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THE SYNTHESIS AND TRANSFORMATION OF COMPOUNDS WITH N=P BOND

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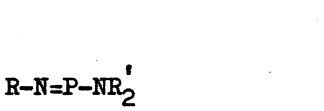
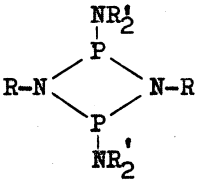
Abstract - 2-Imino-1,3-dioxa-2-phospholanes and 2-imino-4,5-benzo-1,3-dioxa-2-phospholanes have been obtained by Schtaudinger or Kirsanov reactions. Compounds with electronegative substituents at nitrogen are monomeric. If nitrogen atom has aryl radical, 2-imino-1,3,2-dioxaphospholanes are dimerized on N=P bond with formation of 1,3-diaza-2,4-diphosphetidines. 2-Chloro-2-acyliminophospholes react with catechol, o-phenylenediamine and o-aminophenol with the formation of spirophosphoranes. Reactions of phosphazocompounds and catechol give spirophosphorate.

In recent years the chemistry of phosphorus-nitrogen compound has been enriched by a number of new interesting data. The most striking result of recent investigations seems to be the synthesis of compounds of two- and three-coordinated phosphorus with N=P bonds. It should be noted that these compounds have not been obtained for a long time. Numerous attempts of their synthesis resulted only in dimeric products - 1,3-diaza-2,4-diphosphetidines (1).



(1)



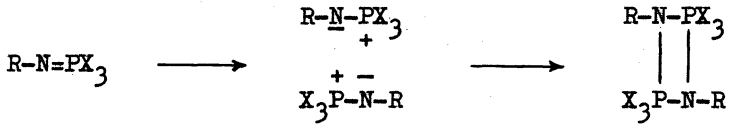
(2)

At one time these failures were responsible for a series of mistakes or too categoric conclusions that monomeric compounds 1 can not exist in individual state. Not long ago the brilliant investigations by O. Scherer and E. Nike demonstrated the possibility of synthesis of monomeric λ^3-phosphazenes as well as their relative stability (2). Furthermore these studies have revealed the importance of steric factors in stabilization and reactivity of organophosphorus compounds.
The case of λ^5-phosphazenes is somewhat different. In contrast to λ^3-phosphazenes most compounds of four-coordinated phosphorus with N=P bond, i.e. λ^5-phosphazenes, are monomeric.
To-day among various compounds of this class only three groups of λ^5-phosphazenes are known as dimers 4 or as being transformed into them under

adequate conditions.

(3) (4)

The first group includes the phosphazenes with chlorine or fluorine atoms at phosphorus (3, 4). It was found that dimerization of phosphazenes 3 takes place when phosphorus atom has electronegative ligands, such as fluorine and chlorine atoms, and nitrogen has alkyl or aryl groups. The charge separation arising from these substituents due to the poor conductivity of electron effects through tetrahedral phosphorus results in the betain structures and their fast dimerization.

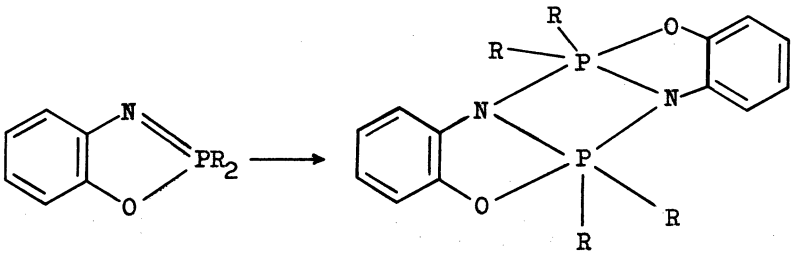


(3) (4)

With the substitution of chlorine or fluorine atoms by more electropositive groups the ability of phosphazocompounds to dimerize is decreased quickly. On the other hand if the nitrogen atom has electronegative groups, for example, acyl radicals, the phosphazocompounds are always monomeric. Electronic influence of substituents at nitrogen atom on the ability of phosphazocompounds to dimerize is clearly seen in the series of trichlorophosphazoarenes (3).

To some extent the bulkiness of substituents at nitrogen also affects the dimerization of phosphazocompounds. As the bulkiness of substituents grows, the dimerization is hindered, and phosphazocompounds are monomeric (similarly to stable λ^5-phosphazenes). For example, trichlorophosphazo-tert-butane or trichlorophosphazotrichloromethane are monomeric. In the case of trichlorophosphazobenzenes the introduction of substituents in ortho-position of aromatic ring hinders the dimerization (3).

For a long time the dimerization was thought to be an inherent property of trichloro- or trifluorophosphazenes only. Yet not long ago A. Schmidpeter et al. (6) and V.A. Gilyarov, M.I. Kabachnik et al. (5) have obtained the second group of λ^5-phosphazenes capable of dimerization, i.e. five-membered heterocycles of phosphorus with endocyclic N=P bond 5, 7. Many azaphospholes appeared dimeric compounds - condensed 1,3-diaza-2,4-diphosphetidines 6, 8 though some azaphospholes are known to be monomeric, incapable of dimerization.



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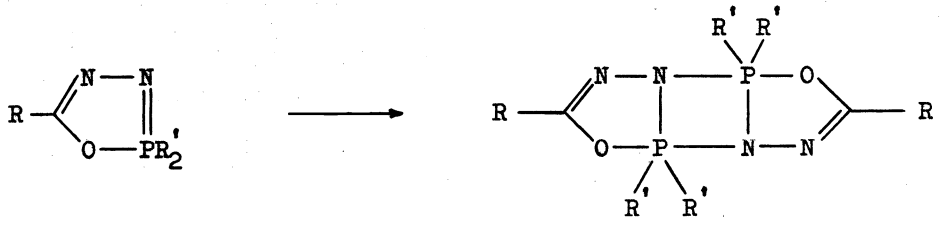
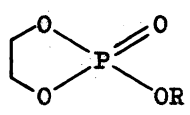
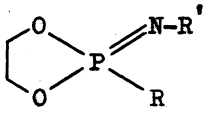


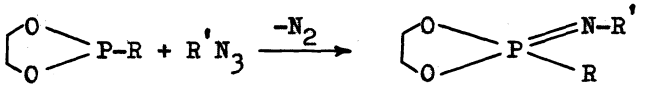
(7) (8)

It is interesting to note that all known six-membered heterocycles with N=P bond, 1,2-azaphosphorines, exist only in the monomeric state and for them the dimerization does not occur.
In dimerization of 1,2-azaphospholes of greatest interest is the formation of dimers even when the phosphorus atom has alkyl, aryl and alkoxyl groups, and not only electronegative atoms of chlorine or fluorine. At present this is not the case for the first group of phosphazocompounds. The unusual behaviour of the five-membered azaphosphole has been explained due to deformation of endocyclic angle at tetrahedral phosphorus resulting from the rigid structure of the cycle. The decrease of endocyclic angle up to 98-100° relieves transformation of tetrahedral phosphorus into trigonal-bipyramidal state characteristic of 1,3-diaza-2,4-diphosphetidines, and therefore the strain of endocyclic angle at phosphorus disappears. Thus for the second group of dimerizable phosphazocompounds both electronic and steric factors are determining in possible monomer-dimer equilibrium.
The above conclusion made it possible to predict the existence of the third group of dimerizable phosphazenes. It is known that the anomalously high reactivity of five-membered heterocycles of phosphorus - 1,3,2-dioxaphospholanes - is due to ring strain which releases on formation of a five-coordinated intermediate, so-called "phospholane effect" (7). The phospholane effect is supposed to take place for that phosphazocompound in which the phosphorus atom is introduced into 1,3,2-dioxaphospholane ring, and the N=P bond occupies endocyclic position. In other words, such compounds 9 might reveal phospholane effect in the dimerization of similar iminophospholanes.

(9)

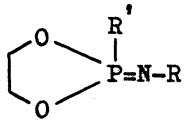
To varify this effect we have obtained 2-imino-1,3-dioxa-2-phospholanes 9 by the Schtaudinger reaction - imination of 1,3,2 λ^3- dioxaphospholanes with azides (8).



(9)

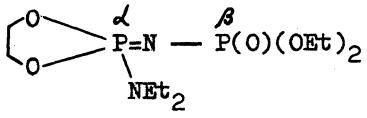
Some compounds were found to be monomeric and the other ones to be dimeric - tricyclic 1,3-diaza-2,4-diphosphetidines.

TABLE 1. Monomeric 2-imino-1,3,2-dioxaphospholanes (9)



R	$P(O)(OEt)_2$			C_6H_5CO	C_6H_5		
R'	NMe_2	NEt_2	OEt	OEt	NMe_2	NEt_2	NBu_2
δ^P	28,70		19,21			20,57	

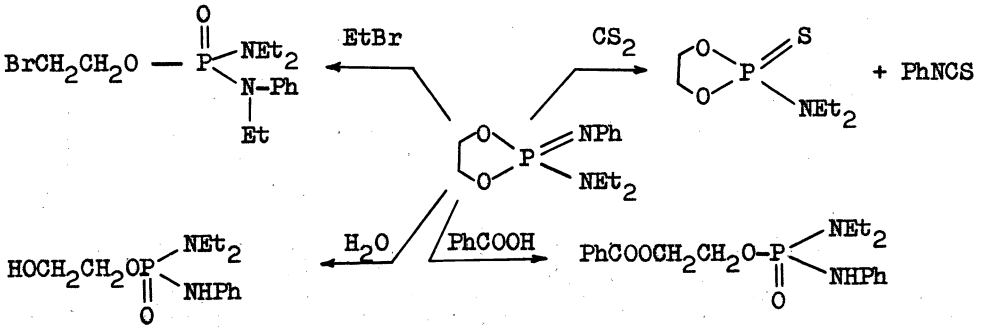
The monomeric 2-imino-1,3,2-dioxaphospholanes 9 are liquids distillable in vacuo. The structure has been confirmed by molecular weight determinations and NMR ^{31}P spectra. For example, NMR ^{31}P spectra of compounds 9a show AB quadruplet of two nonequivalent phosphorus atoms.



(9a)

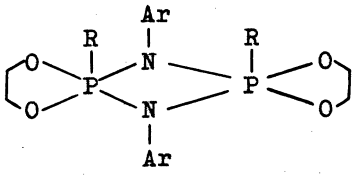
δ_α^P 28.70, δ_β^P - 1.53, J_{PNP} 60 Hz

In the IR spectra of these compounds there are characteristic absorption of N=P bond.
The monomeric iminophospholanes 9 enter the reaction typical for phosphazocompounds, for example, with carbon disulphide. While in reaction with alkyl halides, at hydrolysis or heating, the iminophospholanes undergo imid-amide rearrangement involving the cycle. It should be noted that iminophospholanes 9 have greater reactivity than acyclic phosphazocompounds.



Dimeric 2-imino-1,3,2-dioxaphospholanes 10 of diazadiphosphetidine structure show other properties (Table 2). They are high-melting crystalline compounds with low solubility in organic solvents. They do not react with carbon disulphide and do not undergo other reactions described for monomeric phosphazocompounds. Because of low solubility NMR ^{31}P spectra have been obtained only for some compounds.

TABLE 2. Dimeric 2-imino-1,3,2-dioxaphospholanes (10)

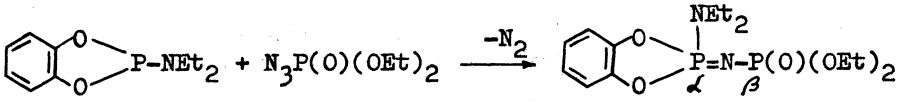


Ar	Ph	Ph	Ph	Ph	Ph	Ph	Tl	Tl
R'	OMe	OEt	OBu	OPh	SEt	F	OMe	OEt
δ^P		-58.23	-58.97					-57.90
		-58.97	-59.51					-58.37

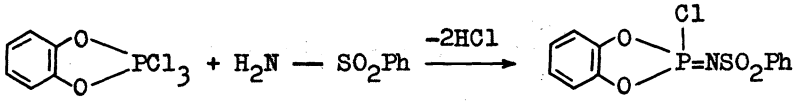
X-ray analysis of one of the compounds (10, Ar=Tl, R=OEt) proved the structure of 1,3-diaza-2,4-diphosphetidine with typical geometry of four-membered

cycle. The coordination of phosphorus atom is trigonal-bipyramidal with atoms of O^2, O^3 and N^2 in equatorial and O^1, N^1 in apical positions. It follows that 2-imino-1,3,2-dioxaphospholanes are monomeric if the nitrogen atom has electronegative acyl groups, such as dialkoxyphosphonyl or carbacyl. If nitrogen atom has phenyl or other aryl radical, the ability of 2-imino-1,3,2-dioxaphospholanes to dimerize depends on the nature of substituents at phosphorus. If the substituent is strong electropositive dialkylaminogroup, the iminophospholanes are monomeric. If the substituent is acceptor or week electrodonor, the iminophospholanes are dimerized on N=P bond. Therefore, the behavior of iminodioxaphospholanes 9 resembles that of 1,3,2-oxazaphospholes and differs from acyclic trialkoxyphosphazocompounds known are monomeric. Obviously, the ring strain effect predominates essentially over electrodonating effects of such groups as alkoxy, aroxy or alkylthio, thus the formation of structures with five-coordinated phosphorus is preferable.

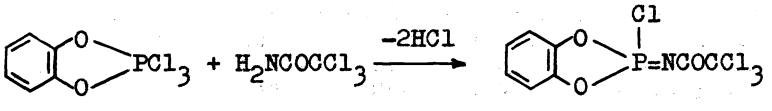
Similar dependence was observed for a series of N-substituted 2-imino-4,5-benzo-1,3,2-dioxaphospholes. N-acyliminobenzodioxaphospholes were obtained by two methods - the Schtaudinger reaction and the Kirsanov reaction (9). P-substituted N-acyliminophospholes were prepared from compounds 11-12 by nucleophilic displacements of chlorine atom.



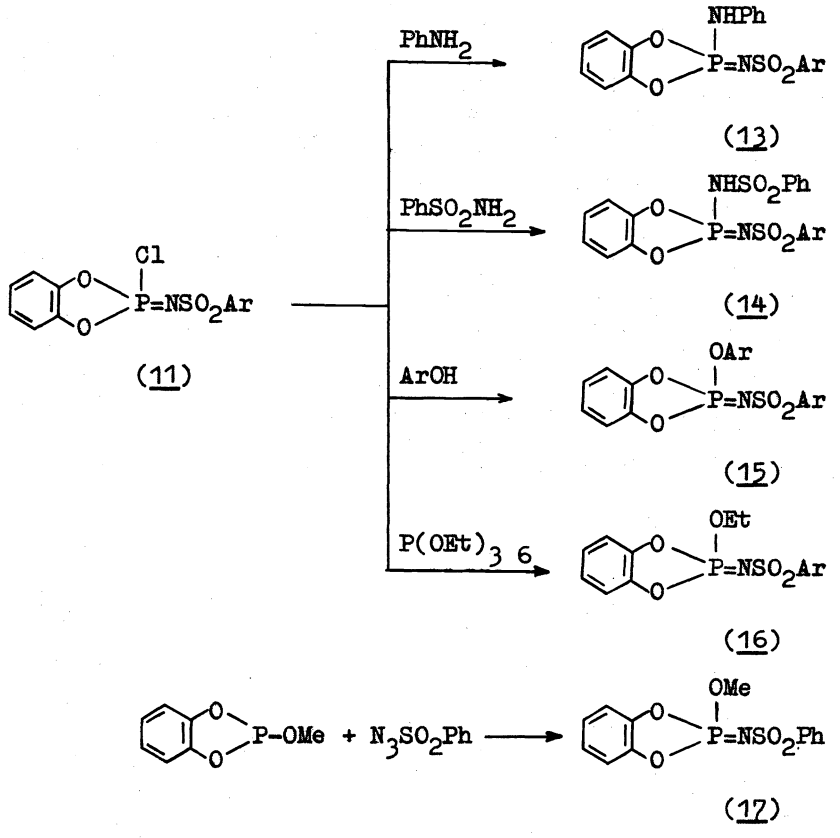
δ^P_α 19.2; δ^P_β - 2.7 ppm



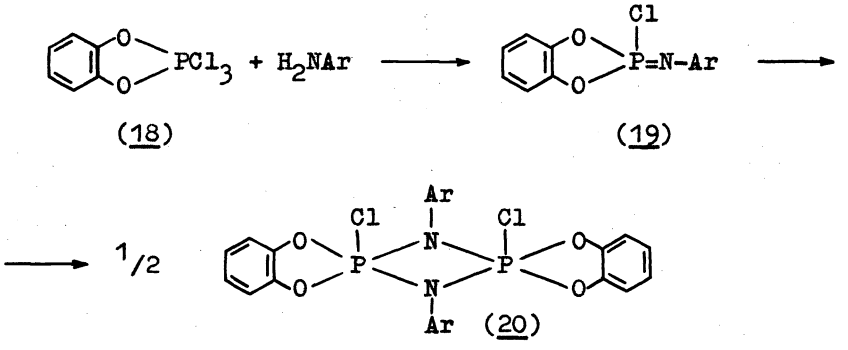
(11), δ^P 9.7 ppm



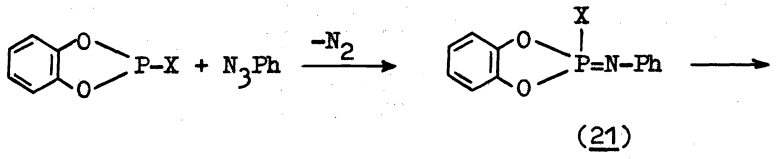
(12)



The compounds 11-17 are monomeric as consistent with IR spectra and molecular weight determinations. NMR ^{31}P spectra of these iminophospholes show only one signal for phosphorus characteristic of monomeric chlorophosphazo-compounds. On the other hand the reaction of trichlorodioxaphosphole 18 with arylamines or their hydrochlorides leads to dimers - tricyclic 1,3-diaza-2,4-diphosphetidines 20 rather than monomeric iminophospholes 19 (10).



The dimeric structures of the compounds 20 were confirmed by mass spectra. Compounds 20 dissolve slowly in phosphorus oxychloride and dioxane at long heating, and values of molecular weights obtained by cryoscopy in fresh solutions are like those of monomers. The repeated measurements of molecular weight in 24 hours give values close to dimers 20. It is most likely that the prolonged heating of these compounds 20 in polar solvents results in slow monomerization and the dimer is reached.
Various P-substituted 2-phenylimino-4,5-benzo-1,3,2-dioxaphospholes 21 obtained by the Schtaudinger reaction were also dimers 22 as shown by mass spectra and NMR ^{31}P spectra data.



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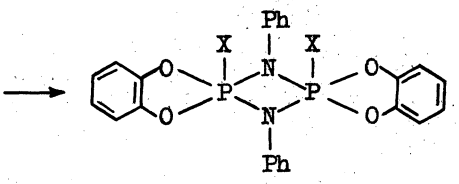
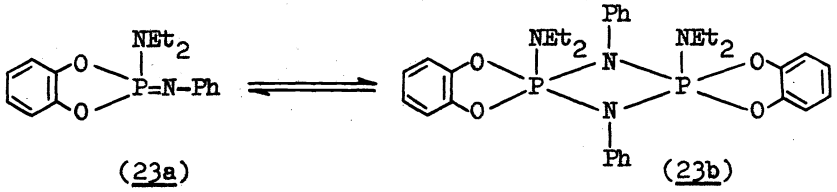


(22)

X	OMe	OEt	OBu	OPh	NMe_2	NEt_2	NBu_2	NHPh
δ^P	-58,0	-60,0	-60,4	-62,4	-55,0	11,8	-55,4	-
($CHCl_3$)						-54,3		

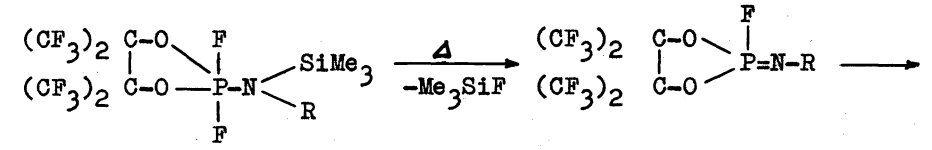
Phenylaminoderivative (22, X = NHPh) has been obtained by onother method - by the reaction of chlorodiazadiphosphetidine 20 with aniline.
Thus the dimerization of 2-imino-4,5-benzo-1,3,2-dioxaphospholes also depends on the nature of substituents at nitrogen atom. In the case of N-acyl derivatives all 2-imino-4,5-benzo-1,3,2-dioxaphospholes are monomeric independently of the nature of substituents at phosphorus atom. If the nitrogen atom of iminogroup has aryl-radical, all 2-imino-4,5-benzo-1,3,2-dioxaphospholes are dimeric. Only in the case of diethylaminogroup at phosphorus the dimer 23b is monomerized in solution and the equilibrium of monomer--dimer is established, which follows from NMR ^{31}P spectra.



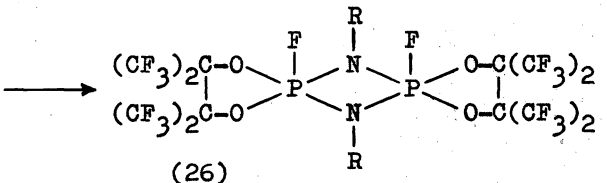
(23a) (23b)

Solvent	δ_α^P	δ_β^P	
C_6H_6	8.7	-54.1	62 : 38
$CHCl_3$	11.8	-54.3	64 : 36
CCl_4	7.5	-53.7	53 : 47

At the same time the compounds 22 with dimethyl- and dibutylaminogroups at phosphorus have the structure of diazadiphosphetidines. The reasons of this anomaly are not clear at present.
On the basis of these results it can be suggested that the cycle of 4,5-benzo-1,3,2-dioxaphosphole has still greater influence on the dimerization of phosphazocompounds than the dioxaphospholane cycles, which is probably due to more ring strain of condensed cycle.
The competitive influence of ring strain of dioxaphospholane cycle and the electronic nature of substituents at phosphorus on the process of dimerization-monomerization can be observed in other compounds. For example, the thermolysis of fluorophosphorane 24 at first is likely to give iminodioxaphospholane 25 but this intermediate 25 is quickly dimerized into 1,3-diaza-2,4-diphosphetidine 26 (11). The bulky substituents at nitrogen of imino-group in this case would hinder dimerization, but the total effect of ring strain and the electronegative atom of fluorine at phosphorus is predominant.



(24) (25)

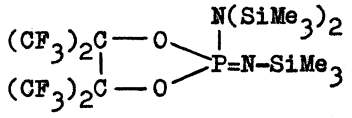


(26)

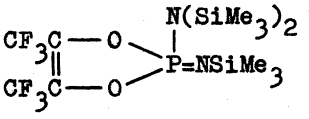
a, R = t-Bu, δ^P - 44.3 ppm

b, R = Me_3Si, δ^P - 47.5 ppm

If aminogroup is introduced into compounds 25 instead of fluorine, the dimerization of compounds 27 does not occur as the influence of substituents is opposite and likely exceeds the influence of ring strain (12).
The compound 28 is monomeric too.

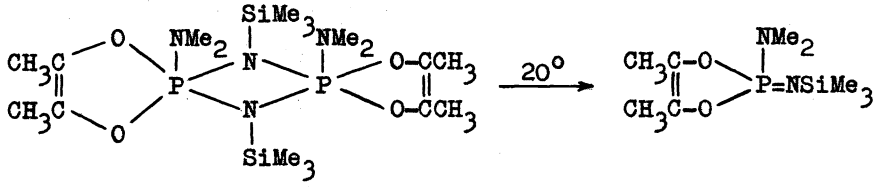


(27), δ^P 8.6 ppm



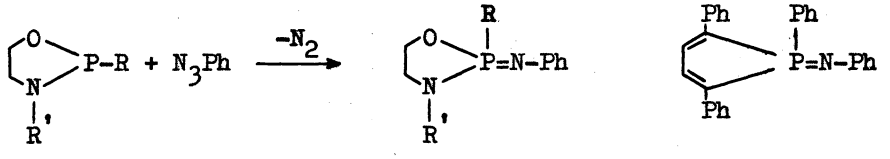
(28), δ^P - 5.3 ppm

Moreover tricyclic diazadiphosphetidine 29 obtained at - 70° gives iminophosphole 30 at increasing temperature (13).



(29), δ^P - 53.1 ppm (30), δ^P 15.9 ppm

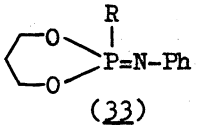
Contrary to 2-imino-1,3,2-dioxaphospholanes, 2-N-phenylimino-1,3,2-oxazaphospholanes 31 are only in monomeric structure. These compounds 31 are relatively strong bases with pKa (CH_3NO_2) 14.5-17.7, in IR spectra there are bands at 1350-1370 cm^{-1} and in NMR ^{31}P a signal near 8 - 20 ppm.



(31) (32)

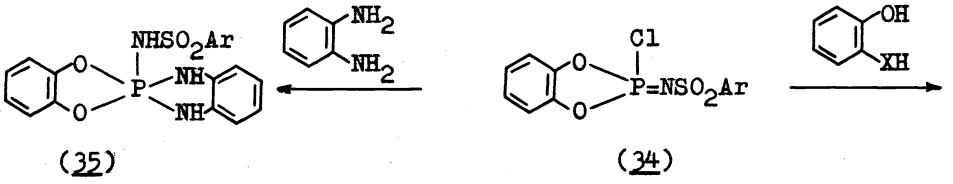
R = OMe, OEt, OPr-i, NEt_2; R' = Me, Ph

1-N-phenylimino-1,2,5-triphenylphosphole 32 is also monomeric (14). Thus, the nature of the phospholane cycle has an important influence on dimerization process. The following studies of a wide range of iminophospholanes will reveal the influence of all possible factors on their properties. The ability to dimerization is expected to occur in iminoderivatives of other phosphorus cycles which show phospholane effect, i.e. have the ring strain. It will be noted that N-arylimino-1,3,2-dioxaphosphorines 31 are monomeric perhaps due to the absence of the ring strain in the cycle (15).

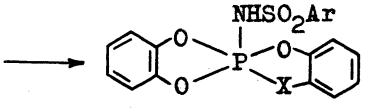


(33)

The ring strain brings about some peculiarities in reactions of monomeric iminophospholes. 2-Chloro-2-N-acylimino-4,5-benzo-1,3,2-dioxaphospholes 34 have a higher reactivity than the acyclic dialkoxychlorophosphazocompounds. They react more easily with the above-mentioned phenols, anilines and arensulphamides. Under some reactions chloroiminophospholes 34 give the compounds of five-coordinated phosphorus. For instance, 2-chloro-2-acyliminophospholes 34 react with catechol, o-phenylene-diamine and o-aminophenol with the formation of 1-N-acylaminospirophosphoranes 35, 36 (16).

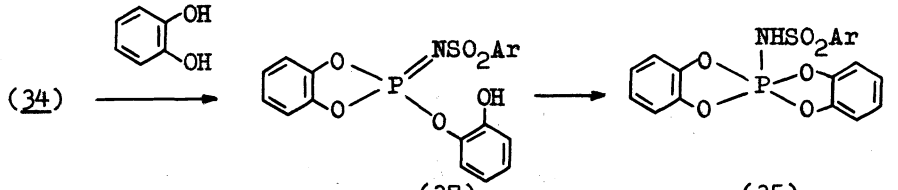


(35) (34)



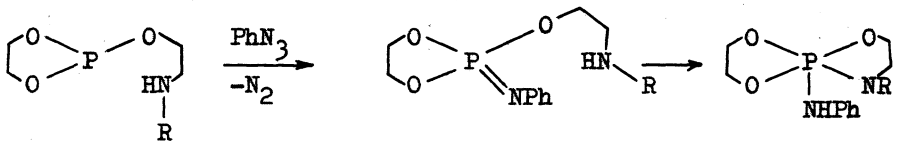
(36) X = O, NH

We consider that the formation of spirophosphoranes 35-36 from chloroiminophospholes proceeds via formation of the substituted iminophospholes with N=P bond such as the compound 37. Then the tautomeric migration of a proton occurs from OH- or NH-groups to nitrogen atom of N=P bond and spirophosphorane is yielded. This process is favoured both by the strained phospholane cycle in the initial molecule and the possibility of formation of the second similar ring resulting from attack of phosphorus atom by nucleophilic ortho-substituent.

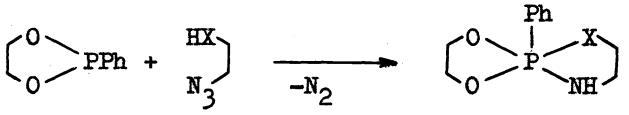


(34) (37) (35)

At first the intramolecular cyclization of iminophospholes into spirophosphoranes has been reported by R. Wolf and coworkers under reaction of phenyl azide and phospholanes 38 (17), and then was observed by J. Cadogan et al. in the reactions of bifunctional azido-compounds with a variety of phosphorus compounds (18).

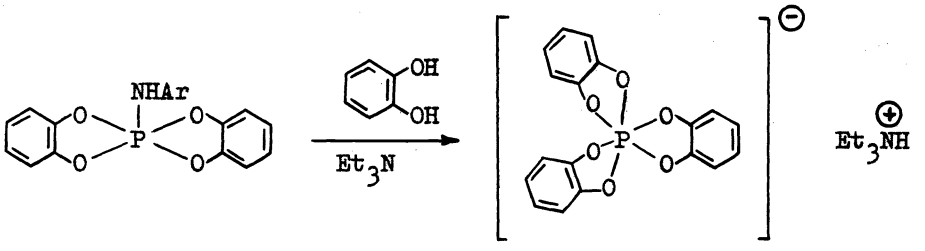


(38) (39) (40)



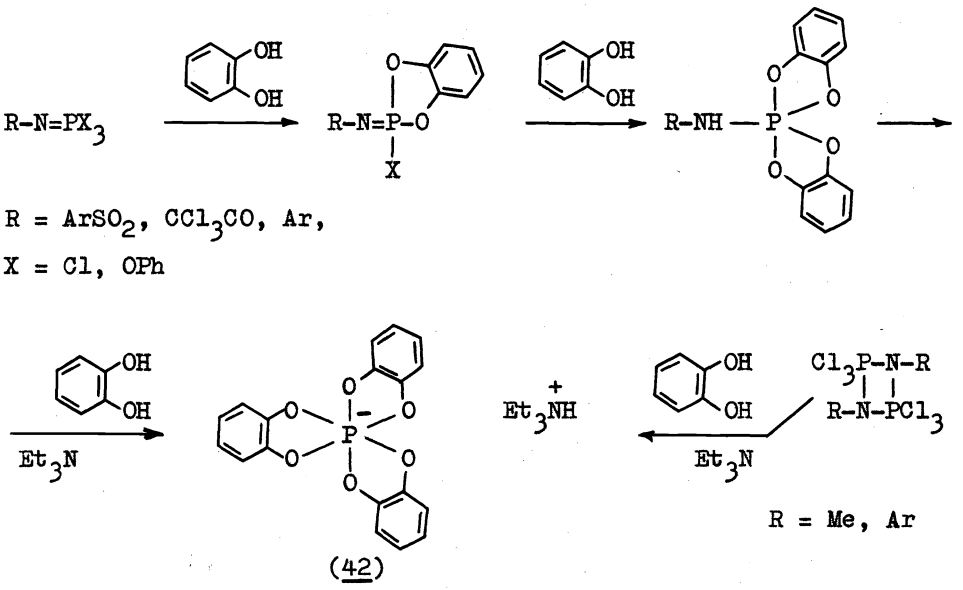
(41)

For these compounds the phosphorane-phosphaze tautomerism such as 37 ⇌ 35 or 39 ⇌ 40 is possible, although neither we nor other scientists have confirmed it by NMR ^{31}P spectroscopy. However the possibility of this tautomerism can not be neglected because for the phosphoryl compounds the tautomeric conversion in spirophosphoranes has been recorded (19). Spirophosphoranes are stable under normal conditions, but at the action of triethylamine they are converted into spirophosphorates 42 (20).



(35) (42)

The action of catechol and triethylamine on spirophosphoranes 35 gives spirophosphorate 42 in high yield.
We have found that spirophosphorate 42 could be isolated from the reactions of trichloro- or triphenoxyphosphazocompounds and catechol in the presence of triethylamine. The reactions have been carried out with trichloro and triphenoxy-N-arylsulphonyliminophosphates, trichloroacetyliminophosphate, triphenoxyphosphazobenzene, a series of 4,5-benzo-1,3,2-dioxaphospholes and N,N'-dimethyl - and N,N'-diphenyl - 2,2,2,4,4,4-hexachloro-1,3-diaza--2,4-diphosphatidines (20). These reactions seem to be common for a wide range of phosphazocompounds having easy leaving groups at phosphorus. Spirophosphorate 42 is known to be obtained from a series of phosphorus chlorides or its oxygen derivatives (21).



(42)

Undoubtedly, the transformation of phosphazocompounds into spirophosphorate 42 proceeds in a number of reactions of successive substitution, as shown in the scheme.

The properties and reactions of iminodioxaphospholanes discussed in the report are first of all due to the specific structure of these five-membered cycles of phosphorus. It should not be excepted that ylides with five-membered phosphorus ring can have some peculiarity in properties too. We hope that further investigations in this field will bring about new interesting results.

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