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Some Unusual Reactions in Organophosphorus Chemistry

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SOME UNUSUAL REACTIONS IN ORGANOPHOSPHORUS CHEMISTRY

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Methylenephosphinophosphorane 1 reacts with azides without evolution of nitrogen to give zwitterionic phosphorazide 3 and iminophosphorazide 4, which are in equilibrium to each other; 1 reacts with hexafluoroacetone (HFA) in a different way to give zwitterionic product 5, which may have the ylidic structure 5'. HFA and thio-HFA react analogously with methylenediphosphines 6 to give corbodiphosphoranes 7. Reaction of 6 with activated alkenes 9 gives monoylide 10, which is a useful synthone for the synthesis of fluorosubstituted conjugated triene 12 and diylides 13 and 14. Reaction of 10 with TOB gives unusually stable betaine 15. Reaction of the other activated alkene 16 with 6 unexpectedly gave the unusual zwitterionic compound 17.

Keywords: Hypervalency; phosphorazides; ylides; zwitterions

Among various organophosphorus compounds containing a structural fragment P—CH₂—P, those in which a methylene group bridges two phosphorus atoms with coordination numbers P^{III} and P^V are of special interest. Such compounds possess unusual chemical properties accounted for by their ability to add some unsaturated reagents to the two phosphorus atoms. Each phosphorus atom increases its coordination number by one to give zwitterionic compounds with positively charged phosphonium and negatively charged phosphate centres.

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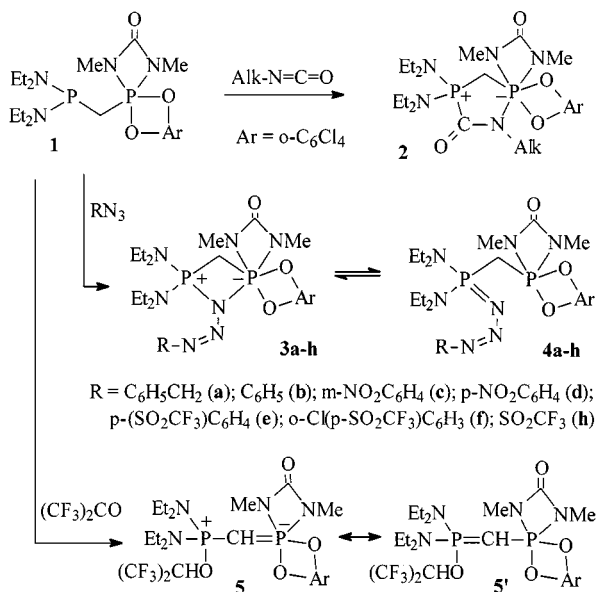


FIGURE 1

Such a type of addition reaction is illustrated, for example, by the interaction of methylenephosphinophosphorane **1** with isocyanates to give zwitterionic product **2**¹ (Figure 1).

Another interesting example of this kind is the interaction of methylenephosphinophosphorane **1** with azides. It takes place without evolution of nitrogen to give zwitterionic phosphorazides **3** and iminophosphorazides **4**. In solution these structural isomers are in equilibrium, the position of which is determined by the electronegativity of the substituent R . The value of the chemical shift of the phosphorus atom with the coordination number 5–6 at room temperature is indicative of the position of the equilibrium. When $\text{R} = \text{C}_6\text{H}_5\text{CH}_2$ (**a**) or C_6H_5 (**b**)² the equilibrium is almost completely shifted to the zwitterionic phosphorazides **3a** ($\delta_{\text{P}} = -154$ ppm) or **5b** ($\delta_{\text{P}} = -142$ ppm), which can be isolated as a stable crystalline colorless products. With trifluoromethylsulfonylazide ($\text{R} = \text{h}$), the formation of iminophosphorane **4h** ($\delta_{\text{P}} = -35$ ppm) was observed by nuclear magnetic resonance (NMR) spectroscopy in solution at temperatures below 0°C . With other azides used the forms **3c-f** and **4c-f** were registered in ^{31}P -NMR spectra simultaneously as common broad signals (for $\lambda^{5-6}\text{P}$) at room temperature or as sharp separate signals at -50°C .

We reasoned that the reaction of **1** with hexafluoroacetone (HFA) could give a zwitterionic product analogous to that of **2**. However, this

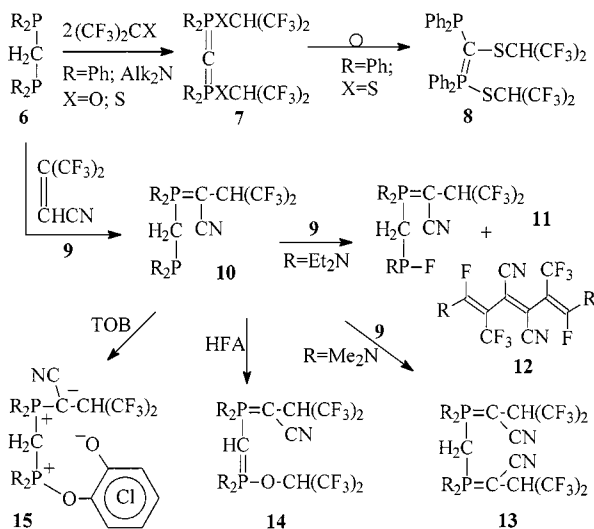


FIGURE 2

reaction gave unexpectedly the ylide **5'**,³ which according to the x-ray data may have an unusual zwitterionic structure **5**.

It turned out that this unusual reaction has a more common character. For example, methylenediphosphines **6** reacts analogously not only with HFA (X = O),⁴ but with thio-HFA (X = S)⁵ to give carbodiphosphoranes **7** (Figure 2). In the latter case (X = S; R = Ph) the carbodiphosphorane is unstable and rearranges into ylide **8**.

The interaction of methylenediphosphines **6** (R = Alk₂N) with (CF₃)₂C=CHCN **9** became an interesting continuation of this work, as **9** can be considered as carbon derivative of HFA or thio-HFA. In equimolar ratio this reaction gives ylide **10**. Further addition of **9** depends on steric hindrance at phosphorus. If R = Me₂N, the expected double ylide **13** can be obtained. If R = Et₂N, the reaction gives conjugated triene **12** and P-F substituted ylide **11**. An addition of HFA to **10** gives the double ylide **14**. The oxidation of **10** with tetrachloro-orthobenzoquinone (TOB) gives the unusual compound **15**, which has a betainic structure with the negatively charged oxygen atom being situated between the two positively charged phosphorus atoms.

An unusual result was obtained when we used in this reaction activated alkene **16**, having a carboxymethyl group (Figure 3). This reaction gave unexpectedly zwitterionic compound **17** with two phosphorus atoms of different coordination numbers and opposite charges. One of the phosphorus atom of **6** loses its original substituents and transforms

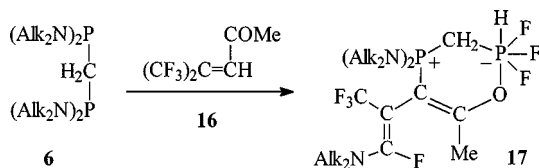


FIGURE 3

into hexacoordinated state, in which it is connected with one hydrogen and three fluorine atoms.

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