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Synthesis, some properties and structural features of 1,2-thiaphosphacyclanes

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Abstract. Synthetic routes to 1,2-thiaphosphacyclanes bearing both tri- and tetracoordinate phosphorus atoms, and their reactivity and structural features based on data from X-ray diffraction analysis are discussed. Particular emphasis is placed on the rare case of ring-chain halogenotropic tautomerism in the series of 1,2-thiaphosphacyclanium salts and related compounds. The bibliography includes 107 references.

I. Introduction

In recent years, there has been an increase in the interest in the chemistry of heterocyclic compounds, development of synthetic routes and investigation of properties of novel types of heterocycles, mostly due to their practical applications, *e.g.*, in agrochemistry and pharmaceutical chemistry. In full measure, this applies to phosphorus-containing heterocyclic compounds. Noteworthy is the known peculiarity of phosphorus-containing heterocyclic compounds compared to their acyclic analogues, which is manifested in the unusual structures (conformational and stereochemical) of the reaction products. Cyclic phosphorus compounds are often invoked with the purpose of studying the mechanisms of chemical transformations of organophosphorus compounds, moreover, they are effectively used as synthons in organic synthesis. Phosphorus-containing heterocyclic compounds, in particular, phosphates, play an important role in biochemical processes.

Among fairly numerous phosphorus-containing heterocyclic compounds known presently, saturated and unsaturated phosphacyclanes [1] and polyheterophosphacyclanes [2–6] have been investigated in most detail. General synthetic procedures have been proposed for the synthesis of 1,3,2-diheterophosphacyclanes based mostly on the interaction of phosphorus acid chlorides with nucleophiles (polyhydric alcohols, thiols and amines). Monoheterophosphacyclanes are represented in the literature mainly by 1,2-oxaphosphacyclanes. Basic publications concerning the synthetic routes to these compounds date from the 1960 – 1980. 1,2-Oxaphosphacyclanes have found wide industrial application, particularly as non-inflammable hydraulic fluids and plasticisers,[7,8] additives to lubricants,[9] flame retardants,[10,11] thermostabilisers of synthetic fibres [12–14] and surfactants.[15] Some P,O-heterocyclic compounds are used as synthons for hard-to-reach compounds.[16–19]

1,2-Monoheterophosphacyclanes having other heteroatoms in the ring, *e.g.*, sulfur or nitrogen, have been investigated to a far lesser extent because of the absence of convenient preparative methods to obtain them. At the same time, cyclic P,S-containing systems represent a highly promising class of organophosphorus compounds. In particular, it is known that some P,S-heterocycles are used as antioxidant additives in motor oils, polymers and agrochemicals,[20–22] and also as co-monomers for polymers possessing complexation properties [23] and ligands for metal complex catalysts.[24] Cyclic esters of phosphorus thioacids are widely used in biochemical studies and as sulfur analogues of nucleotides.[25,26] Some saturated P,S-heterocyclic compounds, such as 2,4-bis-(4-methoxyphenyl)-1,3-dithia-2,4-diphosphetane 2,4-disulfide [27] (currently known as the Lawesson reagent, LR), are of great utility in organic synthesis as mild thiylating agents for carbonyl and phosphoryl compounds and also as reagents in the synthesis of unsaturated 5- and 6-membered heterocyclic compounds containing a P,S-moiety.[28,29]

Though the number of publications concerning the saturated 1,2-thiaphosphacyclanes is rather limited, it seemed expedient to summarise the information on this topic available in the literature taking into account the clear prospects of these compounds. We have paid attention to the synthesis, structural features and tautomerism of this interesting but still poorly investigated class of heterocyclic compounds.

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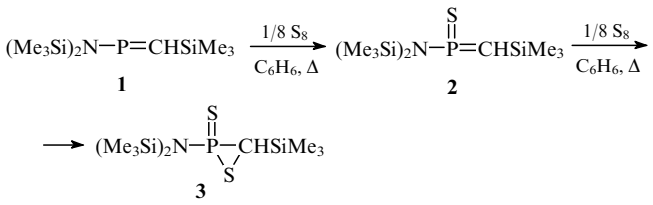
II. 1,2-Thiaphosphiranes

Three-membered saturated P,S-heterocycles, *i.e.*, 1,2-thiaphosphiranes, became available only when synthetic approaches to stable dicoordinate phosphorus compounds were developed.

1. Synthesis of 1,2λ^5-thiaphosphiranes

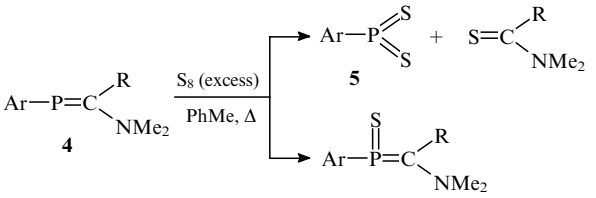
The only general synthetic route to 2-thioxo-1,2λ^5-thiaphosphiranes presently known is based on the addition of elementary sulfur to methylidenephosphines. Niecke and Wildbredt [30] were the first

to obtain a compound with such a heterocycle starting from [bis(trimethylsilyl)amino]trimethylsilylmethylidene-$\sigma^2\lambda^3$-phosphine (**1**).



This reaction proceeds in two steps: the addition of one equivalent of sulfur affords $\sigma^3\lambda^5$-methylidene(thioxo)phosphorane **2** in high yield (90%), which reacts with the second equivalent of sulfur according to the [1 + 2]-cycloaddition affording 2-thioxo-1,2λ^5-thiaphosphirane **3**. A small amount of the latter as a by-product is formed in the first step. If the reaction of methylidenephosphine **1** is carried out directly with two equivalents of sulfur the desired 2-thioxo-1,2λ^5-thiaphosphirane **3** is obtained in virtually quantitative yield.

It should be noted that not all cases of the reactions of phosphaalkenes with sulfur result in the formation of stable $\sigma^3\lambda^5$-methylidene(thioxo)phosphoranes, the pentavalent tricoordinate phosphorus compounds. In particular, the reaction of 2,4,6-tri-*tert*-butylphenyl(dimethylaminomethylidene)phosphines **4** with sulfur yields metadithiophosphonate **5** [31, 32], which does not dimerise to the corresponding analogue of the Lawesson reagent because of the bulky aryl moiety.



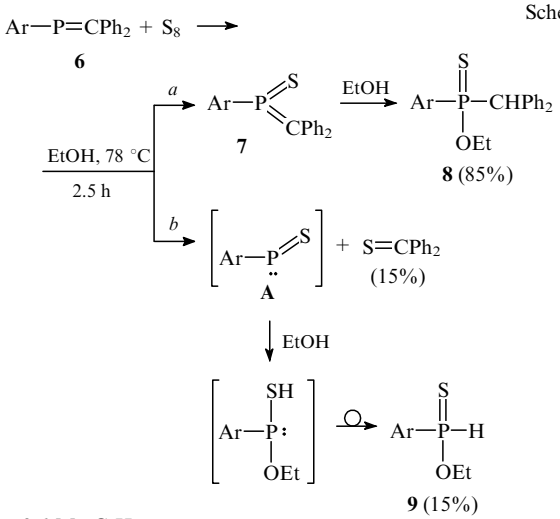
Ar = 2,4,6-$Bu^t_3C_6H_2$, R = H, Me.

No thiaphosphiranes were also found among the addition products of the sulfur to 2,6-dimethylphenyl(diphenylmethylidene)phosphine (**6**) in boiling ethanol,† though in this case methylidene(thioxo)phosphorane **7** is really formed in the first step.[32, 33] It was not possible to isolate phosphorane **7** because of its extreme instability, but its formation was confirmed by NMR and mass spectrometry techniques and also by its reaction with ethanol affording *O*-ethyl 2,6-dimethylphenyl(diphenylmethyl) thiophosphinate **8** (Scheme 1, path *a*, attack on the lone electron pair of the phosphorus atom).[32] Concurrently with the addition of one equivalent of sulfur leading to the phosphorane **7** (path *a*), cleavage of the P=C multiple bond in the starting methylidenephosphine takes place (path *b*), as the energies of these reactions are similar. Such a cleavage results in thiobenzophenone (15%), and after addition of ethanol to an unstable intermediate **A**, *O*-ethyl H-phosphinothioate **9** (15%).

However, if this reaction is carried out in benzene, it is possible to obtain the desired addition product of two sulfur atoms, 2-thioxo-1,2λ^5-thiaphosphirane **10**. Refluxing of methylidenephosphine **6** with 5.7 equivalents of sulfur in benzene for 3 h provided the maximum yield of the product **10** (34%).[32] With a lesser amount of sulfur, a mixture of methylidene(thioxo)phosphorane **7** and the starting methylidenephosphine **6** was formed containing only traces of 1,2λ^5-thiaphosphirane **10**. An increase in the temperature up to 90–100 °C (sealed tube) afforded an analogue of the Lawesson reagent, *i.e.*, compound **11**, which is the dimerisation product of arylmetadithiophosphonate **12**, and

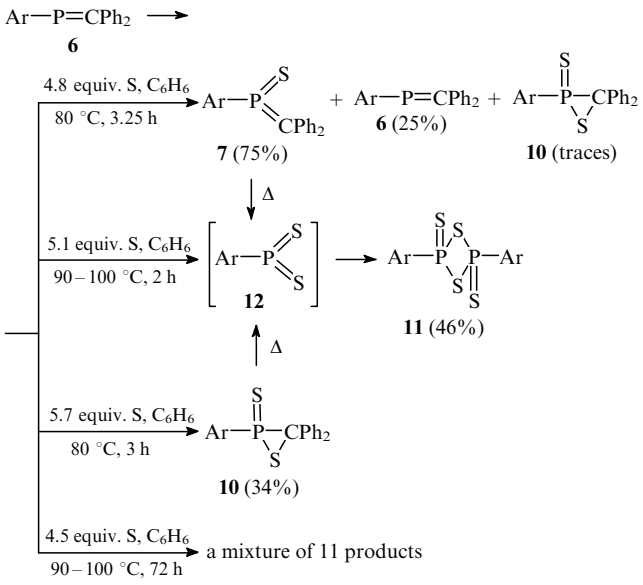
† No reaction of 2,6-dimethylphenyl(methylidene)phosphine with sulfur occurs in EtOH or benzene at room temperature.[32]

Scheme 1



Ar = 2,6-$Me_2C_6H_3$.

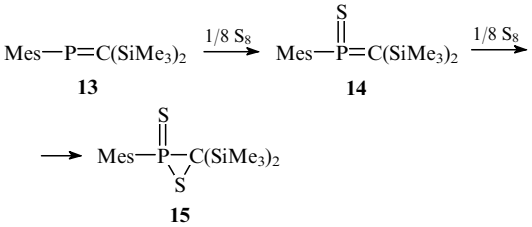
prolonged heating under the above-mentioned conditions gave a mixture of eleven unidentified phosphorus-containing compounds.



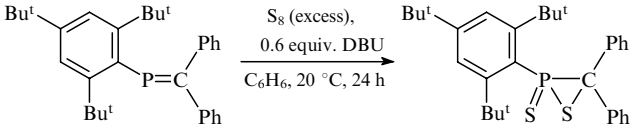
Ar = 2,6-$Me_2C_6H_3$.

Obviously, the stability of methylidene(thioxo)phosphoranes like the stability of 2-thioxo-1,2λ^5-thiaphosphiranes depends on the nature of substituents at the phosphorus atom and at the methylene carbon atom. On the whole, the set of these substitutents is rather limited and comprises bulky groups [$(Me_3Si)_2N$, $(Bu^t)(Me_3Si)N$, Ph, 2,4,6-$Me_3C_6H_2$, 2,4,6-$Bu^t_3C_6H_2$, 2,6-$Me_2C_6H_3$, $SiMe_3$], which stabilise both the starting methylidenephosphine and the addition products of sulfur. The trimethylsilyl group at the methylene carbon atom and bis(trimethylsilyl)amino- [30] and mesityl (Mes) [34, 35] groups at the phosphorus atom manifest the greatest stabilising effect.

The reaction of mesityl[bis(trimethylsilyl)methylidene]phosphine (**13**) with sulfur gives methylidene(thioxo)phosphorane **14** and the corresponding 1,2λ^5-thiaphosphirane **15**, which were obtained in the crystalline form for the first time. This made it possible to carry out the X-ray diffraction investigation (see below).[34]

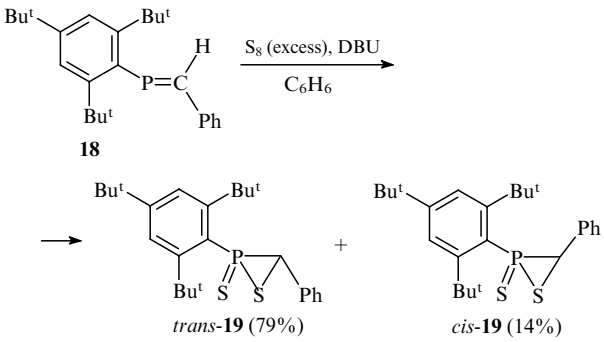


Later, by the example of 2,4,6-tri-*tert*-butylphenyl(diphenylmethylidene)phosphine (**16**) it was shown that the use of bases [*e.g.*, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU)] allows one to perform the addition of sulfur to triarylphosphaalkenes under very mild conditions (under room temperature) and to obtain the corresponding 2-thioxo-1,2λ^5-thiaphosphirane **17** in virtually quantitative yield.[36] At higher temperatures, the yield of the cyclic product decreases significantly due to its instability under these conditions.[37]

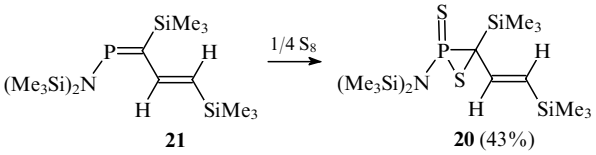


It may be suggested that the presence of different substitutents at the methylene carbon atom of methylidenephosphine would result in the formation of λ^5-thiaphosphiranes as a mixture of two stereoisomers, and this was observed in one study.[38]

The reaction of (*E*)-benzylidene(2,4,6-tri-*tert*-butylphenyl)-phosphine (**18**) with sulfur afforded 1,2λ^5-thiaphosphirane **19** as a mixture of isomers differing in the mutual arrangement of aryl groups. Taking into account the possible steric repulsion of the bulky aryl groups, the authors ascribed the *trans*-configuration to the major isomer.

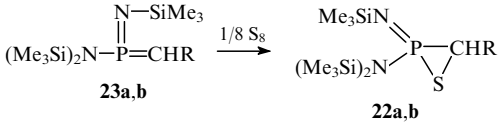


One might also expect the formation of two geometric isomers for the aforementioned 3-trimethylsilyl-2-bis(trimethylsilyl)-amino-2-thioxo-1,2λ^5-thiaphosphirane (**3**),[30] and for λ^5-thiaphosphirane **20,** which is the reaction product of 1-[bis(trimethylsilyl)amino]phosphadiene (**21**) with sulfur.[39]



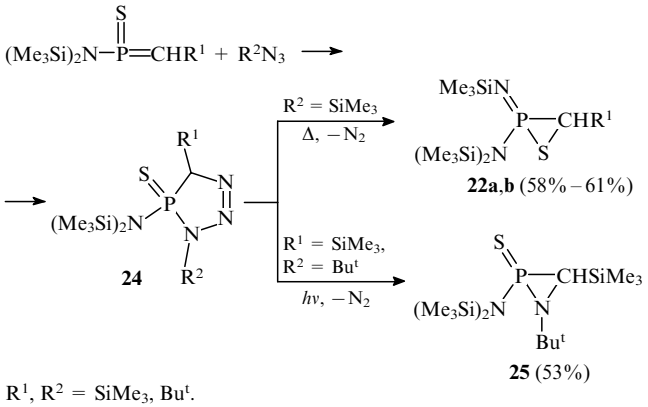
Nevertheless, in these cases the products were isolated as single isomers; their configurations were not discussed by the authors. Evidently, cycloaddition of sulfur to the intermediate methylidene(thioxo)phosphorane is the step determining the type of the λ^5-thiaphosphirane isomer formed. Most likely, this process is stereoselective and results in the sterically least hindered product.

2-Imino-1,2λ^5-thiaphosphiranes **22** are also available by [1 + 2]-cycloaddition of sulfur to methylidene(imino)phosphoranes **23**.[40]



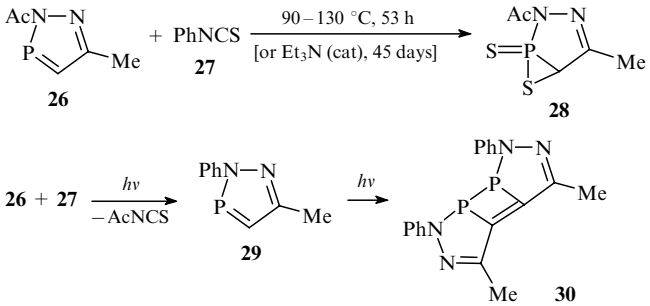
R = SiMe$_3$ (**a**, 72%), Bu^t (**b**, 77%).

Compounds **22** were also obtained starting from methylidene(thioxo)phosphorane by independent synthesis, which involved the addition of trimethylsilyl azide followed by the thermal decomposition of the Δ^1-triazaphospholenes **24** (R^2 = SiMe$_3$) formed.[40] It is noteworthy that the photochemical decomposition of the adduct **24** (R^2 = Bu^t) yields 2-thioxo-λ^5-azaphosphirane **25**.



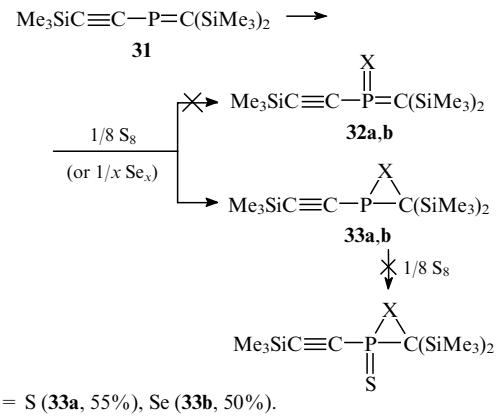
R^1, R^2 = SiMe$_3$, Bu^t.

An unusual reaction of 2-acetyl-5-methyl-1,2,3-diazaphosphole (**26**) with phenyl isothiocyanate (**27**) afforded a fused 2-thioxo-1,2λ^5-thiaphosphirane **28**.[41] The latter can be obtained either upon prolonged heating of the equimolar mixture of reactants or in the presence of a catalytic amount of triethylamine. Changing the reaction conditions (UV-irradiation) causes a change in its direction: the acetyl group at N(2) atom of the starting phosphole is substituted for the phenyl group of phenyl isothiocyanate, giving the product **29**, which is partially dimerised during the reaction affording compound **30**.



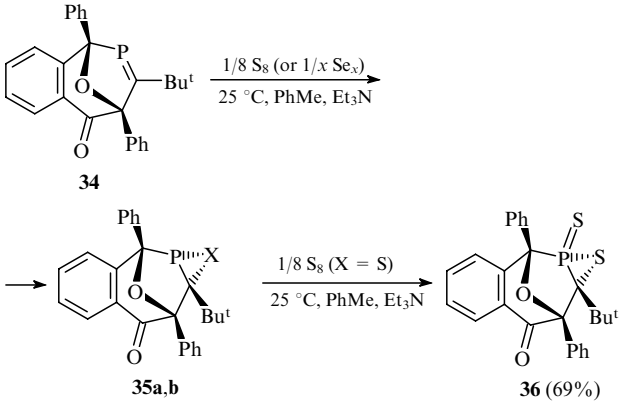
2. Synthesis of 1,2λ^3-thiaphosphiranes

As was mentioned above, the addition of one equivalent of sulfur to methylidenephosphine usually gives rise to methylidene(thioxo)phosphorane rather than to thiaphosphirane or to their mixture with the former predominating. Nevertheless, exceptions from this rule are documented. Thus the reactions of ethynylphosphaalkene **31** with sulfur and selenium do not result in methylidene(thioxo)- (**32a**) and methylidene(selenoxo)phosphoranes (**32b**), but occur as a [2 + 1]-cycloaddition yielding 1,2λ^3-thia- (**33a**) and 1,2λ^3-selenaphosphiranes (**33b**);[42] the latter do not react with the second equivalent of sulfur.



X = S (**33a**, 55%), Se (**33b**, 50%).

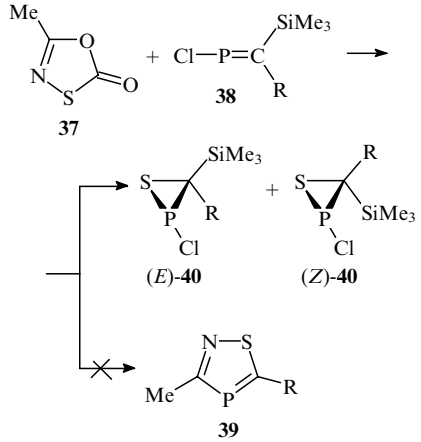
Analogously, in the reaction of tricyclic phosphaalkene **34** with sulfur (or selenium)[43] the sulfur (or selenium) atom adds stereoselectively to the P=C bond with the formation of tetracyclic λ^3-thiaphosphirane (**35a**) [(or λ^3-selenaphosphirane (**35b**)] where the sulfur (or selenium) atom is located *trans* relative to the bridging oxygen atom. However, in this case treatment of the sulfur-containing λ^3-thiaphosphirane with the second equivalent of sulfur under the same conditions readily gives the corresponding 2-thioxo derivative **36**.



X = S (**35a**), Se (**35b**).

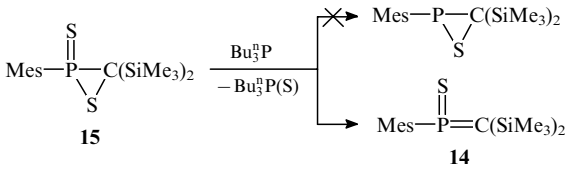
It should be noted that the use of a base (Et_3N) enables one to perform the above reaction under very mild conditions.

The reaction of 5-methyl-1,3,4-oxathiazol-2-one (**37**) with *P*-chloromethylidenephosphine **38** afforded, instead of the expected thiazaphospholenes **39,** a mixture of *E*- and *Z*-isomers of 2-chloro-1,2λ^3-thiaphosphiranes **40** (it is of note, that the interaction of 5-aryl-substituted oxathiazole with phosphines **38** yielded the corresponding thiazaphospholene).[44]

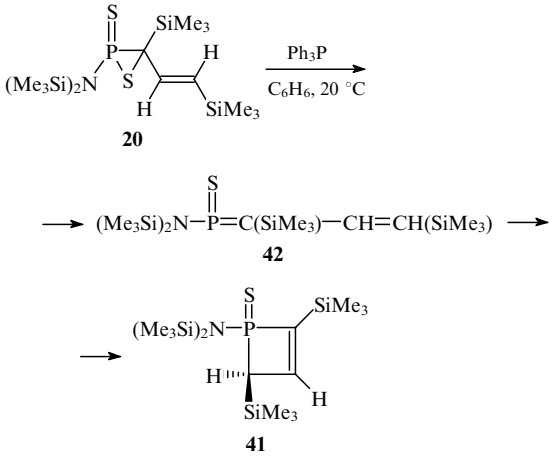


R = Ph (total yield 32%, *E* : *Z* = 75 : 25), $SiMe_3$ (22%).

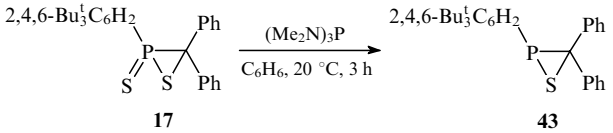
With general considerations in mind, one could suggest desulfurisation of the corresponding 2-thioxo-1,2λ^5-thiaphosphiranes as a possible approach to 1,2λ^3-thiaphosphiranes. However, 2-mesityl-3,3-bis(trimethylsilyl)-2-thioxo-1,2λ^5-thiaphosphirane (**15**) yields the corresponding methylidene(thioxo)-phosphorane **14** rather than the expected λ^3-thiaphosphirane under the action of tributylphosphine.[34, 35]



Desulfurisation of 2-thioxo-1,2λ^5-thiaphosphirane **20** obtained from 1-phosphadiene **21** (see above) with triphenylphosphine affords phosphacyclobutene **41**,[39] which is the intramolecular cyclisation product involving C=C and P=C bonds in the intermediate methylidene(thioxo)phosphorane **42**. The formation of the latter in the reaction was confirmed by ^{31}P NMR spectroscopy.

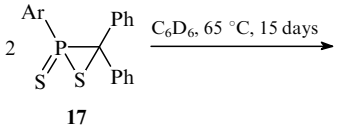


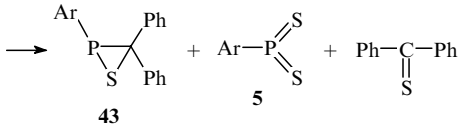
At the same time, 2-thioxo-2-(2,4,6-tri-*tert*-butylphenyl)-3,3-diphenyl-1,2λ^5-thiaphosphirane (**17**) is desulfurised readily giving the corresponding 1,2λ^3-thiaphosphirane **43**.[36, 37] Different phosphines were tested as desulfurisation agents; tris(dimethylamino)-phosphine proved to be the most efficient.



It is believed [37] that the distinction in the results of the reaction of different 2-thioxo-1,2λ^5-thiaphosphiranes suggests that the desulfurisation affording 1,2λ^3-thiaphosphirane [36, 37] is governed by kinetic control, while the reaction giving more stable methylidene(thioxo)phosphorane [34, 35] is governed by thermodynamic control.

It should be noted that triaryl-substituted 2-thioxo-1,2λ^5-thiaphosphirane **17** is unstable and decomposes in deuterated benzene yielding arylmetadithiophosphonate **5**, thiobenzophenone and the corresponding λ^3-thiaphosphirane **43**.[36]

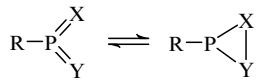




43 **5**

Ar = 2,4,6-$Bu^t_3C_6H_2$.

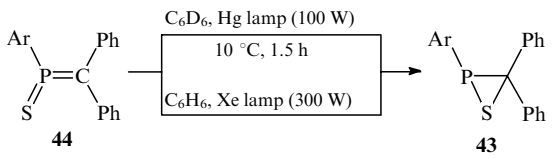
In many respects, the special interest in 1,2λ^3-thiaphosphiranes is caused by the existence of valence isomerism between $\sigma^3\lambda^5$-phosphoranes (**A**) and $\sigma^3\lambda^3$-phosphiranes (**B**).



A ($\sigma^3\lambda^5$) **B** ($\sigma^3\lambda^3$)

Thus thermodynamic conversion of methylidene(imino)phosphorane $Pr^i_2NP(=CHBu^t)(=NBu^t)$ (< 110 °C) and dimethylidenephosphorane $(Me_3Si)_2NP(=CHSiMe_3)_2$ (190 °C) to the corresponding azaphosphirane[45] and phosphirane[46] as well as the reverse transition of diazaphosphiranes (R = Pr^i_2N, Bu^t_2N; X = Y = NBu^t; 50 °C) to diiminophosphorane[47] have been reported earlier. Thermal or photoinduced isomerisation of sterically hindered diphosphene-*P*-sulfide (R = 2,4,6-$Bu^t_3C_6H_2$; X = S, Y = 2,4,6-$Bu^t_3C_6H_2P$) to $\lambda^3\sigma^3$-thiadiphosphirane has been described earlier.[48,49]

Yoshifuji and co-workers[36,37] were the first to obtain both valence isomers **A**($\sigma^3\lambda^5$) and **B**($\sigma^3\lambda^3$) in the individual state and to investigate in detail interconversions of 2,4,6-tri-*tert*-butylphenyl(dimethylidene)(thioxo)phosphorane (**44**) and the corresponding 1,2λ^3-thiaphosphirane **43**. Being irradiated by the light of a mercury[36] or xenon[37] lamp, phosphorane **44** gave λ^3-thiaphosphirane **43** as the main reaction product.



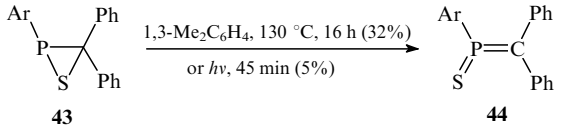
44 **43**

Ar = 2,4,6-$Bu^t_3C_6H_2$.

Irradiation by the Hg lamp (followed by flash chromatography and recrystallisation) and the Xe lamp, yielded 35% and 86% of compound **43** respectively.

The thermal transition of the linear form **44** to the cyclic form **43** for such a type of $\sigma^3\lambda^5$-phosphoranes was not observed. Thus, no traces of the cyclic isomer **43** could be detected upon refluxing of methylidene(thioxo)phosphorane **44** in toluene in the absence of light for 6 days.[36,37] On the contrary, the reverse thermally induced transition of λ^3-thiaphosphirane **43** to methylidene(thioxo)phosphorane **44** did occur.

Investigation of the temperature- and time-dependent transition **43** → **44** showed that the maximum yield of phosphoranes **44** (32%) was achieved upon 16-h reflux of a solution of λ^3-thiaphosphirane **43** in *m*-xylene in the dark. More prolonged heating of compound **43** under these conditions resulted in the decomposition of the methylidene(thioxo)phosphorane **44** that was formed. A decrease in the reaction temperature down to 100 °C along with a simultaneous increase in the heating time (7 days) gave no positive result: the yield of the linear isomer **44** was only 10%. Irradiation of λ^3-thiaphosphirane **43** by the mercury lamp afforded methylidene(thioxo)phosphorane **44** in 5% yield or as traces in a mixture with other unidentified products.



43 **44**

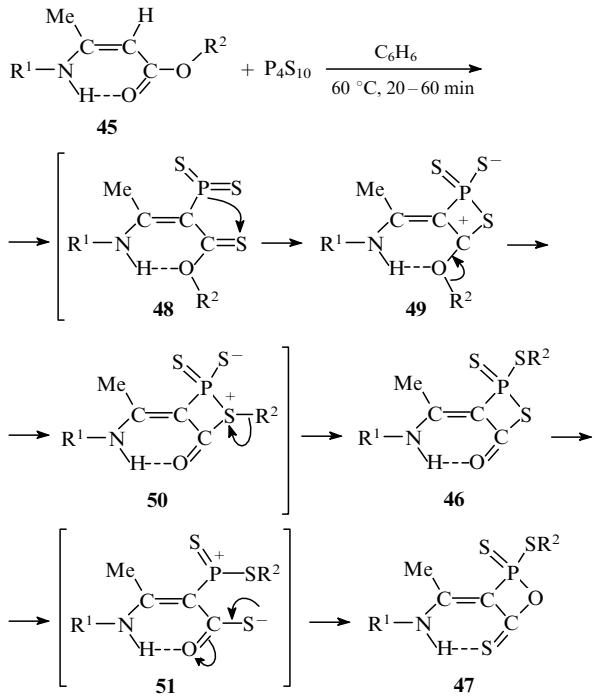
Ar = 2,4,6-$Bu^t_3C_6H_2$.

Thus, in the case of methylidene(thioxo)phosphoranes the conversion of the linear form to the cyclic one is only possible upon irradiation, while the reverse process can be both thermally and photochemically induced, though in the latter case to an considerably lesser extent.

III. 1,2-Thiaphosphetanes

The number of publications devoted to the synthesis of 4-membered 1,2-thiaphosphacyclanes, *i.e.*, 1,2-thiaphosphetanes, is very limited, all the known methods provide only 2-thioxo-1,2λ^5-derivatives.

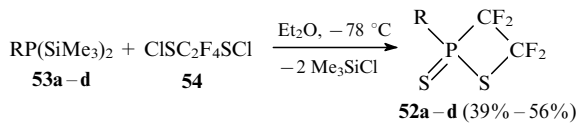
Thus the reaction of alkyl aminocrotonates **45** with P_4S_{10} gives 2-thioxo-1,2-thiaphosphetan-4-ones **46**.[50] However, being heated in benzene (for more than 30 min) or upon chromatographic purification on silica gel the latter rearrange spontaneously to the isomeric oxaphosphetanes **47**. The authors suggested that the possible reaction mechanism involves the addition of a PS_2 fragment and substitution of sulfur for the carbonyl oxygen (intermediate **48**), electrophilic attack by the phosphorus atom of the PS_2 group on the thiocarbonyl sulfur atom with the closure of the P,S-heterocycle **49** and a series of successive rearrangements resulting in migration of the alkyl radical from the oxygen atom to sulfur (intermediates **50**, **51**). Taking into account data from IR spectroscopy (using deuterium exchange), which show that the intramolecular hydrogen bond stabilizing the isomeric heterocycles formed is stronger by far in the thiocarbonyl product **47**, it was proposed that the thiaphosphetane **46** represents a product of kinetic reaction control and the isomeric oxaphosphetane **47**, of thermodynamic control. It should be noted that this method cannot be considered as a preparative one, since the product yields are only 1% – 4%.



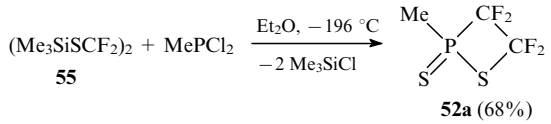
45 **48** **49** **50** **46** **51** **47**

R^1 = Me, Pr^n; R^2 = Me, Et.

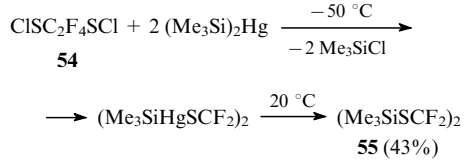
Two approaches to the synthesis of tetrafluoro-1,2-thiaphosphetanes **52** are described.[51] One of them is based on the reaction of [bis(trimethylsilyl)]phosphines **53** with 1,1,2,2-tetrafluoroethane-1,2-bissulfenyl chloride (**54**), which has found application in the preparation of partially fluorinated heterocycles,[52–54] and the second one makes use of the reaction of dichloro(methyl)-phosphine with 4,4,5,5-tetrafluoro-2,2,7,7-tetramethyl-3,6-dithia-2,7-disilaoctane (**55**).



R = Me (**a**), Bu^t (**b**), Ph (**c**), 2,4,6-Bu$^t_3$C$_6$H$_2$ (**d**).

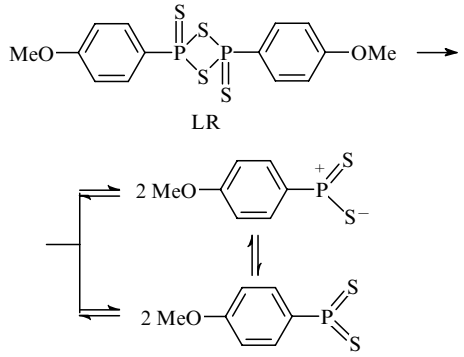


The latter reaction proceeds extremely readily at low temperature and results in the desired heterocycle **52a** in 68% yield, but since the fluorinated agent **55** used in this reaction was obtained in turn from 1,1,2,2-tetrafluoroethane-1,2-bissulfenyl chloride (**54**),[51] the overall yield of the perfluorinated heterocycle **52a** according to this procedure is somewhat lower.



The application of the Lawesson reagent for the synthesis of unsaturated 5- and 6-membered P,S-heterocycles has already been mentioned. This is based on the reactions of the LR with alkenes,[20] the simplest 1,3-dienes [55–58] and α,β-unsaturated ketones.[27,59]

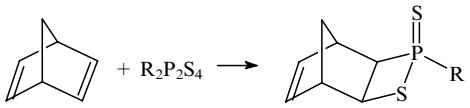
The ability of the LR to enter into cycloaddition reactions with multiple bonds of different types is believed to be connected with its existence in solution [60,61] or at elevated temperatures [28,31] (and all the above reactions take place under rather drastic conditions) in an equilibrium with metadithiophosphonate.[31,32,62] The latter is often referred to as dipolar dithiophosphonium ylide, since its reactivity is similar to that of the Wittig reagents.



The addition of the Lawesson reagent to the double bond of dicyanomethylidene compounds **56** aiming at obtaining 2-thioxo-1,2-thiaphosphetanes **57** was investigated.[63] This was the first example of the application of LR for such a purpose. The putative reaction mechanism involves nucleophilic attack by the monomeric LR fragment on the sp^2-carbon atom resulting in the intermediate **58**, which undergoes intramolecular cyclisation (Scheme 2).

Unsaturated thioamides **59** are formed in this reaction in parallel (as a result of partial hydrolysis of one cyano group in compound **56** under the reaction conditions followed by the substitution of sulfur for the oxygen atom in compound **60** under the action of LR). In the case of benzylidenemalonodinitrile (**56**, R = Ph), the latter reaction pathway is the only one (see Scheme 2).

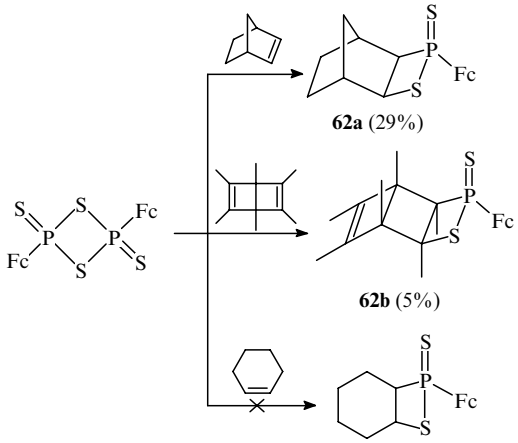
An effective straightforward synthesis of fused 2-thioxo-1,2-thiaphosphetanes has been proposed [58] based on the addition of dithiaphosphetane disulfides $R_2P_2S_4$ to sterically hindered alkenes. Thus exo-[2 + 2]-cycloaddition of $R_2P_2S_4$ to the multiple bond of norbornadiene (NBD) results in a series of stable tricyclic 2-thioxo-1,2-thiaphosphetanes **61**.



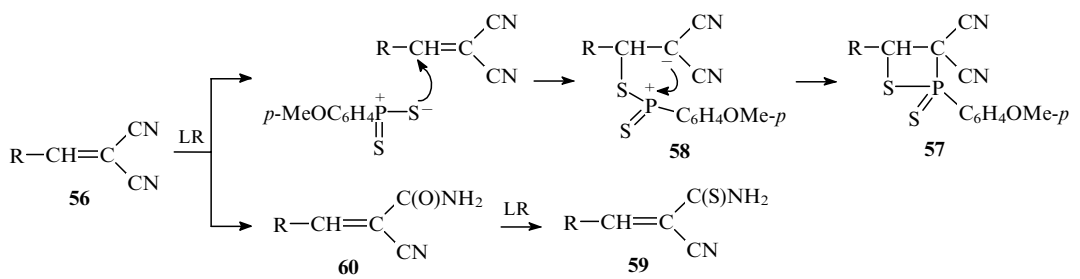
R = 4-MeOC$_6$H$_4$ (**a**), 3-Bu^t-4-OBu^{t}C$_6$H$_3$ (**b**), (C$_5$H$_5$)Fe(C$_5$H$_4$) ≡ Fc (**c**), (C$_5$H$_4$Me)Fe(C$_5$H$_3$Me) (**d**).

The rate of this reaction is determined mostly by the solubility of the starting dithiaphosphetane. Thus bis(methylferrocenyl)dithiadiphosphetane — [(C$_5$H$_4$Me)Fe(C$_5$H$_3$Me)]$_2$P$_2$S$_4$ reacts with NBD at room temperature to give the [2 + 2] adduct **61d** in virtually quantitative yield in 14 h ($CDCl_3$, NMR experiment). The ferrocenyl derivative **61c** is obtained upon heating the reactants in the absence of a solvent at 80 °C for 16 h (the product yield is 69%). The reactions of bis(3-*tert*-butyl-4-*tert*-butoxyphenyl)dithiaphosphetane and the Lawesson reagent itself with NBD afford the target tricyclic compounds **61b** and **61a** in 44% and 13% yields, respectively.

Using $Fc_2P_2S_4$ as an example, an attempt was undertaken to evaluate the scope of the method proposed. The cycloaddition of $Fc_2P_2S_4$ to cyclohexene, norbornene and hexamethylbi-



Scheme 2



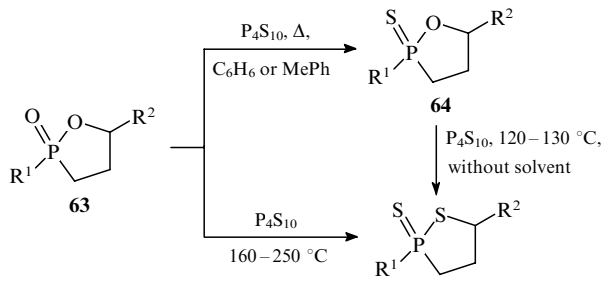
R = C$_6$H$_4$OH-*o*, C$_6$H$_4$OMe-*p*, C$_6$H$_4$NO$_2$-*p*, 2-thienyl.

cyclo[2.2.0]hexa-2,5-diene was investigated.[58] As cyclohexene did not react with $Fc_2P_2S_4$, the authors supposed that only sterically strained alkenes are able to react according to the cycloaddition scheme under such mild conditions giving products of the type **62**.

In conclusion it should be mentioned that the main methods for obtaining 1,2-thiaphosphetanes, excluding the perfluorinated rings, involve the addition of phosphorus pentasulfide and the Lawesson reagent to various unsaturated substrates.

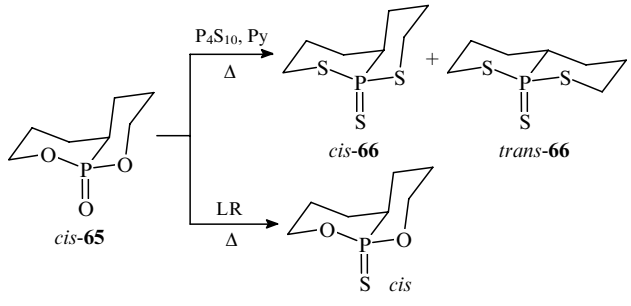
IV. 1,2-Thiaphospholanes and 1,2-thiaphosphinanes

The first representatives of the 5- and 6-membered saturated 1,2-thiaphosphacyclane family have been obtained upon exhaustive replacement of oxygen atoms by sulfur in the well-known 2-oxo-1,2-oxaphosphacyclanes.[24, 64, 65] Such a replacement occurs under the action of an excess of phosphorus pentasulfide on the parent compounds, *e.g.*, 2-oxo-1,2-oxaphospholanes **63**, under drastic conditions (at 160–250 °C). Under milder conditions (reflux in benzene[64] or toluene[24, 65]), only the phosphoryl oxygen atom is replaced affording 2-thioxo-1,2-oxaphospholanes **64**. Their yields range from 17% to 58% depending on the substitutent R^1 at the phosphorus atom. The intermediate 2-thioxo-1,2-oxaphospholanes **64** are thermally stable,[64] in particular, upon distillation (80–130 °C) they do not undergo thione–thiol rearrangement, which would result in the migration of the sulfur atom into the ring. Replacement of the oxygen atom in the oxaphospholane ring by sulfur requires heating of compounds **64** with P_4S_{10} either at 120–130 °C (2 h without a solvent,[64] 6 h in chlorobenzene[65]) or in an autoclave at 250 °C (in toluene).[24]



R^1 = Me, Et, Ph; R^2 = H, Me.

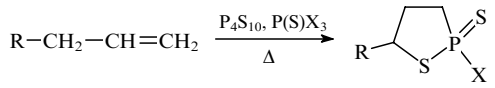
Using this procedure, Polozov and Cremer[66] have performed exhaustive replacement of oxygen atoms by sulfur in both fused 1,2-oxaphospholane rings of the *cis*-isomer of 2,10-dioxaphosphabicyclo[4.4.0]decane 1-oxide **65** (P_4S_{10}, pyridine, reflux).



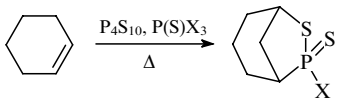
It was found that the stereochemistry of the starting bicycle can be changed during the reaction; the corresponding trithio derivative **66** was obtained as a mixture of *cis*- and *trans*-isomers in a 1.6 : 1 ratio. A milder thiylating agent, LR, enables only a partial replacement of the oxygen atoms in the substrate **65**, and the configuration of the initial *cis*-isomer is retained.

Numerous methods to obtain various 5- and 6-membered 2-oxo-1,2-oxaphospholanes is described in the literature. Evidently, the corresponding 2-thioxo-1,2-thia derivatives may be synthesised from them using phosphorus pentasulfide.

A method different in principle to obtain 2-thioxo-1,2-thiaphospholanes was proposed by Wing.[21, 67] It is based on direct reaction of an unsaturated hydrocarbon, phosphorus pentasulfide and thiophosphoric acid halide under drastic conditions (autoclave, 150–200 °C, 10–18 h). When cyclic alkenes (*e.g.*, cyclohexene) are used as the starting substrates, bicyclic compounds are formed with one of the rings representing 1,2-thiaphospholane. These reaction products are used as antioxidant additives for motor oils, polymers and agrochemicals.

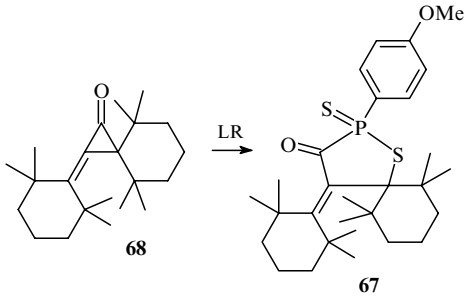


R = H, Me, Et; X = Cl, Br.

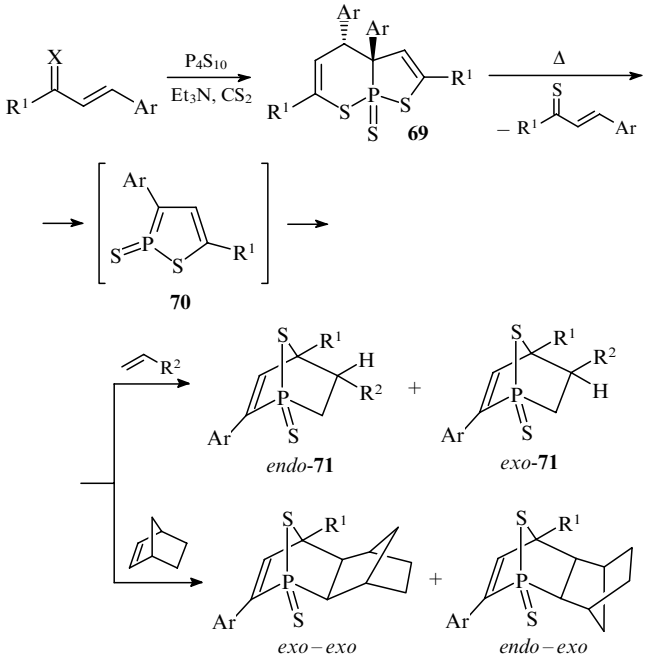


X = Cl, Br.

Conjugated 2-thioxo-1,2-thiaphospholanes **67** substituted in the ring were obtained by the reaction of the Lawesson reagent with a sterically crowded cyclohexylidenecyclopropanone **68**.[68] Nominally, this reaction may be considered as the insertion of the LR monomeric fragment (dithiophosphonium ylide) into the strained C–C bond of the starting cyclopropanone.



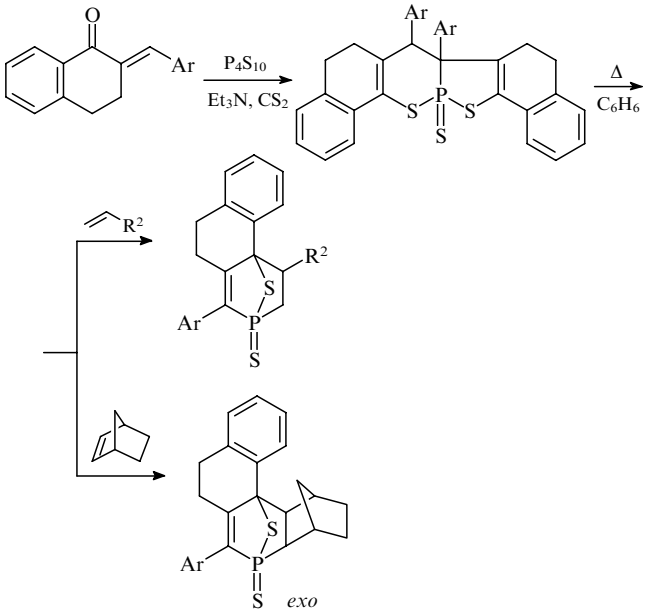
2,9-Dithia-1-thioxophosphabicyclo[4.3.0]nona-3,7-dienes **69** should be mentioned as precursors of another type of fused 2-thioxo-1,2-thiaphospholanes; these are formed in the reaction of α,β-unsaturated ketones with P_4S_{10} in the presence of



X = O, S; Ar = Ph, 4-ClC_6H_4, 4-$MeOC_6H_4$; R^1 = Bu^t, Ph, 4-ClC_6H_4, 4-$MeOC_6H_4$; R^2 = CN, Ph, OBu.

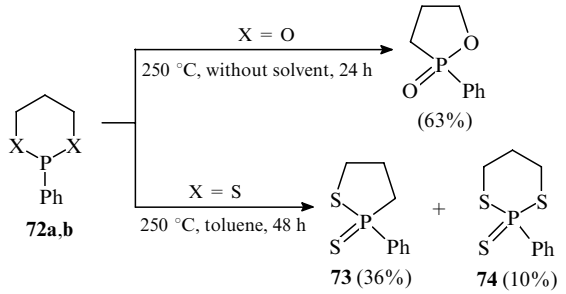
Et_3N.[69–71] Thermolysis of such compounds in benzene occurs with the generation of 2-thioxo-1,2-thiaphospholes **70**, which act as cyclic heterodienes in [4 + 2]cycloaddition reactions with acrylonitrile,[69,70] styrene,[70] butyl vinyl ether [70] and norbornene.[70] In most cases, the cycloaddition products are obtained as mixtures of *exo*- and *endo*-isomers **71** or *exo*–*exo*- and *endo*–*exo*-isomers (in the case of norbornene), usually with the *endo*-isomer (when R^2 = CN, Ph) and *exo*–*exo*-isomer for the norbornene derivative predominating. The configuration of these compounds was established using NMR spectroscopy [69,70] and X-ray diffraction analysis.[71] For butoxy-substituted polycarbocycles, it was not possible to establish the geometry of the molecule.

(*E*)-Arylmethylidene-1,2,3,4-tetrahydronaphthalen-1-one can be used as an α,β-unsaturated ketone, too.[70]



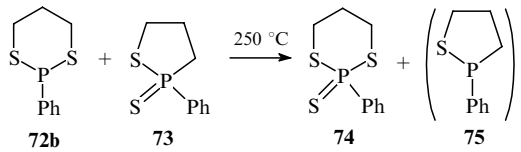
Ar = Ph, 4-ClC_6H_4, 4-$MeOC_6H_4$.

Some processes can be applied for the preparation of both 1,2-oxaphosphacyclanes and their 1,2-thia analogues. Thus an intramolecular thermal isomerisation of the Arbuzov rearrangement type is characteristic of 1,3,2λ³-diheterophosphacyclanes **72** (X = O, S); this occurs with a ring contraction.[24,63] The reaction occurs more readily and in higher yields for the corresponding oxygen derivatives.

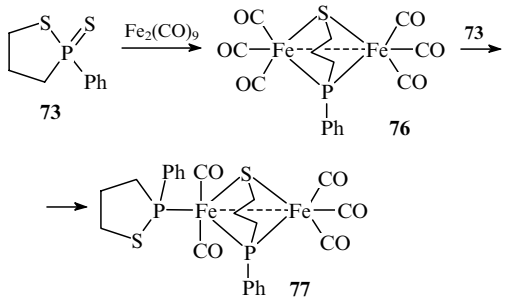


X = O (**72a**), S (**72b**).

In the case of 1,3,2λ³-dithiaphosphinane **72b** (X = S), both 2-thioxo-1,2-thiaphospholane (**73**) and 2-thioxo-1,3,2-dithiaphosphinane (**74**) are formed, the latter being the addition product of sulfur to the substrate. This result is explained by the possible reaction of 1,3,2λ³-dithiaphosphinane **72b** with 2-thioxo-1,2λ⁵-thiaphospholane **73** under drastic reaction conditions.

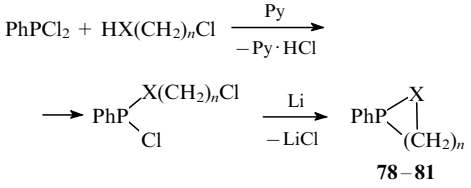


However, the second reaction product, *viz*., 2-phenyl-1,2λ³-thiaphospholane (**75**), was not isolated and the authors failed to detect it by spectroscopic methods. Nevertheless, in the reaction of 2-thioxo-1,2λ⁵-thiaphospholane **73** with $Fe_2(CO)_9$ such a P(III) heterocycle was obtained as a ligand bound to the iron atom. The reaction proceeds in two steps. First, the complex **76** is formed having bridging Fe–S–Fe and Fe–P–Fe bonds, which then reacts with the second molecule of 1,2λ⁵-thiaphospholane **73**. As a result of selective reduction of the P=S group in compound **73**, the complex **77** is formed comprising the 1,2-thiaphospholane ligand.[72]



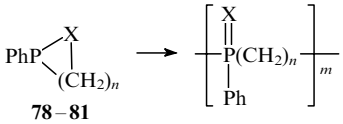
It should be emphasised that the aforementioned synthetic routes to 5- and 6-membered 1,2-thiaphosphacyclanes are limited by the possibility of obtaining products with only a thiophosphoryl group.

An alternative general method for the formation of 1,2-heterophosphacyclic structure has been proposed by Kobayashi and co-workers [23,73] who obtained P,O- and P,S-heterocycles **78**–**81** bearing a three-valent phosphorus atom. This method involves the synthesis of *O*- or *S*-(ω-chloroalkyl) phenylphosphonochloridites followed by their intramolecular cyclisation under the action of metallic lithium.



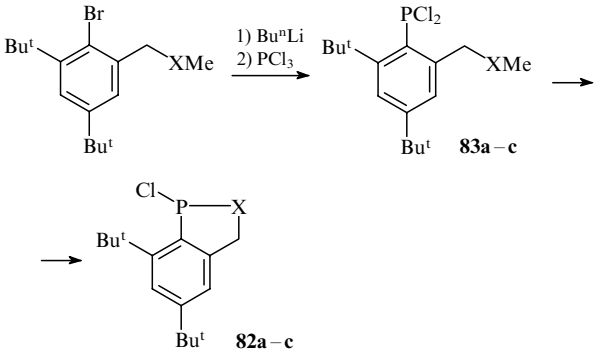
Compound	X	*n*	Yield (%)
78	O	3	37
79	O	4	18
80	S	3	10
81	S	4	5

Independent of the nature of the X atom, 1,2-heterophospholanes (n = 3) are formed in higher yields than 1,2-heterophosphinanes (n = 4); in each class of compounds the yields of oxygen derivatives are higher than those of the sulfur-containing ones. Though in general the yields of both 1,2λ³-oxaphosphacyclanes **78**, **79** and 1,2λ³-thiaphosphacyclanes **80**, **81** in this reaction are moderate, the reaction is rather simple to perform. Compounds **78**–**81** were used as monomers in polymerisation.[23,74] The polymerisation occurs upon either the action of cationic initiators or heating and is accompanied by ring-opening.



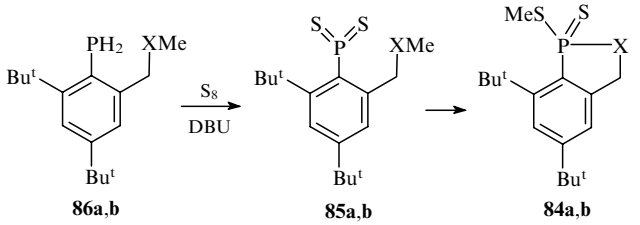
The poly(phosphine oxides) and poly(phosphine sulfides) obtained possess good chelate-forming properties including high extraction capacity towards the ions of some heavy metals.[23] Poly(phosphine sulfides) extract Pd^{2+} and Hg^{2+} cations quantitatively from solutions in a wide range of pH, Cu^{2+} ions are extracted more efficiently in weakly alkaline media. The chelating capacity of poly(phosphine sulfides) exceeds that of the corresponding poly(phosphine oxides) towards Pd^{2+} and Hg^{2+} ions and is comparable for Hg^{2+} ions and significantly lower for uranyl ions UO_2^{2+}.

Fused 2-chloro-1,2λ^3-heterophospholanes **82a**–**c** (X = O, S, Se) are formed as a result of the intramolecular cyclisation of 2,4-di-*tert*-butyl-6-(methylheteromethyl)phenyldichlorophosphines **83a**–**c**.[75] It should be noted that the ease of formation of such heterocyclic compounds decreases in the order Se > O ≫ S.



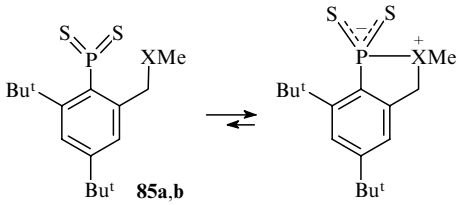
Compound	X	Cyclisation conditions	
		T /°C	t /h
82a	O	25	10
82b	S	25	144
		66	3
82c	Se	< 0	–

2-Thioxo-1,2λ^5-analogues of such fused heterocycles (compounds **84a**,**b**) were obtained by an intramolecular rearrangement of σ^{3}λ^5-metadithiophosphonates **85a**,**b**, obtained in turn by sulfur addition to the corresponding primary phosphines **86a**,**b** in the presense of 1,8-diazabicyclo[5.4.0]undec-7-ene.‡

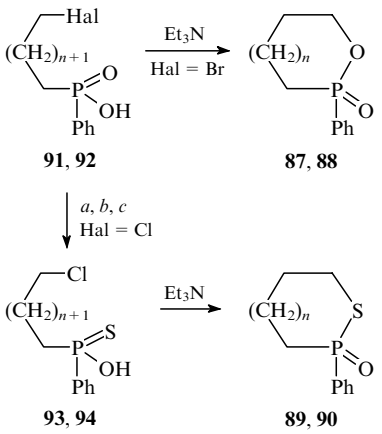


X = S (**a**), Se (**b**).

In this case, too, the cyclisation rate of methylselenomethyl-substituted derivative **85b** was much higher than for its sulfur analoque **85a**. The same applies to the formation of compounds **85a**,**b**. Thus the reaction of the phosphine **86b** with sulfur proceeds within 1 day at ambient temperature resulting in 2-thioxo-1,2-selenaphospholane **84b** in virtually quantitative yield. The formation of dithioxophosphorane **85b** could be observed only by NMR spectroscopy due to its rapid cyclisation. In the preparation of the corresponding 1,2λ^5-thiaphospholane **84a**, the intermediate stable metadithiophosphonate **85a** was isolated in the pure state and its cyclisation proceeded either upon heating of the solution in toluene in a sealed tube for 1 h or on heating without the solvent for 1 min at 180 °C (above the melting point of 171–173 °C). As the chemical shifts of metadithiophosphonates **85** [δ_P = 159.9 (X = Se) and 161.8 (X = S) in $CDCl_3$] in ^{31}P NMR spectra are signifficantly shifted upfield in comparison with the signal of the 2,4,6-tri-*tert*-butylphenyl analogue, 2,4,6-Bu$^t_3$C$_6$H$_2$PS$_2$ (δ_P = 298.2 in $CDCl_3$), the authors suggested the existence of a strong interaction between phosphorus and chalcogen atoms in the methylthio(seleno)methyl substituent as shown below.



To obtain 2-oxo-1,2λ^5- (**87**, **88**) or 2-oxo-1,2λ^5-thiaphosphacyclanes (**89**, **90**), one may use an intramolecular alkylation of ω-chloroalkylphosphinous (**91**, **92**) and -thiophosphinous acids occurring in the presence of triethylamine.[76,77] Virtually no side products are formed during this cyclisation and the reaction kinetics is approximately first order. In this case, too, the five-membered heterocyclic products were formed more rapidly than their six-membered analogues: the ratio of the rate constants for 5- and 6-membered heterocycle formation ($k^5 : k^6$) is 4.3 (for the phosphinate anion) and 30 (for the thiophosphinate anion). It should be noted that despite cyclisation of thiophosphinous acids proceeding under mild conditions and 2-oxo-1,2-thiaphosphacyclanes **89**, **90** being formed in fairly high yields (85%–90%), the starting thioacids **93**, **94** as such were obtained by multi-step procedures complicated by numerous side reactions from the corresponding phosphoryl analogues **91**, **92** in low yields and of 90%–95% purity only.

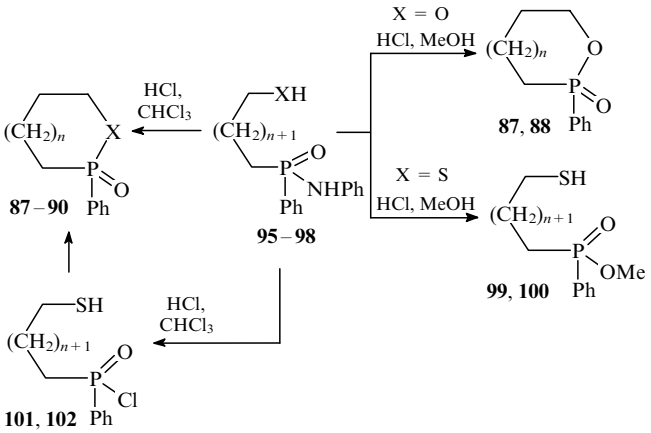


Hal = Cl, Br; n = 0 (**87**, **89**, **91**, **93**), 1 (**88**, **90**, **92**, **94**);
(*a*) $(COCl)_2$; (*b*) P_4S_{10}, $HCONMe_2$ (Cat.), dioxane, reflux;
(*c*) H_2O, acetone.

Harger and co-workers[78,79] carried out the comparative investigation of acid-catalysed cyclisation of ω-hydroxy- (**95**, **96**)[78] and ω-mercaptoalkylphenylphosphinous (**97**, **98**) acid anilides.[79] In this case, the sharp distinction in reactivities of HS and HO groups was observed. Thus oxaphospholanes (**87**) and oxaphosphinanes (**88**) were readily formed in both methanol and chloroform [$k^5 : k^6$ = 70 (in $CHCl_3$) and 50 (in MeOH), at 20 °C, the cyclisation time for the anilide **95** is 1 min and 15 min for the anilide **96**]. At the same time, in MeOH the anilides **97**, **98** were converted into the corresponding esters **99**, **100** due to the nucleophilic substitution of the methoxy group for the anilide residue. In $CHCl_3$ in the presence of gaseous HCl, the cyclisation of anilides **97**, **98** leading to 1,2-thiaphospholane **89** (yield ~75%) and 1,2-thiaphosphinane **90** (yield ~2%) takes place. It should be noted, that such a cyclisation proceeds *via* the intermediate

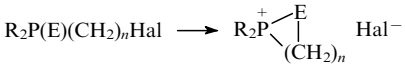
‡ Phosphines **86a**,**b** were obtained by reduction of the corresponding aryldichlorophosphines **83** or *O*-ethyl arylphosphinates with $LiAlH_4$.

formation of phosphinic chlorides **101**, **102**, which were detected in the reaction mixtures by NMR spectroscopy.



X = O: n = 0 (**87**, **95**), 1 (**88**, **96**);
X = S: n = 0 (**89**, **97**, **99**, **101**), 1 (**90**, **98**, **100**, **102**).

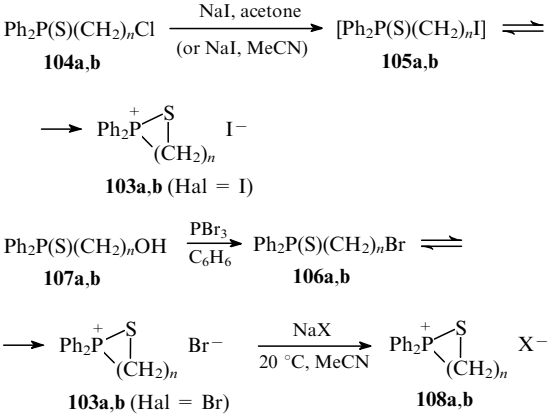
Extensive research to the development of a general approach to 1,2-monoheterophosphacyclanes of diverse structures has been performed by Mastryukova and co-workers in recent years. The method is based on the intramolecular E-alkylation of ω-halogenoalkyl-substituted compounds of tetracoordinate phosphorus bearing a P=E group.



R = Alk, Ar; E = S, O, NR′; Hal = Cl, Br, I; n = 3, 4.

For the first time, this reaction has been employed for the synthesis of 2,2-diphenyl-1,2λ⁴-thiaphosphacyclanium iodides **103a**,**b** (E = S, n = 3, 4; Hal = I), which were obtained by refluxing solutions of the thermally stable ω-chloroalkyldiphenylphosphine sulfides **104a**,**b** in either acetone or acetonitrile with NaI.[80] The reaction proceeds *via* the formation of the corresponding ω-iodoalkyldiphenylphosphine sulfides **105a**,**b**, which was confirmed by ^{31}P NMR spectroscopy. In contrast to ω-chloro-substituted derivatives **104a**,**b**, ω-bromoalkylphosphine sulfides **106a**,**b**, obtained from the corresponding hydroxy derivatives **107a**,**b** and isolated in a pure state, underwent rather easy transformations into cyclic thiaphosphacyclanium bromides **103a**,**b** (Hal = Br) (heating at 100 °C without a solvent).[81,82] Starting from these compounds, one could prepare the corresponding perchlorates and tetrafluoroborates **108a**,**b** by an exchange reaction.[83]

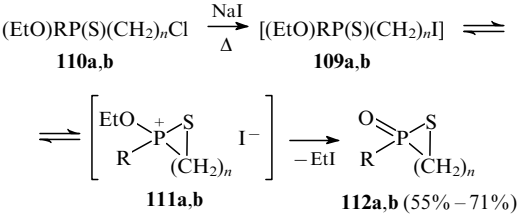
The ease of formation of the cyclic salts **103a**,**b** (Hal = Cl, Br, I) is determined first of all by the nature of the halogen atom and



n = 3 (**a**), 4 (**b**); X = ClO_4, BF_4.

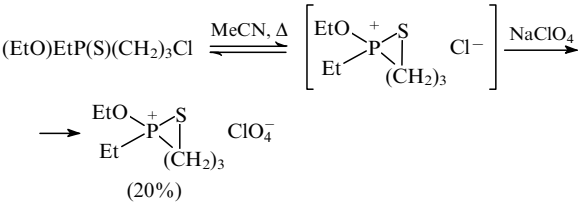
the length of the alkyl chain in the linear starting compound. Thus other conditions being equal, the iodides **105a**,**b** undergo cyclisation more rapidly than bromides **106a**,**b**, whereas chlorides **104a**,**b** do not undergo the intramolecular *S*-alkylation upon either refluxing in acetone or on heating in the absence of a solvent (140 °C, 1.5 h). The 1,2-thiaphospholanium salts (**103a**, n = 3) are formed more rapidly than 1,2-thiaphosphinanium salts (**103b**, n = 4). It should be noted that a tautomeriic equilibrium between the cyclic form and the starting linear compond is established in solutions of 1,2-thiaphosphacyclanium salts, which is a rare case of ring-chain halogenotropic tautomerism (see below).

Intramolecular S-alkylation of ω-iodoalkyl-substituted thiophosphoryl compounds bearing an alkoxy group at the phosphorus atom **109a**,**b** obtained *in situ* from the corresponding chloro derivatives **110a**,**b**,§ dealkylation of the quazi-phosphonium salt formed takes place according to the second step of the Arbuzov rearrangement resulting in 2-oxo-1,2-thiaphosphacyclanes **112a**,**b**.[83–85] In this case, too, five-membered heterocyclic compounds (n = 3) are formed more rapidly than the six-membered ones (n = 4) ($k^5 : k^6 \approx 2$). In addition to the alkyl chain length, the solvent used influences the cyclisation rate: the reaction is faster in acetonitrile than in acetone, which may be connected with both the higher polarity and higher boiling point of MeCN. The nature of the substituent R at the phosphorus atom influences the cyclisation rate to a lesser extent (it decreases in the order Et > Ph > OEt). The yield of 1,2-thiaphosphacyclanes **112a**,**b** is 82%–96% (according to the ^{31}P NMR data obtained for the reaction mixture) and 55%–71% (after isolation by chromatography or recrystallisation).



n = 3 (**a**), 4 (**b**); R = Et, Ph, OEt, NEt_2.

The mechanism of the reaction was established quite reliably as the authors succeeded in isolating the intermediate quasi-phosphonium salt bearing the ethoxy group starting from compound (EtO)EtP(S)$(CH_2)_3$Cl if the nucleophilic chloride anion is replaced by the perchlorate anion.[84,85] It should be noted that this is the first case where the intermediate product of the thione–thiol rearrangement of a phosphorus thioacid ester was isolated as an individual compound.

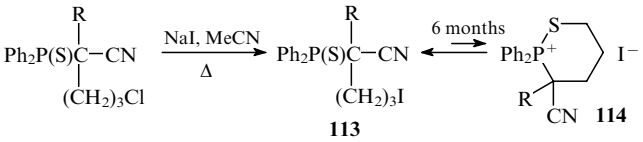


Thus, intramolecular S-alkylation represents a general method for the preparation of thiaphosphacyclanes. A wide range of thiophosphoryl compounds bearing a ω-halogenoalkyl moiety in the molecule undergo the above-mentioned intramolecular transformation. In particular, cyano-substituted mono- and bicyclic 1,2-thiaphosphacyclanes were obtained from ω-halogeno-

§ Chloroalkyl-substituted thiophosphinates and thiophosphonates **110** are thermally stable liquids that can easily be distilled (b.p. = 105–165 °C/2–3 Torr). 3-Chloropropyl(phenyl)thiophosphinate (R = Ph, n = 3) is the only exception, it undergoes the intramolecular thione–thiol rearrangement into 2-oxo-2-phenyl-1,2-thiaphospholane upon distillation *in vacuo* (160–170 °C/2 Torr).

alkyl-substituted thiophosphorylacetonitriles according to this scheme.[86–93]

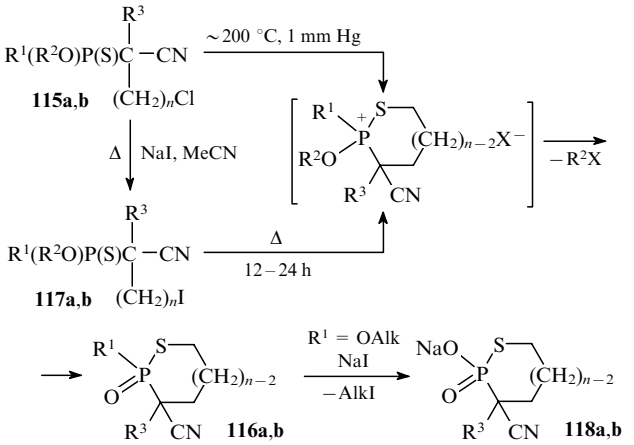
As one would expect, the introduction of an electron-withdrawing cyano group at the α-position with respect to the phosphorus atom results in a decrease in the nucleophilicity of the thione sulfur atom and an increase in the stability of the linear form of cyano-substituted ω-halogenoalkyl sulfides (even the ones with a terminal iodine atom). Thus if non-functionalised ω-iodoalkylphosphine sulfides **105** undergo cyclisation *in status nascendi* under the action of NaI on chloro derivatives **104**, the cyano-substituted analogues **113** cyclise very slowly and in the equilibrium position the proportion of the corresponding phosphacyclanium salt **114** does not exceed 15%.[89]



113 **114**

R = H, Me.

However, the α-CN group favours subsequent dealkylation in the phosphacyclanium salts formed (the intramolecular thione–thiol rearrangement) with at least one alkoxy substituent at the phosphorus atom. Thus, ω-chloroalkyl derivatives **115a**,**b** undergo cyclisation to the 3-cyano-2-oxo-1,2-thiaphosphacyclanes **116a**,**b** upon distillation *in vacuo*.[86–90,93] Under these conditions, the cyano-substituted thiaphospholanes **116a** were formed faster and in higher yields than thiaphosphinanes **116b**. It should be noted, that the radical R^3 at the carbon atom influences sufficiently the yields of the target products (if R^3 = Alk, the yields decrease drastically), while the radical R^1 at the phosphorus atom virtually has no influence on the product yields. The cyclisation of the corresponding ω-iodoalkyl-substituted thiaphosphorylacetonitriles **117a**,**b**, formed *in situ* from the chloro derivatives proceeds under milder conditions. The yields of 3-cyano-2-oxo-1,2-thiaphosphacyclanes obtained in this way are usually higher than those of the same compounds prepared by distillation. If the starting substrate represents the thiophosphonate (R^1 = OAlk), the cyclisation of chloro derivatives **115a**,**b** carried out in the presence of an excess of NaI is accompanied by dealkylation of both alkoxy groups at the phosphorus atom and leads to the formation of sodium salts of the corresponding cyclic acid **118a**,**b** in virtually quanitative yields.[89,93]

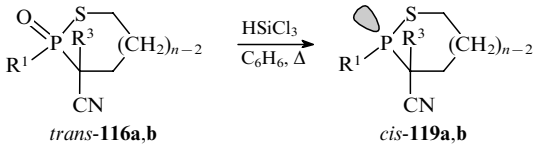


n = 2 (**a**), 3 (**b**); R^1 = Me, Ph, OEt, OPr^n; R^2 = Et, Pr^n, Pr^i, Bu^i; R^3 = H, Me, Et, $(CH_2)_3Cl$; X = Cl, I.

Cyano-substituted thiaphosphacyclanes **116a**,**b** were formed as mixtures of two stereoisomers differing in the mutual disposition of the cyano group and the phosphoryl oxygen atom relative to the ring plane (*cis*-$R_{P*}R_{C*}$ and *trans*-$R_{P*}S_{C*}$). The isomer ratio varies from 7 : 3 to 3 : 7 depending on the cyclisation method.[89] In most cases, the mixtures were separated into individual isomers the structures of which were investigated by X-ray diffraction analysis.

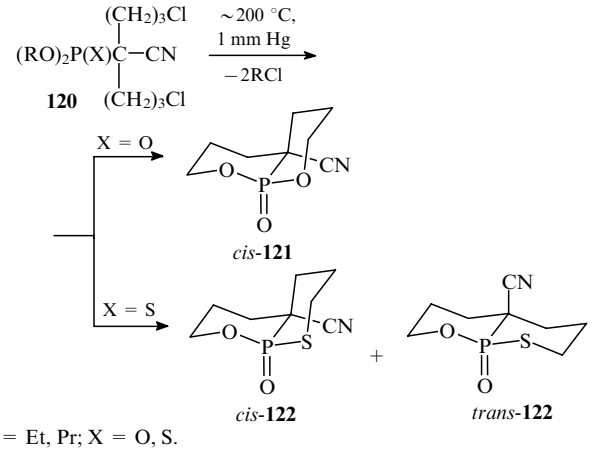
The reversible diastereomeric transformations were found to be a characteristic feature of 3-cyano-2-oxo-1,2λ^5-thiaphosphinanes **116b** where R^3 = H. Thus, the isomeric mixture obtained upon cyclisation transforms with time into a single isomer with the most favourable arrangement of the substituents as regards the general anomeric effect (*cis*-isomer for R^1 = OAlk and *trans*-isomer for R^1 = Me). In benzene solution, the isomer isolated in the pure state gradually transforms into an equilibrium mixture of both isomers.[86] Since no transformation of an isomeric mixture of **116b** R^3 = Alk into an individual isomer and the reverse transformation of any individual isomer into an equilibrium mixture were observed, a carbanion mechanism was suggested for such diastereomeric transformations.[88,90,93] It is believed that the process involves dissociation of a rather acidic hydrogen atom at position 3, the formation of a flattened carbanion and subsequent proton addition with the inversion of configuration of the asymmetric carbon atom in the ring.

The reduction of 3-cyano-2-oxo-1,2λ^5-thiaphosphacyclanes **116a**,**b** by trichlorosilane, which proceeds smoothly with retention of the ring structure, cyano group and stereochemistry, results in the corresponding 1,2λ^5-thiaphosphacyclanes **119a**,**b** possessing a tricoordinate phosphorus atom,[90] which were used as bidentate ligands for Co(II), Ni(II) and Rh(I) complexes.



n = 2 (**a**), 3 (**b**); R^1 = Me, Ph; R^3 = H, Alk.

An efficient route to 6-cyano-2-oxa-10-thia(oxa)phosphabicyclodecane 1-oxides, which were previously accessible with difficulty, was elaborated based on thermal cyclisation of bis(3-chloropropyl)phosphoryl- and -thiophosphorylacetonitriles **120**. This proceeded by an intramolecular P=E alkylation (E = O, S) mechanism.[90–93] 6-Cyano-2,10-dioxaphosphabicyclodecane 1-oxide (**121**) was obtained as a single *cis*-isomer,[91] while its thio analogue with two different cyclic moieties **122** formed as a mixture of *cis*- and *trans*-isomers in a 2.3 : 1 ratio.[92] Both isomers of 6-cyano-2-oxa-10-thia(oxa)phosphabicyclodecane 1-oxide **122** were found to be conglomerates (racemic mixture of homochiral crystals) undergoing spontaneous resolution¶ upon crystallisation.[92]

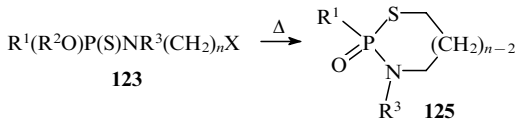


R = Et, Pr; X = O, S.

It should be mentioned, that the intramolecular P=S alkylation (followed by dealkylation of the alkoxy group at the phosphorus atom) proceeds also in the series of *N*-(ω-halogenoalkyl)thiophosphonamidates **123**[94–100] and *S*-(ω-halogenoalkyl)

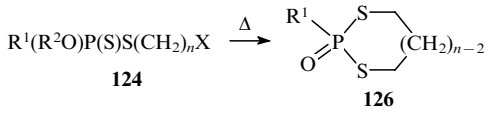
¶ Crystals are formed enriched in one enantiomer.

dithiophosphorates and -phosphonates **124**,[101] to give 1,3,2-diheterophosphacyclanes **125** and **126**, respectively.



123 **125**

n = 2, 3; R^1 = Me, Ph; R^2 = Me, Et, Pr, Bu; R^3 = Me, Et, Ph.



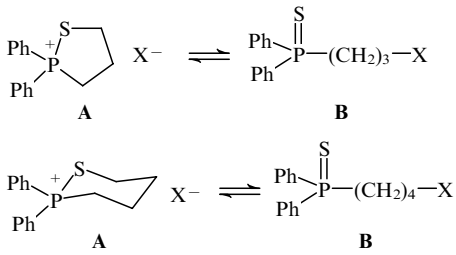
124 **126**

n = 2, 3; R^1 = Me, OPr; R^2 = Et, Pr.

Thus, the intramolecular *S*-alkylation is apparently inherent in various types of thiophosphoryl compounds with an ω-halogenoalkyl fragment. Therefore, there is good reason to believe that the method for the preparation of 2-oxo-1,2-thiaphosphacyclanes by the intramolecular thione–thiol rearrangement is the most common and is of practical importance.

V. Ring-chain tautomerism in the series of 1,2-thiaphosphacyclanes

It was reported,[80–84] that cyclic phosphonium salts **103a**,**b**, called 1,2λ⁴-thiaphosphacyclanium salts, exist in solutions as equilibrium mixtures of a cyclic form (**A**) and a linear ω-halogenoalkylphosphine sulfide (**B**). Such a tautomeric equilibrium belongs to a type of ring-chain anionotropic tautomerism, which occurs in organic chemistry much more rarely than the prototropic one.[102] Moreover, even in cases where both tautomers could be isolated in the individual state, the tautomeric equilibrium in solution is rarely observed especially in the absence of a catalyst.[102]



X = Cl, Br, I.

For the first time, the existence of such a tautomeric equilibrium **A** ⇄ **B** was detected for 2,2-diphenyl-1,2λ⁴-thiaphospholanium iodides (**103a**, Hal = I) and 2,2-diphenyl-1,2λ⁴-thiaphosphinanium iodides (**103b**, Hal = I).[80] However, halogenotropic tautomerism in the series of 1,2-thiaphosphacyclanium salts was investigated in more detail by the example of the corresponding bromides, both the linear (**106a**,**b**) and the cyclic (**103a**,**b**) tautomers of which (Hal = Br) were isolated in the pure state and investigated by X-ray diffraction analysis.[80,81] It was shown that the equilibrium position is attained starting from either the linear or cyclic tautomer. Thus, according to the ^{31}P NMR data, keeping a solution of a five-membered cyclic bromide **103a** (Hal = Br) (or its linear tautomer **106a**) in CH_2Cl_2 at 20 °C yields an equilibrium mixture of the same composition comprising 38% of the cyclic (**A**) and 62% of the linear (**B**) tautomer. In the case of the six-membered bromide **103b** (Hal = Br) (or its linear tautomer **106b**), it takes *ca.* 25 days for the equilibrium to be attained in CH_2Cl_2 and the equilibrium mixture contains 48% of the cyclic (**A**) and 52% of the linear (**B**) tautomers. Thus, with the other conditions being the same (the solvent and temperature), the equilibrium is established faster for five-membered heterocyclic compounds than for the six-memebered ones.

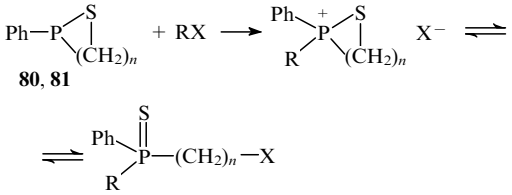
The effect of solvent polarity, ring size and the nature of the anion on the position of the tautomeric equilibrium **A** ⇄ **B** was investigated in detail.[81] As is evident from the data in Table 1, the position of the equilibrium shifts from the linear form to the cyclic one in going from Cl to Br and I. Thus only minor amounts of the cyclic form **A** were determined in acetonitrile solutions of ω-chloroalkyldiphenylphosphine sulfides **104a**,**b** after storage for 6 months, while only the cyclic form **B** was found after keeping the solutions of the corresponding iodides **105a**,**b** in the same solvent. As would be expected for perchlorates, the equilibrium is completely shifted to the cyclic tautomer **A** independent of the solvent polarity. Under the same conditions (solvent, temperature, time), usually an increase in the content of the form **A** is observed in equilibrium mixtures on going from the 1,2-thiaphospholanium salts to 1,2-thiaphosphinanium salts. This fact was explained[80–82] by the higher strain in the five-membered ring.

Table 1. The content of the cyclic form A (%) in solutions of 1,2λ⁴-thiaphosphacyclanium salts **103a**,**b** (Hal = Cl, Br, I) and **108a**,**b** (X = ClO_4) according to ^{31}P NMR data.

Solvent	Hal = Cl		Hal = Br		Hal = I		X = ClO_4	
	n = 3	n = 4	n = 3	n = 4	n = 3	n = 4	n = 3	n = 4
CH_2Cl_2	0	0	38	48	70	85	100	100
$CHCl_3$	0	0	65	85	87	92	100	100
MeCN	9	3	82	82	100	100	–	–

It was also established that the proportion of the cyclic tautomer **A** increases with a decrease in temperature,[80,81] *i.e.*, as in other ring-chain tautomeric systems,[102] the transition of a cyclic form into the linear one is an endothermic process.

A similar equilibrium was described by Kobayashi *et al.*,[23] who studied the mechanism of polymerisation of 1,2λ³-thiaphosphacyclanes, where the initiation step involves the reaction of the latter with RX.



80, **81**

n = 3 (**80**), 4 (**81**); RX = MeOTf, MeI, BnBr.

A mixture of the starting monomer with an equimolar amount of MeOTf, MeI or BnBr in $CDCl_3$ was monitored by ^{31}P NMR and the formation of the corresponding linear form at 80 °C was observed in the cases where halide serves as a counterion. At lower temperature (35 °C), the linear form was not detected. However neither regularities of this process were investigated nor the corresponding tautomers were isolated.

As mentioned above, the decrease in the nucleophilicity of the sulfur atom in linear ω-halogenoalkyl-substituted phosphine sulfides due to the introduction of an electron-withdrawing substituent (*e.g.*, the cyano group) into the α-position relative to the phosphorus atom resulted in the deceleration of the cyclisation, the proportion of the product **114** in the equilibrium mixture not exceeding 15%.[89]

VI. Structural features of 1,2-thiaphosphacyclanes

In a number of papers devoted to 1,2-thiaphosphacyclanes having different ring sizes their structural features revealed from X-ray studies are discussed in detail. Therefore we considered it reasonable to summarise these data. Table 2 presents the principal geometric parameters of 1,2-thiaphosphacyclanes as obtained from X-ray data.

Table 2. The principal bond lengths and bond angles for 1,2-thiaphosphacyclanes according to the literature data.

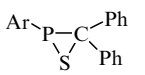
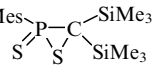
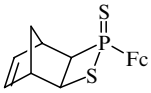
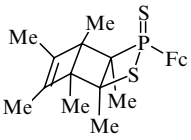
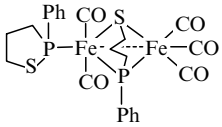
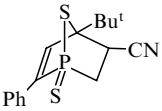
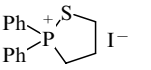
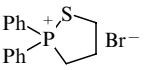
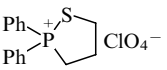
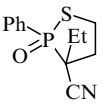
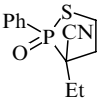
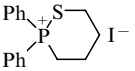
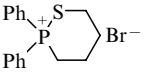
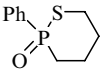
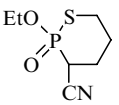
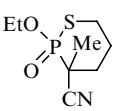
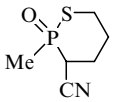
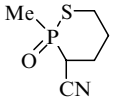
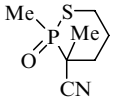
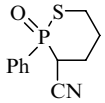
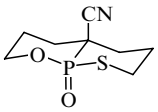
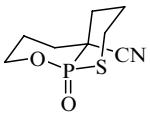
Compound	Structure	Bond lengths /Å				Bond angles /deg		Ref.
		P–S	P–C	S–C	P=X (X = S, O)	P–S–C	S–P–C	
43	 Ar = 2,4,6-$Bu^t_3C_6H_2$	2.113(1)	1.878(2)	1.845(2)		56.18(8)	54.69(7)	36, 37
15		2.049(3)	1.795(7)	1.918(8)	1.932(3)	53.7(2)	59.4(2)	34
61c		2.102(2)	1.844(4)	1.850(6)	1.940(2)	80.1	83.8	58, 103
62b		2.095(1)	1.847(6)	1.880(3)	1.931(1)	79.9(1)	83.7(1)	58, 103
77		2.087(2)	1.907	1.832		97.2	95.3	72
71 (Ar = Ph, R^1 = Bu^t, R^2 = CN) [a]		2.088(3) 2.073(2)	1.827(8) 1.829(7)	1.860(7) 1.866(6)	1.923(3) 1.929(3)	82.3(2) 82.6(2)	93.0(3) 94.4(2)	104
103a (Hal = I)		2.068(2)	1.805(4)	1.850(6)		93.0(2)	101.1(1)	80
103a (Hal = Br)		2.062(2)	1.818(5)	1.842(7)		93.3(2)	100.3(2)	81
108a (X = ClO_4)		2.052(2)	1.812(5)	1.844(7)		93.8(2)	99.4(2)	83
cis-**116a** (R^1 = Ph, R^3 = Et)		2.078(1)	1.857(2)	1.827(3)	1.477(1)	95.7(1)	97.2(1)	89
trans-**116a** (R^1 = Ph, R^3 = Et) [a]		2.0751(4) 2.0832(4)	1.869(1) 1.873(1)	1.834(1) 1.840(1)	1.4805(8) 1.4817(8)	94.93(4) 95.20(4)	95.84(4) 97.87(3)	89
103b (Hal = I)		2.051(2)	1.778(5)	1.837(5)		97.6(1)	107.6(1)	80
103b (Hal = Br)		2.048(2)	1.790(5)	1.833(5)		97.3(1)	108.1(2)	81
112b (R = Ph)		2.082(1)	1.790(3)	1.828(3)	1.474(2)	96.8(2)	103.4(1)	84
cis-**116b** (R^1 = OEt, R^3 = H)		2.044(1)	1.817(4)	1.807(6)	1.456(3)	99.2(1)	105.5(1)	86
cis-**116b** (R^1 = OEt, R^3 = Me)		2.056(1)	1.836(1)	1.832(2)	1.469(1)	99.54(8)	105.8(1)	88

Table 2 (continued).

Compound	Structure	Bond lengths /Å				Bond angles /deg		Ref.
		P–S	P–C	S–C	P=X (X = S, O)	P–S–C	S–P–C	
trans-**116b** (R^1 = Me, R^3 = H)		2.062(2)	1.838(3)	1.835(3)	1.488(2)	97.9(2)	103.9(1)	86
cis-**116b** (R^1 = Me, R^3 = H)		2.065(2)	1.833(2)	1.845(3)	1.484(2)	100.13(7)	113.13(8)	89
cis-**116b** (R^1 = Me, R^3 = Me)		2.054(2)	1.836(2)	1.832(2)	1.470(4)	99.54(8)	105.79(5)	89
trans-**116b** (R^1 = Ph, R^3 = H) [a]		2.059(1) 2.061(1)	1.839(2) 1.832(2)	1.827(2) 1.838(2)	1.477(2) 1.479(1)	99.1(1) 97.96(9)	103.45 103.56	89
trans-**122** (see [a, b])		2.04(1) 2.076(9)	1.824(2)	–	1.471(6)	93(1) 98(1)	–	89
cis-**122** (see [b])		2.020(1)	1.823(2)	1.821(4)	1.463(2)	96.2(2)	105.46(8)	89

[a] Parameters for two independent molecules. [b] The compounds represent conglomerates, which undergo crystal-induced spontaneous resolution (data for the major enantiomer are shown). The structures are disordered due to superposition of two enantiomers (7 : 3 for *trans*-**122** and 17 : 3 for *cis*-**122**).

The structures of two 1,2-thiaphosphiranes **43** and **15**, with a tri-[36,37] and tetracoordinate[34] phosphorus atom, respectively, were investigated by X-ray diffraction analysis. In λ^5-derivative **15** with the phosphine sulfide group, the P–C and P–S bond lengths in the three-membered ring are somewhat shorter than in the λ^3-derivative **43**, which results in the corresponding elongation of the S–C bond in compound **15**. Presumably, this is connected with the presence of bulky trimethylsilyl groups at the carbon atom in compound **15**. It is interesting to note that with allowance for the difference in the chemical structure, *i.e.*, with the presence of the sulfur atom in the ring, compound **15** is virtually isostructural with its precursor, methylidene(thioxo)phosphorane **14** Mes–P(S)=C$(SiMe_3)_2$.[34]

In the series of 1,2-thiaphosphetanes, the representatives of the smallest group of 1,2-thiaphosphacyclanes, only for two ferrocenyl-substituted thiophosphoryl compounds **61c** and **62b**[58,103] are X-ray data available. In these compounds, the four-membered ring is part of a fused cage system, both compounds being represented by *exo*-isomers. The four-membered ring in both compounds is flattened (the maximum deviation from the plane PCCS is 0.05 and 0.14 Å for **61c** and **62b** respectively). The minor deviation from planarity in compound **62b** is caused by steric hindrance due to methyl substituents. The increase in the S=P–C angle in **62b** is evidence for this fact.

X-Ray diffraction studies of the iron complex **77** with the 1,2λ^3-thiaphospholane P-monodentate ligand was carried out.[72] The ligand is characterised by the longest $P-C_{cyclo}$ bond (1.907 Å) of all the 1,2-thiaphosphacyclanes shown in Table 2. In addition, the P–S bond length in this compound (2.087 Å) also exceeds the analogous bond lengths in other 1,2-thiaphospholanes with the exception of compound **71** (Ar = Ph, R^1 = Bu^t, R^2 = CN)[104] having a norbornene structure, where the five-membered ring may be considered as a 1,2-thiaphospholane only formally (the sulfur atom serves as a bridge between the bridgehead phosphorus and carbon atoms). The parameters of the 1,2-thiaphospholane ring in compound **71** are similar to the expected values with the exception of the P–S–C angle (82.3° and 82.6°) due to considerable steric strain in the bicyclic skeleton. It should be noted that in this case the values of the angle are similar to those in phosphetanes.

According to X-ray data for 5- and 6-membered 1,2-thiaphosphacyclanium salts **103a** (Hal = I, Br), **108a** (X = ClO_4) and **103b** (Hal = I, Br)[80,81,83] differing only in their anions, these compounds are isostructural. In addition, the orientaion of the two phenyl rings bound to the phosphorus atom relative to the planes of both the 5- and 6-membered rings is practically the same in all compounds. Thus, their structures do not depend on the nature of the anion or packing character. In all the structures under investigation, the phosphorus atom has a slightly distorted tetrahedral configuration with an endocyclic angle reduced to 100.3(2)° and 108.1(2)° in the thiaphospholane and thiaphosphinane rings, respectively.

Five-membered rings in 1,2-thiaphosphacyclanium salts **103a** (Hal = I, Br) and **108a** (X = ClO_4) have envelope conformations with an average deviation of the C(4) atom from the plane formed by the other atoms of 0.6 Å. 1,2-Thiaphosphinanium salts **103b** (Hal = I, Br) possess chair conformations. On going from five-membered to six-membered rings contraction of the P^+-S bonds (on average, from 2.065 to 2.050 Å) and S–C bonds (from 1.846 to 1.835 Å) is observed.

The presence of shortened contacts of the type 'cation – halide anion' ($P^+-S\cdots Hal^-$) is a characteristic feature of these compounds, and analysis of the known structural data showed that such contacts with the halide ions in compounds containing the P^+-S bond were previously unknown. In compounds **103a** (Hal = I, Br), **108a** (X = ClO_4) and **103b** (Hal = I, Br), the phosphorus, sulfur and halogen atoms are virtually colinear [the average value of the P–S–Hal bond angle is 175.3(1)°], which points to the directionality of the contact. Taking into account the difference in the van der Waals distances, the contact strength for the same ring is virtually independent of the nature of the halogen.

Thus the difference in the S···Hal$^-$ distances in five-membered rings for the bromide **103a** (Hal = Br) and the iodide **103a** (Hal = I) (0.16 Å) almost coincides with the difference in van der Waals radii for Br and I (0.17 Å). Owing to these contacts, the sulfur atom in such structures acquires a trigonal configuration. On going from five- to six-membered thiaphosphacyclanium halides, significant contraction of the S···Hal$^-$ distance is observed (this correlates with the interion contact strength) by 0.19 and 0.18 Å in iodides and bromides, respectively. Based on the correlation of the P—S and S···Hal$^-$ bond lengths with the ring size, it was suggested that this contact is caused by the donor–acceptor interaction of the halogen lone electron pair with the antibonding orbital of the P—S bond (n – σ*-interaction).

Despite the similarity on the whole of the geometric parameters of five-membered phosphonium salts **103a** and **108a** with those of cyano-substituted *cis* and *trans*-2-oxo-1,2λ^5-thiaphospholanes **116a**,[89] the elongation of the P—S bond and contraction of the S—C bond in the latter should be mentioned. The same regularity is observed when comparing the bond lengths in salts **103b** (Hal = I, Br) with those in 2-oxo-1,2λ^5-thiaphosphinane **112b** (R = Ph).[84]

The introduction of the cyano group in position 3 of the 2-oxo-1,2-thiaphosphinane ring[86,88,89] resulted in the contraction of the P—S bonds (*cf.* structures **112b** and **116b** with different substituents R^1 and R^3, Table 2). At the same time, the P—S bond in 3-cyano-2-oxo-1,2-thiaphosphinanes **116b** (R^1 = OEt, R^3 = Me; R^1 = Me: R^3 = H, Me; R^1 = Ph, R^3 = H) is longer† than the P—S bond in the corresponding thiaphosphinanium salts **103b** (Hal = I, Br). It should be mentioned also that in both five- and six-membered rings the presence of the cyano group leads to a significant elongation of the P—S bond, especially in the case of transoid arrangement of the phosphoryl oxygen atom and the CN fragment.

According to an X-ray investigation[92] of single crystals of *cis*- and *trans*-isomers of phosphabicyclo[4.4.0]decane 1-oxide **122,** these compounds represent conglomerates (racemic mixture of homochiral crystals) which undergo the crystal-induced spontaneous resolution. Thus in the crystals of both isomers, the superposition of two enantiomers P_R and P_S (7 : 3 for *trans*-**122** and 17 : 3 for *cis*-**122**) is observed. On the whole, the geometry of compounds obtained is similar to that of the known phosphabicyclo[4.4.0]decane 1-oxides with two symmetric 1,2-oxaphosphinane rings.[91,105–107] The P(1)O(2)C(4)C(8) torsion angles in compounds *cis*-**122** and *trans*-**122**, which characterise the mutual disposition of the phosphoryl and cyano groups, are equal to −48.4° and 179°, respectively.

In conclusion, it may be mentioned that in general the length of an ordinary P—S bond in 1,2-thiaphosphacyclanes independent of the ring size and coordination number of the phosphorus atom varies within a rather narrow range 2.049–2.095 Å. The longest P—S bond was detected in 1,2-thiaphosphirane **43** (2.113 Å) and phosphetane **61c** (2.102 Å), and the shortest one in phosphabicyclo[4.4.0]decane 1-oxide **122** (2.02 and 2.04 Å). The P—C bond length also varies insignificantly: the shortest P—C bond was found in 1,2-thiaphosphirane **15** and in five- and six-membered 1,2-thiaphosphacyclanium salts **103b** (Hal = I, Br) and **108a** (X = ClO_4). The bond angles S—P—C in all compounds shown in Table 2 are in keeping with the regular values corresponding to the size of the heterocycle (in three- and four-membered cycles, the bond angles decrease in compliance with the normal tendency connected with the presence of strained small rings).

VII. Conclusion

The material presented in this review is evidence of the essential progress in the field of synthesis of 1,2-thiaphosphacyclanes having the phosphorus atom in different valence states and coordination. Such general synthetic routes should be noted as sulfur addition to methylidenephosphines resulting in 2-thioxo-1,2λ^5-thiaphosphiranes; the addition of phosphorus pentasulfide or the Lawesson reagent to a variety of unsaturated substrates leading to 2-thioxo-1,2λ^5-thiaphosphetanes; the reaction of phosphorus pentasulfide with available five- or six-membered 2-oxo-1,2-oxaphosphacyclanes yielding 2-thioxo-1,2λ^5-thiaphospholanes and -thiaphosphinanes; and intramolecular S-alkylation of ω-halogenoalkyl-substituted thiophosphoryl compounds, which give easy access to a wide range of mono- and bicyclic 2-oxo-1,2λ^5-thiaphosphacyclanes, including those functionalised in the ring. The existence of convenient synthetic routes may open prospects for the further use of this type of organophosphorus compounds in fine organic synthesis, agriculture and some technical areas.

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References

1. L D Quin *The Heterocyclic Chemistry of Phosphorus Systems Based on the Phosphorus-Carbon Bond* (New York: Wiley-Interscience, 1981)
2. R A Cherkasov, V V Ovchinnikov, M A Pudovik, A N Pudovik *Usp. Khim.* **51** 1305 (1982) [*Russ. Chem. Rev.* **51** 746 (1982)]
3. M A Pudovik, V V Ovchinnikov, R A Cherkasov, A N Pudovik *Usp. Khim.* **52** 640 (1983) [*Russ. Chem. Rev.* **52** 361 (1983)]
4. N A Polezhaeva, R A Cherkasov *Usp. Khim.* **54** 1899 (1985) [*Russ. Chem. Rev.* **54** 1126 (1985)]
5. R A Cherkasov, N A Polezhaeva *Usp. Khim.* **56** 287 (1987) [*Russ. Chem. Rev.* **56** 163 (1987)]
6. V F Mironov, M A Pudovik, O G Sinyashin *Ross. Khim. Zh.* **69** 13 (1999) [a]
7. US P. 2 916 510; *Chem. Abstr.* **54** 5571 (1960)
8. US P. 2 953 591; *Chem. Abstr.* **55** 5346 (1961)
9. US P. 2 648 695; *Chem. Abstr.* **48** 8252 (1954)
10. Germ. P. 2 346 787; *Chem. Abstr.* **83** 44 266 (1975)
11. Germ. P. 2 454 189; *Chem. Abstr.* **85** 78 634 (1976)
12. Jpn. P. 63 280 728; *Chem. Abstr.* **111** 40 152 (1989)
13. Jpn. P. 63 130 595; *Chem. Abstr.* **110** 39 511 (1989)
14. Jpn. P. 62 185 710; *Chem. Abstr.* **108** 96 114 (1988)
15. L Germanaud, S Brunel, Y Chevalier, P Le Perchec *Bull. Soc. Chim. Fr.* 699 (1988)
16. L D Quin, B G Marsi *J. Am. Chem. Soc.* **107** 3389 (1985)
17. L D Quin, J Szewczyk, K M Szewczyk, A T McPhail *J. Org. Chem.* **51** 3341 (1986)
18. L D Quin, B Pete, J Szewczyk, A N Hughes *Tetrahedron Lett.* **29** 2627 (1988)
19. L D Quin, X-P Wu, N D Sadanani, I Lukes, A S Ionkin, R O Day *J. Org. Chem.* **59** 120 (1994)
20. US P. 4 042 523; *Chem. Abstr.* **87** 204 150 (1997)
21. US P. 4 231 970; *Chem. Abstr.* **94** 84 303 (1981)
22. US P. 4 908 045; *Chem. Abstr.* **112** 201 939 (1990)
23. S Kobayashi, M Suzuki, T Saegusa *Macromolecules* **19** 462 (1986)
24. F Mathey, D Thavard *J. Organomet. Chem.* **117** 377 (1976)
25. I Tworowska, W Dabkowski, J Michalski *Phosphorus Sulfur Silicon Relat. Elem.* **177** 1855 (2002)
26. P Guga, A Okruszek, W J Stec *Top. Curr. Chem.* **220** 169 (2002)
27. H Z Lecher, R A Greenwood, K C Whitehouse, T H Chao *J. Am. Chem. Soc.* **78** 5018 (1956)
28. M P Cava, M I Levinson *Tetrahedron* **41** 5061 (1985)
29. R A Cherkasov, G A Kutyrev, A N Pudovik *Tetrahedron* **41** 2567 (1985)
30. E Niecke, D-A Wildbredt *J. Chem. Soc., Chem. Commun.* 72 (1981)
31. J Navech, J Majoral, R Kraemer *Tetrahedron Lett.* **24** 5885 (1983)
32. T A Van der Knaap, F Bickelhaupt *J. Organomet. Chem.* **277** 351 (1984)
33. T A Van der Knaap, T C Klebach, R Lourens, M Vos, F Bickelhaupt *J. Am. Chem. Soc.* **105** 4026 (1983)
34. M Caira, R H Neilson, W H Watson, P W Neilson, Z M Xie *J. Chem. Soc., Chem. Commun.* 698 (1984)
35. R H Neilson *Phosphorus Sulfur Relat. Elem.* **18** 43 (1983)

† With the exception of compound **116b** (R^1 = OEt, R^3 = H).

36. K Toyota, K Shimura, H Takahashi, M Yoshifuji *Chem. Lett.* 1927 (1994)
37. K Toyota, H Takahashi, K Shimura, M Yoshifuji *Bull. Chem. Soc. Jpn.* **69** 141 (1996)
38. M Yoshifuji, K Toyota, N Inamoto *Tetrahedron Lett.* **26** 1727 (1985)
39. B A Boyd, R J Toma, R H Neilson *Tetrahedron Lett.* **28** 6121 (1987)
40. E Niecke, J Böske, B Krebs, M Dartmann *Chem. Ber.* **118** 3227 (1985)
41. B A Arbuzov, E N Dianova, E Ya Zabotina *Izv. Akad. Nauk SSSR, Ser. Khim.* 169 (1986) [b]
42. R Appel, C Casser *Chem. Ber.* **118** 3419 (1985)
43. S G Ruf, J Dietz, M Regitz *Tetrahedron* **56** 6259 (2000)
44. G Märkl, W Hölzl *Tetrahedron Lett.* **30** 4501 (1989)
45. E Niecke, A Seyer, D-A Wildbredt, W W Schoeller *Angew. Chem., Int. Ed. Engl.* **20** 675 (1981)
46. E Niecke, M Leuer, D-A Wildbredt, W W Schoeller *J. Chem. Soc., Chem. Commun.* 1171 (1983)
47. E Niecke, K Schwichtenhövel, H G Schöfer, B Krebs *Angew. Chem., Int. Ed. Engl.* **20** 963 (1981)
48. M Yoshifuji, K Shibayama, N Inamoto, K Hirotsu, T Higuchi *J. Chem. Soc., Chem. Commun.* 862 (1983)
49. M Yoshifuji, K Ando, K Shibayama, N Inamoto, K Hirotsu, T Higuchi *Angew. Chem., Int. Ed. Engl.* **22** 418 (1983)
50. U Dabrowska, J Dabrowski *Chem. Ber.* **109** 1779 (1976)
51. H W Roesky, U Otten *J. Fluorine Chem.* **46** 433 (1990)
52. H W Roesky, N Benmohamed *Chem. Ztg.* **11** 417 (1986)
53. H W Roesky, N Benmohamed, K Keller, N Kewelch, N Nolteneyer, G M Scheldrick *Z. Naturforsch., B* **42** 1249 (1987)
54. H W Roesky, A Thiel, M Noltemeyer, G M Sheldrick *Chem. Ber.* **118** 2111 (1985)
55. T Sasaki, K Shimizu, M Ohno *Chem. Pharm. Bull.* **32** 1433 (1984)
56. A Ecker, I Boie, U Schmidt *Monatsh. Chem.* **104** 503 (1973)
57. A Ecker, I Boie, U Schmidt *Angew. Chem., Int. Ed. Engl.* **10** 191 (1971)
58. M R St J Foreman, A M Z Slawin, J D Woollins *J. Chem. Soc., Dalton Trans.* 1175 (1999)
59. S Sheibye, R Shabana, S-O Lawesson, C Roemming *Tetrahedron* **38** 993 (1982)
60. T B Rauchfuss, G A Zank *Tetrahedron Lett.* **27** 3445 (1986)
61. M R St J Foreman, A M Z Slawin, J D Woollins *J. Chem. Soc., Dalton Trans.* 3653 (1996)
62. R Appel, F Knoch, H Kunze *Angew. Chem.* **95** 1008 (1983)
63. M D Khidre, El-S M A Yakost, M R H Mahran *Phosphorus Sulfur Silicon Relat. Elem.* **133** 119 (1998)
64. B A Arbuzov, L Z Nikonova, O N Nuretdinova *Izv. Akad. Nauk SSSR, Ser. Khim.* 648 (1973) [b]
65. H-J Kleiner *Liebigs Ann. Chem.* 324 (1980)
66. A M Polozov, S E Cremer *Phosphorus Sulfur Silicon Relat. Elem.* **147** 337 (1999)
67. US P. 4 540 526; *Chem. Abstr.* **104** 34 193 (1986)
68. W Ando, H Hayakawa, N Tokitoh *Tetrahedron Lett.* **28** 1803 (1987)
69. H Yamaguchi, S Kametani, T Karalasa, T Saito, S Motoki *Tetrahedron Lett.* **23** 1263 (1982)
70. H Tanaka, S Kametani, T Saito, S Motoki *Bull. Chem. Soc. Jpn.* **58** 667 (1985)
71. T Uchida, K Kozawa, T Saito, S Motoki *Bull. Chem. Soc. Jpn.* **57** 1990 (1984)
72. F Mathey, M-B Comarmond, D Moras *J. Chem. Soc., Chem. Commun.* 417 (1979)
73. S Kobayashi, M Suzuki, T Saegusa *Bull. Chem. Soc. Jpn.* **58** 2153 (1985)
74. S Kobayashi, M Tokunoh, T Saegusa *Macromolecules* **19** 466 (1986)
75. K Kamijo, K Toyota, M Yoshifuji *Chem. Lett.* 567 (1999)
76. A Chaudhry, M J P Harger, P Shuff, A Tompson *J. Chem. Soc., Chem. Commun.* 83 (1995)
77. A Chaudhry, M J P Harger, P Shuff, A Tompson *J. Chem. Soc., Perkin Trans. 1* 1347 (1999)
78. S Collison, M J P Harger *J. Chem. Res.* (*S*) 28 (2000)
79. M J P Harger *J. Chem. Res.* (*S*) 296 (2000)
80. I M Aladzheva, O V Bykhovskaya, D I Lobanov, K A Lyssenko, M Yu Antipin, T A Mastryukova, M I Kabachnik *Mendeleev Commun.* 48 (1996)
81. D I Lobanov, I M Aladzheva, O V Bykhovskaya, P V Petrovskii, K A Lyssenko, M Yu Antipin, T A Mastryukova, M I Kabachnik *Phosphorus Sulfur Silicon Relat. Elem.* **128** 165 (1997)
82. I M Aladzheva, I V Leont'eva, D I Lobanov, P V Petrovskii, K A Lysenko, T A Mastryukova, M I Kabachnik *Zh. Obshch. Khim.* **68** 1417 (1998) [c]
83. I M Aladzheva, O V Bykhovskaya, D I Lobanov, P V Petrovskii, K A Lysenko, T A Mastryukova, M I Kabachnik *Zh. Obshch. Khim.* **68** 1421 (1998) [c]
84. O V Bykhovskaya, I M Aladzheva, D I Lobanov, P V Petrovskii, K A Lysenko, T A Mastryukova *Zh. Obshch. Khim.* **71** 393 (2001) [c]
85. I M Aladzheva, O V Bykhovskaya, D I Lobanov, P V Petrovskii, K A Lysenko, T A Mastryukova *Khim. Geterotsikl. Soedin.* 105 (2002) [d]
86. I L Odinets, N M Vinogradova O I Artyushin, P V Petrovskii, K A Lyssenko, M Yu Antipin, T A Mastryukova *Mendeleev Commun.* 158 (1999)
87. N M Vinogradova, I L Odinets, O I Artyushin, K A Lyssenko, P V Petrovskii, T A Mastryukova *Phosphorus Sulfur Silicon Relat. Elem.* **144–146** 589 (1999)
88. I L Odinets, N M Vinogradova, K A Lyssenko, M Yu Antipin, T A Mastryukova *Mendeleev Commun.* 216 (2000)
89. I L Odinets, N M Vinogradova, K A Lyssenko, M Yu Antipin, P V Petrovskii, T A Mastryukova *Heteroat. Chem.* **13** 1 (2002)
90. I L Odinets, N M Vinogradova, K A Lyssenko, M Yu Antipin, P V Petrovskii, T A Mastryukova *Phosphorus Sulfur Silicon Relat. Elem.* **177** 1787 (2002)
91. N M Vinogradova, K A Lyssenko, I L Odinets, P V Petrovskii, T A Mastryukova, M I Kabachnik *Phosphorus Sulfur Silicon Relat. Elem.* **132** 265 (1998)
92. I L Odinets, N M Vinogradova, P V Petrovskii, K A Lyssenko, T A Mastryukova *Heteroat. Chem.* **11** 163 (2000)
93. T A Mastryukova, I L Odinets, N M Vinogradova, K A Lyssenko, P V Petrovskii *Pol. J. Chem.* **75** 1103 (2001)
94. Ph Savignac, Ng Thanh Thuong, P Chabrier *C.R. Hebd. Seances Acad. Sci., Ser. C* **266** 1791 (1968)
95. Ph Savignac, Ng Th Thuong, P Chabrier *C.R. Hebd. Seances Acad. Sci., Ser. C* **267** 183 (1968)
96. Ph Savignac, P Chabrier *C.R. Hebd. Seances Acad. Sci., Ser. C* **267** 1166 (1968)
97. Ph Savignac, J Chenault, P Chabrier *C.R. Hebd. Seances Acad. Sci., Ser. C* **270** 2086 (1970)
98. Ph Savignac V H Tenlade *Phosphorus Sulfur Relat. Elem.* **21** 23 (1984)
99. Ph Savignac *Phosphorus Sulfur Silicon Relat. Elem.* **56** 183 (1991)
100. O I Artyushin, P V Petrovskii, T A Mastryukova *Phosphorus Sulfur Silicon Relat. Elem.* **177** 2227 (2002)
101. R M Kalyanova, P V Petrovskii, T A Mastryukova *Phosphorus Sulfur Silicon Relat. Elem.* **177** 2225 (2002)
102. R E Valters, W Flitsch, in *Ring-Chain Tautomerism* (New York: Plenum, 1985) p. 271
103. M R St J Foreman, A M Z Slawin, J D Woollins *Chem. Commun.* 855 (1997)
104. T Uchida, K Kozawa, T Sarro, S Motok *Bull. Chem. Soc. Jpn.* **57** 1985 (1984)
105. S E Cremer, A G Sommese, O Rodriques *Phosphorus Sulfur Silicon Relat. Elem.* **75** 107 (1995)
106. S Bellard, S Postle, G M Sheldric *Acta Crystallogr., Sect. B* **34** 1032 (1978)
107. T M Lane, O P Rodriques, A G Sommese, S E Cremer *Acta Crystallogr, Sect. C* **51** 251 (1995)

[a] — *Mendeleev Chem. J. (Engl. Transl.)*
[b] — *Russ. Chem. Bull., Int. Ed. (Engl. Transl.)*
[c] — *Russ. J. Gen. Chem. (Engl. Transl.)*
[d] — *Chem. Heterocycl. Compd. (Engl. Transl.)*