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INVESTIGATIONS OF PHOSPHORANES WITH P-H BOND DURING THE REACTION OF AMINOPHOSPHINE WITH ALCOHOLS

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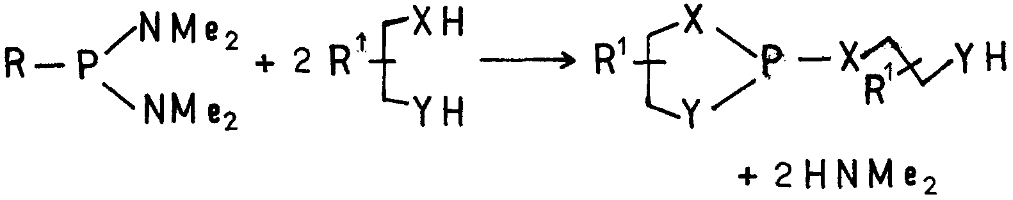
During the alcoholysis of an aminophospholane one has observed a phosphorane which might result from the decomposition of a probably hexacoordinated phosphorus species;this is a contribution to the knowledge of the P_{III}-N alcoholysis mechanism.

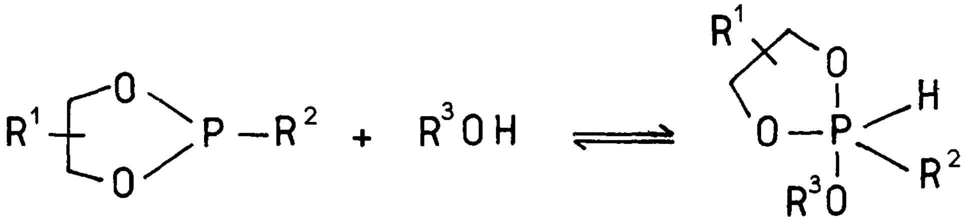
We have, previously, described the formation of phosphoranes with a hydrogen ligand from the reaction of bifunctional compounds on a diaminophosphine (1) :

(a)



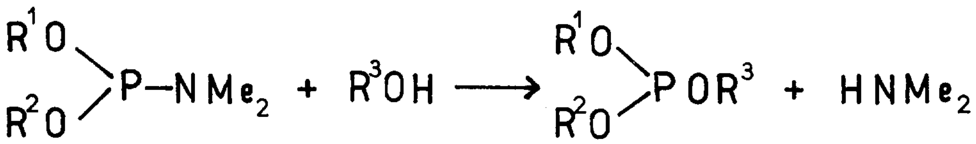
We had pointed out, at that time, that such compounds may be formed in numerous reactions involving P(III) and may very probably be detected under suitable experimental conditions. Since then we have observed (2) the reaction of hydroxyl compounds with 2-alkyl and 2-aryl 1,3,2-dioxaphospholanes which give rise to an equilibrium between phosphorane and phospholane :

(b)



We have now extended these studies to the reactions of alcohols with aminophosphines ; a classic method for the synthesis of phosphites (3) :

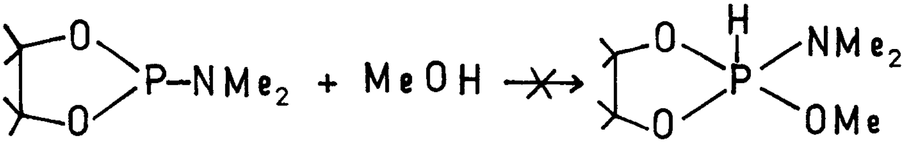
(c)



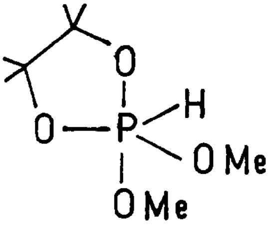
A 1:1 stoichiometric mixture of 2-N,N dimethylamino 4,4,5,5-tetramethyl 1,3,2-dioxaphospholan 1 and methanol (both carefully purified) prepared at room temperature in an inert atmosphere, has been studied by ^{1}H and ^{31}P nmr.

We observe, in addition to the starting material and the products, a phosphorane which does not contain the N,N -dimethylamino group bonded to phosphorus. Therefore, this reaction cannot be the result of a simple addition of methanol on the aminophosphine as we had previously thought (2) (4 to 9).

(d)



An examination of the ^{1}H nmr spectrum showed definitively that we have the phosphorane 3 :



$\delta^{31}P$ (ppm)	$^{1}J_{PH}$ (Hz)	δ_{OCH_3} (ppm)	$^{3}J_{P-H}$ (Hz)	$^{4}J_{H-H}$ (Hz)	δ_{CH_3} (ppm)	$\delta_{H(P)}$ (ppm)
+ 26	694	3,22	20,2	0,45	1,1	5,75

(under the same conditions, isopropanol gives an analogous phosphorane but in low yield : $\delta^{31}P = + 34$ ppm $^{1}J_{PH} = 683$ Hz).

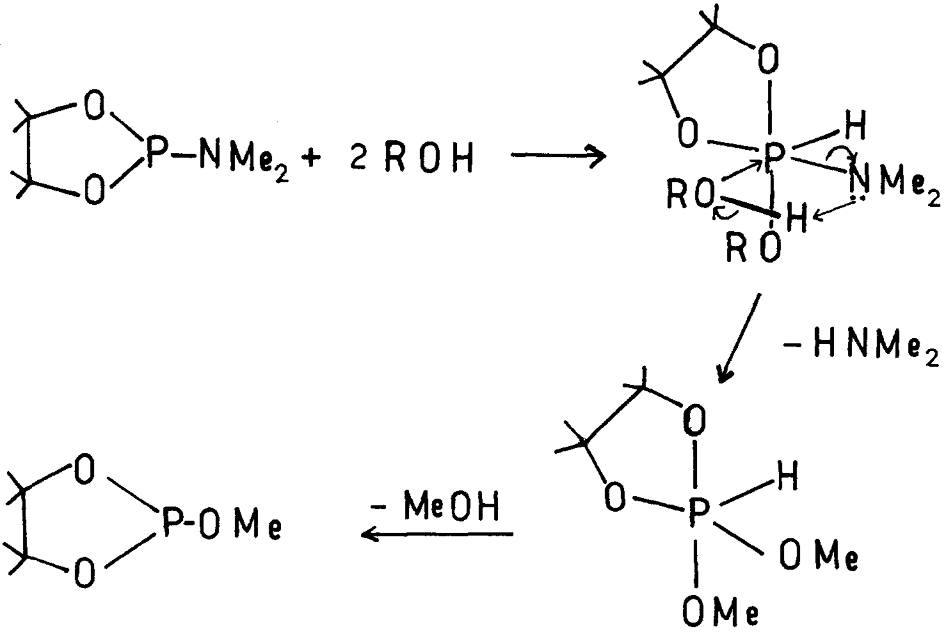
The ratio of P_V : (P_{III} total) in the mixture, as calculated from the nmr spectra, is observed to pass a maximum of about 0.15 after 30 min. at 33 °C ; subsequently diminishing to zero when the aminophospholane has been totally consumed.

If the reaction is repeated using a 1:2 mixture of aminophospholane to alcohol, one observes the reaction to be more rapid. In this case the ratio of P_V : (P_{III} total) reaches a maximum of approximately 0.30.

Thus, it might be hypothesized that this compound is formed as the result of the addition of the alcohol, present in the reaction medium, on the phosphite 5 * : this secondary reaction is favoured by the presence of amine formed during the course of the primary reaction (c) (6).

This hypothesis is not supported because when we mix stoichiometric quantities of methanol and 2-methoxy 4,4,5,5-tetramethyl 1,3,2-dioxaphospholan at room temperature, with added amine, we do not observe the formation of the phosphorane 4. These observations lead us to the conclusion that the formation and the decomposition of the phosphorane 3 will be consecutive at one stage during the course of which the aminophosphine complexes with two molecules of methanol (possibly in a concerted manner) giving rise to a transitory hexacoordinate phosphorus species (scheme 1).

(e)



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* Under the same conditions such an addition has been observed, for example, in the case of the transesterification of 4,4,5,5-tetramethyl 2-phenoxy 1,3,2-dioxaphospholan with methanol ; in the ^{31}P nmr spectrum of the mixture, there was a doublet of weak intensity:

$$\delta^{31}P = 25 \text{ ppm} \qquad ^{1}J_{HP} = 680 \text{ Hz} \qquad ^{3}J_{PH} = 21,3 \text{ Hz}$$

In conclusion these observations are a novel contribution to mechanistic studies of the alcoholysis of P_{III}-N bonds (9).

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