

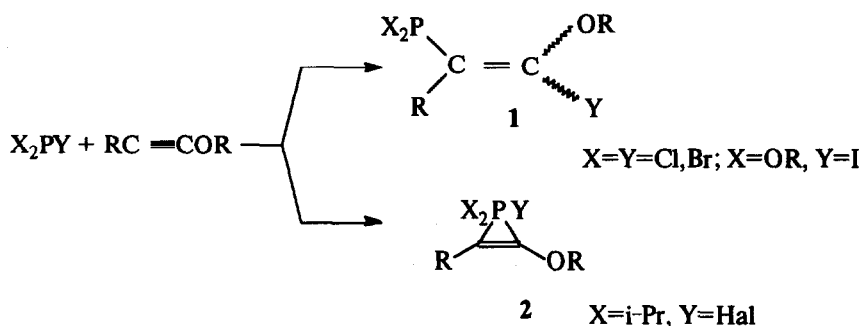
The Addition of Phosphorus Halides to Ynamines. Ring-Chain Tautomerism of Phosphirene with Isomeric Open Structure

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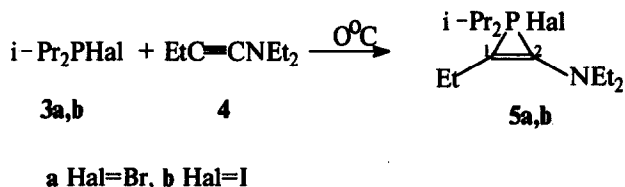
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Abstract: *The reaction of halogenodiisopropylphosphines 3a-c with 1-diethylamino-1-butyne 4 in dichloromethane leads to new phosphirenes 5. In benzene or pentane mixtures of phosphirenes 5c and isomeric open structure 6 have been obtained. Ring-chain tautomerism for 5c and 6 have been observed for the first time.*

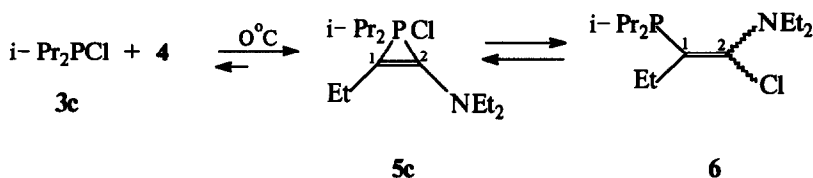
Recently it was shown in our laboratory that the addition of phosphorus trihalides to triple bond of ynethers leads to the formation of β -halogeno- β -alkoxyalkenyl phosphines 1. On the other hand, halogenodialkylphosphines and ynethers react with the formation of phosphirenes 2¹.



Here we report the reactions of halogenophosphines 3a-d and ynamine 4 leading to phosphirenes 5, β -halogeno- β -aminoalkenylphosphines 6 or their mixtures depending on the nature of reagents and solvents used. The reaction of a 1 molar solutions of bromo- or iododiisopropylphosphines 3a,b (1 equiv.) in pentane, benzene or dichloromethane with ynamine 4 (1 molar solution at the same solvent, 1 hour, 20°C) gives pale-yellow solutions of phosphirenes 5a,b in C₆H₆ or CH₂Cl₂ or pale-yellow solids from pentane in high yields.



For chlorodiisopropylphosphine **3c** the reaction product depends (under the same conditions) to a considerable extent on the solvent used. In dichloromethane only **5c** is formed; however a 1:9 mixture of **5c** and **6** is formed in pentane and a 1:1 mixture in benzene.



The mixture of **5c** and **6** is a colorless oil. We have found that these isomers are in equilibrium, which can be easily shifted if the solvent is changed. When pentane is evaporated and benzene is added, the 1:9 mixture of **5c** and **6** quickly turns into 1:1 mixture of these isomers. Also phosphirene **5c** turns into 1:9 mixture of **5c** and **6** when dichloromethane is evaporated and pentane is added (the transformations were monitored by ^{31}P NMR). It has to be noted that these transformations are reproducible and can be brought about repeatedly in both directions. The equilibrium between **5c** and **6** is the first example of ring-chain tautomerism for a phosphirene and its isomeric open structure.

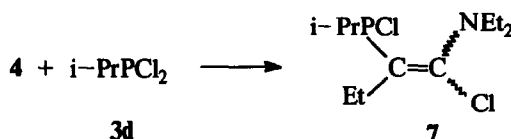
Obviously, P-Hal bond in **5** is partly ionic and the extent of ionization increases both in polar solvents and on going from Hal=Cl to Hal=I. A strong upfield shift of the ^{31}P resonance of **5c** in pentane or C_6D_6 (about 17–25 ppm) in comparison with CD_2Cl_2 (see Table), and an upfield shift of the ^{31}P resonance of **5c** (about 9–26 ppm) in comparison with **5a,b** in the same solvents, confirm the decrease in P-Hal bond ionization and the increase in phosphorane character of **5** in the sequence $\text{I} < \text{Br} < \text{Cl}$.

So, easier ionization of P-Hal bond in **5a,b** in comparison with **5c** and easier ionization of P-Cl bond of **5c** in CD_2Cl_2 in comparison with C_6D_6 and pentane leads to an increase in positive charge on the phosphorus atom and to an increase in stability of the phosphirenes. The question whether the phosphirenes possess aromaticity remains undecided². The data can be interpreted to demonstrate the possibility of weak aromatic stabilization of phosphirene **5c** in comparison with the open structure **6**.

Table. Selected spectral data of compounds 5a-c, 6 and 7³.

Compound	Solvent	δP^4	δC^1 (J _{PC} , Hz)	δC^2 (J _{PC} , Hz)
5a, Hal=Br	C ₆ D ₆	-66	85.7 (34.5)	127.2 (0)
	CD ₂ Cl ₂	-60		
5b, Hal=I	C ₆ D ₆	-60		
	CD ₂ Cl ₂	-58	85.1 (22.5)	126.0 (5.7)
5c, Hal=Cl	pentane	-94		
	C ₆ D ₆	-86	92.1 (99.5)	146.5 (27.6)
	CD ₂ Cl ₂	-69		
6	C ₆ D ₁₂	16	133.9 (28.5)	153.8 (26.5)
7	CD ₂ Cl ₂	111	136.8 (44.7)	149.0 (25.2)

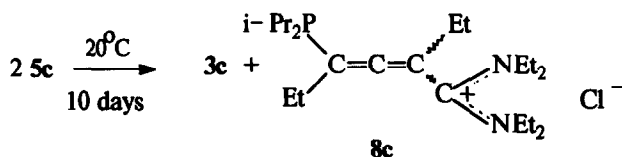
The addition of isopropyldichlorophosphine to ynamine 4 yields only chloroenamine 7 in the same conditions as for 5a-c.



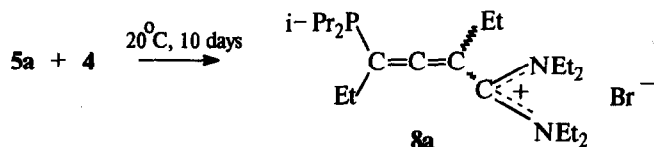
No cyclization from 7 to the isomeric phosphirene was observed, probably due to a decrease in nucleophilicity of the phosphorus atom in 7.

The easy interconversion of 5c and 6 as well the value of ²J_{PC} couplings (25–26 Hz) can serve as confirmation of E-configuration of 6 and 7 (see ref. 5 on the stereochemistry of β-phosphorus-substituted alkenyl alkyl ethers).

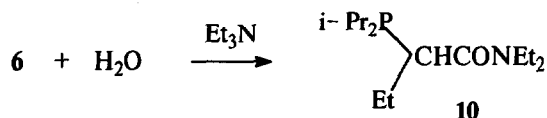
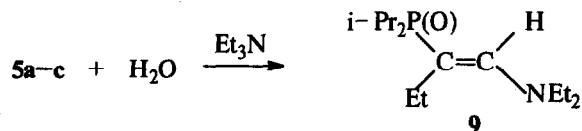
While 5a,b are stable for several days at room temperature, and the mixture of 5c and 6 is stable in pentane or benzene solutions, in dichloromethane 5c is unstable to undergo quantitative transformation into the amidinium salt 8c⁶ and an equivalent of chlorophosphine 3c.



Supposedly 5c reacts with ynamine 4, which is present in small quantities in equilibrium with 5c. We have carried out the reaction of 5a with 4 and we have shown that 8a is actually formed in this reaction.



The hydrolysis of a pentane solution of **5c** and **6** by 2 equiv. of water in THF in the presence of triethylamine at -80°C gives mixtures of corresponding products **9** and **10**, whereas the hydrolysis of dichloromethane solutions of **5a,b** under the same conditions leads only to **9**⁷.



REFERENCES AND NOTES.

1. Kazankova, M.A., Rodionov, I.L., Lusikova, E.V., Lutsenko, I.F. In *Trudy VIII Vsesoyusnoi Konferenzii po Khimii Fosfororganicheskikh Soyedineniy*. Moscow, Nauka, 1987, pp.82–90.
2. Mathey F. *Chem Rev.* 1990, **90**, pp.997–1025.
3. The structures of all new compounds were confirmed by NMR ^{13}C , ^1H , ^{31}P , and IR spectra. NMR spectra were recorded on a VXR-300 Varian spectrometer, δP and δC are given in p.p.m. and refer to 85% H_3PO_4 and TMS as standards.
4. δP of **5a-c** varies over a range of 3–5 p.p.m. depending on concentration.
5. Lazhko E.I., Luzikova E.V., Michailov G.Yu., Kazankova M.A., Ustynyuk Yu.A., *J. Gen. Chem. (USSR)*, 1988, **58**, pp.1247–1258.
6. **8c**: IR $\nu(\text{C}=\text{C}=\text{C})$ 1920 cm^{-1} ; ^{31}P -NMR (CH_2Cl_2) 12; ^{13}C -NMR (CD_2Cl_2): 106.7 (d, 32.3, $\text{C}_{\text{sp}^2}\text{-P}$), 206.28 (d, 16.3, $=\text{C}=\text{C}$), 97.2 (d, 7.9, $\text{C}-\text{C}(\text{NEt}_2)_2$), 168.3 (d, 2.9, $\text{C}(\text{NEt}_2)_2$).
7. **9** (E-isomer): ^{31}P -NMR (C_6D_6) 16; ^{13}C -NMR (C_6D_6): 93.5 (d, 94.7, $\text{C}_{\text{sp}^2}\text{-P}$), 146.2 (d, 15.5, $\text{C}_{\text{sp}^2}\text{-H}$); ^1H -NMR (CD_2Cl_2): 6.3 (d, 17, 1H, H-P). **10**: ^{31}P -NMR (C_6D_6) 51.7; ^{13}C -NMR (C_6D_6) 171.7 (d, 7.7, $\text{C}=\text{O}$), 40.1 (d, 29.0, CH-CO). Bp. $90\text{--}120^{\circ}\text{C}$ at 1 mm Hg (for mixture **9** and **10**).

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