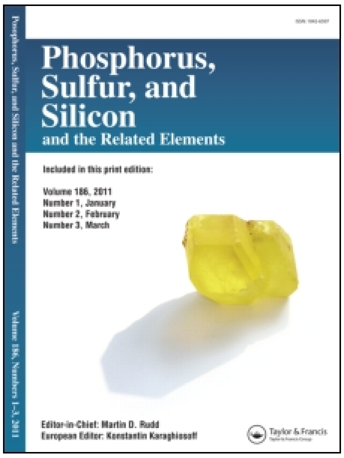

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METHYLENEPHOSPHINOPHOSPHORANES. UNUSUAL ADDITION REACTION IN ORGANOPHOSPHORUS CHEMISTRY.

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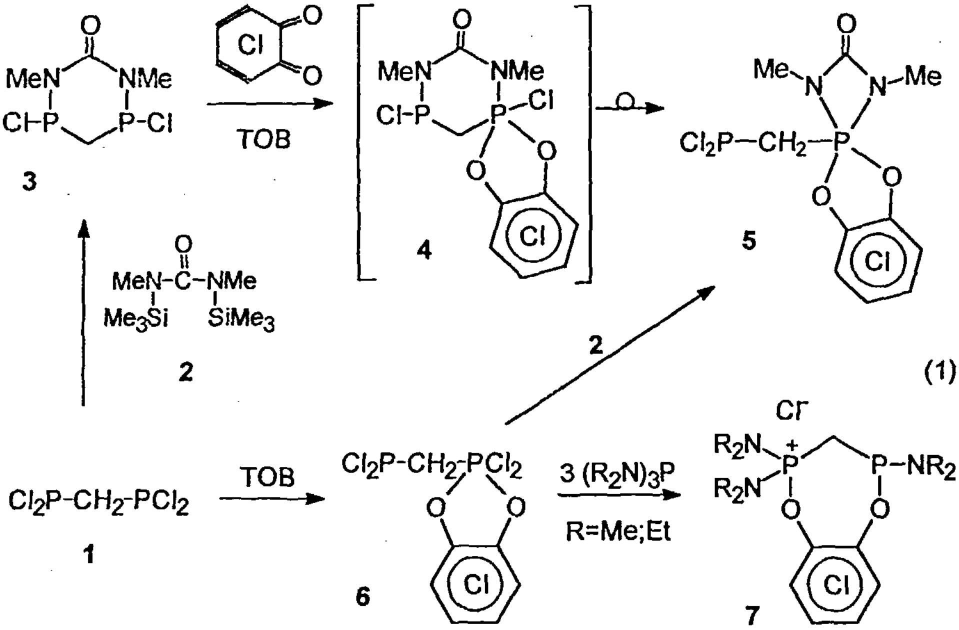
Abstract: Intermediate **4** is unstable and rearranges into **5**. Substitution of chlorine atoms in **5** by dialkylamino groups gives **8** and **9**. **8** reacts with TEA to give phosphaalkene **10**, which slowly dimerizes into **11**. Methylenephosphinophosphorane **9** shows unusual properties. It adds isocyanates to two phosphorus atoms to give zwitterionic structural isomers **12a,b**. The structure of **12a** was resolved by X-ray analysis. **9** reacts with azides unexpectedly giving the zwitterionic product **13**. Reaction of **9** with hexafluoroacetone is unusual and leads to the ylid **14a,b**. According to the X-ray data it exists in zwitterionic form **14b** and displays a new type of coordination at phosphorus atom. HFA can react in a similar way with other phosphines. For example, with **15** it gives the double ylid **16**.

Methylenephosphinophosphorane, isocyanate, addition, hexafluoroacetone, oxydation

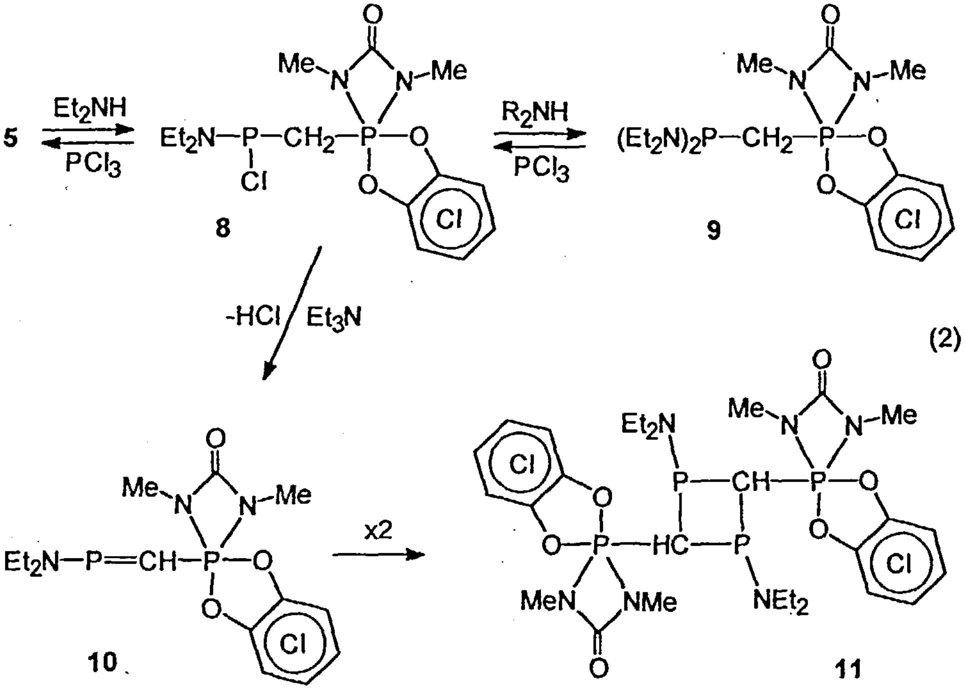
The reaction of methylenebis(dichlorophosphine) **1** with silylated urea **2** leads to 1,5-Diaza-2,4-diphosphorinan-6-one **3**.[1] Oxydation of one phosphorus atom of **3** by tetrachloroorthobenzoquinone (TOB) occurs easily but it does not give the expected product **4** which is unstable and undergoes an interesting rearrangement into methylenephosphinophosphorane **5**. The oxydation of **1** by TOB leads to another methylenephosphinophosphorane **6**. The reaction of **6** with silylated urea **2** also gives compound **5**. Thus methylenephosphinophosphorane **5** can be obtained in two ways, both of them include the formation of unstable intermediate product **4**. The reaction of **6** with tris(dialkylamino)phosphine proceeds with the substitution of chlorine atomes by dialkylaminogroups and causes an interesting rearrangement into seven-membered heterocyclic system **7** which includes both phosphorus atoms. (Fig. 1)

Chlorine atoms in **5** can be stepwise substituted by dialkylaminogroups to give derivatives **8** and **9**. Using PCl_3 it is possible to conduct the reverse transformations from **9** to **8** and then to **5**. Under the action of triethylamine **5** loses HCl and forms the C-spirophosphoranesubstituted phosphaalkene **10**. **10** is stable in solution within several hours and then dimerizes into **11**. (Fig. 2).

The methylenephosphinophosphorane **9** is especially interesting. It possesses unusual chemical properties. For example, it adds methyl- and ethylisocyanate to two

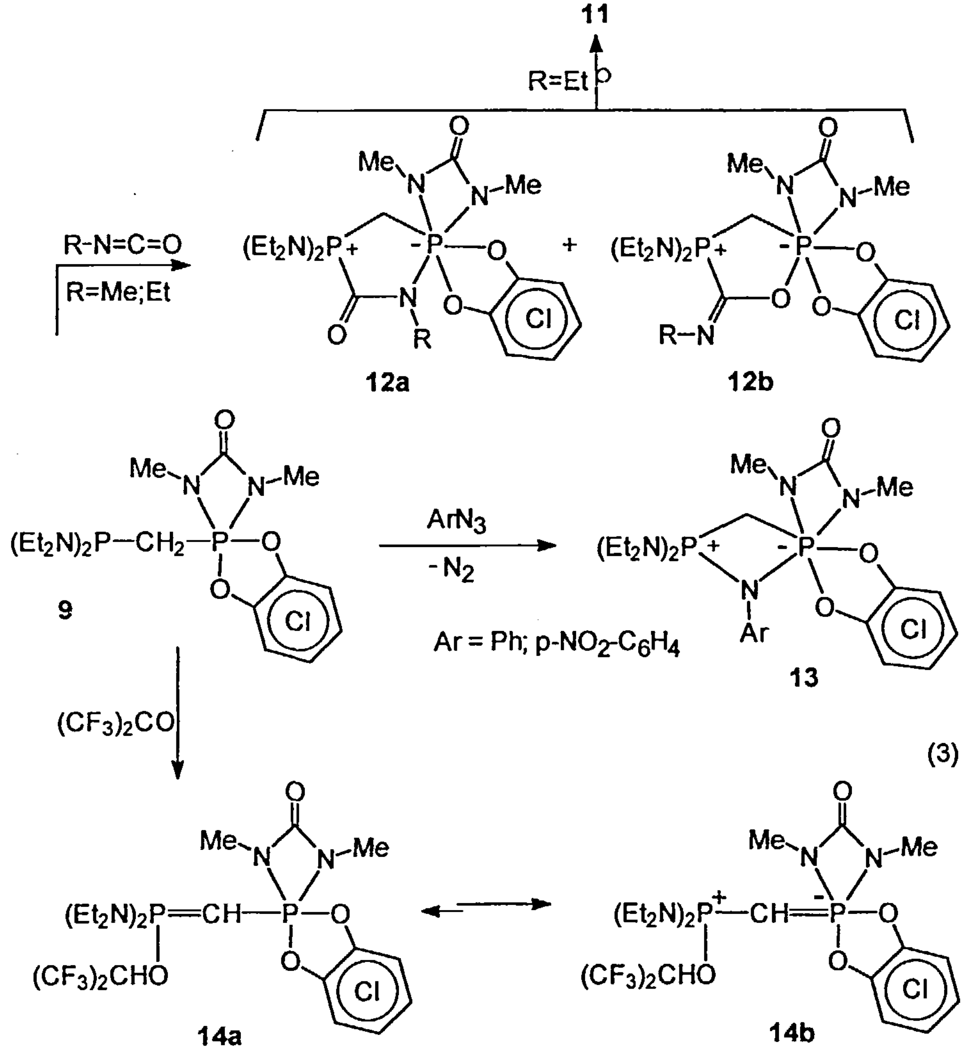

3
TOB
4
5
2
2
1
TOB
6
3 (R2N)3P
R=Me;Et
7
Cl⁻

(1)


5
Et2NH
PCl3
8
R2NH
PCl3
9
-HCl
Et3N
10
x2
11

(2)

phosphorus atoms turning them into tetra- (λ^4P^+) and hexa-coordinate state (λ^6P^-) with formal opposite charges.[2] The reaction gives two structural isomers **12a** and **12b** in the ratio 7 : 1 which are in equilibrium. This is a new type of addition reaction in organophosphorus chemistry. The structure of **12a** was determined by X-ray analysis. The two bonds connecting the isocyanate fragment to the two phosphorus atoms are longer than expected. Accordingly the isocyanate fragment dissociates from the rest of the molecule in solution very easily. It is interesting that the isomers **12a,b** (R=Et) rearrange slowly in solution of chloroform at room temperature into the dimer **11**. This reaction obviously includes the intermediate formation of the monomeric phosphaalken **10**. (Fig. 3).

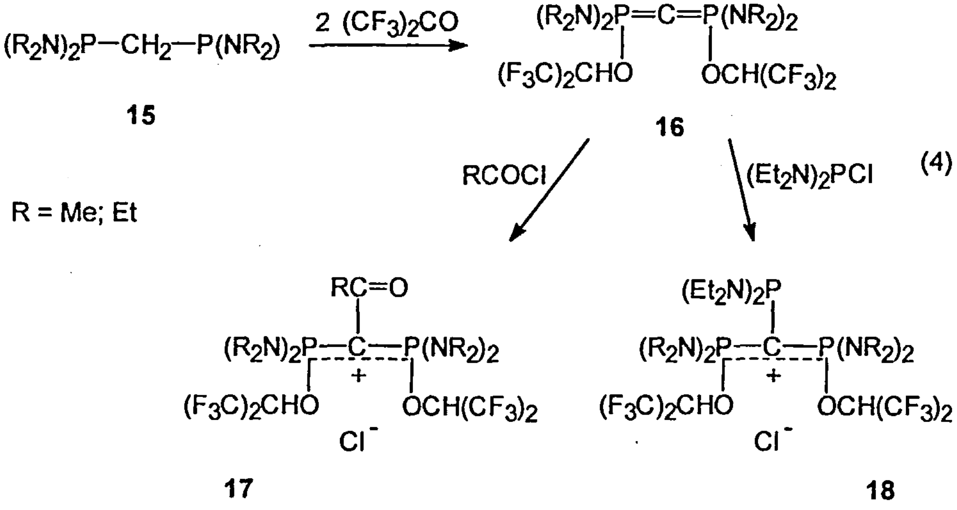


(3)

The interaction of **9** with azides is also unusual. It does not give the normal Staudinger reaction product. The reaction proceeds with the expected evolution of nitrogen but again with the participation of both phosphorus atoms and leads to the zwitterionic product **13**.

The reaction of **9** with hexafluoroacetone (HFA) is very interesting. It does not lead not to the expected cyclic oxidation product but to compound **14**, which can be considered as an addition product of the P-H ylid, isomeric to **9**, to the carbonyl function of HFA.[3] Even if an excess of HFA was used, no other products except **11** were observed. X ray analysis of **14** showed that the λ^5P-C bond is even shorter than the ylidic λ^4P=C bond and that it has a pronounced double character. From these data the structure **14b** of negatively charged penta-coordinate phosphorus with a double bond can be postulated (Fig. 3).

It turned out, that HFA reacts in a similar way with some other phosphines as well. For example methylenediphosphine **15** easily adds two equivalents of HFA giving the double ylid **16** (Fig. 4). The reaction proceeds obviously in two steps, through the monoylid intermediate which cannot be detected as its further reaction with HFA is more rapid than its own formation. Compound **16** is stable in solution and can be prepared in good yield. It is readily available and presents an interesting starting material which can be derivatized in different ways. For example, it reacts with chloroanhydrides of carboxylic acids or with PCl_3 with the formation of salts **17** and **18** respectively.



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