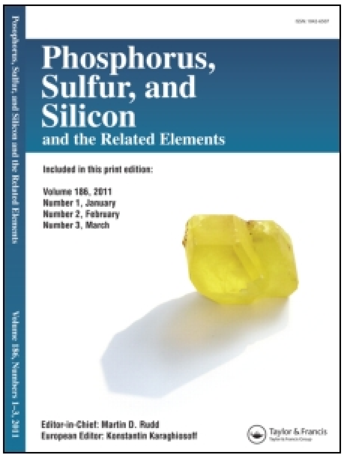

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NUCLEOPHILIC ADDITION-OXIDATION REACTIONS OF σ^3, λ^3 DIALKYL(SILYLAMINO)PHOSPHINES WITH MONO AND DISUBSTITUTED ACETYLENES

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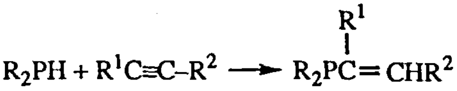
Abstract: Dialkyl(silylamino)phosphines R_2PNT_2 undergo a nucleophilic addition-oxidation reaction with either mono- or di-substituted acetylenes which is followed by a silyl migration to form phosphoranimines with unsaturated substituents. The reaction route depends on the substituent on the acetylenic carbon atom. Reactions of the acetylenes with dialkyl(silylamino)phosphines show high chemo and regio selectivity for addition to the triple bond in the formation of the alkene phosphoranimines. The reaction of (silylamino)-phosphines with α,β-acetylenic carbonyl compounds is more complicated; the reaction route depends critically on the substituents at both the carbonyl and the β-acetylenic carbon atoms.

INTRODUCTION

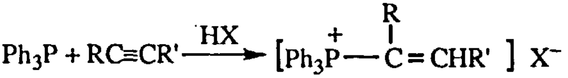
It is well known that σ^3, λ^3 phosphines are good nucleophiles and their reactions with a variety of organic compounds have been studied in detail.[1] The first step of the reaction is nucleophilic attack of P^{III} at the electrophilic center of the organic substrate. In the second step an addition or elimination reaction occurs to form stable product.[1] Thus, primary and secondary phosphines add to activated acetylenes to yield tertiary alkenyl phosphines.[2-4]



$$R_2PH + R^1C{\equiv}C{-}R^2 \longrightarrow R_2P\overset{R^1}{\overset{|}{C}}{=}CHR^2$$

$$R = H \text{ or } Ph;\quad R^1,\ R^2 = H \text{ or } Ph$$

Tertiary phosphines react with acetylenes to give alkenylphosphonium salts [2-6]



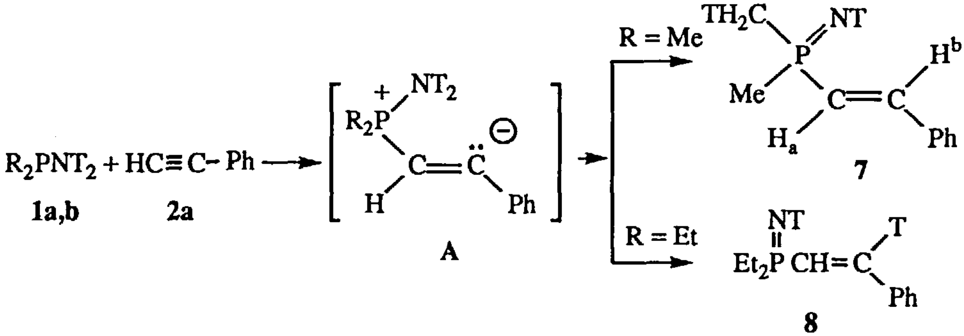
$$Ph_3P + RC{\equiv}CR' \xrightarrow{HX} [Ph_3\overset{+}{P}{-}\overset{R}{\overset{|}{C}}{=}CHR'\ ]\ X^-$$

In the past 20 years simple syntheses of secondary and tertiary silylaminophosphines have been developed[7] and this has stimulated the study of their reactivity with organic compounds containing different functionalities. These phosphines are good nucleophilic reagents which react easily with polar compounds. The reactions are accompanied by silyl group elimination or migration to give stable σ^4,λ^5 phosphoranimines[7-10]

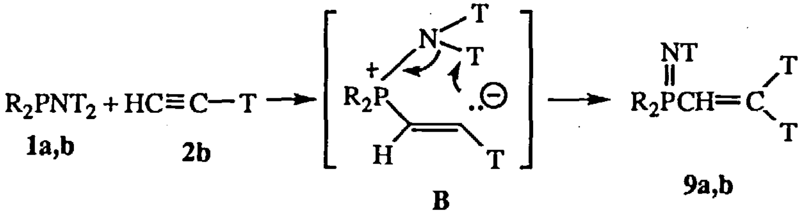
In view of the fact that phosphines react with triple bonds, it was of interest to investigate the reactivity of silylaminophosphines with mono- and disubstituted acetylenes as a route to unsaturated phosphines. Herein we describe the results obtained for reactions of dialkyl(silylamino)phosphines **1a-e** with phenylacetylene **2a**, trimethylsilylacetylene **2b**, phenylpropargylaldehyde **3**, 4-phenyl-3-butyn-2-one **4**, 3-butyn-2-one **5** and ethylpropiolate **6**.

RESULTS AND DISCUSSION

Me_2PNT_2 **1a** and Et_2PNT_2 **1b** react very slowly with phenylacetylene **2a** at room temperature reaching completion only after 30 days. The first step of the reaction appears to be nucleophilic attack of phosphorus on the unsubstituted acetylenic carbon atom presumably with formation of Zwitterion A:

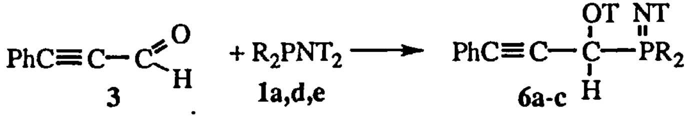


In the second step, **1a** and **1b** gave different oxidation products; in the case of **1a** the proton migration from one of methyl groups at phosphorus to the carbanion of A occurs and, after Me_3Si group migration from the N-atom to the methylene group at phosphorus, the alkene phosphoranimine **7** was obtained. In the case of **1b**, direct migration of the Me_3Si group from the nitrogen to the terminal carbon of the carbanion A gave the alkene phosphoranimine **8**. The structures of **7** and **8** were established by NMR spectra and elemental analysis. The reaction of Me_2PNT_2 **1a** and Et_2PNT_2 **1b** with trimethylsilylacetylene **2b** is an addition-oxidation process with migration of the Me_3Si from the nitrogen to the terminal carbon of the carbanion **B** and dialkyl 2,2-bistrimethylsilyl-1-ethenylphosphoranimines **9a,b** was obtained:



This reaction was carried out without solvent in a sealed ampoule at 120°C. After 30 days heating the phosphoranimines **9a,b** were obtained in good yield (75-80%). The structures of **9a** and **9b** were elucidated by NMR and elemental analysis.

The reaction of (silylamino)phosphine with acetylene carbonyl compounds is more complicated. The route depends on the substituents at the carbonyl and the β-acetylenic carbon. Dialkyl (silylamino)phosphines **1a,d,e** were reacted with phenylpropargylaldehyde **3** in CH_2Cl_2 at -78°C. As was shown for other carbonyl compounds[12] only addition-oxidation of **1a,d,e** to the C=O group was observed:

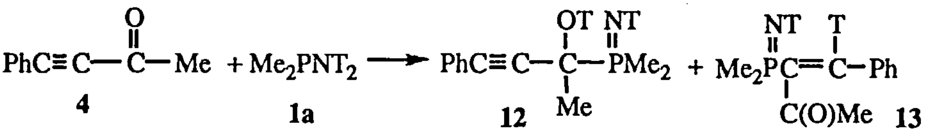


$$\underset{\mathbf{3}}{PhC{\equiv}C{-}CHO} + \underset{\mathbf{1a,d,e}}{R_2PNT_2} \longrightarrow \underset{\mathbf{6a\text{-}c}}{PhC{\equiv}C{-}\overset{OT}{\underset{H}{C}}{-}\overset{NT}{\overset{\|}{P}}R_2}$$

R: (a) Me; (d) ^iPr; (e) TCH_2

Structures of the acetylenic phosphoranimines **6a-c** were deduced from NMR and elemental analysis. This reaction is again **1a,d,e** highly chemo-, regio-, and stereoselective.

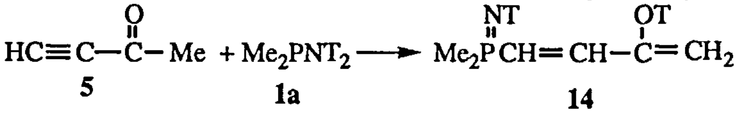
The formation of a similar acetylenic phosphoranimine (**12**) was also found in the reaction of 4-phenyl-3-butyne-2-one (**4**) with (silylamino)phosphine **1a** at -78°C. In this case, however, the main product (**13**) resulted from the addition of **1a** to the α-acetylenic carbon atom with subsequent migration of the trimethylsilyl group to the β-acetylenic carbon atom:



$$\underset{\mathbf{4}}{PhC{\equiv}C{-}\overset{O}{\overset{\|}{C}}{-}Me} + \underset{\mathbf{1a}}{Me_2PNT_2} \longrightarrow \underset{\mathbf{12}}{PhC{\equiv}C{-}\overset{OT}{\underset{Me}{C}}{-}\overset{NT}{\overset{\|}{P}}Me_2} + \underset{\mathbf{13}}{Me_2\overset{NT}{\overset{\|}{P}}\underset{C(O)Me}{C}{=}\overset{T}{C}{-}Ph}$$

The ^{31}P NMR spectrum of the crude product showed three signals at 19.2 ppm, 3.7 ppm and 2.6 ppm respectively for **12** and the (E) and (Z) isomers of **13**. These two examples show that the reaction path strongly depends on the particular substituents at β-acetylenic and carbonyl carbon atoms. The reaction is neither chemo-, regio-, nor stereoselective.

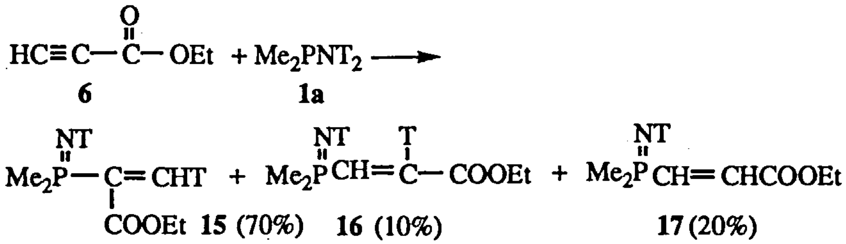
The reaction of **1a** with 3-butyne-2-one **5** yields a different product because the electron donating CH_3 group decreases the electrophilicity of the carbonyl carbon atom facilitating the addition of **1a** to triple bond. At -78°C in CH_2Cl_2 the reaction of 3-butyne-2-one **5** with **1a** was accompanied by polymerization. The polymerization process continued during distillation and so **14** was isolated only in low yield:



$$\underset{\mathbf{5}}{HC{\equiv}C{-}\overset{O}{\overset{\|}{C}}{-}Me} + \underset{\mathbf{1a}}{Me_2PNT_2} \longrightarrow \underset{\mathbf{14}}{Me_2\overset{NT}{\overset{\|}{P}}CH{=}CH{-}\overset{OT}{C}{=}CH_2}$$

The structure of 1,3-butadienyl phosphoranimine **14** was also deduced from ^1H, ^{13}C and ^{31}P NMR spectra.

To evaluate the influence of a substituent at C=O on the reaction, we studied the reactivity of **1a** with ethyl propiolate **6**. In diethyl ether at -50°C a mixture of products was obtained:



$$\underset{\mathbf{6}}{\mathrm{HC{\equiv}C{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}OEt}} + \underset{\mathbf{1a}}{\mathrm{Me_2PNT_2}} \longrightarrow$$

$$\underset{\mathbf{15}\ (70\%)}{\mathrm{Me_2\overset{\overset{\displaystyle NT}{\|}}{P}{-}\underset{\underset{\displaystyle COOEt}{|}}{C}{=}CHT}} + \underset{\mathbf{16}\ (10\%)}{\mathrm{Me_2\overset{\overset{\displaystyle NT}{\|}}{P}CH{=}\overset{\overset{\displaystyle T}{|}}{C}{-}COOEt}} + \underset{\mathbf{17}\ (20\%)}{\mathrm{Me_2\overset{\overset{\displaystyle NT}{\|}}{P}CH{=}CHCOOEt}}$$

The main product of the reaction was the phosphoranimine **15**, which arises from nucleophilic addition of **1a** to the α-acetylenic carbon atom. The structure of compound **15** is in accord with the NMR spectral data. Finally, the phosphoranimine **17** probably results from the presence of a trace of water or the abstraction of proton from the solvent in the first step of the reaction. Reacting **1a** with **6** in dichloromethane gave only **17**.

The phosphines **1d-e** reacted with **3** in the same fashion as **1a**. Individual products however could not be isolated from the reaction of **1d** or **1e** with **4**, **5** or **6** because the reaction mixture polymerized very rapidly.

CONCLUSION

The investigations described herein illustrate the reactivity of the dialkyl(silylamino)phosphines toward variously substituted acetylenes. For the first time we have shown a nucleophilic addition-oxidation reaction of σ^3, λ^3 (silylamino)phosphines to the C≡C triple bond. Extensions of these reactions will provide new approaches for the synthesis of alkenylphosphoranimines.

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