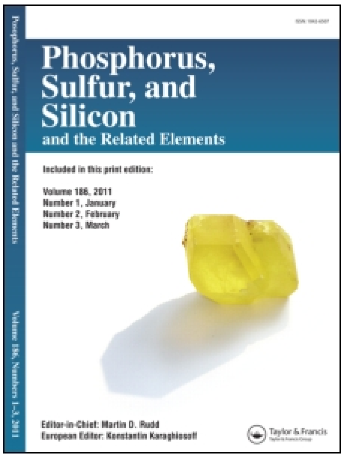

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

SPIROPHOSPHORANES - STRUCTURE REACTIVITY

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To cite this Article Burgada, Ramon(1976) 'SPIROPHOSPHORANES - STRUCTURE REACTIVITY', Phosphorus, Sulfur, and Silicon and the Related Elements, 2: 1, 237 — 249

To link to this Article: DOI: 10.1080/03086647608078955

URL: http://dx.doi.org/10.1080/03086647608078955

Phosphorus and Sulfur
1976, Vol. 2, pp. 237-249

SPIROPHOSPHORANES – STRUCTURE REACTIVITY †

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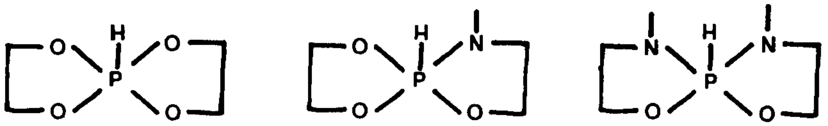
The first part of this article will deal with the reactions of spirophosphoranes with a P–H bond. These compounds contain two five-membered rings and have four oxygen atoms, or three oxygen atoms and one nitrogen atom, or two oxygen and two nitrogen atoms directly bonded to the phosphorus atom, which in all cases bears an hydrogen atom (Scheme 1). The most remarkable property of these compounds is undoubtedly their ability to give rise to a tautomeric equilibrium between the tri- and penta-coordinated structures $P_{III} \rightleftarrows P_V$.

Scheme 2 shows the first example of this type of equilibrium, which was suggested in 1967,[1] and confirmed by infrared spectroscopy in 1968,[2] and by P^{31} nmr at various temperatures in 1970-71.[3] This suggestion was based on an attempt to conciliate a chemical property, which had previously been described in our laboratory,[4] and that we shall discuss later, and spectroscopic results, particularly those obtained by P^{31} nmr. It was later demonstrated in our laboratory, and in the laboratories of Professors Mathis, Barrans and Wolf in Toulouse with many examples, that the phenomenon was quite general and could be represented by Scheme 2.



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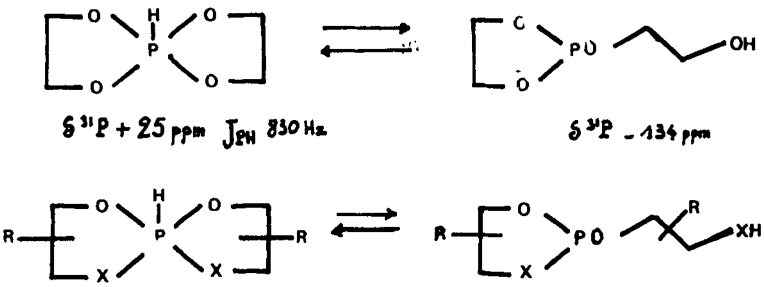

X = O or NH or NR

2

In the spirophosphorane which has one nitrogen atom, the split essentially occurs between the phosphorus and the nitrogen. We will not discuss here the various factors which determine the equilibrium such as the electronic factors, the steric factors, or the symmetry properties of the tri- and penta-coordinated molecules, or the external factors such as the solvent and the temperature. All this has been discussed in a number of articles and was reviewed recently.[5] Since the pentacoordinated phosphorus structure and the tricoordinated phosphorus structure bearing a nucleophilic XH function are very different, we looked for a specific reaction for each one of them. Our interest being to find evidence for the equilibrium itself even when one of the forms exists in such small quantities that it is no longer detectable by spectroscopic methods.

In scheme 3 we can see that the action of phenyl isocyanate on tetra-oxygenated spirophosphoranes leads to the formation of pentacoordinated derivatives such as 3 and 4 and not to a tricoordinated derivative such as

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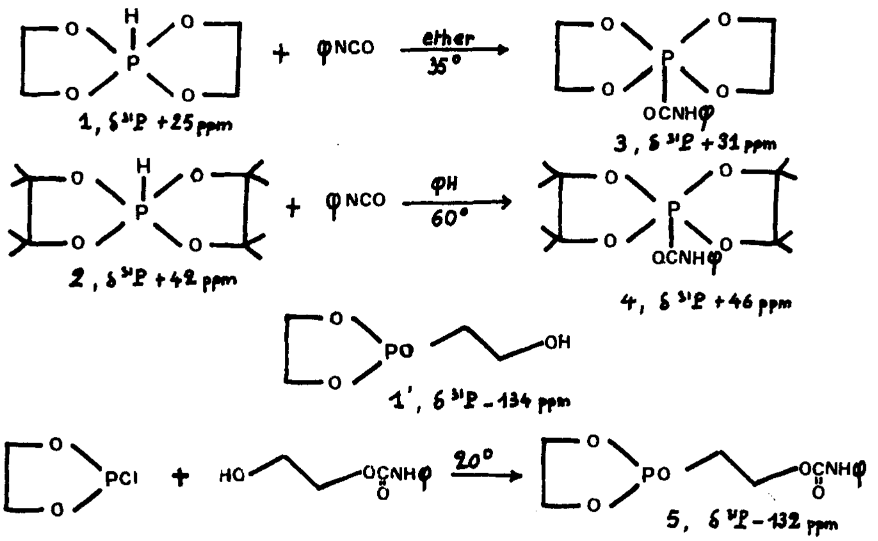
† Plenary Lecture. The Vth International Conference of Organic Phosphorus Chemistry, Gdansk, Poland, September 1974.

5. This occurs although spirophosphorane 1 is present to the extent of 10-20% as the tautomer 1′ which has a free OH group that could form a carbamate with the isocyanate; a reaction which should lead to the tricoordinated compound 5.



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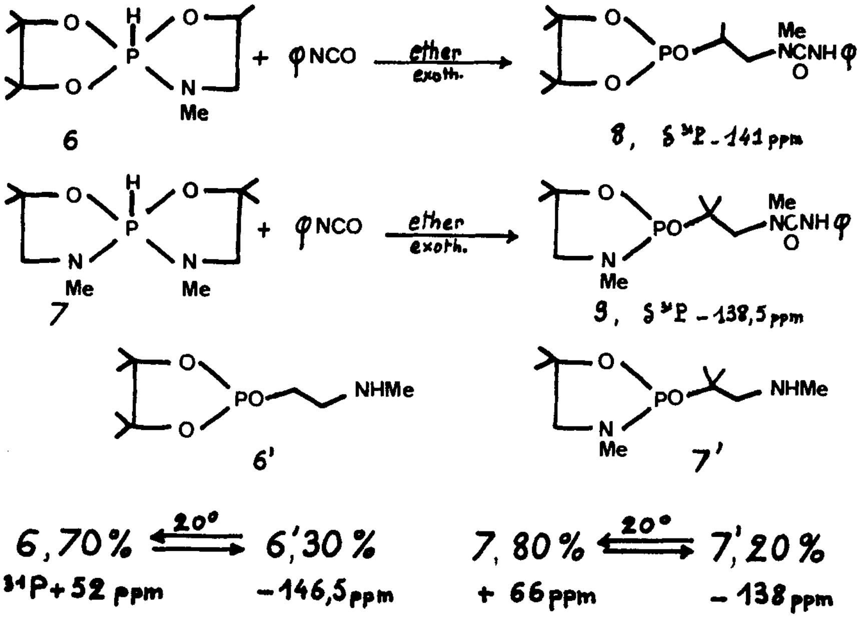
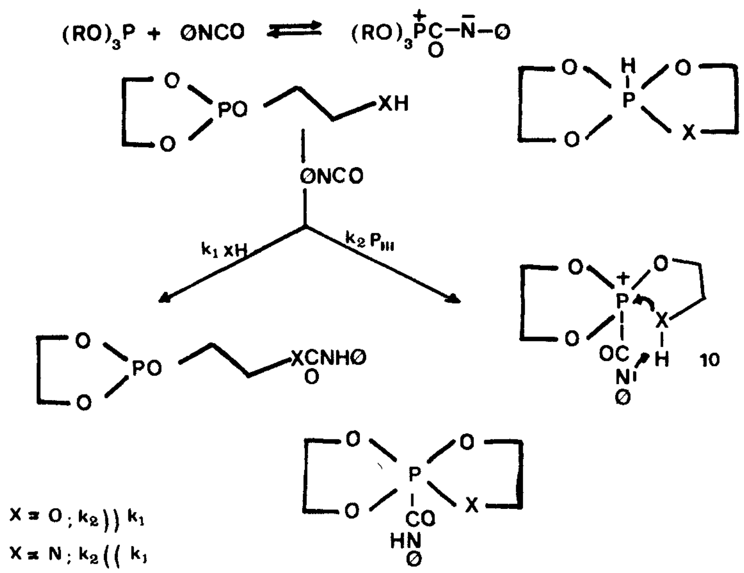


4

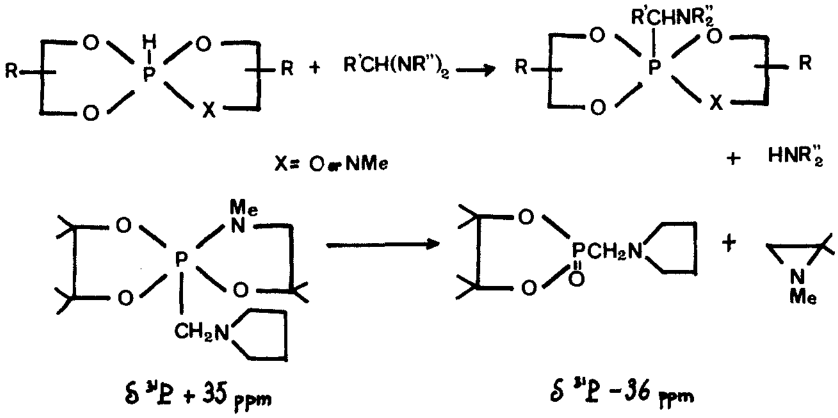
Let us now examine the case of the spirophosphorane which bears a nitrogen atom (Scheme 4). We can see that, in this case, there is only the formation of tricoordinated derivatives although spirophosphoranes 6 and 7 respectively show 30% and 20% of the tricoordinated form 6′ and 7′ at 20°. We can therefore conclude that the reactions of the isocyanate are independent of the tautomeric equilibrium, but depend on the nature of the nucleophilic XH function, which is free by equilibrium.

For the trimerization of isocyanates catalyzed by trialkyl phosphites, Hudson and his coworkers have suggested a mechanism which starts with the first slow step shown in Scheme 5.[6] By analogy and drawing upon the tricoordinated form of spirophosphorane, we can envisage the formation of an intermediate such as **10**; furthermore it is well known that the speed of the reaction of amines with isocyanates is much greater than the speed of the reaction of alcohols with these same isocyanates. In view of this observation, the mechanism which we suggest is coherent with our results; it involves the tricoordinated form of spirophosphoranes. The reaction is a function of the rates k_1 and k_2 of reaction of the nucleophilic centers, XH, and the tricoordinated phosphorus, with the carbonyl function of the isocyanate.



5

Let us now examine the reaction of aminals (Scheme 6). As opposed to the case with isocyanates, aminals react with tetraoxygenated or nitrogen-containing spirophosphoranes to lead exclusively to pentacoordinated derivatives. These are the unstable α-aminospirophosphoranes that can easily be decomposed into α-aminophosphonates. The formation of the α-aminospirophosphorane occurs only if the amine which is simultaneously formed is eliminated from the reaction mixture as soon as it is formed. However if the corresponding amine is added to the pure α-aminospirophosphorane, isolated by crystallization or distillation, there is no reaction or regression to the starting products. This observation enables us to conclude that the starting materials are in equilibrium with an intermediate compound which can evolve irreversibly to the α-aminospirophosphorane (Scheme 7).



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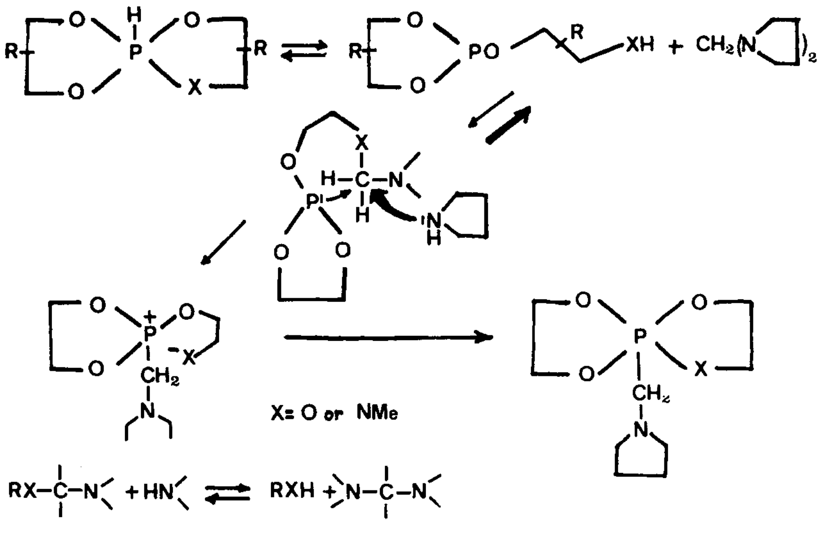
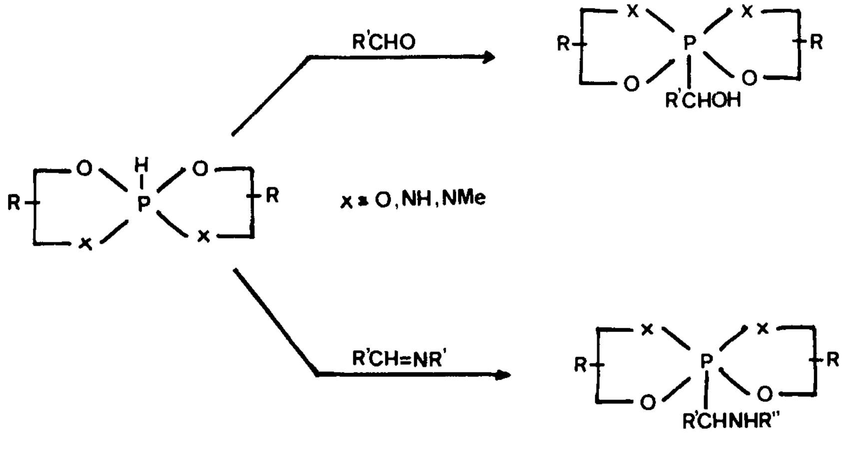


7

Here also we suggest a mechanism involving the tricoordinated form of the spirophosphorane. The first step is reversible and it is a reaction of the XH function of the aminal in agreement with the well known classical scheme; the second step, which is a nucleophilic intramolecular attack of the tricoordinated phosphorus on the carbon atom of the XCH_2N group, is rendered irreversible by the elimination of the amine. The reactions of spirophosphoranes with a P–H bond on aldehydes[7] and imines[8] (Scheme 8), which we have previously described, can be explained by a mechanism close to the one we have just discussed.

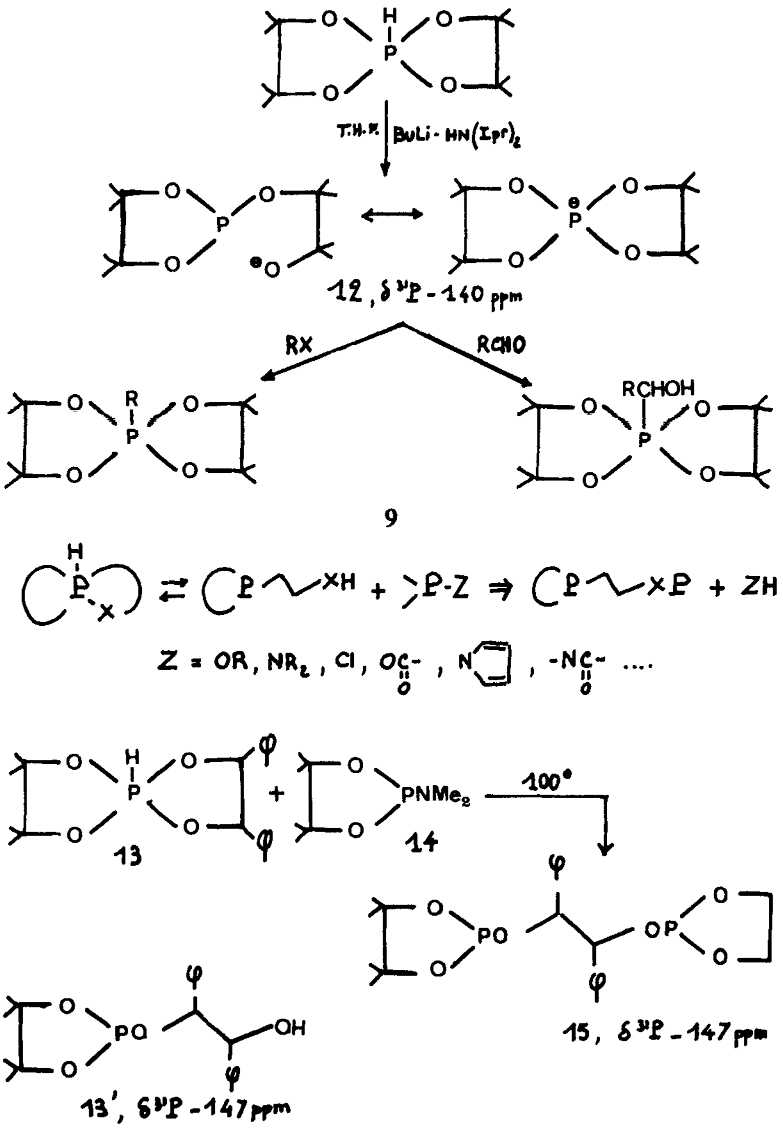


8

Starting with a spirophosphorane containing a P–H bond it is thus possible, using the direct reaction we have just seen, to obtain a spirophosphorane containing a phosphorus-carbon bond in which a carbon atom bears a functional group. Another synthetic route is possible through the metallation of spirophosphoranes (Scheme 9). This metallation can be obtained with sodium hydride, sodium amide, or even better by using the amide ion itself obtained through the butyl lithium-isopropyl amide interchange.[9] We have obtained positive results with yields ranging from 60-90% with a large number of halides and aldehydes.

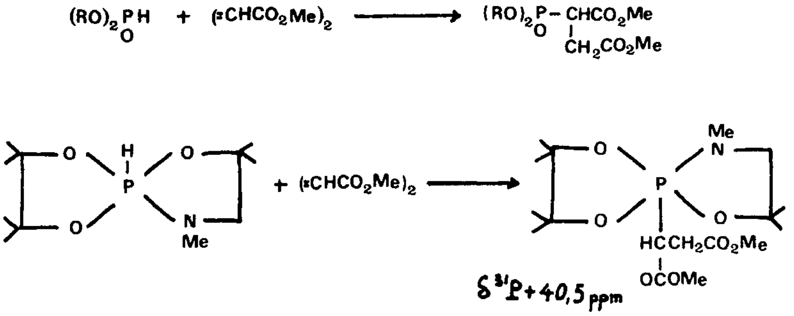
The tricoordinated form of spirophosphoranes are not always detectable by spectroscopic methods; we have therefore looked for, and suggested, a chemical test to show the presence of this tricoordinated form[5,10] (Scheme 10).

This test is based on the following hypothesis: the tricoordinated form obtained through the opening of the spirophosphorane cycle is accompanied by the formation of a nucleophilic XH function that can split the P–Z bond of a reagent and shift the equilibrium concertedly to the right. This can be obtained by the transformation of the XH bond to an XP bond with elimination of ZH.[5,10] The test is independent of the position of the equilibrium: it is therefore usable even if the tricoordinated form only exists in trace amounts. We have chosen the $N(CH_3)_2$ group as the radical Z, and volatile dimethylamine thus formed can be continuously measured outside the reaction medium. This enables a rough estimate of the rate of reaction to be obtained. Among many examples, we have chosen to show the case of the spirophosphorane 13; its tricoordinated form 13′ is not detectable by P^{31} nmr at 100°. As a general rule, the percentage of the tricoordinated form increases with the temperature. Through reaction with the aminophosphine 14, we obtained the diphosphite 15 in quantitative yield. This test is applicable to the majority of tetraoxyspirophosphoranes and also to those which contain nitrogen.



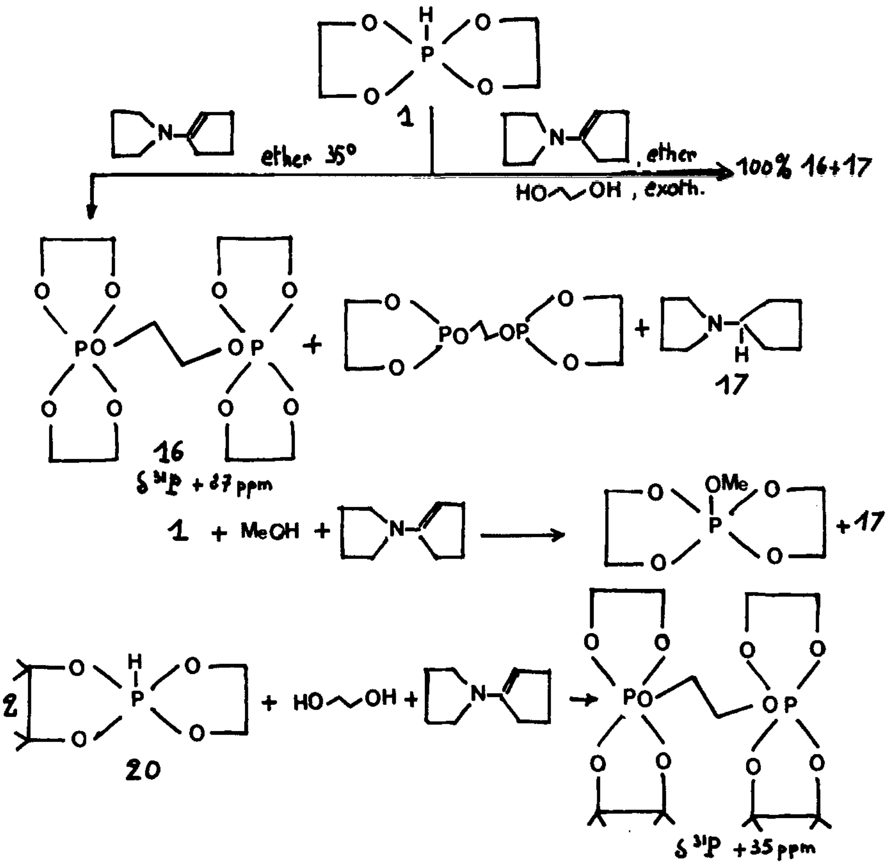
10

In recent articles,[5,10] arguments have been discussed for a reaction of the P–Z group, solely on the P_{III} form and not on the P_V form of the spirophosphorane. In the reactions so far discussed, a carbon-pentacoordinated phosphorus bond was formed from a hydrogen-pentacoordinated phosphorus bond exactly as in the hydrogen phosphonates, in which it is possible to create a carbon-phosphorus bond from a hydrogen-phosphorus bond. Scheme 11, which shows the addition of the dimethyl maleic ester to hydrogen phosphonate[11] or a spirophosphorane, is an example of this comparison.



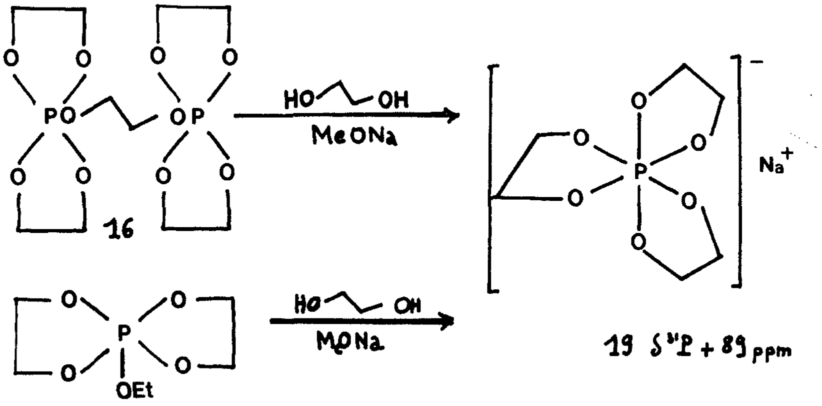
$$(RO)_2\underset{O}{P}H + (=CHCO_2Me)_2 \longrightarrow (RO)_2\underset{O}{P}-\underset{CH_2CO_2Me}{CHCO_2Me}$$

11



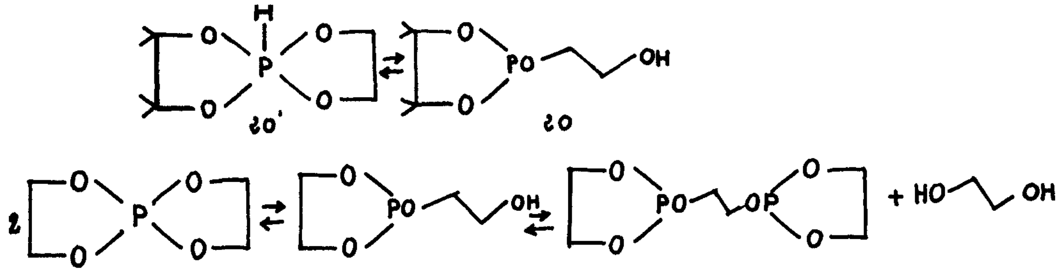
12

Let us now examine the case of the creation of an oxygen-pentacoordinated phosphorus bond starting from a hydrogen-pentacoordinated phosphorus bond of a spirophosphorane. So far, only two types of reactions giving this result are known. Originally we thought that the first reaction presented (Scheme 12) would lead to a condensation product between the spirophosphorane and the enamine analogous to the products obtained by condensation of hydrogen phosphonates and enamines.[12] However, the products which are obtained are a dispirophosphorane, a diphosphite, and the amine corresponding to the reduction of the enamine used as starting material. If the reaction is performed in presence of one mole of ethylene glycol, the dispirophosphorane and an amine are obtained in practically quantitative yields. The third reaction simply shows that it is possible to replace the glycol with a simple alcohol, thus obtaining a family of phosphoranes which can be prepared through the use of tricoordinated phosphorus derivatives and peroxides after the method of Denney and his coworkers.[13] Compound **16** was identified by microanalysis and by its spectroscopic parameters (Figure 1). The structure of the dispirophosphorane **16** is confirmed by its ability to form the hexacoordinated derivative **19** already prepared and described by Denney and his coworkers.[14] (Scheme 13.)



13

Our results are still too incomplete to give an hypothesis concerning the mechanism of reaction. However, it should be noted that the spirophosphorane **1** reacts with the enamine even in the absence of alcohol or glycol; however, the reaction is much slower compared to spirophosphorane **20** which only reacts when glycol is present (Scheme 12). This can be explained by the fact that spirophosphorane **1** can liberate the glycol necessary to the reaction through a series of equilibria which we have shown to occur.[10] Spirophosphorane **20**, which has 4 methyl groups on the ring, is not as reactive when in its tricoordinated form and cannot give rise to second part of the equilibrium with liberation of the glycol (Scheme 14).



14

The second reaction that can give an oxygen-pentacoordinated phosphorus bond from an hydrogen-pentacoordinated phosphorus bond is reported in scheme 15. It is shown here as the reaction between the tricoordinated form of a tetraoxygenated spirophosphorane or as the reaction of an ionized tricoordinated form of an aminospirophosphorane with a diketone.[15] The pentaoxyspirophosphorane **21** can also be obtained by nucleophilic attack of the glycol on pentacoordinated compound **23** with liberation of dimethylamine.[16] This leads to the second part of this paper in which we examine some properties of spirophosphoranes in which the fifth ligand is constituted by a nitrogen atom or an oxygen atom.

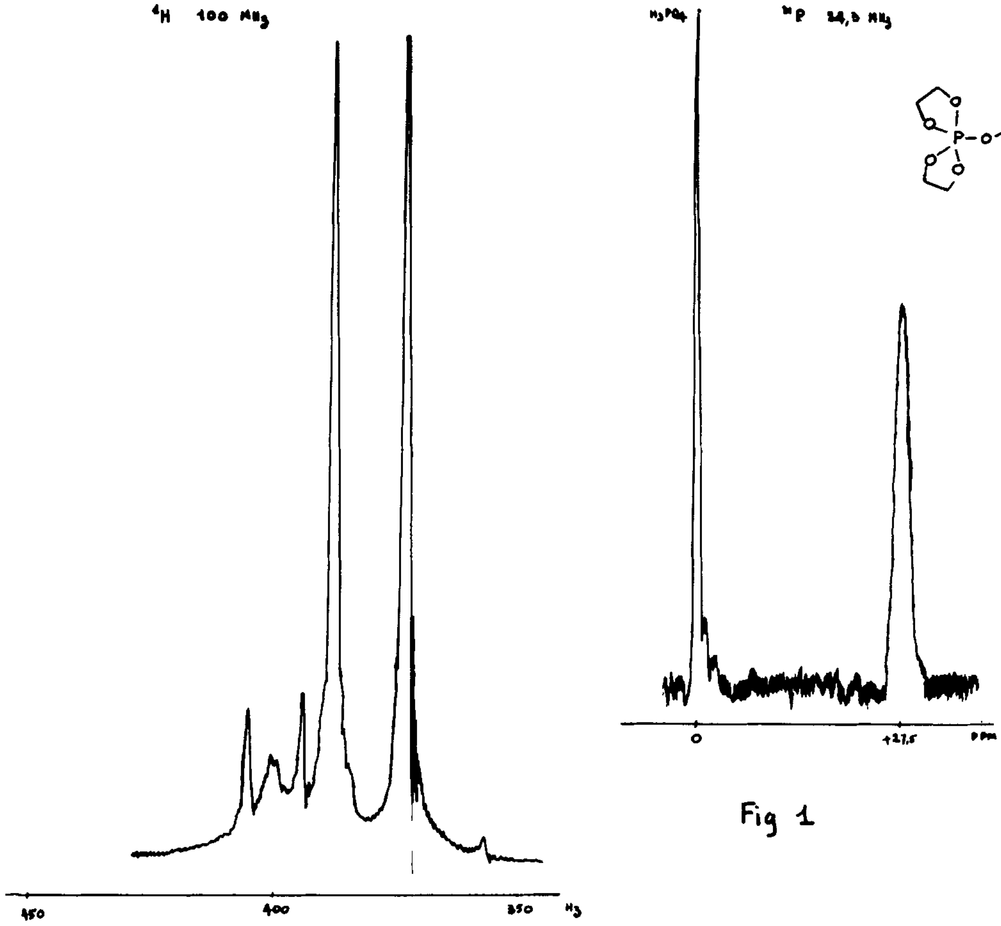
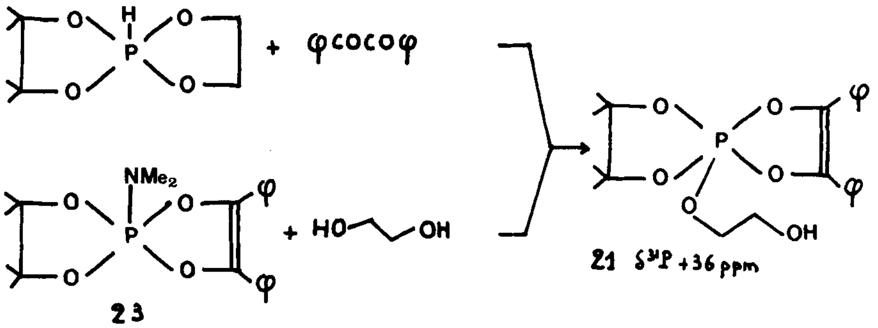
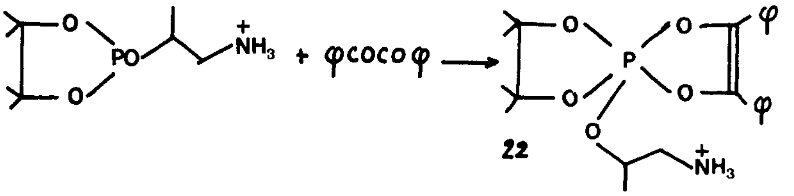


Fig 1



23

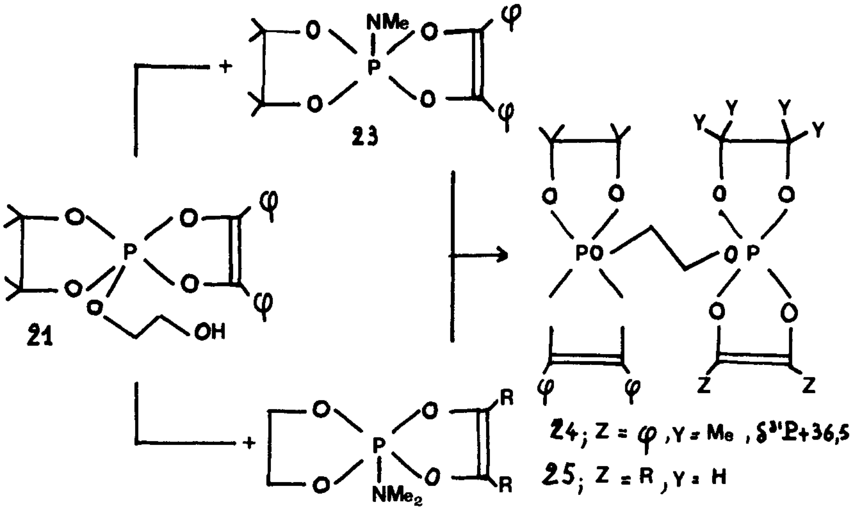
21 δ³¹P +36 ppm



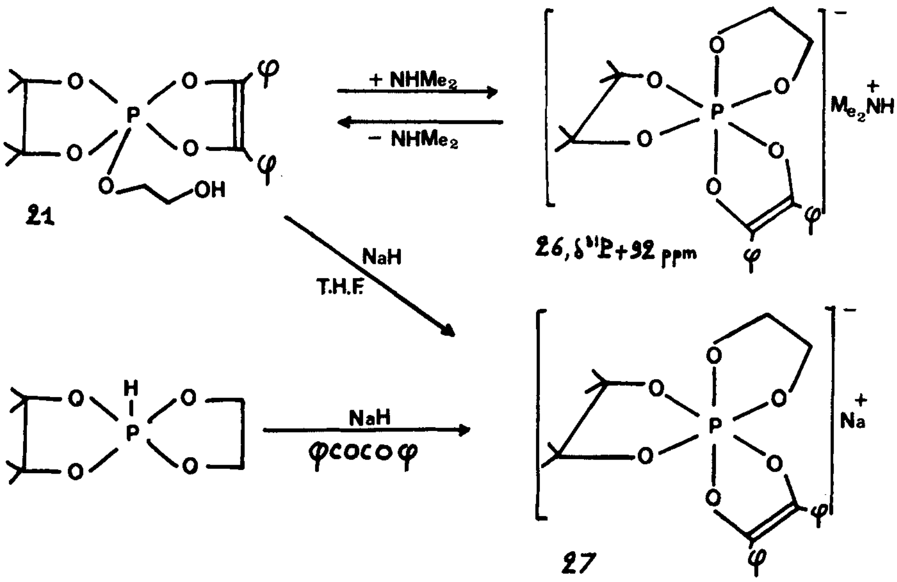
22

Essentially we shall use as models for these examples compounds 21 and 23, which are particularly interesting for the study of nucleophilic substitution on pentacoordinated phosphorus and for the formation of hexacoordinated phosphorus derivatives. Scheme 16 shows that, thanks to its functional OH group, compound 21 can react with another molecule of aminospirophosphorane such as 23 thus forming symmetrical or unsymmetrical dispirophosphoranes such as 24 and 25. Lastly compound 21 can, in basic media, give hexacoordinated derivatives. If dimethylamine is added to spirophosphorane 21 (Scheme 17), a stable hexacoordinated derivative 26 is formed. Slight heating of 26 drives out the dimethylamine with formation of the spirophosphorane 21.

The following reactions show two possible routes to hexacoordinated compounds with the replacement of the ammonium cation by the non-volatile sodium cation, thus increasing the stability of the hexacoordinated complex. Of course, it is possible to envisage a number of variations of the same principle with this reaction; however, we shall only give a few examples here to show that this is not a unique case, but rather a general phenomenon.

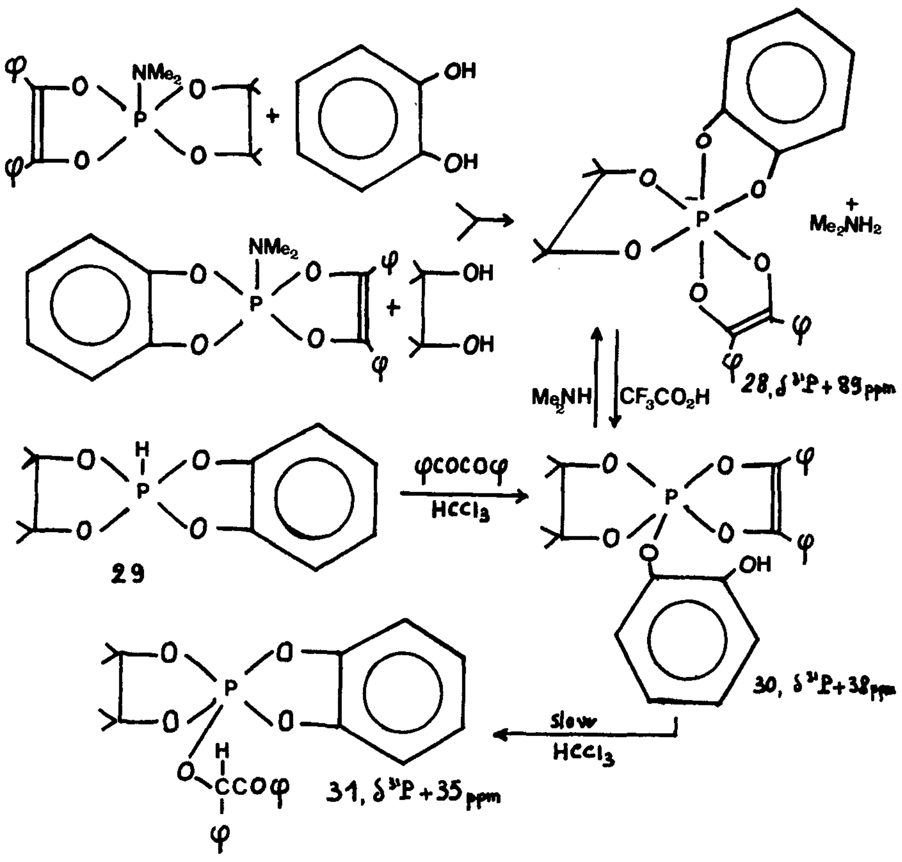


16



17

The first two reactions (Scheme 18) which are nucleophilic substitutions on the pentacoordinated phosphc rus in basic media lead to the hexacoordinated compound 28. The third reaction is, we believe, very interestin it is carried out in neutral media, and it leads to the spirophosphorane 30 through a nucleophilic attack of the tricoordinated form of 29 on the diketone. Still in neutral media, compound 30 slowly changes to form 31. The driving force for this intramolecular rearrangement being attributable to a gain in stability arising from th replacement of the non-saturated ring by a catechol ring. This phenomenon is quite general in the chemistry of spirophosphoranes, and relative stability can be classified according to the nature of the ring.



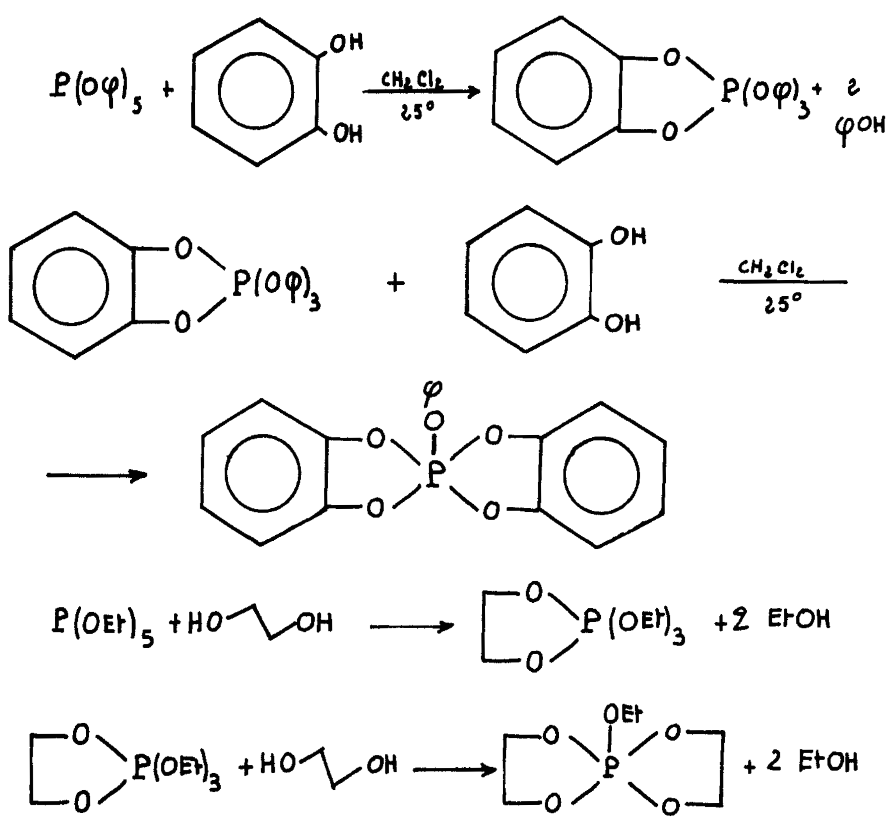
18

Scheme 19 shows another example of displacement reactions in which the exchange is due to a gain of stability arising from the replacement of two ligands by an unsaturated[17] or by a saturated ring.[13]

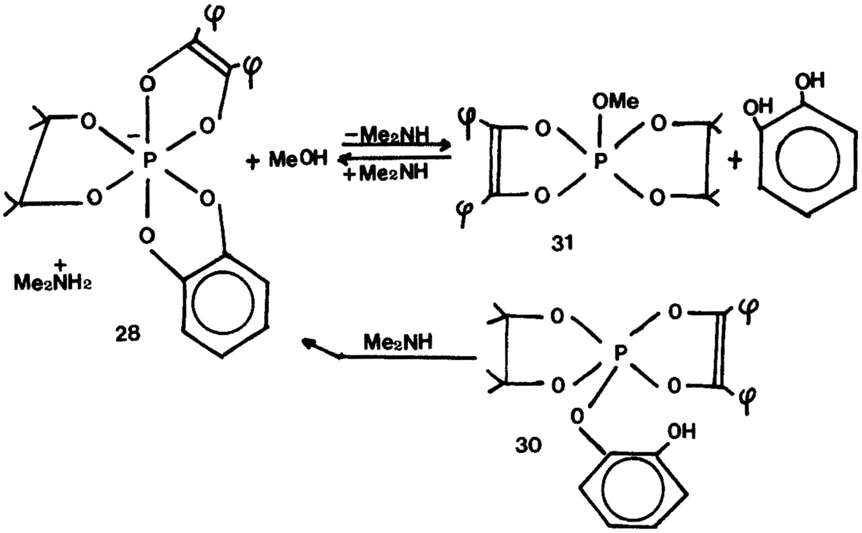
Let us now return to Scheme 18. If dimethylamine is added to spirophosphorane 30 before it has changed to compound 31, the medium is now basic and there will be immediate formation of the hexacoordinated complex 28. Compound 31 is stable in basic media. The addition of trifluoroacetic acid to 28 gives back spiro phosphorane 30 which we can now consider as being formed temporarily during the first and second reaction: of scheme 18, but which cannot be observed spectroscopically because of the rapid evolution of dimethylamine due to the basicity of the medium.

In the last example (Scheme 20) of an exchange reaction, we can again observe the influence of a base on the evolution of this system.

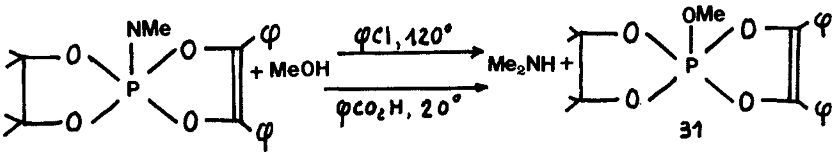
The final part of this paper concerns the influence of acids on the reaction which we have just seen. In ord to carry out the methanalysis of spirophosphorane 23, thus obtaining the methoxylated compound 31, it is necessary to heat the reaction mixture to 120° for few hours (Scheme 21). In the presence of one mole of carboxylic acid,[18] however, the reaction is extremely fast even at 20°.

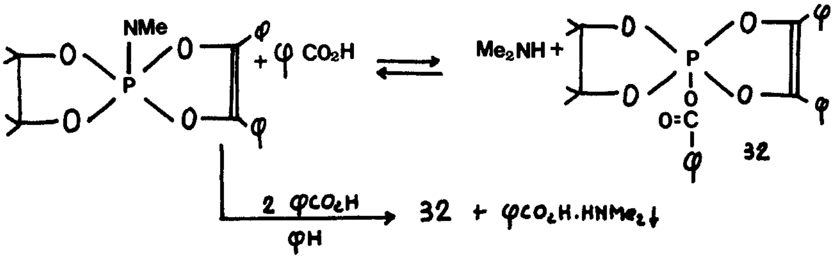

P(Oφ)5
OH
OH
CH2Cl2
25°
P(Oφ)3
+ 2 φOH
φ
O
P
P(OEt)5
+HO
OH
P(OEt)3
+2 EtOH
OEt
+ 2 EtOH

19


φ
O
P
+ MeOH
−Me2NH
+Me2NH
OMe
OH
+
Me2NH2
28
31
Me2NH
30

20





21

Nifant'ev and his coworkers have observed an identical phenomenon during the alcoholysis of the nitrogen-tricoordinated phosphorus bond.[19] In fact we have shown that, in the cases of both tri- and pentacoordinated phosphorus, the increase in the speed of the reaction is not due to a catalytic effect but rather to the formation of the very reactive acyloxy intermediate;[18,20] in the present case it is an acyloxy spirophosphorane derivative which is formed through the equilibrium shown here. In the presence of two equivalents of acid, the dimethylamine is eliminated as an insoluble salt and the acyloxy spirophosphorane can be isolated in crystalline form. Of course, the presence of methanol leads to the pentaoxy spirophosphorane 31. A few years ago, Ramirez and coworkers[17] suggested that base-catalyzed nucleophilic substitutions at five-coordinated oxyphosphoranes involved intermediates with octahedral hexacoordinated phosphorus. Professor Ramirez has informed me that stable crystalline adducts with hexacoordinated phosphorus, related to the postulated intermediates in the displacement reactions, have now been isolated (paper scheduled for publication in *J. Am. Chem. Soc.*).

ACKNOWLEDGMENTS

I should like to acknowledge my collaborators: Doctor Daniel Bernard and Claude Laurenco, who have played a key part in this work.

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