## SOME PHYSICAL AND CHEMICAL PROPERTIES OF THE PHOSPHORUS-NITROGEN BOND

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# SOME PHYSICAL AND CHEMICAL PROPERTIES OF THE PHOSPHORUS-NITROGEN BOND [†]

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This lecture is dedicated to the memory of Dr Hafiz Boudjebel, who worked for two years in our laboratory and unfortunately died in a plane crash near Tangier in December 1973.

We began working on organic compounds of phosphorus twenty years ago. We encountered many interesting problems, and, having to choose between them for this occasion, eventually decided to speak about the phosphorus-nitrogen bond and a few related questions. We could gather many experimental facts, which Hercule Poirot would describe as the pieces of a puzzle, and we are trying to arrange them according to a nice logical pattern. The pattern is by no means complete now, but some main lines begin to appear; both spectroscopic and chemical evidence give some hints concerning the respective electrophilicity and nucleophilicity of phosphorus and nitrogen, or, to put it another way, on the hybridization state of both atoms and on the order of the P–N bond.

## STEREOCHEMISTRY OF PHOSPHORUS NITROGEN COMPOUNDS

The geometry of molecules containing the phosphorus-nitrogen bonds gives some information on the nature of this bond, and it is useful to review some facts.

Kuczkowski[54] proved that $F_2P–PH_2$ is perfectly *trans*; hydrazine is well known to be gauche (Hamada et al.[44]). In both cases, the tricoordinated atoms are pyramidal (Fig. 1). Morris and Nordmann[73] found that $F_2P–N(CH_3)_2$ in the crystal has a plane of symmetry which contains both N–C and the N–P bonds; this can be considered as an extreme case of gauche conformation. Nitrogen in this compound should then be in an $sp^2$ hybridization state, and the comparatively short P-N distance (1.628 Å; P-P distance, 2.218; N-N, 1.451; mean between P-P and P-N, 1.83) suggests that the order of this bond is greater than one.

M. C. Labarre et al.[55] compared data from magnetooptical rotation, dipole moments and magnetic resonance and concluded that such a partial bonding in fact does exist to an extent which depends on the nature of the substituents.
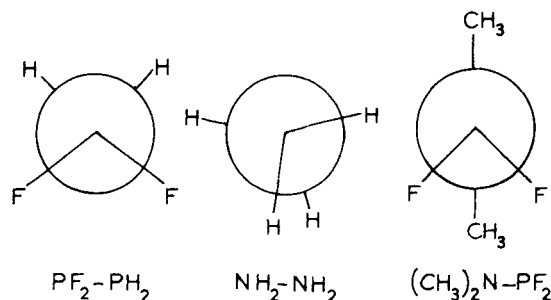


FIGURE 1    Conformation of $F_2P–NH_2$ (after Kuczkowski et al., Ref. 54), $H_2N–NH_2$ (after Hamada et al., Ref. 44), $F_2P–N(CH_3)_2$ (after Morris and Nordmann, Ref. 73).

The hybridization state of a nitrogen atom can be estimated from the consideration of spin coupling constants between directly linked $^{15}N$ and $^1H$ nuclei; such $J$ constants increase with increasing $s$ character of the orbital by which the nitrogen atom links to hydrogen (Binsch et al.,[9] Axenrod et al.[2,3]). The values measured by Cowley et al.[30,32] for $^1J(^{15}N^1H)$ in P(III)–N–H systems are consistent with an hybridization state of nitrogen near $sp^2$.

Two factors can tend to force nitrogen into an $sp^2$ or near $sp^2$ state: the ability of phosphorus to attract

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electrons from the lone pair of nitrogen and the electron transfer from phosphorus towards nitrogen along the single bond. The first effect is expressed as the result of a CNDO 2 calculation by Bach et al.[6] which gives for the P–N bond an order significantly greater than one, owing to the fact that the orbital occupied by the lone pair of nitrogen is a combination of N-$2p$ and P-$3d$. On the other hand Czismadia, Cowley et al.[33,34] pointed out that the second effect can be very important. A nitrogen atom linked to phosphorus (and not conjugated with a $\pi$ system) could be planar even if the N-to-P coordination is unimportant.

If we turn now to derivatives of tetracoordinated phosphorus, we find a work by Bullen et al.[17] (see also Ref. 16); in crystalline phenylphosphorodiamidate (Fig. 2), one nitrogen atom is quasi-planar, the P → O bond being approximately in the same plane as the P–NH$_2$ system (see also Ghouse et al.[38]).
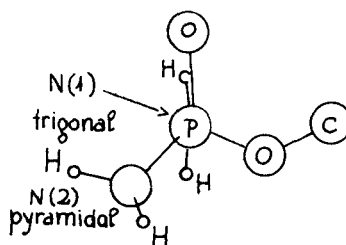


FIGURE 2    Conformation of phenylphosphorodiamidate (after Bullen and Dann, Ref. 17).

There are few determinations of the geometry of compounds containing a pentacoordinated phosphorus atom linked to nitrogen. The amino group in F$_4$P–NH$_2$ seems to be in the same plane as the two apical fluorine atoms (Cowley[31]) (Fig. 3).
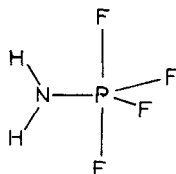


FIGURE 3    Stereochemistry of F$_4$P–NH$_2$ (after Cowley and Schweiger, Ref. 31).

In any case, nitrogen bound to phosphorus does not always seem to be in an $sp^2$ state. Dimethylamino-difluorophosphine itself in the gas phase has a geometry with a pyramidal nitrogen atom different to that reported by Morris (Holywell et al.[46]). In the crystal of phenylphosphorodiamidate the second nitrogen atom is pyramidal. In both cases, the geometry of nitrogen depends upon intermolecular interactions. The nitrogen atom in (C$_6$H$_5$)$_2$P(O)–N(CH$_3$)$_2$ has been reported by Haque and Gauglan to be non planar.[45]

## ROTATIONAL ISOMERISM AROUND THE P–N BOND

The structures described above for P(III) and P(IV)-N systems imply the existence of a barrier to rotation which was studied for aminophosphines (sensu lato) by Cowley et al.[27-29] as well as by French workers (Charrier et al.,[25] Simonnin et al.[85]) on the basis of dynamic nuclear magnetic resonance experiments.

Another aspect of the same problem is the existence of rotational isomerism. Dr Ayed[4] prepared many aminophosphines containing an NH group, and he established with R. Mathis et al.[5,70] that the NH-stretching absorption band is in most cases double (Fig. 4); the relative intensities of both components depending on the bulk of the group R. In the case of 3, the band is simple; this could be due to a weak attraction between the NH group and one of the phenyl groups.
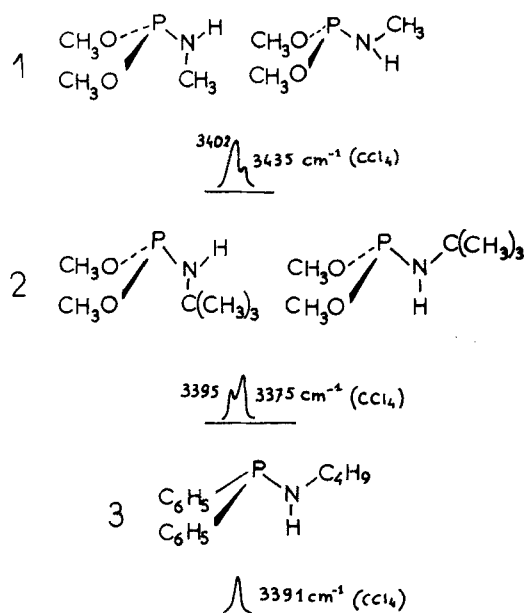
FIGURE 4    Infrared absorption bands of the NH group in aminophosphines as evidence for rotational isomerism (after R. Mathis, N. Ayed et al., Ref. 70).

In phosphoramides only one NH-stretching band is observed but two in amides of thionophosphoric acid (Nyquist et al.,[74-76] R. Mathis, J. Khemdoudi, and T. Bouissou[72]). These latter compounds seem therefore to exist in two forms (Fig. 5), whereas in phosphoramides *sensu stricto* one of them (form 4 according to Nyquist) is heavily favored so that the other one is undetectable.
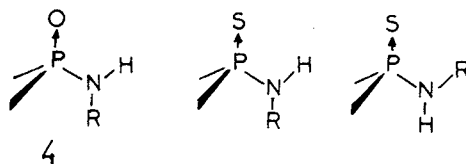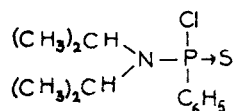


FIGURE 5    Rotational isomerism in P(IV)–N derivatives.

The barrier to rotation for compound 5 has been measured by Jennings.[52]



# ELECTRONIC STATE OF THE NITROGEN ATOM AND NH-STRETCHING VIBRATION

Beside measurement of the spin coupling constant $J(^{15}N^{1}H)$, which requires $^{15}N$ enriched compounds, another

method can give reliable information on the hybridization state of nitrogen, namely the spectroscopic study of the NH-stretching vibration (this work was initiated by H. W. Thompson. it has been reviewed in Ref. 62). The pertinent characteristics are:

i)   the frequency of the fundamental band corresponding to the stretching vibration, $\nu_{0\to1}$;

ii)  the intensity of this absorption band in neutral medium, $A_{0\to1}$;

iii) the effect of the nature of the solvent upon frequency;

iv)  the anharmonicity of the vibration measured by the difference $2\Delta\nu_{1\to2} = 2\nu_{0\to1} - \nu_{0\to2}$.

There is a good correlation between $A_{0\to1}$, solvent effect and anharmonicity: if the solvent effect is higher (which I will describe by "higher acidity", even though this is not quite correct), the anharmonicity is less and the intensity of the fundamental band is greater. Those quantities depend[62] (see also Filimonov[35]) upon inductive effect, but they depend still more upon the hybridization state of the nitrogen atom: an $sp^2$ NH group is more acidic than an $sp^3$ group in cases where the inductive effect should be approximately the same. The relation between the fundamental frequency and molecular structure is not straightforward: negative inductive effect tends to lower it, and higher $s$ character in the NH bond tends to raise it. In any case, measuring some or all of these quantities allows one to locate most NH groups on a scale going from aliphatic amines to pyrrole through arylamines and carboxylic amides. I shall give here the results obtained for some of the compounds studied in our laboratory using mostly solvent effect and anharmonicity (for the intensity of NH-stretching band in spirophosphoranes, see R. Mathis et al.[67]).

It can be seen from Tables I, II, III that the acidity of an NH group linked to phosphorus is sensitive to the nature of the substituents borne by each atom of the P—N bond: it is raised by negative inductive effect, or by conjugation of nitrogen with an aromatic ring. It is sensitive also to the coordination number of phosphorus. The P(III)—NH compounds lie in the range from aromatic amines to carboxylic amides. The P(IV)—NH and P(V)—NH compounds range from carboxylic amides to pyrrole and even higher. This can be summarized by

$$P\,(III)-NH \qquad \begin{array}{l} P\,(IV)-NH \\[4pt] P\,(V)-NH \end{array}$$

The idea of a variable hybridization state of the nitrogen atom can be tested. The first example is a spirophosphorane. In most of the spirophosphoranic compounds studied the NH groups are in an equatorial position according to Mutterties' rule. Compound 18, on the contrary, must have one apical and one equatorial NH group. In this case there is a striking difference between the two groups: one of them is much less acidic than the other one; it is certainly in the apical position and therefore farther from the phosphorus atom.
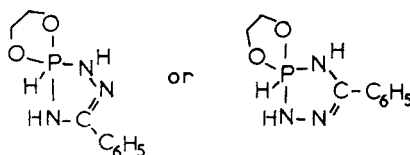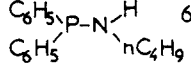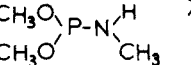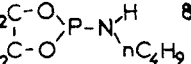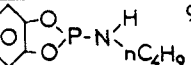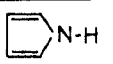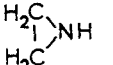


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TABLE I

Spectral properties of NH groups linked to tricoordinated phosphorus atoms (after R. Mathis, Ref. 70; N. Ayed, Refs. 4, 5.)

| COMPOUND | NH stretching | | |
| --- | --- | --- | --- |
| | $\nu_{0-1}$ CCl$_4$ | $\Delta\nu_{0-1}$ CCl$_4$ - dioxane | $2\nu_{0-1}^- - \nu_{0-2}$ |
| $\begin{array}{c} C_6H_5 \\ \backslash \\ C_6H_5 \end{array} P-N \begin{array}{c} H \\ \backslash \\ nC_4H_9 \end{array}$   6 | 3392 | 45 | 165 |
| $\begin{array}{c} CH_3O \\ \backslash \\ CH_3O \end{array} P-N \begin{array}{c} H \\ \backslash \\ CH_3 \end{array}$   7 | 3435 3402 | 68 (mean) | 156 154 |
| $\begin{array}{c} H_2C-O \\ \vert \\ H_2C-O \end{array} P-N \begin{array}{c} H \\ \backslash \\ nC_4H_9 \end{array}$   8 | 3412 3385 | 70 (mean) | 146 153 |
| benzo $\begin{array}{c} O \\ \backslash \\ O \end{array} P-N \begin{array}{c} H \\ \backslash \\ nC_4H_9 \end{array}$   9 | 3405 3372 | 87 (mean) | 144 146 |
| $\Box$ N-H | 3497 | 139 | 139 |
| H-CO-NH-CH$_3$ | 3466 3429 | 77 (mean) | |
| C$_6$H$_5$-NH-CH$_3$ | 3433 | | 156 |
| $(nC_6H_{11})_2$ NH | 3334 | | 180 |
| $\begin{array}{c} H_2C \\ \vert \\ H_2C \end{array}$ NH | 3325 | 13 | |

Another test is the comparison between a series of three dioxaphospholane derivatives with tri-, tetra- and pentacoordinated phosphorus and the corresponding benzodioxaphospholane analogs (Table IV).

Each of the three ethylene compounds 8, 19, 16 is less acidic than the corresponding phenylene analog, 9, 20, 17. This can be explained as follows: in the ethylene compound the oxygen atoms donate electrons to the phosphorus atom rendering it less apt to accept electrons from nitrogen. In the phenylene compound one of the lone pairs of each oxygen atom is more or less delocalized over the aromatic system and donates less to phosphorus, and the N-to-P coordination is enhanced. Of course, the spectral properties of the NH group linked to phosphorus depend on the nature of the other substituents linked to nitrogen; however the influence of the phosphorus moiety can be expressed in terms of variable hybridization of the nitrogen atom.

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## TABLE II

Spectral properties of NH groups linked to tetracoordinated phosphorus atoms (after M. Barthelat, Ref. 8; R. Mathis, Ref. 64).
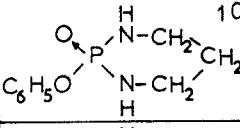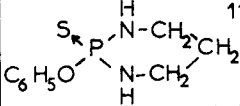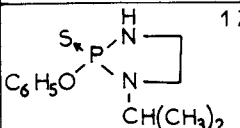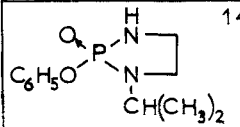
| COMPOUND | NH stretching | | |
|---|---|---|---|
| | $\nu_{0-1}$ CCl$_4$ | $\Delta\nu_{0-1}$ CCl$_4$ - dioxane | $2\nu_{0-1} - \nu_{0-2}$ |
| **10** | 3413 | 113 | 166 |
| **11** | 3417 | 122 | 160 |
| **12** | 3430 / 3421 | 120 / 111 | 154 |
| **13** | 3450 | 220 | 138 |
| **14** | 3429 | 113 | 155 |

## TABLE III

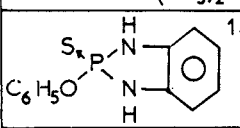Spectral properties of NH groups linked to pentacoordinated phosphorus atoms (after R. Mathis et al., Refs. 63, 67, 68, 71; see also M. Barthelat, Ref. 7, R. Mathis et al., Ref. 66).
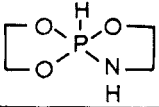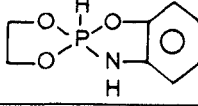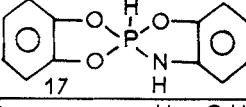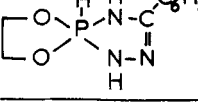
| COMPOUND | NH stretching | | |
|---|---|---|---|
| | $\nu_{0-1}$ $CCl_4$ | $\Delta\nu_{0-1}$ $CCl_4 - $ dioxane | $2\nu_{0-1} - \nu_{0-2}$ |
| 15  | 3486 | 94 | 140 |
| 16  | 3474 | 164 | 137 |
| 17  | 3465 | 205 | 135 |
| 18  | 3479 3462 | 120 62 | 138 150 |

## TABLE IV

Solvent effect on the NH-stretching frequency in some P(III)—NH, P(IV)—NH and P(V)—NH compounds.



8    $\nu_{CCl_4} - \nu_{dioxane} = 70$ cm$^{-1}$

9    87 cm$^{-1}$

19    122 cm$^{-1}$

20    160 cm$^{-1}$

16    164 cm$^{-1}$

17    205 cm$^{-1}$
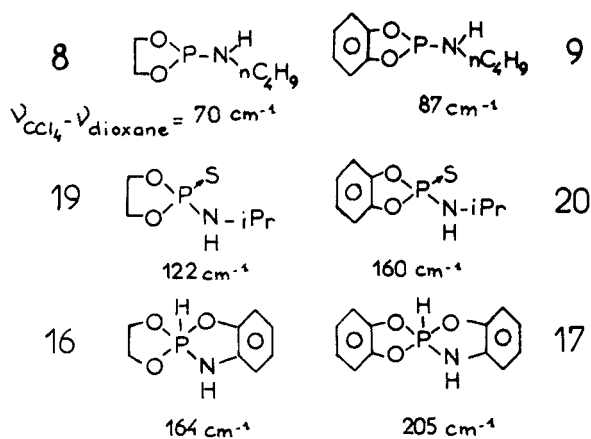
## SPECTRAL PROPERTIES AND REACTIVITY OF THE P–N BOND IN DERIVATIVES OF TERVALENT PHOSPHORUS

If the rough picture thus constructed is reasonable, it should suggest some correlations between chemical and spectroscopic properties. We will now consider such correlations. Some exchange reactions, (1), (2), (3), between aminophosphines and protic or aprotic reagents have been studied in our laboratory and in that of R. Burgada.[18]

$$H-N\begin{matrix}R'\\R'\end{matrix} \rightarrow \ \rangle P-N\begin{matrix}R'\\R'\end{matrix} + H-N\begin{matrix}R\\R\end{matrix} \tag{1}$$

$$\rangle P-N\begin{matrix}R\\R\end{matrix} + \left\{ \begin{array}{l} H-O-R' \rightarrow \rangle P-O-R' + HN\begin{matrix}R\\R\end{matrix} \tag{2} \\[2em] CF_3CO-OCH_3 \rightarrow \rangle P-OCH_3 + CF_3CON\begin{matrix}R\\R\end{matrix} \tag{3} \end{array} \right.$$
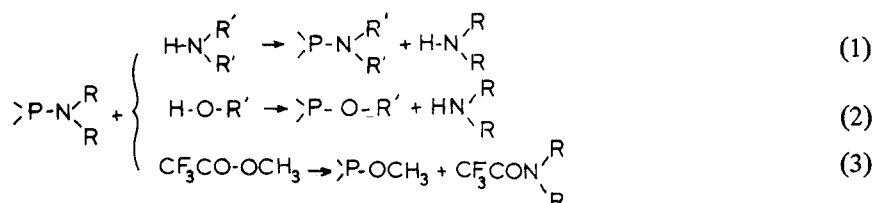
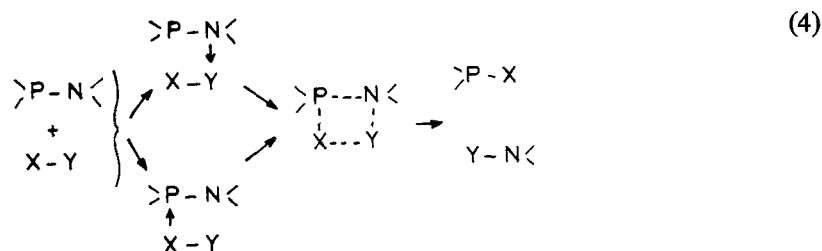Such reactions can be interpreted as occurring through a tetragonal transition state or intermediate (4).

$$\tag{4}$$



Two sets of factors can contribute to lower the activation energy:

i)   nucleophilicity of atom X and electrophilicity of phosphorus;

ii)  nucleophilicity of nitrogen and electrophilicity of atom Y.

If the first set of factors is important, the cycle effects demonstrated by Hudson and coworkers[14,15,41-43] [47,48] should appear (see also Aksnes[1]). It is not at all obvious that nitrogen should be the nucleophilic site in the P(III)–N bond. Laurent, Jugie, and Wolf,[50] for instance, showed that the aminophosphine 21 coordinates to borane through the phosphorus atom as does 22 (Fleming[36]). But 22 coordinates to BF₃ through nitrogen presumably because BF₃ is harder than BH₃ and N harder than P.
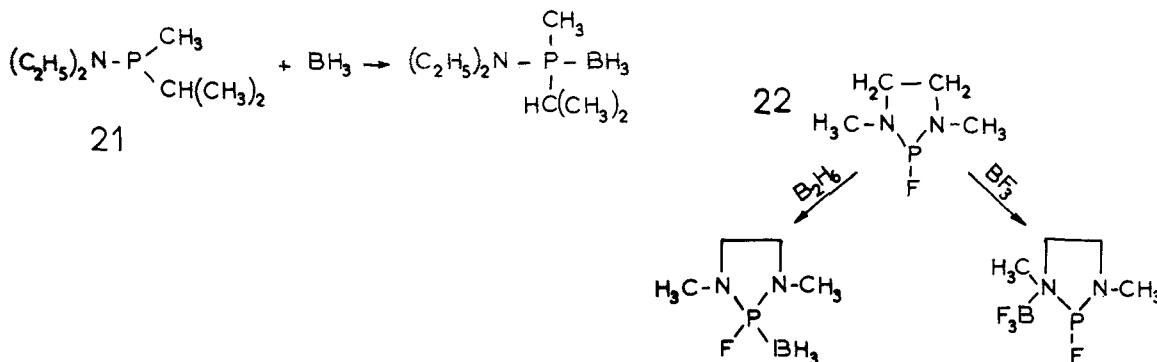
Brown et al.[14] proved that acyl chlorides react with the P(III)—N bond in either of two ways (5) and (6) according to the nature of X (see also Pudovik[80]).



$$X_2 P-NR_2' + R-C-Cl$$

$$\begin{array}{c} \overset{\oplus}{X_2 P-NR_2'} \\ | \\ R-C-O \end{array} \quad Cl^{\ominus} \longrightarrow products \tag{5}$$

$$\begin{array}{c} \overset{\oplus}{X_2 P-NR_2} \\ | \\ R-C-O \end{array} \longrightarrow products \tag{6}$$
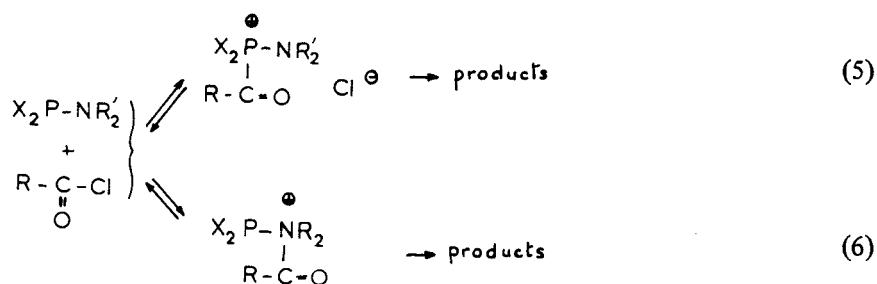
There appears to be a delicate balance between strength-weakness and hardness-softness of both atoms in determining the site of attack. Borowitz[10,11] demonstrated the effect of substituents on the hard-soft character of tervalent phosphorus (see also Hudson;[51] Smith[86]).

In the reactions with which I intend to deal now, nitrogen seems to be the nucleophilic site.

*Aminolysis of Aminophosphines*

As can be seen from Table V, the rate of reaction (1) increases with increasing strength of the attacking amine and with decreasing strength of the leaving amine. An extreme case is that of pyrrole which is a very poor nucl nucleophile: pyrrole is unable to break the P—N bond in 23 and it is ejected from its phosphino derivatives by all secondary amines hitherto used in this reaction. This can be interpreted by supposing that the major factor in determining the reaction rate is the ease of the nucleophilic attack of nitrogen on phosphorus and not the ease of protonation of the P—N nitrogen by the attacking amine (Lafaille[56-58]). It can also be seen that the aminolysis is more rapid if phosphorus is more electrophilic which can happen in two ways: first, if the substituents on phosphorus are more electron-withdrawing; secondly, if the electron density on nitrogen is lower (e.g. in pyrrole derivatives) thus diminishing the N-to-P coordination (Table VI).

TABLE V
Reactivities of different amines towards the P—N bond (Lafaille et al., Ref. 58).

## TABLE VI
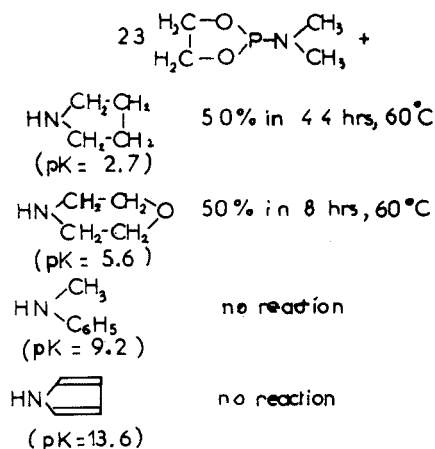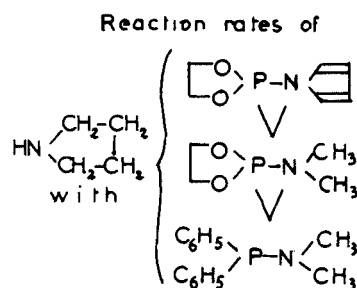### Reactivity of an amine towards different aminophosphines (Ref. 58).



## Alcoholysis of Aminophosphines

Reaction (2) (see, for instance, Pudovik,[79] Petrov,[78] Burgada,[87] Bernard[88]) was studied mechanistically and revealed some unexpected features; our first results are summarized in Figure 6 (Lafaille[56]).
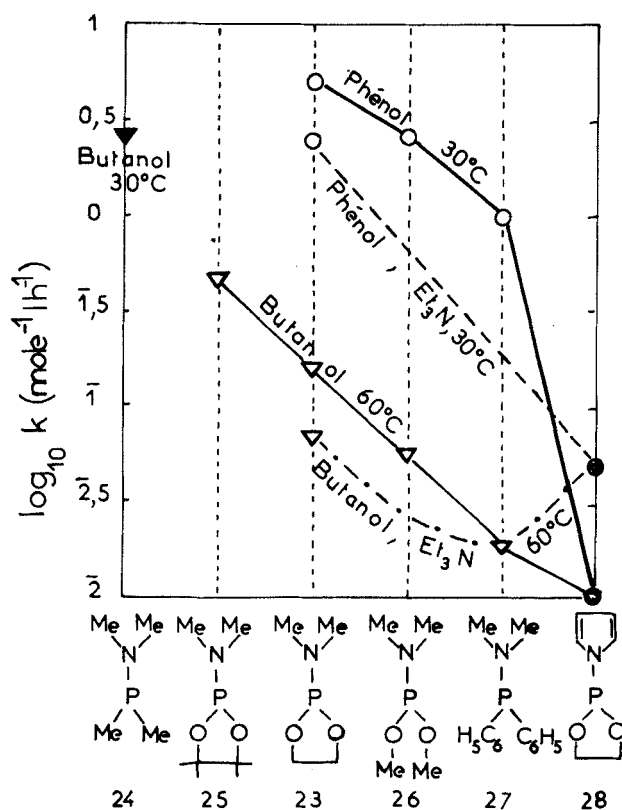


FIGURE 6    Reaction rates of aminophosphines with alcohols and phenol (Lafaille, Ref. 56).

It can be seen that reactivities of compounds 24, 25, 23, 26, 27, 28 towards n-butanol decrease in that very order which can reasonably be considered, with the puzzling exception of 27, as that of decreasing nucleophilicity of nitrogen. On the other hand, phenol reacts more readily than n-butanol (which is less acidic) with 23, 26, 27. This strongly suggests that the rate determining factor is the ability of the hydroxyl group to protonate nitrogen in the respective aminophosphine. This is corroborated by two facts: addition of a base reduces the rate of reaction of 23 against both butanol and phenol, presumably by hydrogen bonding of the OH group; and acetic acid reacts very rapidly (Burgada[20]). The case of the pyrryl derivative 28 is very interesting: first, the difference between phenol and butanol is somewhat less than for other aminophosphines; secondly, addition of a base enhances, in both cases, the reaction rate. Here we must take into account a possible attack of nucleophilic oxygen on electrophilic phosphorus.

## A Cycle Effect

I have already mentioned cycle effects. I can give one example of them. The reaction rates of piperidine against 24 and 27 (Table VII) are similar; the activation energies however are quite different. This is just what might be expected for a reaction occurring through nucleophilic attack on phosphorus which relieves the ring strain in the transition state (Lafaille[57]).

<div align="center">

TABLE VII

Ring effect on aminolysis of the P—N bond (Ref. 57).

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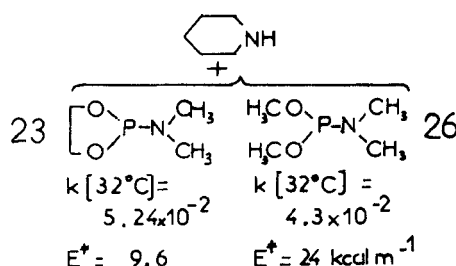


## An Aprotic Exchange Reaction Between Aminophosphines and Methyl Trifluoroacetate (MTF)

Most aminophosphines are cleaved by methyl trifluoroacetate (3); a reaction investigated by Burgada.[19] The nucleophilicity of nitrogen here again plays a major role as exemplified by the case of 28 which does not react with methyl trifluoroacetate. There does not seem to be a very great difference between the reactivities of MTF with 23 and with 26. If this is true, this would mean that the electrophilicity of phosphorus does not play a major role.
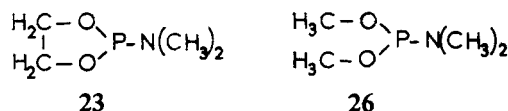


Ayed[4,5] tested the reactivity of several N-monosubstituted aminophosphines towards MTF. In these substances, the spectral properties of the NH group are a good indicator of the electronic state of nitrogen. It is quite clear from Figure 7 that increasing the bulk of the alkyl substituent R linked to nitrogen diminishes the rate of the reaction of aminophosphine with MTF in each of the series 1-2-3, 4-5-6, 7-8-9, but consideration of the series 1-4-7, 2-5-8, 3-6-9 shows that in each of them the reactivity decreases in the order:
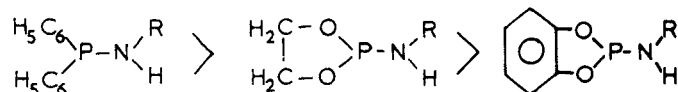
This last order is that of increasing "acidity" of the NH group as measured by the solvent effect on the frequency of the NH stretching vibration or by the respective anharmonicity (Table VII). The order is the same as that of decreasing basicity of nitrogen.
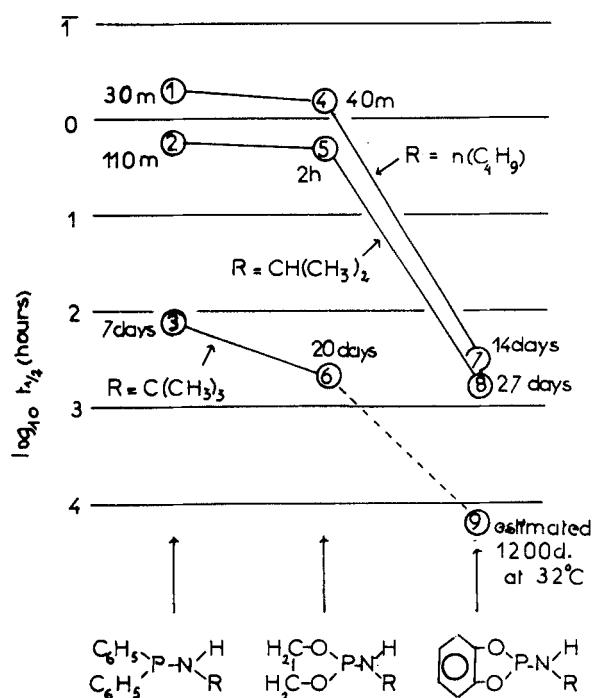


FIGURE 7    Reactivity of aminophosphines towards methyl trifluoroacetate at $40°C$ (Ayed, Refs. 4,5).

TABLE VIII

Comparison between reactivity of the P–N bond and spectral properties of the NH group (Refs. 4,5).

| | $\begin{array}{c}C_6H_5\\C_6H_5\end{array}$P-N$\begin{array}{c}H\\R\end{array}$ | $\begin{array}{c}H_2C-O\\H_2C-O\end{array}$P-N$\begin{array}{c}H\\R\end{array}$ | ⟨○⟩$\begin{array}{c}O\\O\end{array}$P-N$\begin{array}{c}H\\R\end{array}$ |
|---|---|---|---|
| Reactivity towards $CF_3COOCH_3$ | | > | > |
| $\nu_{NH}(CCl_4)-\nu_{NH}(dioxan)$ | 45 to 50 cm$^{-1}$ | 65 to 70 | 90 to 100 |
| $2\nu_{0\to1}NH-\nu_{0\to2}NH$ | 160 to 170 cm$^{-1}$ | 150 to 155 | 145 to 150 |

If the amino moiety in the aminophosphine is kept the same the nitrogen will be less nucleophilic if phosphorus is more electron-withdrawing. Let us consider compounds 29, 30, 31, 23, 32, 33 (Table IX). The

difference in reactivity between **23** and **32** can be explained by the "phenylene effect" already referred to. The comparison between **29, 30** and **31** suggests that the intracyclic nitrogen atom is conjugated weakly with the phenyl group in **30**, strongly with the carbonyl in **31**; its ability to donate electrons to phosphorus decreases in the order **29, 30, 31** and, in the same order, the ability of phosphorus to attract electrons from the extracyclic nitrogen atom increases rendering the latter less nucleophilic. Comparison of **29, 32** and **33** allows one to compare the "electron donating" powers of intracyclic nitrogen and oxygen; nitrogen seems to be a somewhat better "donor".

An unanswered question: why does the extracyclic P—N bond in **29** cleave much more easily than the intracyclic one?

## TABLE IX

Effect of structure on the reactivity of aminophosphines towards methyl trifluoroacetate (after Burgada, Ref. 19).
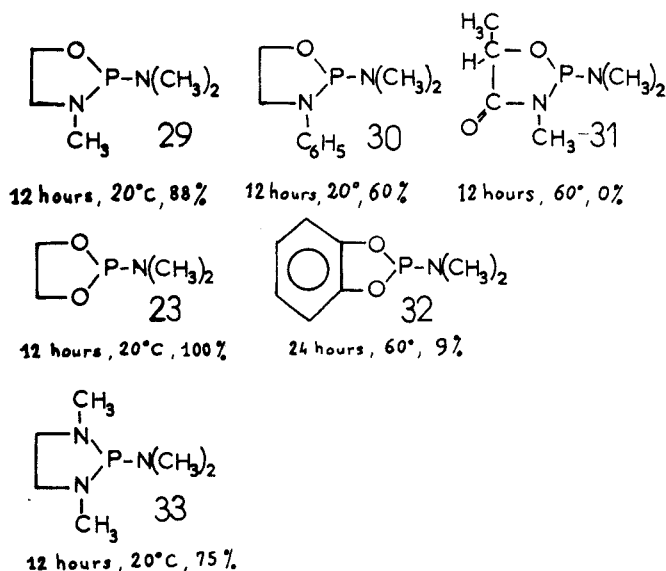


We have tried to gain some information about the supposed partial double bond character of the P—N link from the P—N stretching force constant. To do this, we had to locate the P—N stretching absorption band in the spectra. This identification is not straightforward (Rauchle et al.,[81] Chittenden and Thomas,[26] R. Mathis et al.[69]). However we are reasonably sure of having located this band in several compounds. Its frequency varies considerably from 790 cm$^{-1}$ in **28** to 1005 cm$^{-1}$ in **34**. This can be readily explained if the order of the P—N bond is one in the pyrrylphosphine and significantly greater in **34**.
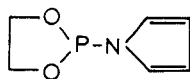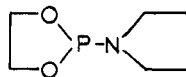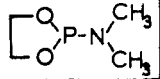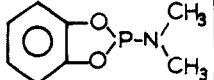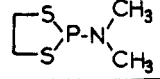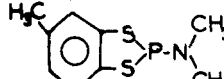


**28** $\nu_{P-N} = 790$ cm$^{-1}$        **34** $\nu_{P-N} = 1005$ cm$^{-1}$

In order to compare, for instance, the compounds of Table X, knowledge of the P—N stretching frequency was not sufficient, owing to the coupling between the P—N stretching movement and the symmetrical $PO_2$ or $PS_2$ stretching coordinate in the normal vibration. A coarse calculation of the appropriate force constant was made, with reasonable bond angles and reasonable P—O force constants (Fritzowsky[37]). The amino moiety in

these four compounds being unchanged, it can be supposed that an increase in the force constant is due to an increased conjugation between nitrogen and phosphorus which should render nitrogen less nucleophilic. The comparison with the reactivity of the same substances with MTF is satisfying.

TABLE X

Stretching force constant of the P–N bond, reactivity towards methyl trifluoroacetate (Boudjebel, Ref. 12, Burgada, Ref. 19), and rotation around the bond (Refs. 12, 19).

| Compound | $\nu_{P-N}$ (cm$^{-1}$) $k_{P-N}$ ($10^5$ dyne cm$^{-1}$) | percent of exchange with $CF_3CO\text{-}OCH_3$ (%, temperature, time) | free enthalpy of activation for the rotation about the P. N bond (kcal. mole$^{-1}$) |
|---|---|---|---|
|  | 969<br>4,95 | 100; 20°C ; 12 h. | |
|  | 978<br>5,05 | 9; 60°C; 12 h. | 7,8 |
|  | 960<br>5,05 | 24; 60°C; 42 h. | 7,6 (estimated) |
|  | 967<br>5,15 | <5; 60°C; 42 h. | 8,9 |

The P–N bond seems to be more double in the "dithia" system than in the "dioxa" one, and the former is less reactive. In each phenylene derivative the P–N bond is more double than in the corresponding ethylene analog and it is less reactive towards MTF. It can be noted that application of Gordy's formula[40] leads to a bond order ca. 1.5 if the force constant is $5 \times 10^5$ dyne cm$^{-1}$.

## COMPETITION BETWEEN THE CLEAVAGE OF P–N, P–O, AND P–S BONDS

H. Goncalves and H. Boudjebel[39] investigated the alcoholysis of amino- and of methoxy-derivatives of 1-,3-,2-dithiaphospholane. There is good evidence that the alcoholysis of the P–N bond in these compounds is reversible; this has been checked in the case of 35 and 36 where secondary reactions are unimportant under certain conditions:
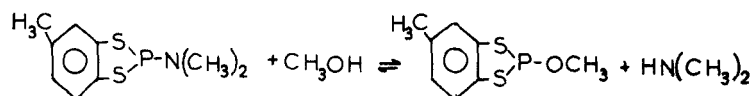


35                                                    36

In the case of derivatives of aliphatic dithiols two secondary reactions take place (Scheme 1), namely alcoholysis of the P–S bonds (both of them simultaneously), and attack of the dimethylamino compound by the freed dithiol giving a "diphosphite" type compound (analogous compounds had been prepared by Burgada, H. Germa, and M. Willson[21,22]).
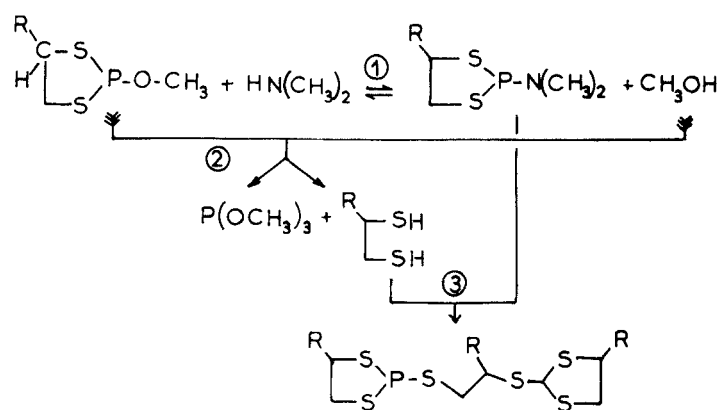
*Scheme 1*

There are several conspicuous problems about these reactions, and we lack kinetic data to solve them at the present time. However we think it possible to make some good suggestions. The diathiol alone does not attack the methoxy compound; here we can offer two hypotheses: first, the dithiol in the presence of a base is able to attack the methoxyl-phosphorus bond; secondly, the dithiol attacks the amino compound formed by the aminolysis of the P—O bond of the starting material. We prefer the second hypothesis.

Methanol, either in neutral or in basic solution, cleaves both P–S bonds to give trimethylphosphite. In the absence of a base, the reaction is slow, but if dimethylamine is added it becomes much more rapid. Here again, two hypotheses can be made: first, the amino compound is formed and afterwards cleaves more rapidly than the methoxy compound; secondly, trimethyl phosphite is formed in all cases directly from the methoxydithiaphospholane, but this attack by methanol is catalyzed by a base (8).
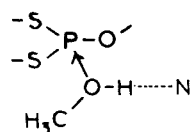


(8)

In our opinion the second hypothesis seems more satisfying, even though we lack convincing argument to support it. It has the advantage of explaining the difference in reactivity between the dithiaphospholane derivatives and their cyclic analogs. A nucleophilic attack on phosphorus would relieve a ring strain in cyclic compounds; the reaction being, therefore, easier for these compounds than for acyclic ones. Indeed the major reaction which occurs when 37 is heated with methanol in benzene solution proceeds as well without methanol and trimethyl phosphite is obtained only when a large excess of the alcohol is used, or if a base is added, or both.



37
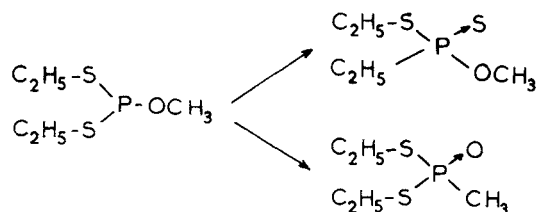
The behavior of derivatives of dithiaphospholane differs surprisingly from that of the isologous dioxa compounds. Burgada and Lafaille[23] proved that **38** undergoes cleavage of the ring according to (9) and (10) in neutral medium. Both steps are reversible which is the first difference with methoxydithiaphospholane.



$$(9)$$



$$(10)$$
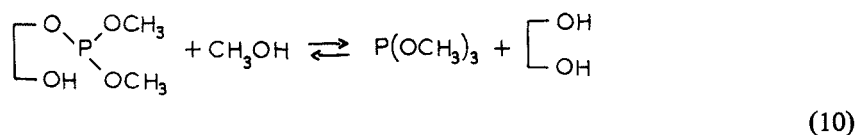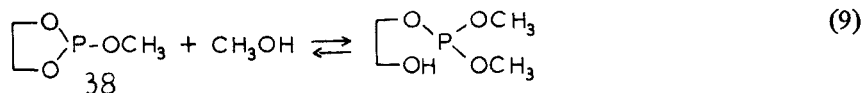
A second difference lies in the fact that these reactions are inhibited and not favored in the presence of a base. It can be surmized that reactions (9) and (10) proceed *via* an attack by the proton of methanol on the intracyclic oxygen atoms; an idea which we plan to check in the near future.
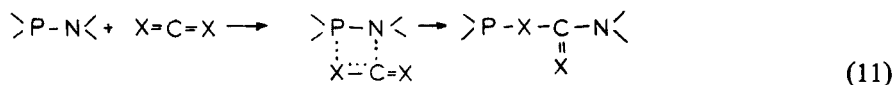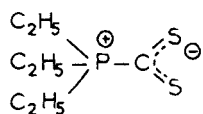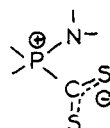
## INSERTION REACTIONS WITH AMINOPHOSPHINES

Carbon dioxide and carbon disulfide are known to react with aminophosphines *sensu lato* (Oertel et al.,[77] Jensen et al.[53]) to give insertion compounds according to (11).



$$(11)$$

Triethylphosphine with $CS_2$ gives us an adduct to which Margulis and Templeton[60,61] assigned structure **39**.



**39**                                              **40**

Some aminophosphines (Jensen[53]) are able to give such zwitterionic adducts as **40** which can rearrange to the isomeric insertion derivatives. However it seems very likely that the latter can be formed directly by nucleophilic attack by nitrogen according to equation (11).

H. Boudjebel[12,13] tried such reactions on derivatives containing the $S_2PN$ system. Carbon dioxide did not react; perhaps in this case oxygen is too hard a base to achieve the insertion by the formation of a phosphorus-oxygen link. Carbon disulfide gave the thiocarbamates (for instance **41** and **42**) which we expected with both cyclic and acyclic $S_2PN$ compounds.
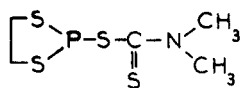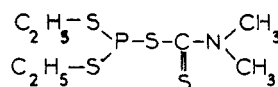


**41**                                              **42**

M. Willson observed another reaction which was rather unexpected but which perhaps results from an insertion followed by rearrangement (Scheme 2). Such a reaction bears some similarity to ones described by Burgada.[24]

*Scheme 2*
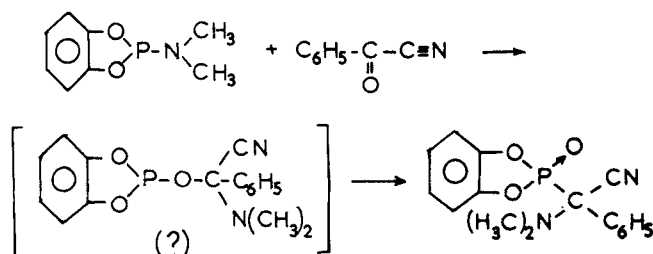


A quite different result is obtained when benzoyl cyanide reacts with **23** or with **25** (Scheme 3).

*Scheme 3*
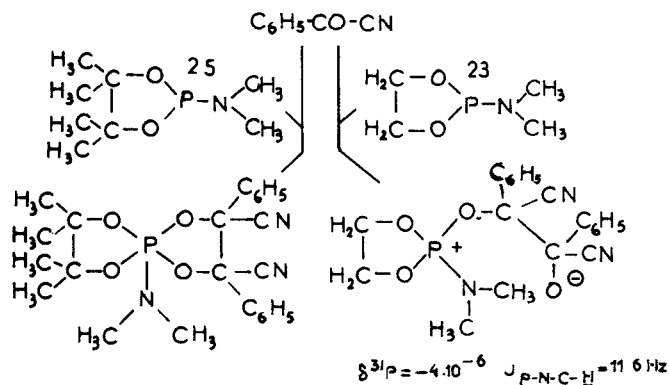


## NUCLEOPHILIC ATTACK AT TETRACOORDINATED PHOSPHORUS

In this last section I will mention a reaction which can lead to the formation of a P(IV)—N bond and which gives rise to interesting questions. Monique Revel and J. Navech[82-84] studied the reaction between amines and cyclic phosphate esters derived from α-diols. Three types of products were obtained suggesting that the nucleophile can attack three sites in the phosphate molecule according to Scheme 4.

Path 1 in this scheme leads to a zwitterionic compound **43**; path 2 to a phosphoramide **44** (which, of course, cannot be formed if the starting amine is tertiary); path 3 gives an amonium phosphate **45**. The interpretation of path 3 is not obvious, because a direct nucleophilic attack on the aromatic carbon seems to be very unlikely. It is more satisfying to suppose that nitrogen can attack *two* sites only (paths 1 and 2); attack on phosphorus should lead to a presumably bipyramidal transition state or intermediate; the latter could go over the the phosphoramide **44** by ring opening, or to the ion pair **45** by internal rearrangement

(Scheme 5).

*Scheme 4*
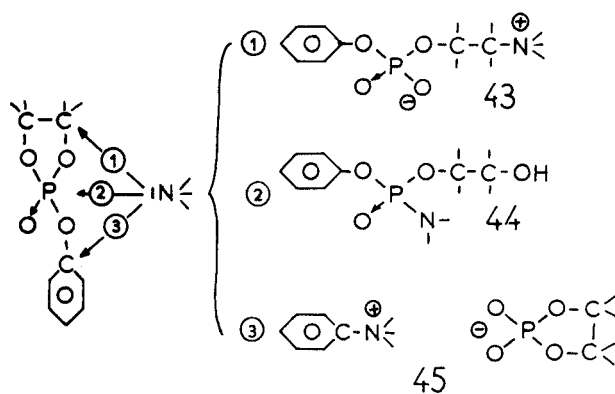


*Scheme 5*
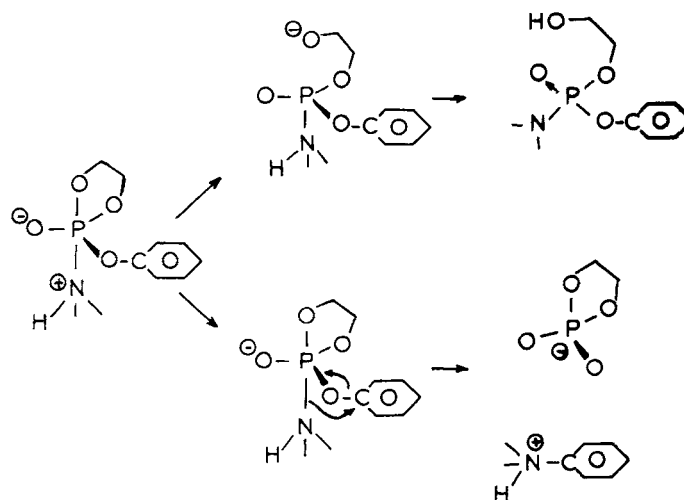


The course of the reaction is sensitive both to the presence of methyl substituents on the dioxaphospholane carbons and to the nature of the amine. The balance between the three pathways seems to be, once more, a matter of softness-hardness.

REFERENCES

1. G. Aksnes and K. Bergesen, *Acta Chem. Scand.* 19, 931-4 (1965).
2. T. Axenrod, P. S. Pregosin, M. J. Wieder, and G. W. A. Milne, *J. Am. Chem. Soc.* 91, 3681-2 (1969).
3. T. Axenrod, M. J. Wieder, G. Berti, and P. L Barili, *J. Am. Chem. Soc.* 92, 6066-8 (1970).
4. N. Ayed, These de Specialite, Toulouse, 15.6.1974.

5.   N. Ayed, R. Mathis, R. Burgada, and F. Mathis, *C. R. Acad. Sci.* **278** C, 1085-8 (1974).
6.   M. C. Bach, C. Brian, F. Crasnier, J. F. Labarre, C. Leibovici, and A. Dargelos, *J. Mol. Struct.* **17**, 23-36 (1973).
7.   M. Barthelat, B. Garrigues, and R. Mathis, *C. R. Acad. Sci.* **277** C, 415-8 (1973).
8.   M. Barthelat, R. Mathis, A. Bousquet, J. Navech, and F. Mathis, *Spectrochim. Acta* **29** A, 79-91 (1973).
9.   G. Binsch, J. B. Lambert, B. W. Roberts, and J. D. Roberts, *J. Am. Chem. Soc.* **86**, 5564-9 (1964).
10.  G. B. Borowitz and I. J. Borowitz, *Phosphorus* **2**, 91-6 (1972).
11.  I. J. Borowitz and R. K. Crouch, *Phosphorus* **2**, 209-19 (1973).
12.  H. Boudjebel, These de Specialite, Toulouse, 13.11.1973.
13.  H. Boudjebel, H. Goncalves, and F. Mathis, unpublished results.
14.  C. Brown, R. F. Hudson, and R. J. G. Searle, *Phosphorus* **2**, 287-91 (1973).
15.  C. Brown, R. F. Hudson, V. T. Rice, and A. R. Thompson, *Chem. Commun.* 1255 (1971).
16.  G. J. Bullen, F. S. Stephens, and R. J. Wade, *J. Chem. Soc.* A, 1804-11 (1969).
17.  G. J. Bullen and P. E. Dann, *Acta Cryst.* B29, 331-7 (1973).
18.  R. Burgada, Chimie Organique du Phosphore, Colloque international du CNRS, Paris, 247-56 (1969).
19.  R. Burgada, *Bull. Soc. Chim.* 136-43 (1971).
20.  R. Burgada, *Bull. Soc. Chim.* 4161 (1972).
21.  R. Burgada, H. Germa, M. Willson, and F. Mathis, *Tetrahedron* **27**, 5833-52 (1971).
22.  R. Burgada, H. Germa, and M. Willson, *Tetrahedron* **29**, 727-40 (1973).
23.  R. Burgada, L. Lafaille, and F. Mathis, *Bull. Soc. Chim.* 341-2 (1974).
24.  R. Burgada and J. Roussel, *Bull. Soc. Chim.* 192-200 (1970).
25.  C. Charrier, M-P. Simonnin, *C. R. Acad. Sci.* **264** C, 995-7 (1967).
26.  R. A. Chittenden and L. C. Thomas, *Spectrochim. Acta* **22**, 1449-63 (1966).
27.  A. H. Cowley, M. J. S. Dewar and W. R. Jackson, *J. Am. Chem. Soc.* **90**, 4185-6 (1968).
28.  A. H. Cowley, M. J. S. Dewar, W. R. Jackson, and W. B. Jennings, *J. Am. Chem. Soc.* **92**, 1085-6 (1970).
29.  A. H. Cowley, M. J. S. Dewar, W. R. Jackson, and W. B. Jennings, *J. Am. Chem. Soc.* **92**, 5206-13 (1970).
30.  A. H. Cowley and J. R. Schweiger, *Chem. Commun.* 1492-3 (1970).
31.  A. H. Cowley and J. R. Schweiger, *Chem. Commun.* 560-61 (1972).
32.  A. H. Cowley and J. R. Schweiger, *J. Am. Chem. Soc.* **95**, 4179-85 (1973).
33.  I. G. Csizmadia, A. H. Cowley, M. W. Taylor, L. M. Tel, and S. Wolfe, *Chem. Commun.* 1147-8 (1972).
34.  I. G. Csizmadia, A. H. Cowley, M. W. Taylor, and S. Wolfe, *Chem. Commun.* **11**, 432-3 (1974).
35.  V. N. Filimonov and D. S. Bystrov, *Opt. i Spektr.* **12**, 66-72 (1962).
36.  S. Fleming, M. K. Lupton, and K. Jekott, *Inorg. Chem.* **11**, 2534-40 (1972).
37.  N. Fritzowsky, A. Lentz, and J. Goubeau, *Z. Anorg. Allg. Chem.* **386**, 203-7 (1971).
38.  K. M. Ghouse, R. Keat, H. H. Mills, J. M. Robertson, T. S. Cameron, K. D. Howlett, and C. K. Prout, *Phosphorus* **2**, 47-8 (1972).
39.  H. Goncalves, R. Burgada, M. Willson, H. Boudjebel, and F. Mathis, unpublished results.
40.  W. Gordy, *J. Chem. Phys.* **14**, 305-20 (1946).
41.  R. Greenhalgh and R. F. Hudson, *Phosphorus* **2**, 1-9 (1972).
42.  R. Greenhalgh and R. F. Hudson, *Chem. Commun.* 1300 (1968).
43.  R. Greenhalgh, J. E. Newberry, R. Woodcock, and R. F. Hudson, *Chem. Commun.* 22 (1969).
44.  Y. Hamada, A. Y. Hirakawa, K. Tamagake, and M. Tsuboi, *J. Mol. Spectr.* **35**, 420-35 (1970).
45.  M. Haque and C. N. Gauglan, *Chem. Commun.* 921 (1966).
46.  G. C. Holywell, D. W. H. Rankin, B. Beagly, and J. M. Freeman, *J. Chem. Soc.* A, 785-90 (1971).
47.  R. F. Hudson and C. Brown, *Acc. Chem. Res.* **5**, 204-11 (1972).
48.  R. F. Hudson and A. Mancuso, *Chem. Commun.* 522-3 (1969).
49.  R. F. Hudson and A. Mancuso, *Phosphorus* **1**, 265-70 (1972).
50.  R. F. Hudson and A. Mancuso, *Phosphorus* **1**, 271-6 (1972).
51.  R. F. Hudson and R. J. G. Searle, *Chimia* **20**, 117-19 (1966).
52.  W. B. Jennings, *Chem. Commun.* 867-8 (1971).
53.  K. A. Jensen, O. Dahl, and L. Engels-Henrisen, *Acta Chem. Scand.* **24**, 1179-90 (1970).
54.  R. L. Kuczkowski, M. W. Schiller, and R. W. Rudolf, *Inorg. Chem.* **10**, 2505-08 (1971).
55.  M-C. Labarre and Y. Coustures, *J. Chim. Phys.* **70**, 534-43 (1973).
56.  L. Lafaille, unpublished results.
57.  L. Lafaille, unpublished results.
58.  L. Lafaille, R. Burgada, and F. Mathis, *C. R. Acad. Sci.* **270**, 1138-40 (1970).
59.  J-P. Laurent, G. Jugie, and R. Wolf, *J. Chim. Phys.* **66**, 409-13 (1969).
60.  T. N. Margulis and P. W. Templeton, *J. Am. Chem. Soc.* **83**, 995-6 (1961).
61.  T. N. Margulis and D. H. Templeton, *J. Chem. Phys.* **36**, 2311 (1962).
62.  F. Mathis, "Les liaisons NH, PH, SH et SiH" in *Structure et proprietes moleculaires* (A. Kirrmann, Ed.) (Masson, Paris, 1970).
63.  R. Mathis, *C. R. Acad Sci.* **268** C, 1229-31 (1969).
64.  R. Mathis, M. Barthelat, R. Kraemer, J. Navech, and F. Mathis, *Spectrochim. Acta* **29**A, 63-78 (1973).
65.  R. Mathis, M. Barthelat, L. Lopez, and J. Barrans, *C. R. Acad. Sci.* **276** C, 649-52 (1973).
66.  R. Mathis, M. Barthelat, Y. Charbonnel, and J. Barrans, unpublished results.

67.    R. Mathis and R. Burgada, *C. R, Acad. Sci.* **274** C, 1156-8 (1972).
68.    R. Mathis, R. Burgada, and M. Sanchez, *Spectrochim. Acta* **25**A, 1201-10 (1969).
69.    R. Mathis, L. Lafaille, and R. Burgada, *Spectrochim. Acta* **30**A, 357-70 (1974).
70.    R. Mathis, N. Ayed, Y. Charbonnel, and R. Burgada, *C. R. Acad. Sci.* **277** C, 493-6 (1973).
71.    R. Mathis, Y. Charbonnel, and J. Barrans, *C. R. Acad. Sci.* **275** C, 539-42 (1972).
72.    R. Mathis, J. Khemdoudi, and T. Bouissou, unpublished results.
73.    E. D. Morris and C. E. Nordmann, *Inorg. Chem.* **8**, 1673 (1969).
74.    R. A. Nyquist, *Spectrochim. Acta* **19**, 713-29 (1963).
75.    R. A. Nyquist, E. H. Blair, and D. W. Osborne, *Spectrochim. Acta* **23**A, 2505-21 (1967).
76.    R. A. Nyquist, M. N. Wass, and W. W. Mulder, *Spectrochim. Acta* **26**A, 611-25 (1970).
77.    G. Oertel, H. Malz, and H. Holtschmidt, *Chem. Ber.* **97**, 891 (1964).
78.    K. A. Petrov, V. P. Evdakov, K. A. Bilevich, V. P. Padchenko, and E. E. Nifant'ev, *Zh. Obshch. Khim.* **32**, 920-3 (1962).
79.    A. N. Pudovik, M. A. Pudovik, S. A. Terenteva, and V. E. Belskii, *Zh. Obshch. Khim.* **41**, 2407-13 (1971).
80.    A. N. Pudovik, E. S. Batyeva, and V. A. Alfonsov, *Zh. Obshch. Khim.* **42**, 1235-8 (1972).
81.    F. Rauchle, W. Pohl, B. Blaich, and J. Goubeau, *Ber. Bunsenges. Phys. Chem.* **75**, 66-71 (1971).
82.    M. Revel, J. Navech, and F. Mathis, *Bull. Soc. Chim.* 105-10 (1971).
83.    M. Revel and J. Navech, *C. R. Acad. Sci.* **268** C, 121-4 (1969).
84.    M. Revel, M-T. Boisdon, and J. Navech, *C. R. Acad. Sci.* **269** C, 182-4 (1969).
85.    M-P. Simonnin, C. Charrier, and R. Burgada, *Org. Magn. Reson.* **4**, 113-20 (1972).
86.    N. L. Smith, *J. Org. Chem.* **28**, 863-5 (1963).
87.    R. Burgada, G. Martin, and G. Mavel, *Bull. Soc. Chim.* 2154 (1963).
88.    D. Bernard, P. Savignac, and R. Burgada, *Bull. Soc. Chim.* 1657-8 (1972).