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SYNTHESIS, PROPERTIES AND STRUCTURES OF PHOSPHORUS-NITROGEN HETEROCYCLES

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Abstract – The synthesis, properties and structures of heterocyclic molecules containing phosphorus and nitrogen are described in this review. A systematic synthesis of a ring compound needs one or more bifunctional starting molecules that react in a special way to form new bonds and to obtain the ring. Oligomers or polymers can be obtained besides other products resulting from leaving groups necessary to form the new bonds. Hydrazine for example is one of the simplest bifunctional compounds that must be able to introduce two vicinal nitrogen atoms into a cycle, as it will be shown further.

CONTENT

INTRODUCTION

The role of aromatic heterocycles containing phosphorus and nitrogen has been recognized and established in the regulation of enzymatic activity, function, folding and stability of biological systems.[1-6] In the Figure 1 are presented few structures of several aromatic heterocycles containing phosphorus.[1]

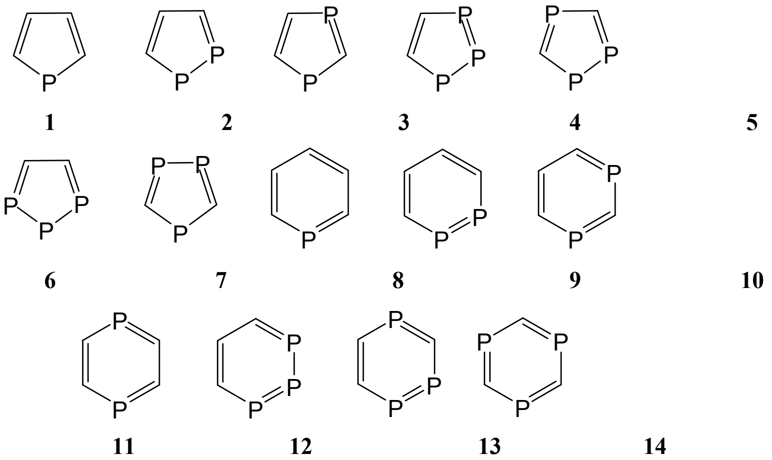


Figure 1. Structures of several aromatic heterocycles containing phosphorus [1]

In addition, these heterocyclic compounds showed a significant role in the design of organic nanotubes, biological receptor models and ionophores was recognized as well.[7,8] A lot of studies were performed on aromatic systems (benzene, tryptophan, phenylalanine, tyrosine etc).[9-12]

These heterocyclic systems (**1-14**) considered in the Figure 1, provide also a possibility to realize a large number of complexes with metals. The phospholes and phosphinines can form strong complexes with metal ions (Li^+, Mg^{2+}, Ca^{2+}, Na^+, K^+).[1] There are about a dozen crystal structures which have Li^+ and Na^+ bound to phosphorus systems.[13,14]

In this review further it will be shown several methods of synthesis and several properties of few heterocycles containing phosphorus and nitrogen.

1. Nonalternating inorganic heterocycles containing hydrazine as building block. Hydrazine derivatives of phosphoric and thiophosphoric acid

A lot of different possibilities to obtain heterocycles containing phosphorus were developed during the last decades. Here several examples will be described.

For example, using the phosphorus halogenated ester **15**, the heterocycle **16** can be obtained (Figure 2) in around 13% yield, by a chemical process which occurs in anhydrous conditions using pyridine as base and tetrahydrofuran as solvent. The heterocycle **16** was purified after several recrystallisations.[15]

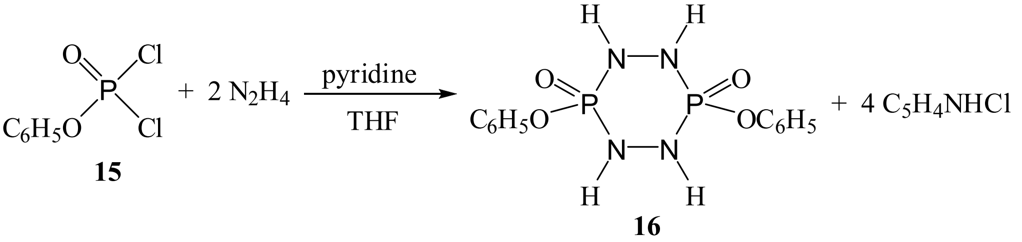


Figure 2. The synthesis of a heterocycle containing phosphorus and nitrogen (**16**), from phenyl phosphorodichloridate (**15**) in THF and pyridine

The ^{31}P NMR and ^{1}H NMR spectra and determinations of molecular weight were in good agreement with the assumed structure for the heterocycle **16**. The melting point of it was around 259-260 °C. The reaction of heterocycle **16** with KOH in ethanol, under reflux, produces the carbon-free dipotassium-salt **17** (Figure 3).

This salt (**17**) can not be oxidized to the corresponding azo-compound **18** (Figure 3).[16] No color change was observed, as in the case of noncyclic hydrazidophosphonates.[17]

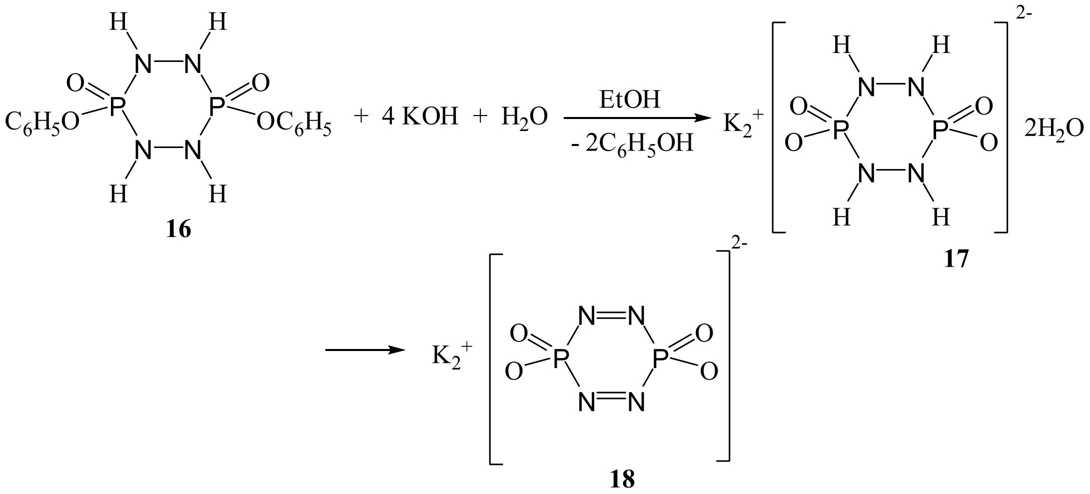
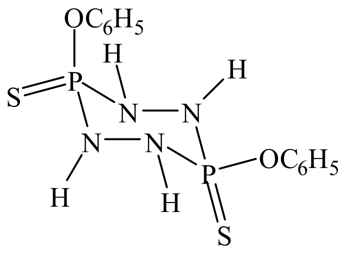


Figure 3. Reaction of compound **16** with KOH to form the carbon-free dipotassium-salt

On the other hand, the decomposition of it occurs under nitrogen.[16] Resynthesizing the phenylester of the corresponding dithio-ring compound described by Tolkmith and Britton[18] gave the same results. In this case two isomers can be isolated with preparative chromatography on silica gel.[15] A *cis*- and t*rans*-isomers (Z and E isomers) would be expected as well. Both isomers **19** and **20** were anticipated to possess a cyclohexane ring conformation (Figure 4). The trans-isomer **20** exists in two different conformations.



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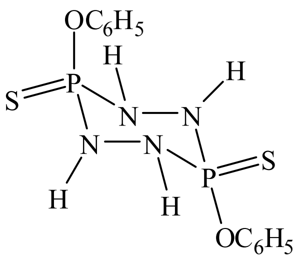

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Figure 4. Isomers containing phosphorus and nitrogen in the ring

X-ray structure determinations of the both isomers (**19** and **20**) provide interesting results. The *trans*-isomer adopts the expected centrosymmetric chair conformation with S atom in the equatorial positions and the *cis*-isomer is in a twist-conformation that possesses a two symmetry axis. Both (S atom and phenoxy–groups) are in the "isoclinals positions" (Figure 4).[15]

2. Monomethylhydrazine derivatives of phosphorus (III) and (V) compounds

Another interesting heterocycles are the compounds derivate from hydrazine, containing as well phosphorous and nitrogen atoms in the ring (for example the structure **21**, Figure 5).[15]

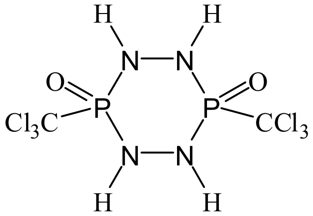

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Figure 5. Heterocycles derived from hydrazine

Because of the fast proton exchange processes of the NH groups there is no possibility of monitoring conformational changes in solution by NMR-spectroscopy of molecules with this type of structures (**21**). The results of the X-ray diffraction determinations could be singular and maybe due to crystal packing effects too. But in *N*-methyl-substituted compounds, it could be expected that the NMR-spectra would reveal some more information.

The chemical reaction of monomethylhydrazine with phenoxy-thiophosphoryl-dichloride **22** (Figure 6) in the presence of base in excess, produces a mixture of three dihydrazides isomers (**23**, **24** and **25**). These dihydrazides were isolated by chromatographic method.[15]

The molar ratio of **23**:**24**:**25** compounds is around 10:2:1, at a temperature between 0 °C and 40 °C. At lower temperatures (below 0 °C) only the compound **23** is formed. The identity of the isomers is easily recognized with NMR-spectroscopy.

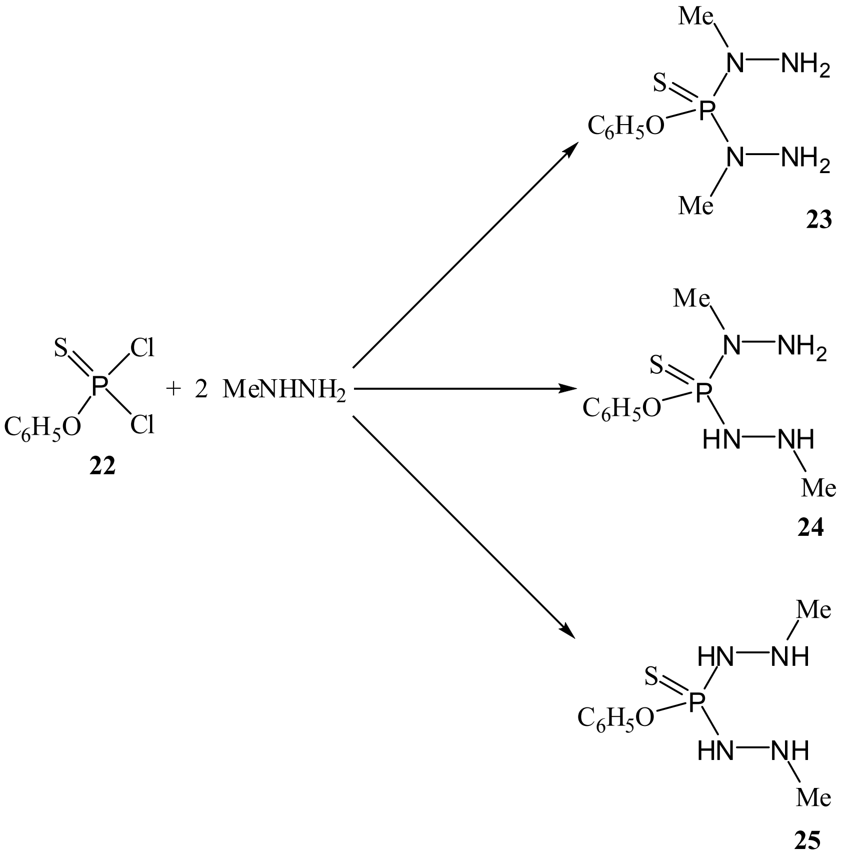

Figure 6. The reaction of monomethylhydrazine with phenoxy-thiophosphoryl-dichloride

From the compounds **23** and **24** other two heterocycles (**26** and **27**, Figure 7) containing phosphorus and nitrogen in the cycle could be synthesized. The process occurs at low temperature by the reaction of **23** and/or **24** in the presence of excess base. The symmetrical compound **26** exists also in the *cis*- and the *trans*-conformations. The same it was found in the case of the asymmetrical ring compound **27**.[15] The isomers of **27** can be separated with good results by column chromatography. They have the melting range between 135 °C and 161 °C. In the same time the mixture of the both isomers **26** and **27** has a melting range between 115 °C and 157 °C.

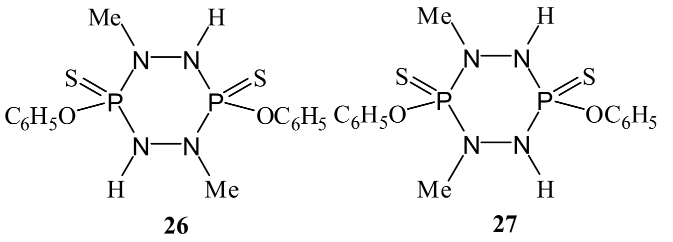

Figure 7. Different heterocycles obtained from **23** and **24**, in the presence of excess base

These compounds (**26** and **27**) could be also obtained by the dimerisation reaction of **28** (Figure 8), a monochloro-monohydrazido derivative.

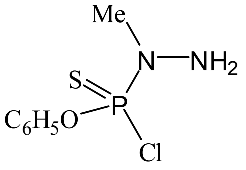

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Figure 8. Structure of the monochloro-monohydrazido derivative **28**

3. Spirocycles containing two or more phosphorus atoms combination of hydrazine rings and cyclophosphazenes

Bifunctional compounds such as alkane-diols, diamines or aminoalcohols for instance yield spirocompounds. Hexachlorocyclotri(phosphazene) **29** is a known and easily accessible molecule that could reacts with organic amines (**30**) to form usually vicinal disubstituted products (**31a** and **31b**, Figure 9).[15] At room temperature in THF as solvent, the compound with the structure **31a** (4,4,6,6-tetrachloro 6-phenoxy-cyclotri(phosphazene)-2-spiro-3-cyclodi(phosphadiazane)-6-sulfide) could be synthesized in about 70% yield. In the same time the compound with the structure **31b** could be obtained as well.

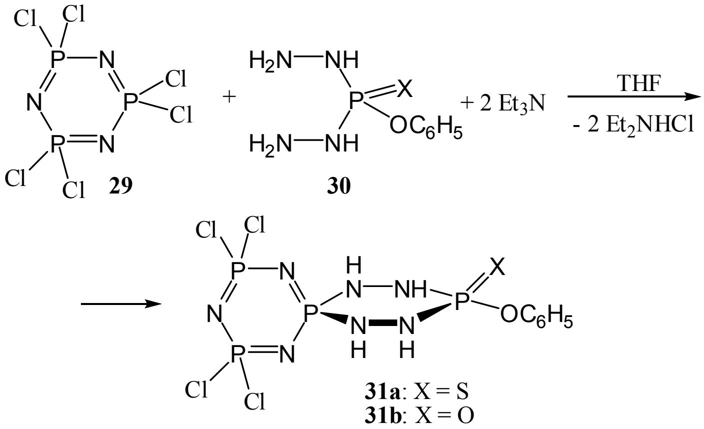
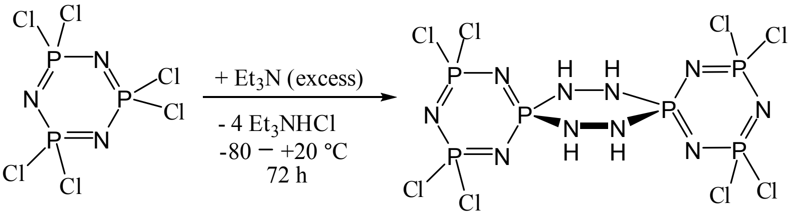


Figure 9. Synthesis of two vicinal disubstituted heterocycles containing phosphorus and nitrogen, from hexachlorocyclotri(phosphazene)

The structure of the products **31a** and **31b** was proved by several spectroscopic methods (IR, NMR and MS). The hexachlorocyclotri(phosphazene) **29** also reacts directly with the absolute hydrazine to yield the dispiro-system **32** (Figure 10). The process occurs in a temperature range between –80 °C and 20 °C. The reaction process it takes 72 hours to be complete.[15]



29 **32**

Figure 10. The reaction of hexachlorocyclotri(phosphazene) with absolute hydrazine

Also in the literature are described heterocyclic compounds containing seven-membered ring (**33**, Figure 11). The compound **33** almost resembles a cyclophosphazene, but contains a N-N single-bond in the ring. It is described in the literature with its X-ray structure.[15]

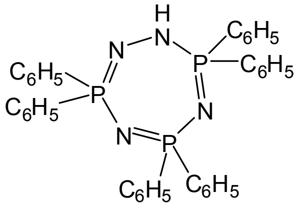


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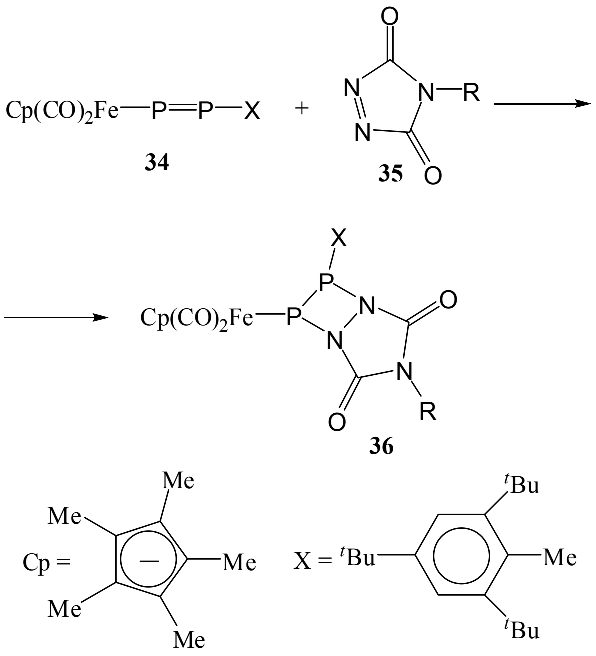
Figure 11. The structure of a cyclophosphazene derivative containing N-N and N=N bonds in the ring

The number of atoms which form the cycle could vary. For instance a four-membered hydrazine-ring could be formed in a (2–2) cycloaddition reaction of a phosphene (**34**) with an N-substituted azodicarbonimide (**35**). The resulting bicyclic molecule (**36**) may be considered a diphosphane hydrazine derivative (Figure 12).[19]



34 **35** **36**

Figure 12. The (2–2) cycloaddition reaction of a phosphene with an N-substituted azodicarbonimide

The corresponding phosphonic acid derivatives as diazaphosphiridine-3-oxides **38** are also known. They have been obtained from the *N*-chlorinated diamides **37** by HCl elimination (Figure 13).[20] Moreover, the monosubstituted phosphanes (such as supermesitylphosphane for example) react with the diethylester of azodicarbonic acid to yield the diazaphosphoridine as intermediate. This compound spontaneously isomerizes to the corresponding diiminophosphorane.[21]

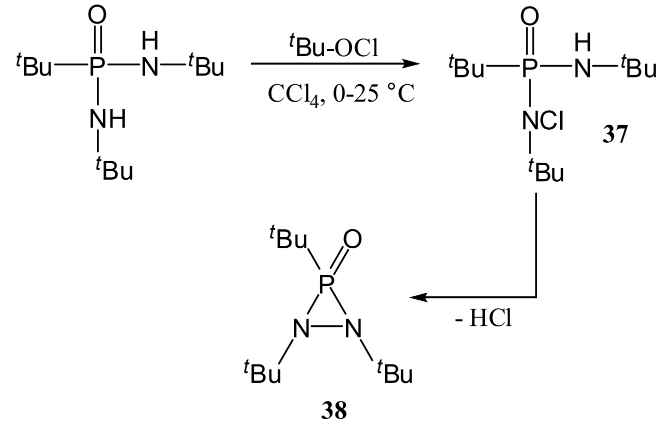
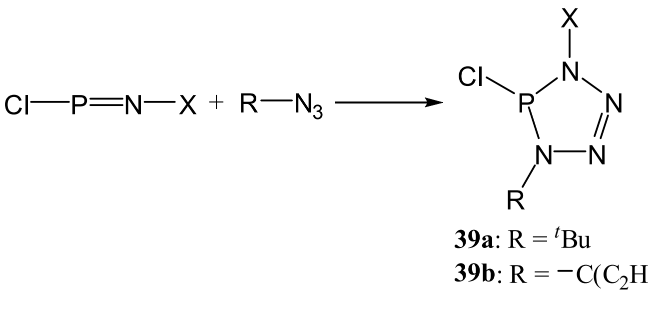


Figure 13. The synthesis of diazaphosphiridine-3-oxides compounds by HCl elimination from *N*-chlorinated diamides

Another way to obtain such heterocycles with phosphorus and nitrogen in the ring is describes in the Figure 14. This is the formation of a five-membered ring by oxidation of a diamide of the phosphonic acid. This means that a new N-N bond is formed during the ring closure (**39a** and **39b**). The hydrazine is not present in one of the starting materials, but is formed during the ring synthesis.[22]



39a: R = ^{t}Bu
39b: R = $-C(C_2H_5)_3$

Figure 14. Synthesis of 4-alkyl-5-chloro-1*H*-1,2,3,4,5-tetrazaphosphole

Similar compounds containing phosphorus (III) and N-N single bonds in the ring have been synthesized below the room temperature, from iminophosphanes and organic azides with bulky substituents (the structure **40**, Figure 15).[23]

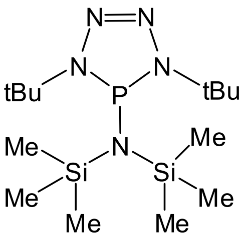


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Figure 15. Structure of 1,2,3,4,5-tetrazaphosphole derivative containing P(III)

Above the ambient temperature, these compounds lose nitrogen and are transformed into the corresponding bis(imino)phosphoranes.[23-26] It should be mentioned here that as early as 1921, a reaction of triphenylphosphane with hydrogen azide led to a compound, that was described as a salt $[(C_6H_5)_3P\text{-}NH_2]\text{-}N_3$,[27] later turned out to be a 2–3 cycloaddition product (the structure **41**, Figure 16) of triphenylphosphaneimine and hydrogen azide.[28]

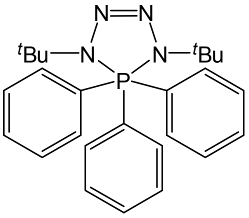

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Figure 16. Structure of a 2–3 cycloaddition heterocycle product of triphenylphosphaneimine and hydrogen azide containing P(V)

A cyclic dimmer product obtained from the reaction of *N*-trimethylsilylpyrazole and phosphoruspentafluoride **42** (Figure 17) has a tricyclic structure (**43**, Figure 18).[29]

The ring adopts a flat boat conformation. The phosphorus atoms are octahedral coordinated.[29] The by-product **43** proved to be an eight-membered ring molecule containing a P–O–P unit in the ring. The X-ray structure shows the central ring having a boat chair conformation (Figure 18).[30]

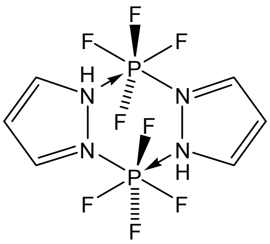

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Figure 17. The structure of phosphoruspentafluoride

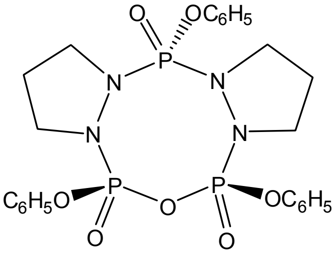

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Figure 18. Cyclic dimmer obtained by the reaction of *N*-trimethylsilylpyrazole and phosphoruspentafluoride **42**

It could be mentioned also that quite a lot of interesting chemistry on the borderline between inorganic and organic chemistry has been published related to cyclic hydrazine derivatives, for instance Schiff–base derivatives of thiophosphoric acid dihydrazides and dendrimers and other polymers containing these and similar building blocks. Since the compounds are no "inorganic" ring systems in a rigid sense, no details are given here, but a few main publications are cited.[31-37]

4. Heterocycles containing phosphorus from *N,N*-bis[(–)-norpseudoephedrine]

The chemical reaction from the *N,N*-bis[(−)-norpseudoephedrine] oxalyl and $P[NMe_2]_3$ produces the epimer helix of tricyclic phosphorane **44** (Figure 19).[38,39] The phosphorane **44** react with borane and produces further a mixture of two isomeric compounds: the structures **45** and **46**. These phosphorane derivatives with structures **45** and **46** presented in the Figure 19, in borane excess finally could produce two reduced isomers: **47** and **48**.[39]

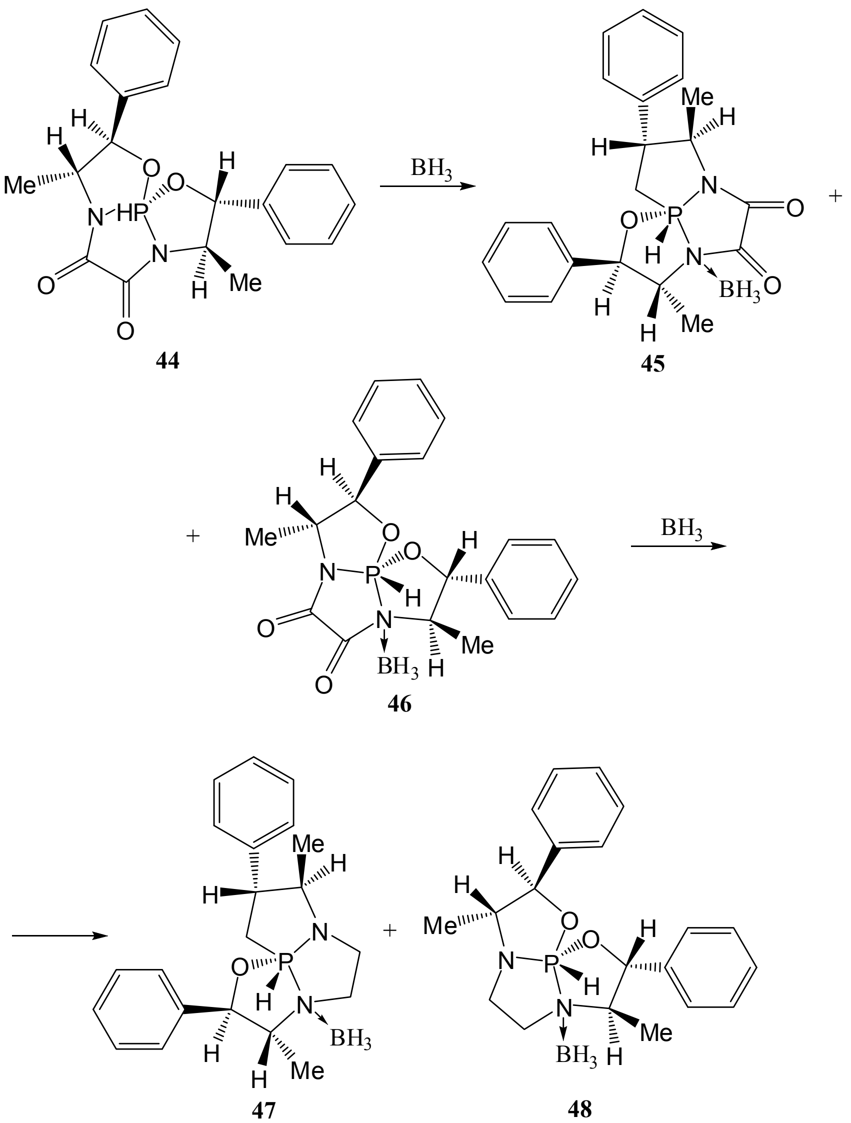


Figure 19. Reaction of the *N,N*-bis[(−)-norpseudoephedrine]oxalyl with $P(NMe_2)_3$ afforded isomer **44**.[39]

The non-symmetrical optically active oxalyl derivative was reacted with dialkyldichlorotin compounds providing optically active binuclear diorganotin compounds, with a delocalized pentacyclic framework and two non-equivalent pentacoordinated (TBP) tin atoms.[40] The metallic atoms are strongly coordinated by the oxygen atoms from the amide; the relevance is due to their stable rigid structures, suitable models for NMR and X-ray diffraction studies of hypervalent metallic atoms.

All of these compounds are interesting derived heterocycles from the family of ephedrines. These ligands have been used to obtain linear and cyclic organic derivatives, heterocycles and complexes with metal ions, all having high potential as optically active compounds. Their use as fine reagents for asymmetric synthesis or optically active catalytic agents in industry is a strong motivation for the study of these simple but in the same time relevant molecules. Much investigation is still needed in order to obtain a better understanding of the stereochemistry and of the dynamic behavior in the molecules resulting from chiral organic ligands and other elements different from carbon.[38]

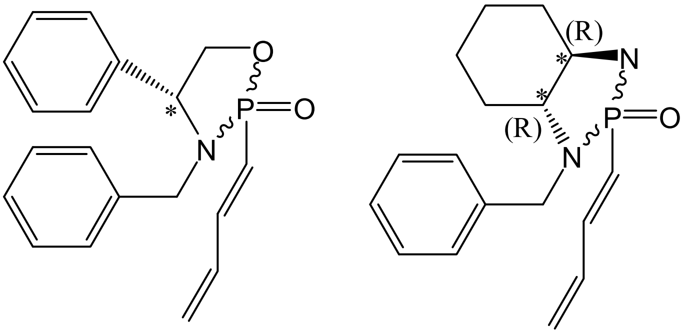
5. Synthesis of novel chiral 1-phosphono-1,3-butadiene for asymmetric hetero Diels-Alder cycloadditions[41]

The chiral 1-phosphonodienes bearing a bicyclic (*R*,*R*)-1,3,2-dioxaphospholane or a (*R*,*R*)-1,3,2-diazaphospholidine auxiliary are important dienes for the asymmetric Diels–Alder processes. They showed a very high reactivity towards model nitroso and azodicarboxylate dienophiles. Aminophosphonic acids and their related compounds represent an important class of pharmacologically active molecules.[41,42] These described chemical synthesis regarding α-aminophosphonic derivatives, despite the fact that the interest for β-, γ- and δ-homolog is still growing. As a part of a research program[41,43] dedicated to the synthesis of aminophosphonic compounds, it was studied the hetero Diels-Alder (HDA) cycloadditions of achiral 1-phophonodienes with activated nitrogen containing dienophile (nitroso and azodicarboxylate compounds).[44]

The HDA reaction is very compatible with the asymmetric development.[45,46] This led to consider the asymmetric HDA cycloadditions of nitrogencontaining dienophiles and chiral phosphonodienes as an entry towards aminophosphonic chirons. Several examples of chiral phosphonodienophiles are illustrated by Wyatt,[47,48] and King[49] with chirality either directly surrounding the phosphorous atom itself or being placed elsewhere on the chiral auxiliary. It exist only one previous report by Wyatt, in which the use of a chiral 4-phenyl-1-phosphonodiene was mentioned, versus a cyclic azodicarboxylate dienophile (4-phenyl-1,2,4-triazolin-3,5-dione) leading to the corresponding cycloadduct (with good yield but also with low stereoselectivity).[47]

Two different methods could be used to obtain a chiral phosphonodiene (Figure 20):

- the direct introduction of the chirality on the phosphorus atom (diene **49**) (Figure 20).
- the introduction of the chirality on an adjacent atom, with a nitrogen relay nearby the phosphorus atom (e.g., diene **50**) (Figure 20).



49 **50**

Figure 20. Two examples of chiral phosphonodienes

The first method (the direct introduction of the chirality on the phosphorus atom) was abandoned, because the synthesis of diene **50** produces in fact a mixture of diastereoisomers, impossible to be separated. In the second method, it was used C_2-symmetry auxiliaries (bicyclic 1,3,2-dioxaphospholane)[50] and 1,3,2-diazaphospholidines[51] derived from (*R*,*R*)-1,2-dihydroxy- and (*R*,*R*)-1,2-diaminocyclohexane.

Few other chiral dienes (**51a–d**) have been selected for a study of their hetero Diels–Alder reactions with the dienophiles **52a–c**, to obtain the isomers **53** (R) and **54** (S). All of these structures (**51–54**) are presented in the Figure 21, where where R’ is H in **51a**, Me in **51b**, Pr in **51c** and Bn in **51d**, R’’ is Me in **52a**, 2–Tol in **52b** and COOMe in **52c**, and Y is O in **52a** and **52b**, and NR’’ in **52c**.

For the both conformers of dienes **51a–d**, the substituents attached to the nitrogen atoms were found in a pseudo–equatorial position. In agreement with the previous observations (Bennani and Hanessian)[51] there is an obvious differentiation of the preferred orientation of R’ groups on either size of the chiral auxiliary. By increasing the hydrophobicity of the R’ groups of the diene, a stronger sterical hindrance appears and an increase in the selectivity was observed. For the dienophile **52a** the selectivity increased twice passing from diene **51a** to diene **51d**, while for dienophile **52b** the increase in selectivity was more pronounced when going from diene **51a** to diene **51d**.

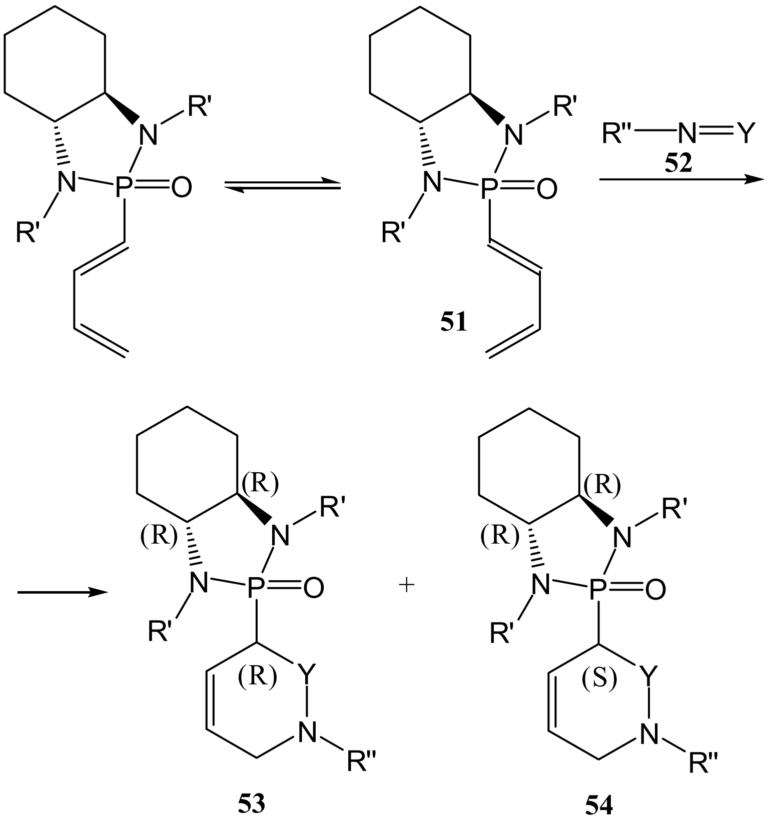


Figure 21. Asymmetric HDA cycloadditions of chiral phosphonodienes (**51a–d**) and dienophiles (**52a–c**): partners selected for the theoretical study

The cycloadditions of dienophile **52c** with dienes **51a–d** clearly showed a synergy effect due to the steric hindrance of both the R' and R'' substituents. The highest level of stereo selectivity was obtained with diene **51d**.

This prediction has been confirmed. It was synthesized in two steps the chiral diene **51d**, from the compound **55**, in 62% yield (Figure 22). The structure of the product **51d** was confirmed by X-ray diffraction analysis.

Experimentally, under classical thermal conditions, the reaction of diene **51d** with **52b** led to a 1:1 mixture of separable diastereomers **56** and **57**, after 12 hours in refluxing (Figure 22). This can be attributed to a low energetic discrimination between the both conformers of chiral diene **51d** and to the high asynchronicity of bond formation with the nitroso-partner.[41] The selectivity was not influenced by the polarity of the solvent.[41]

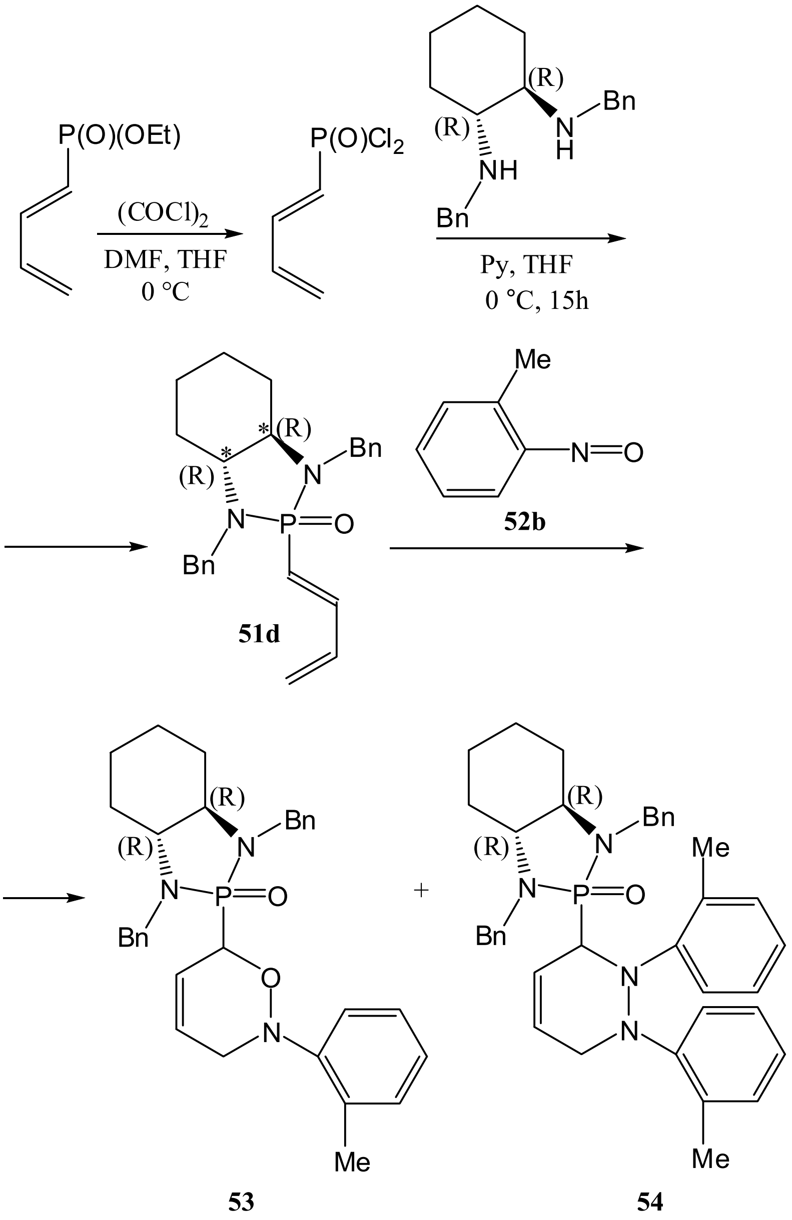


Figure 22. Synthesis and cycloadditions of phosphonodiene **51d**.

CONCLUSIONS

The present paper makes an overview of literature data from the last decades, for different synthesis methods and properties of several classes of heterocycles containing phosphorus in the ring. Many compounds described here contain phosphorus and nitrogen in the cycle.

The work in the field of heterocycles with phosphorus atoms in the ring contributes to the general image of the ring structures and the ring conformations. The importance of hydrazine and their derivatives as ring building has been described as well.

The combination of different ligands derived from ephedrine produces new heterocyclic compounds, optically active. These heterocycles can be used as fine reagents for asymmetric synthesis or optically active catalytic agents in the industry. This is a strong reason to study more these compounds, in order to understand their stereochemistry and their behavior.

All of these compounds containing phosphorus described are new interesting heterocycles with many applications.

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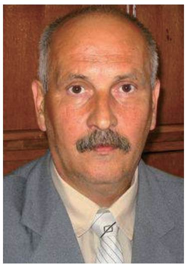

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