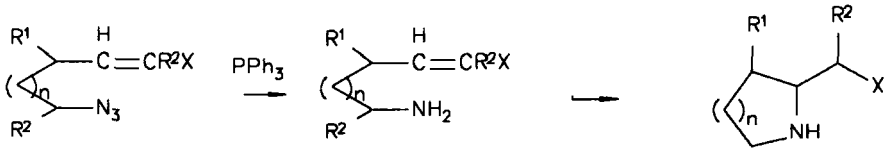
48a

λ^5-Phosphazenes derived from aliphatic azides [1] are easily hydrolyzed in the air atmosphere. This property has been recently used in the reduction of azido compounds to functionalized primary amines under very mild reaction conditions and in excellent yields. This general chemoselective method involves the treatment of functionalized azides with triphenylphosphine followed by addition of a slight excess of water at room temperature.[147,148] Under these reaction conditions acid and basic labile functional groups are preserved. Aminoalkohols **48b** have been obtained in this way. Likewise, this method can achieve the regioselective reduction of azide groups bonded to a primary carbon atom in the presence of azides bonded to secondary and tertiary carbon atoms.[148,149]

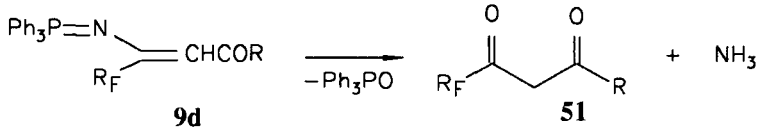


48b

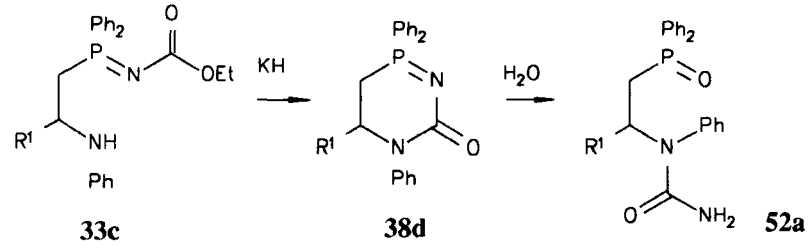
Water hydrolysis of functionalized λ^5-phosphazenes can be applied to the preparation of primary amines bearing an electrophilic double bond in the ω-position. The intramolecular 1,4-Michael type addition of this *"in situ"* functionalized primary amines **48c** leads to functionalized pyrrolidines and piperidines **50** [149] as well as thienopyrroles [150] under very mild reaction conditions.



In like manner, *N*-vinylic λ^5-phosphazenes are unstable in moist solvent and hydrolyzed to carbonyl compounds in quantitative yields [36] through the corresponding enamines.[100] This reaction has been used in the synthesis of perfluoroalkyl β-diketones **51**[101] by acid hydrolisis of λ^5-phosphazenes **9d**.



Cyclic λ^5-phosphazenes are also very easily hydrolysed with water. For instance, in the cyclocondensation reaction of β-amino compounds derived from *N*-ethoxy-carbonyl λ^5-phosphazenes **33c** in the presence of a base, the corresponding cyclic compounds **38d** are not obtained, but the hydrolysed phosphine oxide **52a** are isolated.[91]

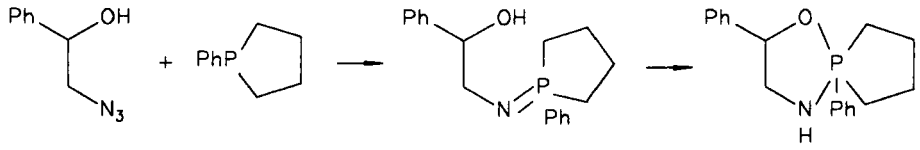


b) Acids Addition

Treatment of λ5-phosphazenes with mineral acids in the presence of water leads to the formation of primary aminophosphonium salts, which undergo hydrolytic cleavage.[21,144] However, these aminophosphonium salts can be stable in some cases when anhydro acids are used. [63] Thus, reaction of *C*α-functionalized λ5-phosphazenes **35** with HI results in nitrogen protonation giving the amino phosphonium salts **49b** regioselectively with the enamine functionality remaining intact. [89]

35 **49b**

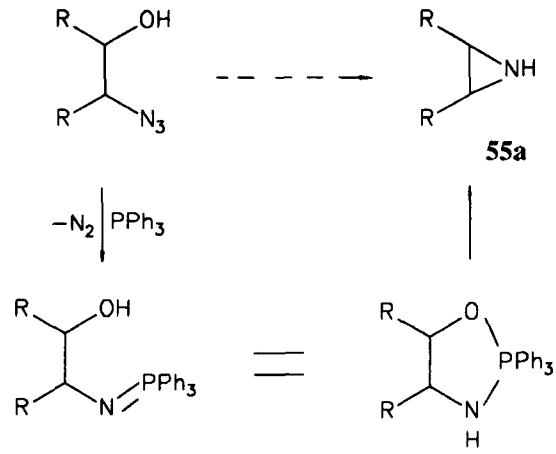
While intermolecular protonation of λ5-phosphazenes requires mineral acids, intramolecular protonation of *N*-functionalised λ5-phosphazenes can be carried out with less acid compounds such as alcohols [151] or amines [122,123] (see valence tautomerism, section II) giving rise to the penta-coordinate amino(oxy)-phosphoranes **54** *via* the functionalized λ5-phosphazenes **53**.



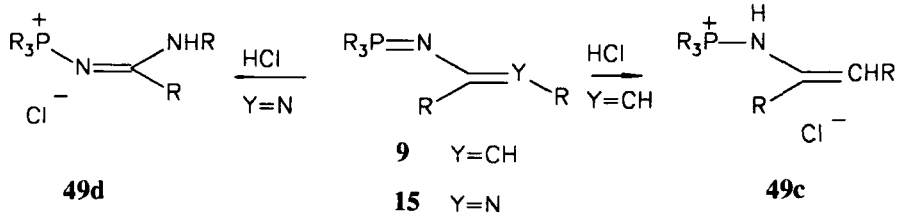
53 **54a**

The reaction of 2-azido-alcohols with phosphines leads to stereospecific synthesis of aziridines **55a**.[152-155] The reaction of 2-azido-alcohol with an *erythro* or *threo* configuration and triphenylphosphine leads to *trans*- or *cis*-aziridines in a highly selective

fashion.[153-155] Formation of aziridines proceeds *via* the 2-hydroxyalkyl λ^5-phosphazenes **53b** and the heterocyclic valence-tautomers 1,3,2-λ^5-oxaza-phospholidines **54b**.[155] This metodology has been recently used in the preparation of aziridine-carboxylic esters of high optical purity.[156.157]



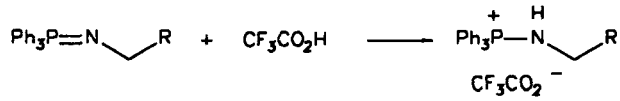
In the case of *N*-vinylic λ^5-phosphazenes **9** the presence of a double bond in conjugation with the λ^5-phosphazene moiety introduces the problem of site selectivity. Addition of HCl to *N*-acyl [92] and *N*-vinylic λ^5-phosphazenes [38,40] leads to the amino phosphonium salts **49c** through 1,2 addition. *N*-imidoyl λ^5-phosphazenes **15** presents different reactivity, whose reaction with hydrochloric acid affords the iminophosphonium salts **49d** formed by conjugated 1,4-addition of the mineral acid to the λ^5-phosphazene compound. [59]



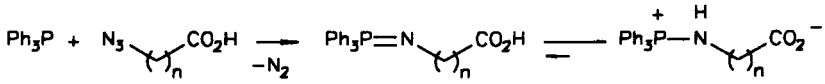
c) Addition of Carboxylic Acids and Related Compounds. Synthesis of Amides

i. Carboxylic Acids. Synthesis of Amides and Peptides

As has already been shown above, λ^5-phosphazenes exhibit basic properties and may undergo protonation on the nitrogen atom if they are treated with compounds containing mobile hydrogen atoms. Strong carboxylic acids such as trifluoracetic acid protonate λ^5-phosphazenes affording the corresponding phosphonium salts **49e**,[158] while in the case of λ^5-phosphazenes derived from ω-azidocarboxylic acid[158,159] zwitterionic structures **49f** are obtained.

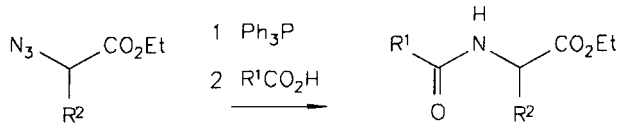


49e



49f

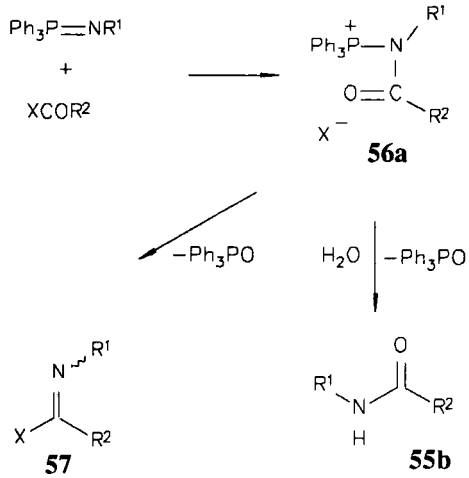
Besides a simple acid-base process, the reaction between λ^5-phosphazenes derived from triarylphosphines and aliphatic[34,158] or aromatic carboxylic acids[144,158] leads to a good method of preparation of amides; the best results are obtained when triethylphosphine replaces triphenylphosphine.[160] The isolation of λ^5-phosphazenes is not necessary, and carboxamides are obtained by *"one pot"* reaction of carboxylic acids, azides and phosphine. This coupling reaction is also a useful method for the preparation of allylic amides[146] and for the synthesis of small peptides **55a**.[161]



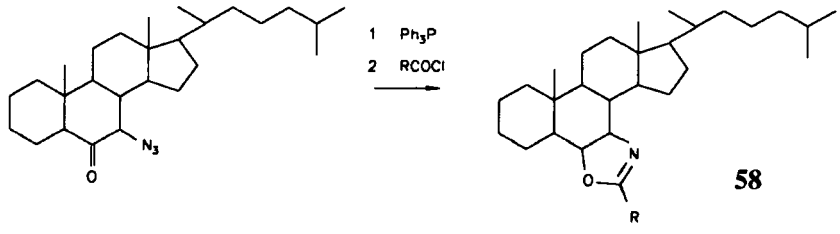
55a

ii. Acyl Halides. Synthesis of Amides and Haloimines

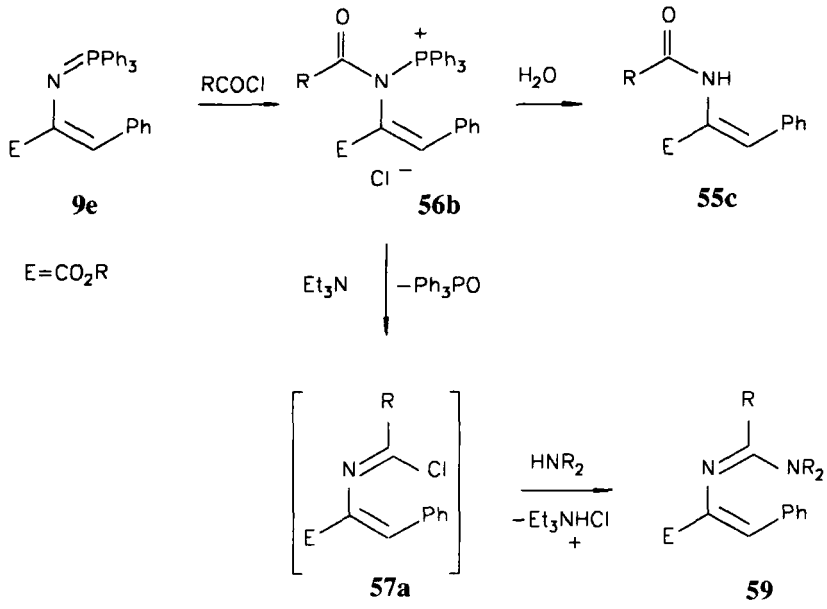
Acyl halides also add to λ^5-phosphazenes giving rise to the formation of the hygroscopic *N*-acylated compounds **56a**.[162,163] The hydrolysis of these compounds affords amides **55b**,[162,164] while in anhydrous reaction conditions, haloimines **57** are formed with the loss of phosphine oxide.[164,165]



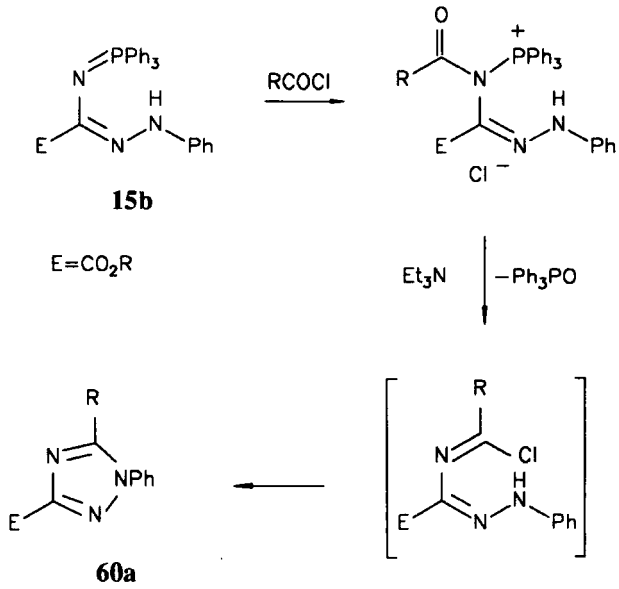
This reaction affords a method for the preparation of amides under very mild reaction conditions and λ^5-phosphazenes has been also used as synthetic intermediates in the preparation β-lactam antibiotics.[166] On the other hand, the condensation of λ^5-phosphazenes with acyl halides yields imidoyl halides **57**.[165] This process has been also applied to the preparation of heterocyclic systems.[163] Thus, while the reaction of simple λ^5-phosphazenes with dicarbonyl halides [167] yields azepine derivatives, the three component reaction between azido-ketones, acyl halides and triphenylphosphine affords not only 1,3-oxazoles[168] but also steroids containing the 1,3-oxazole ring **58**.[169]



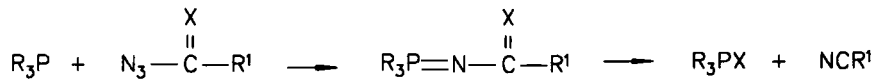
N-acylation of λ5-phosphazenes is not limited to simple compounds, *N*-acrylic λ5-phosphazenes **9e** also produce these reactions and lead to *N*-acylated aminophosphonium salts **56b**. Hydrolysis of these compounds gives the acyl α,β-dehydroaminoacid derivatives **55c**. In addition, this reaction can be used for the synthesis of 2-azadienes **59**, without the isolation of aminophosphonium salts **56b**, when λ5-phosphazenes react with acetyl chloride followed by addition of amino derivatives in the presence of triethylamine. Formation of azadienes could be assumed *via* the elimination of phosphine oxide leading to the haloimine **57a** and subsequent reaction with the amino derivative.[164]



Other functionalized derivatives has been also used in the preparation of heterocyclic compounds. 1,2,4-Triazoles **60a** are prepared in good yield by reaction of *N*-functionalized λ5-phosphazenes **15b** with acyl halides.[170] Likewise, the reaction of λ5-phosphazenes derived from pyrazole gives bicyclic compounds such as pyrazolo pyridinium salts.[29]



On the other hand, *N*-acyl- λ^5-phosphazenes [93,143] and their thio analogs [72,143] decompose with formation of nitriles. This process takes place by heating acylated derivatives and in the case of *N*-thioacyl compounds, it is spontaneously produced.[171]

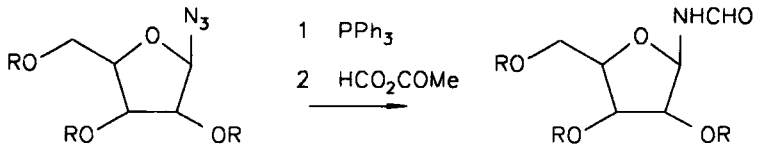


N-nitroso phosphonium salts generated by means of reaction of λ^5-phosphazenes with nitrosyl chloride presents similar behaviour and even decompose at -70°C giving phosphine oxide and diazonium chloride.[47] However, ethoxycarbonyl λ^5-phosphazenes lead to the formation of isocyanate derivatives.[172]

iii. Carboxylic Acid Anhydrides. Synthesis of Amides

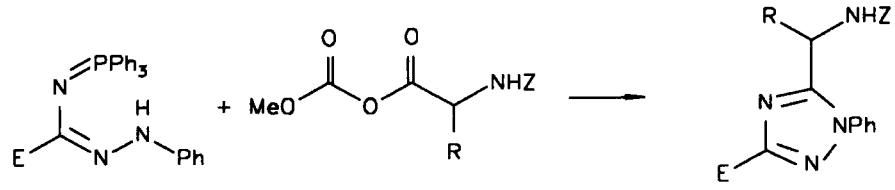
Reaction of acid anhydrides with λ^5-phosphazenes has been used only recently for the conversion of azides into amides. *N*-substituted phthalimides can be obtained, under essentially neutral conditions, by mixing or heating alkyl (aryl) azide, triphenylphosphine

and phthalic anhydride. This reaction has also been applied in the domain of carbohydrates.[173] The use of mixed anhydrides such as acetic formic anhydride similarly offers an entry to the preparation of glycofuranosyl formamides **62**.[174]



62

The reactivity of λ5-phosphazenes with acid anhydrides has also been applied to the preparation of heterocyclic compounds. Thus, *N*-funtionalized λ5-phosphazenes **15b** derived from phenylhydrazones react with cyclic anhydrides,[175] as well as mixed anhydrides derived from aminoacids,[176] to form substituted 1,2,3-triazoles **60b**.

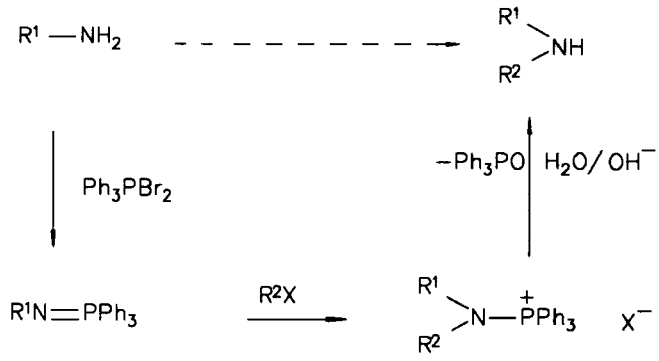


E=CO2R

60b

d) Alkylation Reactions. Synthesis of Secondary Amines

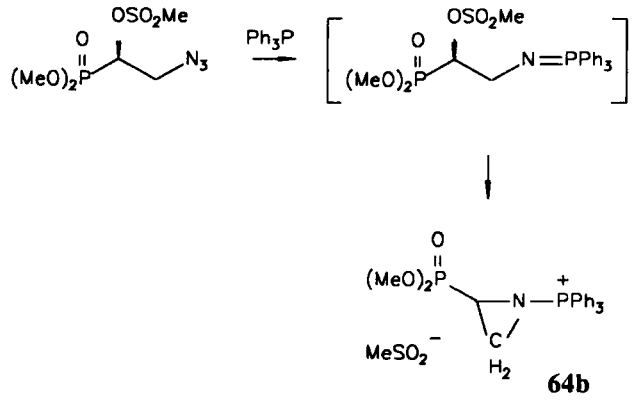
Treatment of λ5-phosphazenes with alkyl halides leads to the stable and isolable *N*-monoalkylated phosphonium salts **63a**. Alkaline hydrolysis of these compounds affords secondary amines. This methodology is one of the most convenient general methods for the monoalkylation of primary amines and are uncontaminated by bis-alkylated products.



63a

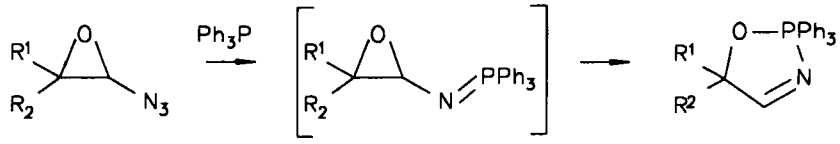
This reaction is especially suitable for the monoalkylation of primary aromatic amines [47,162,177] through the alkylation-alkaline hydrolysis sequence. However, the alkylation of *N*-alkyl λ^5-phosphazenes is limited to the use of methyl and ethyl halides[63] as alkylating agents. Higher alkyl halides are dehydrohalogenated by the strongly basic *N*-alkyl λ^5-phosphazene group and give no alkylated products. However, *N*-aryl-λ^5-phosphazenes are much less basic, and this side reaction does not affect the yield of *N*-alkylated phosphonium salts **63a**.[177] Similar monoalkylation reactions with methyl iodide has been observed for λ^5-phosphazenes derived from aminosugars.[33]

On the other hand, when the alkylating agent is present in the λ^5-phosphazene compound, intramolecular alkylation can take place. Reaction of 2-iodoalkyl azides with triphenylphosphosphine directly yields *N*-aziridyl phosphonium salts in a stereospecific fashion.[178] Similar reactivity is shown by other functionalized methanosulfonate derivatives giving rise to the synthesis of substituted aziridines.[155] This reaction has been used in the preparation of aziridinyltriphenylphosphonium mesylate **64b**, a precursor of optically active aminophosphonic acids.[179]



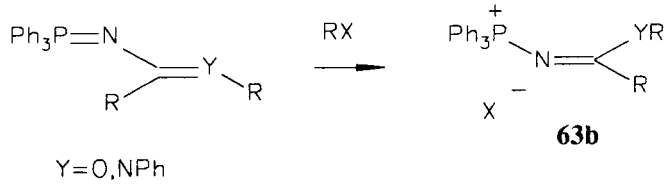
64b

The nucleophilic character of λ5-phosphazenes also has been shown in the reaction of these compounds with oxiranes leading to aziridines.[180] The reactivity of λ5-phosphazenes with oxiranes has been recently applied in the preparation of silylated heterocyclic compounds [181] as well as in the synthesis of 2,5-dihydro-1,3,2-oxaza-phospholes **65** by the treatment of 2-azido-oxiranes with triarylphosphines.[182]



65

Alkylation of simple λ5-phosphazenes with alkyl halides leads to aminophosphonium salts (1,2-addition) and the presence of a functional group conjugated with the λ5-phosphazenes makes 1,4-addition possible. Reaction of *N*-functionalized λ5-phosphazenes such as *N*-heterocyclic,[66] *N*-acyl [80,183] and *N*-imidoyl[59] derivatives with alkylating agents affords the iminophosphonium salts **63b**.



Y=O,NPh

63b

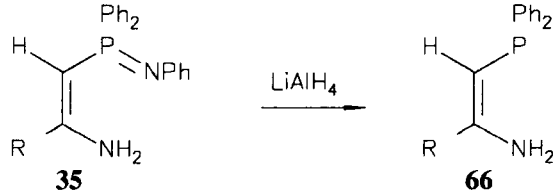
e) Oxidation and Reduction

The reactions of λ^5-phosphazenes with oxidative and reductive agents have been scarcely studied. However, an elegant synthesis of nitrocomponds has been described[184] which involves the ozonolytic conversion of λ^5-phosphazenes into nitro compounds at low temperature. Cycloaddition of ozone to the phosphorylated compound probably provides an unstable adduct, which decomposes into the phosphine oxide and the nitro derivative. This process is limited to those substrates, that are tolerant of ozone at -78°C. Apart from this restriction, the process seems to be predictable and reliable. It is of interest to discover other oxidative reagents that can replace ozone.

$$Ph_3P{=}NR \xrightarrow{O_3} Ph_3PO + O_2NR$$

Photoreduction of *N*-aryl and *N*-alkyl λ^5-phosphazenes to phosphines has been reported [185] when these compounds were irradiated in inert solvents. However, λ^5-phosphazenes which possess nitrogen-substituents, capable of strong delocalization of the nitrogen lone pair (e.g benzene sulfonyl, benzoyl) are photostable.

On the other hand, *N*-aryl λ^5-phosphazenes can be chemically reduced to phosphines making use of lithium aluminium hydride (LAH). Reduction of *N*-aryl *P,P,P*-alkyl-diaryl- [135] and *N*-aryl *P,P,P*-aminoalkyldiaryl-λ^5-phosphazenes [91] leads to the formation of alkyldiaryl- and aminoalkyldiaryl-phosphines, respectively. Similarly, β-enamino λ^5-phosphazenes **35** are reduced with LAH to form the functionalized phosphine **66** without modification of the enamine moiety.[135]

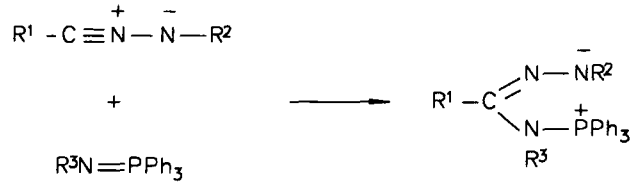


35 **66**

f) Reaction with Compounds Containing Multiple Bonds

i. 1,3 Dipoles

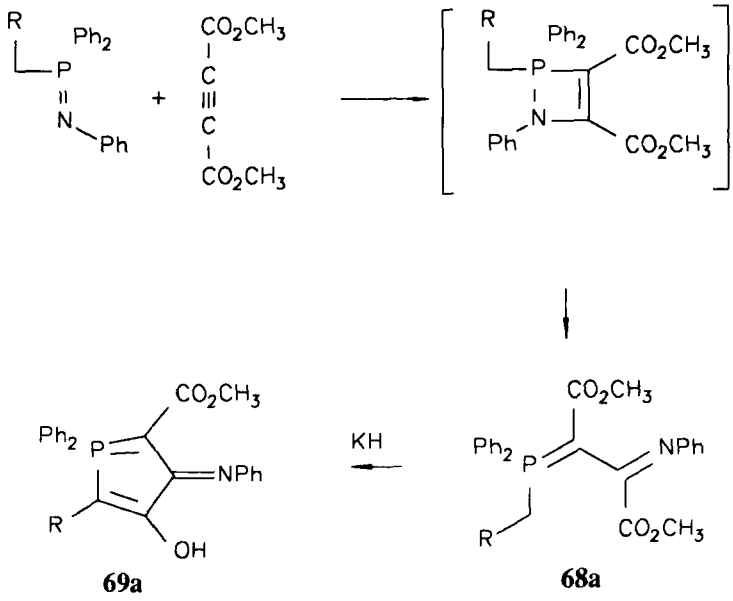
λ^5-phosphazenes can be used as dipolarophiles in 1,3-dipolare cycloadditions[186]. However, with nitrile oxides or nitrones, cycloadducts are not obtained; only the subsequent breakdown products are isolated. Similarly nitrile imines react with λ^5-phosphazenes to yield the corresponding betaines **67**,[186] not the expected cycloadducts.



67

ii. Acetylenic Compounds and Nitriles

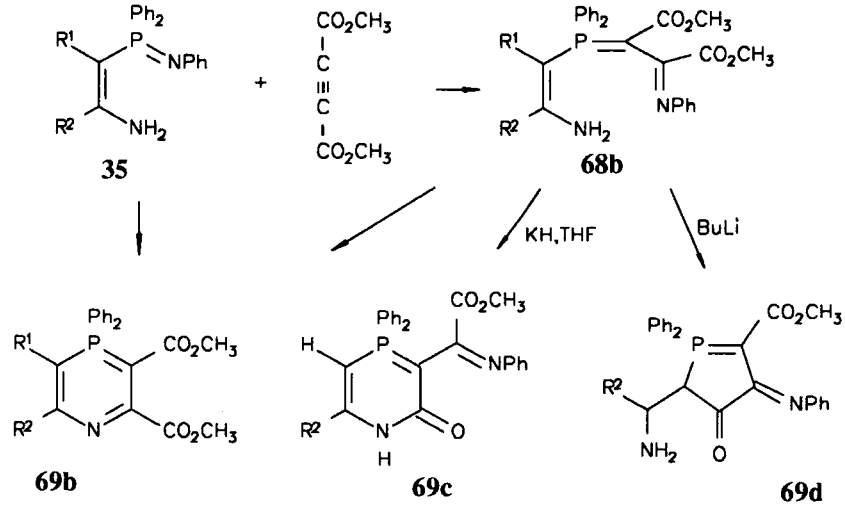
Treatment of λ^5-phosphazenes with acetylene dicarboxylic esters leads to stabilized phosphoranes **68a**.[187-190] Formation of these compounds can be explained through [2+2]



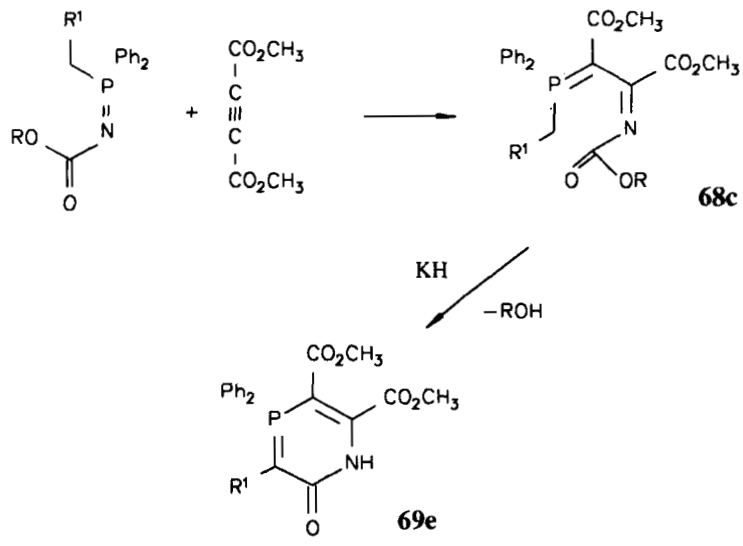
69a **68a**

cycloaddition of the P=N linkage of λ^5-phosphazenes to the carbon-carbon triple bond of acetylene dicarboxylate to give the non-isolable 1-aza-2-phosphete followed by an electrocyclic ring opening. Functionalized phosphorus ylides **68a** obtained by this process can be used for the preparation of stable 3H-λ^5-phospholes **69a**.[189]

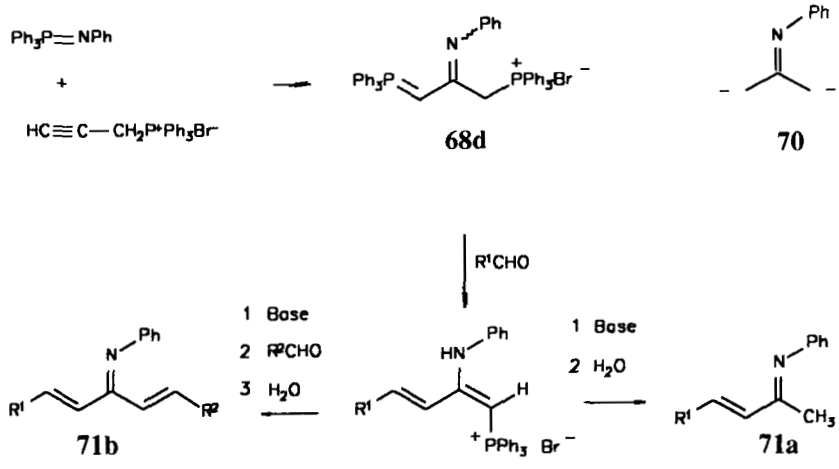
Functionalized λ^5-phosphazenes react similarly. Thus, *N*-phenyl β-enamino λ^5-phosphazenes **35**, reacts with dimethyl acetylendicarboxylate (DMAD) to give stable 1:1 adducts and can be exploited in the preparation of six and five membered phosphorus containing heterocycles. Heating stabilized phosphorus ylides **68b** results in *N*-cyclocondensation affording 1-aza-4λ^5-phosphinines **69b**, [191] while 1-aza-2-oxo-4λ^5-phosphinines **69c** and enamino λ^5-phosphole derivatives **69d** are obtained when adducts **68b** are treated with KH and BuLi, respectively [192].



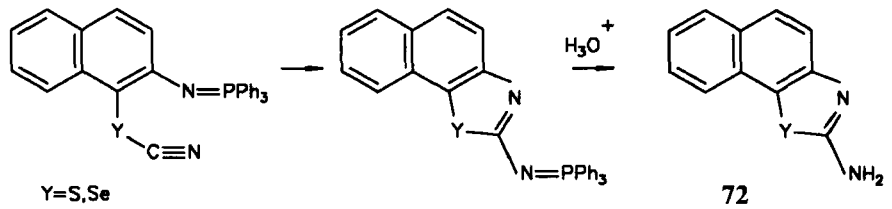
N-functionalized λ^5-phosphazenes with electron-withdrawing groups at the nitrogen atom also react with activated acetylenes leading to conjugated phosphorus ylides **68c** in a similar way to that described for simple λ^5-phosphazenes. Subsequent metallation with KH affords aza λ^5-phosphininones **69e**.[193]



Monoacetylenic acid esters such as methyl propiolate shows a similar reactivity pattern to that observed by the acetylendicarboxylic acid esters.[190] In this context, propargylic phosphonium salts react also with λ5-phosphazenes giving rise to the formation of phosphoranes **68d**.[194,195] These reactive intermediates can be considered as *N*-phenylimino acetone dianion equivalents **70**. Wittig reaction with aldehydes and subsequent treatment with base and aqueous work-up leads to α,β-unsaturated ketimines **71a**,[196] while when a second aldehyde is added 2-vinyl-1-azadienes **71b** are obtained.[195]



Activated nitriles react with λ^5-phosphazenes in a similar way to that described for acetylenic derivatives with formation of new *N*-functionalized λ^5-phosphazenes.[100] An intramolecular cyclisation reaction involving a process of this type was observed when λ^5-phosphazene intermediates containing thio- and seleno-cyanates were used in the preparation of 1,3-thia- and 1,3-selena-azoles **72**.[197]



72

g) Reaction with Carbonyl Compounds and Related Derivatives.

Aza-Wittig Reaction

Like phosphorus ylides, λ^5-phosphazenes undergo reactions with carbonyl derivatives and related componds such as aldehydes, ketones, isocyanates, isothiocyanates, carbon dioxide and carbon disulfide. In all cases, a C=N double bond is formed to replace a C=O or C=S double bond, the driving force appears to be the formation of the phosphine oxide or sulfide. This method provides one of the best methods for the construction of carbon-nitrogen double bonds under mild reaction conditions and in the absence of acid or base derivatives.

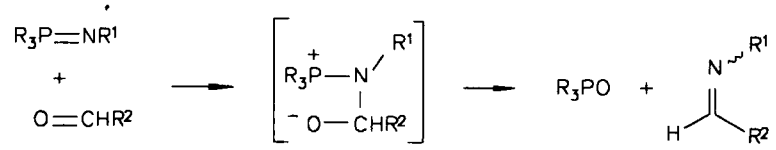
X=O,S

i. Intermolecular Aza-Wittig Reactions

A. Reactions with Aldehydes and Ketones. Synthesis of Iminic Compounds

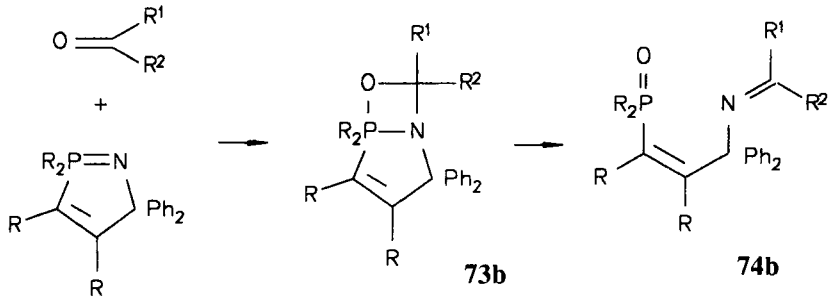
The reactivity of carbonyl compounds with λ^5-phosphazenes has been known for a long time since it was reported[21] that heating N-phenyl λ^5-phosphazene with benzaldehyde

at 100°C and with benzophenone at 150°C led to the corresponding imines **74a**. Kinetic studies of the reaction of λ5-phosphazenes with aldehydes [13,119] indicate that a betaine intermediate **73a** having a considerable degree of localized charge is involved.



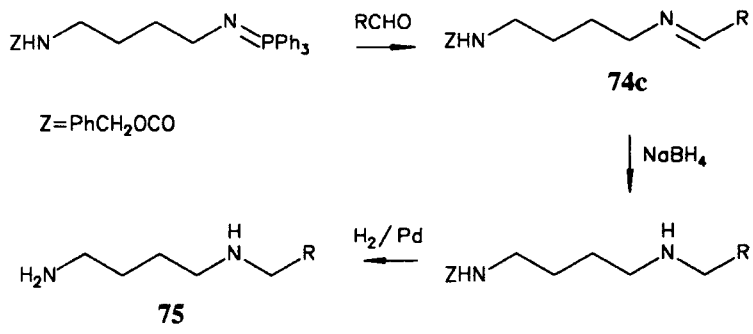
73a **74a**

However, experimental observations can be also explained in terms of a concerted 4-membered transition state **73b** [198] like the Wittig reaction [199] of the isoelectronic phosphoranes. Experimental evidence for a cyclic intermediate was observed by the reaction of cyclic λ5-phosphazenes with ketones leading to the crystalline [2+2]-cycloadducts **73b**.[200] Unlike ketones, aldehydes react with cyclic λ5-phosphazenes to give the ring-opened products **74b**.

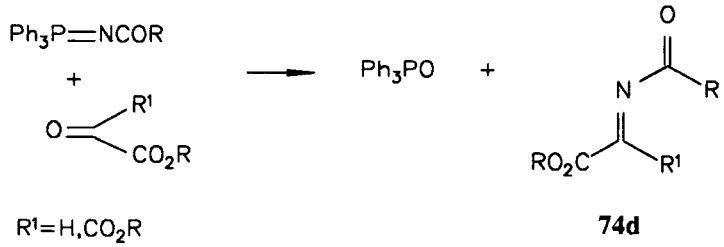


73b **74b**

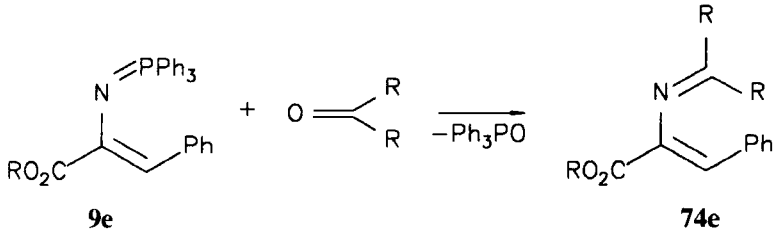
This reaction has been used in the preparation of *N*-unsubstituted imines,[55,56,76] diimines,[201] *N*-(trimethylsilyl)methyl) imines,[30] allylic imines[146] as well as imines derived from aminosugars[33] lactams[166] and fluorinated ketenimes.[202] A combination of the aza-Wittig reaction and reduction of the iminic compound **74c** with sodium borohydride has been recently reported for the synthesis of alkyl substituted polyamines **75**, valuable for biological studies.[203]



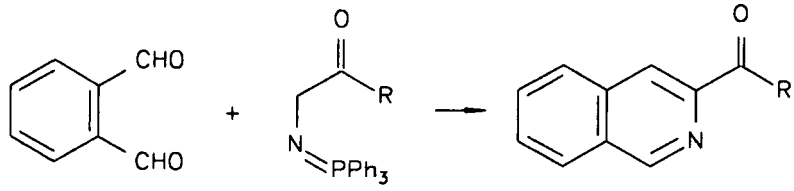
Electron-withdrawing substituents at the *N*-atom of λ^5-phosphazenes reduce the nucleophilic character of the nitrogen, but aza-Wittig reactions can still occur. Thus, *N*-alkoxycarbonyl and *N*-carbonyl λ^5-phosphazenes reacts with glyoxalates [204,205] and ketomalonates [205,206] to give di- and triacylimines **74d**, which are moderately reactive dienophiles for Diels-Alder cycloaddition.



In this context, *N*-vinylic λ^5-phosphazenes can react with carbonyl compounds leading to the formation of triazoles [207] as well as quinazolines [208] when *N*-hydrazoyl- or *N*-imidoyl-λ^5-phosphazenes are used. However, the reaction of *N*-acrylic λ^5-phosphazenes **9e** with aldehydes [41] and ketones [38] leads to 2-aza-1,3-butadienes derived from α,β-dehydraminoacids **74e**.



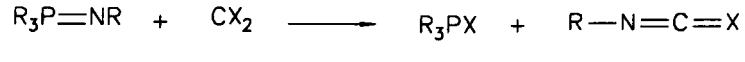
This methodology provides an easy entry to heterocyclic compounds making use of diketones.[209] In a similar way, functionalized aldehydes such as 2-azido-1-cyclopenten-1-carboxaldehyde lead to the formation of bisannulated pyridines [210] or tetrahydrocyclopentapyrazoles, [211] while the condensation of *o*-phthaldehyde with N-carbonyl methyl λ5-phosphazenes affords isoquinolines **74f**,[212] the reaction must be carried out at 0°C in order to avoid the formation of pyrazines by reaction of two molecules of the λ5-phosphazene. [213]



74f

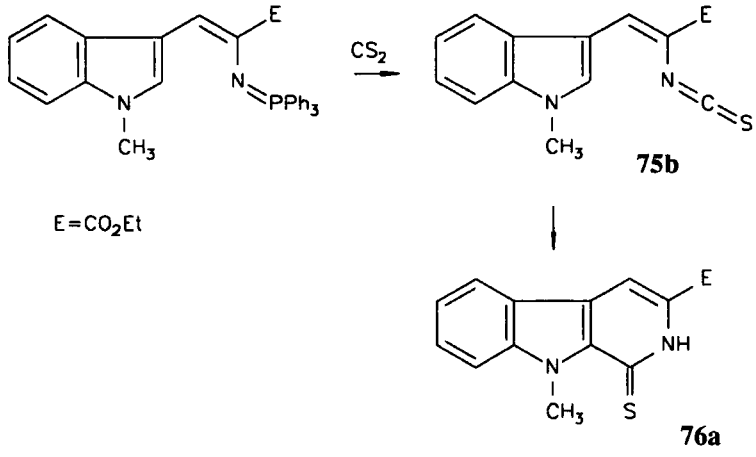
B. Reaction with Carbon Dioxide and Carbon Disulfide. Synthesis of Isocyanates and Isothiocyanates

The reaction of heterocumulenes such as carbon dioxide and carbon disulfide with λ5-phosphazenes was known as early as the beginning of this century.[1,21] However, a real interest has recently been shown in this kind of reaction owing to their use in the preparation of a wide range of alkyl-,[30,214] adamantyl-[215] aryl-[214] isocyanates as well as isothiocyanates **75a**.

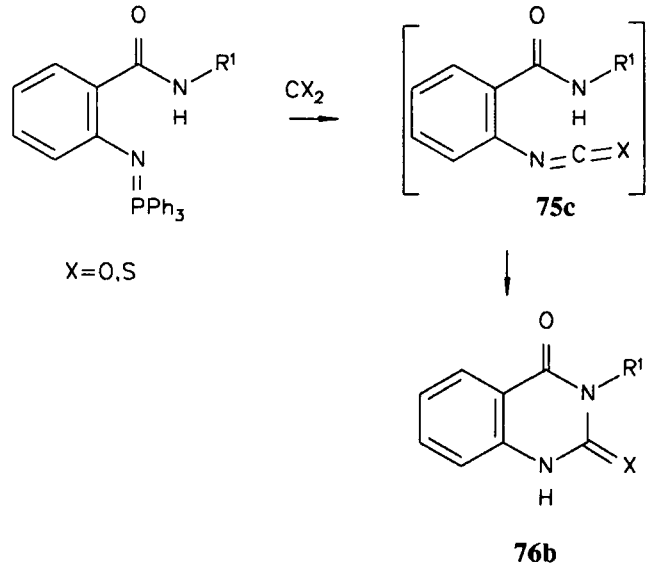


75a

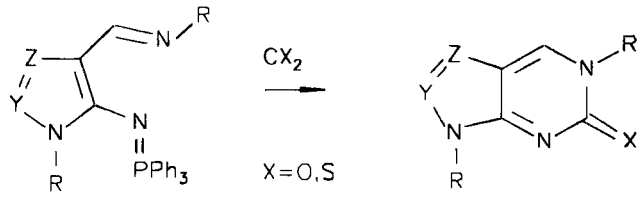
Functionalized heterocumulenes obtained by this method can be used in the preparation of heterocyclic compounds. The treatment of *N*-vinylic λ5-phosphazenes with carbon disulfide leads to pyrimido-indole **76a**, the formation of which can be explained through the intermediacy of the conjugated isothiocyanate **75b**.[28]



The reaction with carbon disulfide has made feasible the development of a new methodology for the preparation of heterocyclic compounds *via* a tandem aza-Wittig/ heterocumulene-mediated annelation strategy. Thus, λ^5-phosphazenes derived from *N*-substituted *o*-azido benzamides react with carbon dioxide or carbon disulfide to form functionalized quinazolinones **76b**.[216]



This strategy, based on the combination of an aza-Wittig reaction followed by electrocyclic ring closure of the obtained heterocumulene, has been used for the synthesis of fused heterocycles such as pyrazolo-pyridones,[42] pyridono-indoles [217] and, when λ5-phosphazenes derived from imino-pyrazole, thiazole and triazole were used, the corresponding functionalized fused pyrimidones **76**.[29,218]



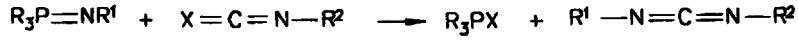
YZ=(CH)4

Y=N; Z=CH,N,S

76c

C. Reaction with Isocyanates and Isothiocyanates. Synthesis of Carbodiimides.

Both aliphatic and aromatic λ5-phosphazenes react with phenyl isocyanate [1,21] and phenyl isothiocyanate under slight warming producing diphenylcarbodiimide [219] and triphenylphosphine oxide or sulfide exothermically. This reaction has been used in the preparation of symmetrical dialkyl,[30,215] diaryl carbodiimides **77a** [220] as well as carbodiimides derived from nucloesides. [221]

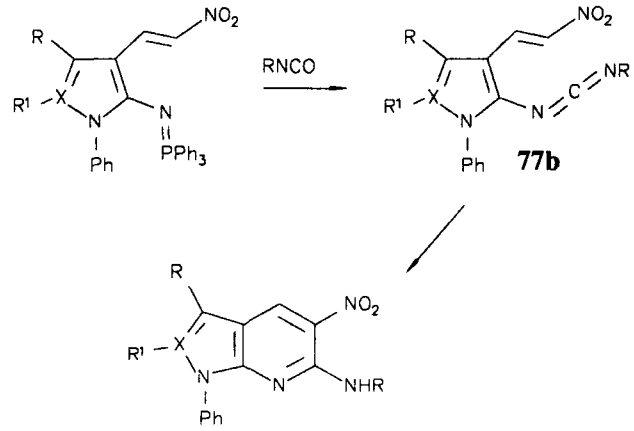


X=O,S

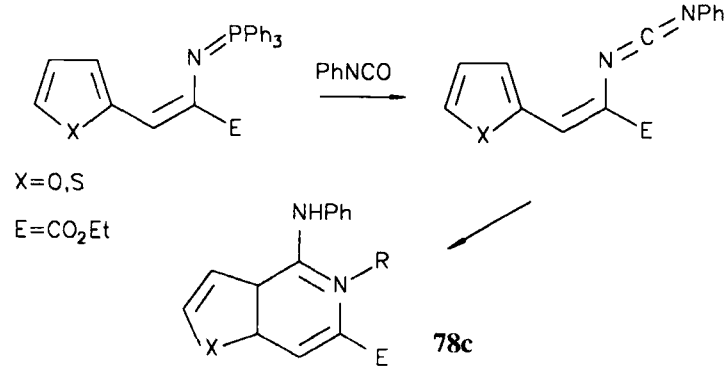
77a

Wittig-type reaction is not restricted to simple λ5-phosphazenes, since *N*-vinylic compounds can also react with phenyl isocyanates giving rise to the formation of conjugated carbodiimides. [41,222,224] Unsaturated heterocumulene systems of this type are very useful *synthons* in the synthesis of heterocyclic compounds, as diene substrates in Diels-Alder reactions.[222,223] Thermal cyclisation processes [222,224] were also reported for the preparation of benzo-pyridines.[222] Similarly, synthesis of bicyclic compounds derived from pyrimidines is described. [188]

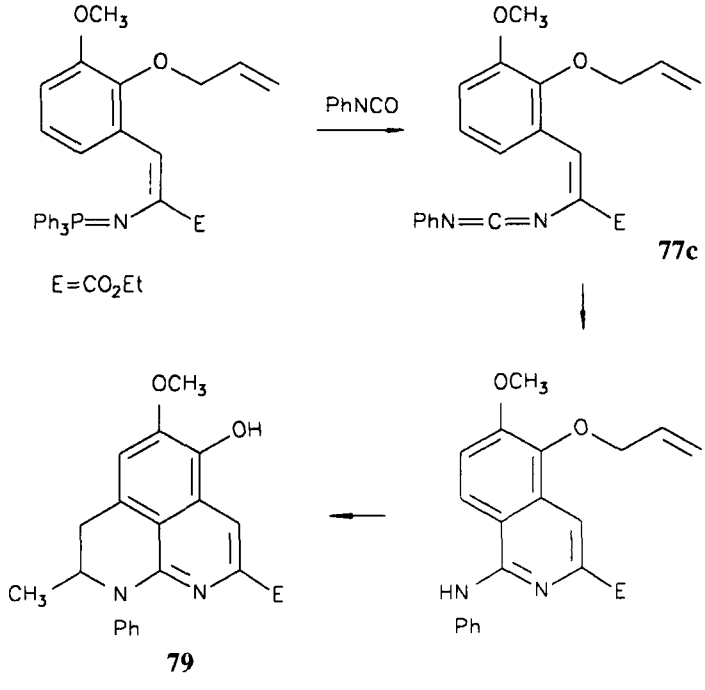
This reaction is very useful in the synthesis of a wide range of organic compounds. The tandem aza-Wittig reaction/carbodiimide-mediated annulation reaction has been used in the synthesis of quinazoline derivatives, [216] fused pyrimidines [29,218] and imidazo triazines [224] *via* reaction of isocyanate derivatives with functionalized λ^5-phosphazenes. Likewise, aza-Wittig reaction of λ^5-phosphazenes derived from functionalized pyrazoles and indoles with alkyl and aryl isocyanates lead to the corresponding pyrazol- **78a**[42] and indol-pyridines **78b.** [217]



On the othe hand, thieno- and furo-pyridine derivatives **78c** has been prepared by reaction of λ^5-phosphazenes derived from azido heteroaryl acrylates and triphenyl phosphine with aromatic isocyanates. [225]

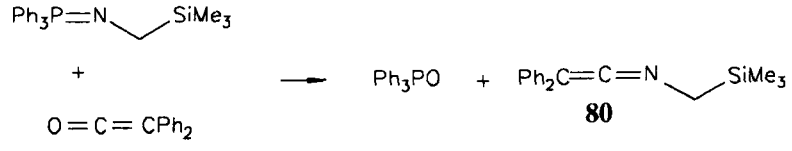


Recently, cyclisation of conjugated carbodiimides **77c** obtained from λ5-phosphazenes has been also [226] used in an elegant synthesis of 1,9-diazaphenalen derivatives **79**, based on a new method of two consecutive pyridine annelations. The synthesis involves a consecutive aza-Wittig reaction/ Electrocyclic ring-closure/ Claisen rearrangement/ Intramolecular amination process.



D. Reactions with Other Reagents

Diphenyl ketene also reacts with λ5-phosphazenes under similar conditions to those described for other heterocumulenes, leading to ketenimines. This reaction was used by Staudinger [1] and has been applied in the preparation of *N*-aryl-,[1] *N*-acyl-,[227] *N*-cyanoalkyl[227] and *N*-trimethylsilylmethyl- ketenimines **80**.[30]

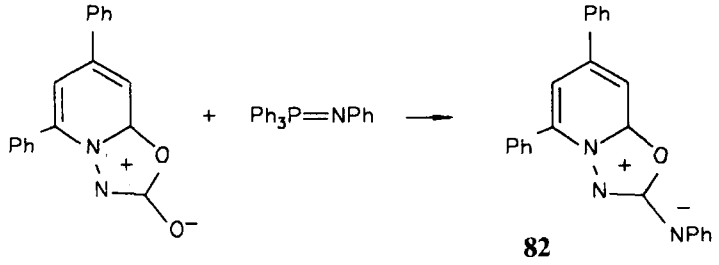


Sulfur dioxide shows a similar reactivity pattern to that described for carbon dioxide and its reaction with *N*-phenyl triphenyl λ^5-phosphazene leads to the formation of thionylaniline **81**.[21] In spite of the potential synthetic interest of this reaction, it is surprising that this method has been scarcely used in organic synthesis.

$$Ph_3P{=}NPh + SO_2 \longrightarrow Ph_3PO + Ph{-}N{=}S{=}O$$

81

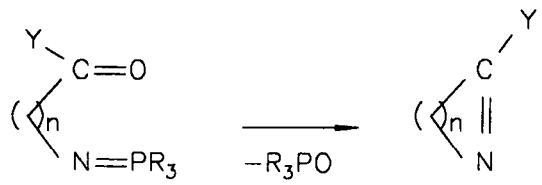
Wittig-type reactions proceed also when substituted thioureas react with *N*-aryl λ^5-phosphazenes leading to an efficient method for the preparation of *N,N',N''*-trisubstituted guanidines.[228] Similarly, fused mesoionic heterocycles such as oxadiazolopyridylium aminides **82** has been prepared from *N*-phenyl λ^5-phosphazenes.[229]



82

ii. Intramolecular Aza-Wittig Reactions. Iminocyclisation

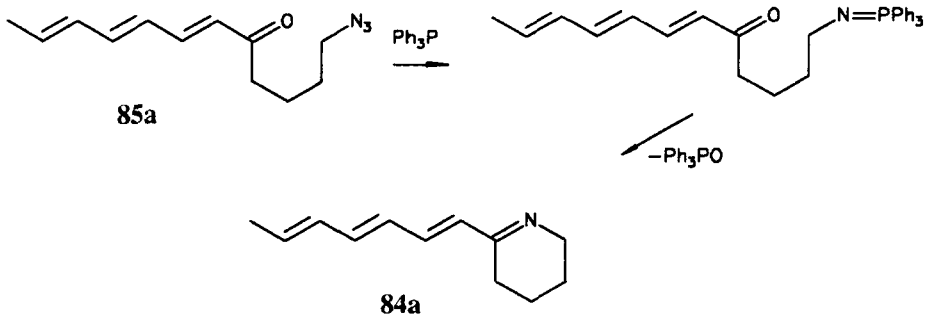
The intermolecular synthesis of carbon-nitrogen double bonds from λ^5-phosphazenes and carbonyl compounds is well known. In many instances, when both the carbonyl and λ^5-phosphazene group are in the same molecule, the entropic assistance provided in the intramolecular aza-Wittig reaction is enough to promote the formation of cycloimines **84** when *N*-functionalized λ^5-phosphazenes containing carbonyl compounds **83** are used. Carboxylic esters and amides, in which the carbonyl group is less reactive than aldehydes, ketones and heterocumulenes also undergo this intramolecular reaction, giving rise to the formation of heterocyclic compounds.



83 **84**

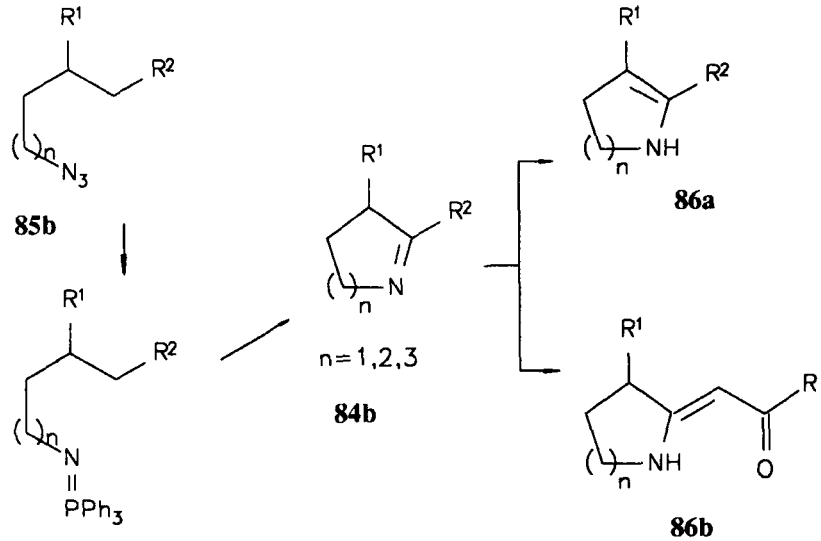
A. λ5-Phosphazenes Derived from Aldehydes and Ketones

Compounds of this class are easily available through reaction of azido ketones with phosphines. The first example of the intramolecular version of this reaction was the formation of the pyridine ring in the last step of the synthesis of the alkaloid nigrifactine **84a** [230] from the azido ketone derivate **85a**.

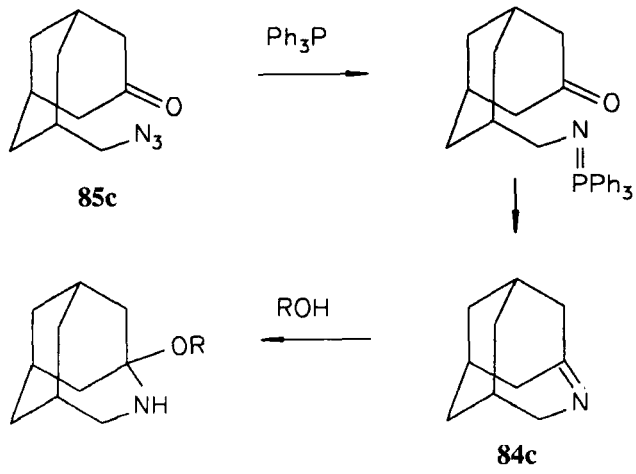


85a **84a**

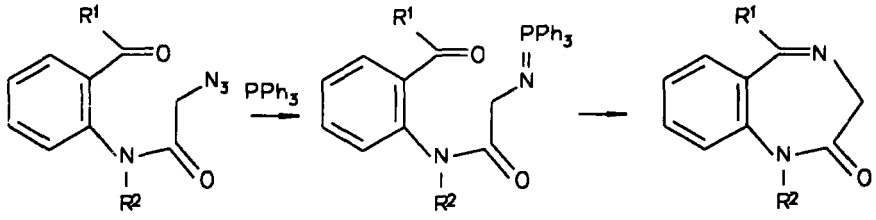
Cyclisation of the λ5-phosphazenes derived from azido ketones also has been applied in the synthesis of 1,2-dehydroproline methylamide [231] and pyrroline systems.[232] A wide range of 5, 6 and 7 membered heterocycles can be conveniently prepared from azido ketones **85b** by an intramolecular aza-Wittig reaction. This reaction provides a method for the preparation of imines **84b**,[233] cyclic enamines **86a**,[234] enaminones **86b**, [235] isoquinoline[236] as well as tetracyclic imines derived from indole[237] under anhydrous conditions.



Furthermore, this method also provides a general and regioselective route to bridgehead imines from ketoazides and oxacyl azides using the Staudinger reaction followed by an intramolecular aza-Wittig reaction.[238] The reactive bridghead imine, 4-aza-4-homobrend-3-ene, its 5-oxo derivative and the 4-aza-homoadamant-3-ene **84c** are generated by this process, and are trapped subsequently by the solvent, either methanol or ethanol.

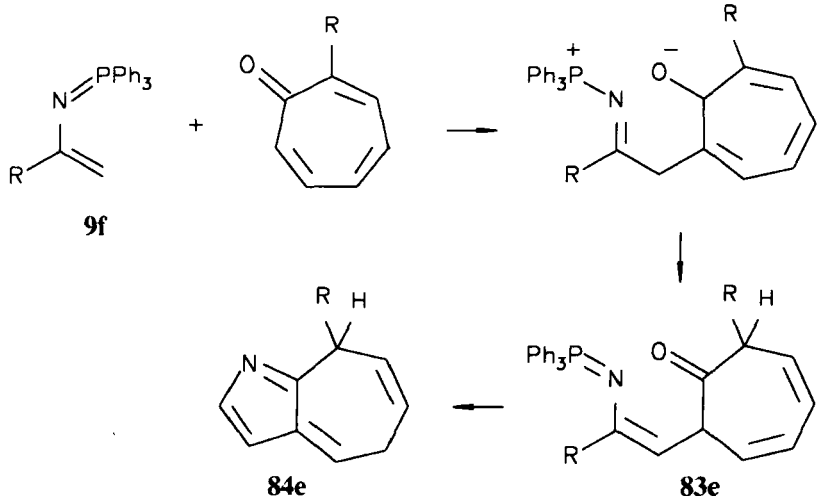


It is noteworthy that this strategy has been also used in the synthesis of drugs, such as the seven membered heterocycles diazepam [239] and nitrazepam [239,240] from azido-acetanilides and triphenylphosphine. Likewise, intramolecular reaction between the λ5-phosphazene group and a carbonyl moiety has been applied to the synthesis of benzo-1,4-diazepin-2-ones **84d** when λ5-phosphazenes **83d** derived from 2-azido acetamido-benzaldehyde and benzophenone **85d** were used.[241]



85d **83d** **84d**

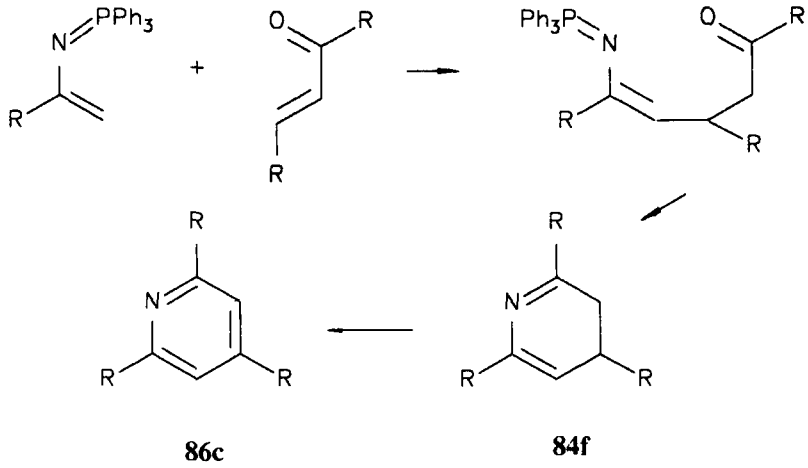
In the reactions described in this section the key intermediates *N*-carbonylalkyl λ5-phosphazenes were generated from azido ketones and phosphines. A second alternative involves the formation of the *N*-functionalized λ5-phosphazenes, precursor of the cyclic compounds, by reaction of *N*-vinylic λ5-phosphazenes **9f** and ketones through a tandem conjugated 1,4-addition (enamine type alkylation)/ aza-Wittig reaction. This



9f **84e** **83e**

strategy allows the preparation of substituted pyrroles [242] when λ^5-phosphazenes derived from α-azidostyrene react with α-bromo ketones. Similarly annelation reactions occured when *N*-vinylic λ^5-phosphazenes were treated with tropone derivatives, leading to in the formation of 1-aza-annulene ring systems **84e**.[243]

This methodology involving carbon-carbon bond formation through Michael addition of the *N*-vinylic λ^5-phosphazenes to α,β-unsaturated ketones followed by aza-Wittig reaction also has been applied to the formation of six membered heterocycles. Thermal reaction of *N*-vinylic λ^5-phosphazenes with α,β-unsaturated ketones gives an enamine-type alkylation and subsequent intramolecular aza-Wittig reaction to the pyridine derivatives **86c**.[244,36] Cyclic α,β–unsaturated ketones show similar behaviour, leading to pyridophane ring systems. [245]

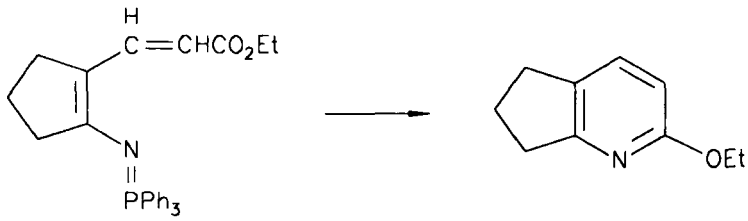


86c **84f**

B. λ^5-Phosphazenes Derived from Esters

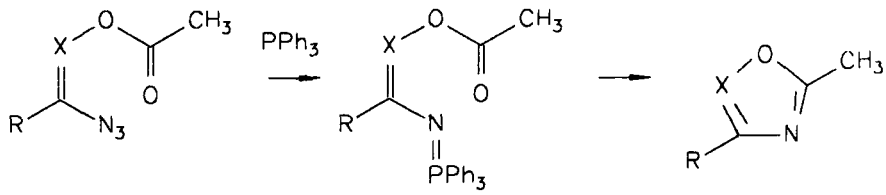
Intramolecular aza-Wittig reaction is not restricted to the λ^5-phosphazenes derived from ketones, but other less reactive carbonyl compounds, can also undergo this reaction to form cyclic imines. This method has been used in the preparation of lactams,[215] selective temporary protection of complex carbohydrates [246] and in the preparation of quinoline [247]

and isoquinoline [248] ring systems. Cyclopentapyridines **84g** has been also obtained by intramolecular aza-Wittig reaction of the *N*-functionalized λ5-phosphazenes **83g**. [249]



83g **84g**

The synthetic potential of this intramolecular version of the aza-Wittig reaction involving cyclisation of the carbonyl group from carboxylic esters has been applied to the preparation of five membered nitrogen heterocycles. Accordingly, benzoxazoles **84h**, [250] 1,2,4-oxadiazoles **84i** [251] and oxazole **84j** [252] derivatives have been prepared from the corresponding functionalized azides. *N*-Carbonyl λ5-phosphazenes show a similar reaction pattern, leading to benzoxazin-4-ones. [253]



84h RX=(CH)4

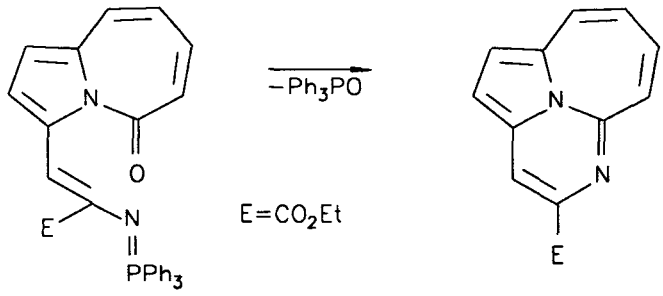
84i X=N

84j X=CR

C. λ5-Phosphazenes Derived from Amides

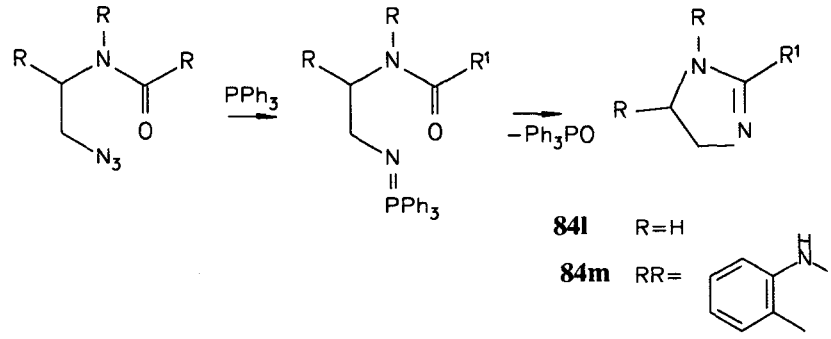
Only a few examples are known where the carbonyl group of an amide is involved in the formation of carbon-nitrogen double bond. This methodology was first used in the

preparation of the tricyclic system 5-aza-cycl[4,3,2]azine-4-carbonic ester **84k** through thermal intramolecular aza-Wittig from *N*-functionalized λ^5-phosphazenes **83k**. [254]

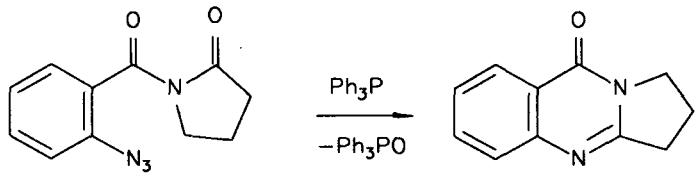


83k **84k**

Recently, this synthetic strategy has been applied to the preparation of five membered heterocycles. A new process for producing imidazolines **84l** [159] and imidazo-benzimidazoles **84m** [255] was also reported.



Reaction of imide carbonyl groups in the intramolecular aza-Wittig reaction leads to an efficient route to imino lactam derivatives.[256] Likewise, the application of this reaction to the synthesis of six membered heterocycles provides a new entry to the preparation of natural products derived from quinazolines such as deoxyvasicinone **84n**.[257]



84n

In conclusion, the foregoing summary forms the basis for the expectation that λ5-phosphazenes will play an important role in the design of new carbon-nitrogen bond forming processes for the construction of acyclic and heterocyclic derivatives. We look forward with interest to new developments in this rapidly expanding field of chemistry.

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