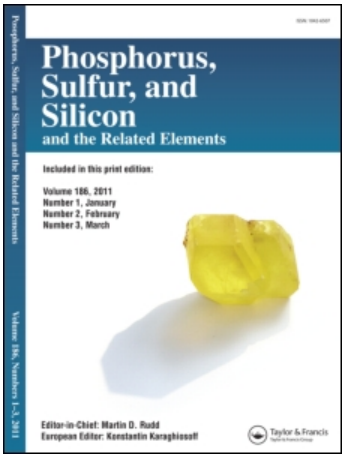

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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To cite this Article Regitz, M. , Heydt, H. , Wagner, O. , Schnurr, W. , Ehle, M. and Hoffmann, J.(1990) 'Transformation of Phosphaalkynes into 1H- and 2H-Phosphirenes[1]', Phosphorus, Sulfur, and Silicon and the Related Elements, 49: 1, 341 — 344
To link to this Article: DOI: 10.1080/10426509008038975
URL: http://dx.doi.org/10.1080/10426509008038975

Phosphorus, Sulfur, and Silicon, 1990, Vols. 49/50, pp. 341–344
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TRANSFORMATION OF PHOSPHAALKYNES INTO 1H- AND 2H-PHOSPHIRENES[1]

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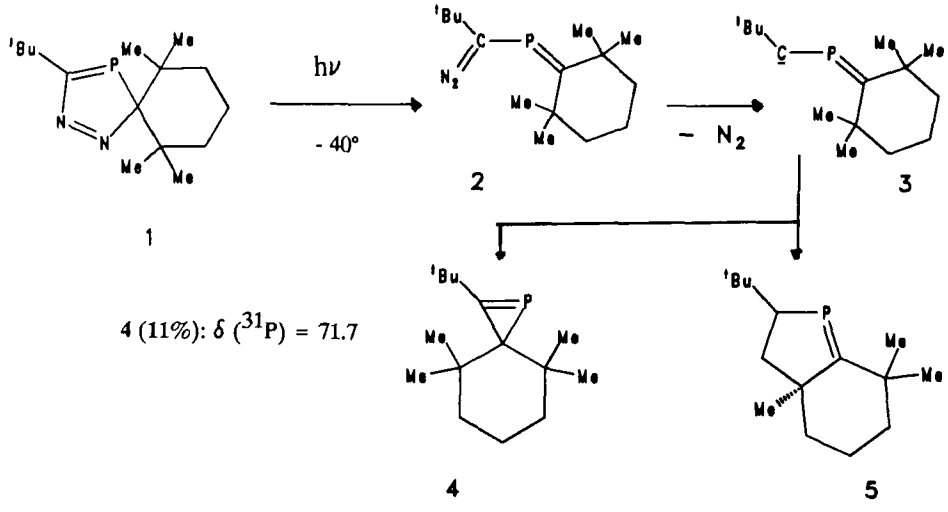
Abstract The 2H-phosphirene **4** is synthesized from the spirocyclic 3H-1,2,4-diazaphosphole **1** by low temperature photolysis. The isomeric 1H-phosphirenes **7** are formed by a [2+1]-cycloaddition process of chloro carbenes, generated from diazirines, onto the triple bond of phosphaalkynes. When the 1-chloro-1H-phosphirenes **7** are allowed to react with a series of nucleophiles substitution occurs yielding the 1H-phosphirenes **9**, **11** and **12**. The existance of a phosphirenium cations, for instance **13** is discussed.

In contrast to open chained phosphaalkenes the cyclic isomers are rarely unknown. This is especially true for the simplest cyclic phosphaalkene, the 2H-phosphirene.

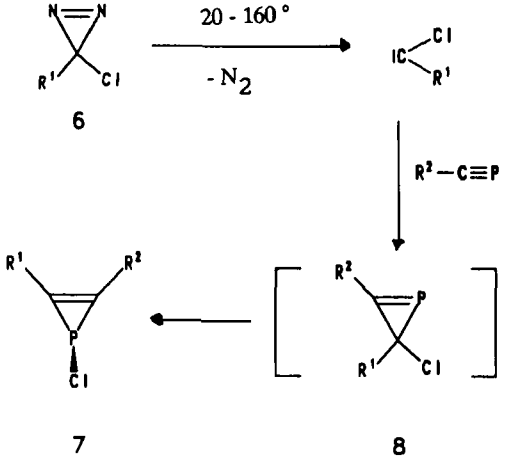
The synthetic target - a 2H-phosphirene - was achieved by the low temperature photolysis of the spirocyclic 3H-1,2,4-diazaphosphol **1**[2] . The ring opening of **1** to the phosphavinyl-diazoalkane **2** is followed by the nitrogen elimination to furnish the phosphavinylcarbene **3**, which gives rise to two reaction pathways yielding a mixture of products: one of which is the first 2H-phosphirene **4** formed by a intramolecular [2+1]-cycloaddition process, while the other is the anelated 1-phosphacyclopentene **5**, which was formed by the carbene insertion into a C/H-bond. Bulb-to-bulb destillation and subsequent chromatography on silica gel results in a 1:5 ratio of the two products in a combined yield of 55%. It has to pointed out that comparable results are also obtained when the tetramethyl substituted six-membered ring is replaced by the the five- or seven-membered analogues.



The high field shift of the phosphorus atom at about 72 ppm was at first suprising but we are able to perform a X-ray structure from a metal complex of **4** which unequivocally confirms the P/C double bond in a three-membered ring[3].

When The diazirines **6** are thermolyzed in a large excess of phosphaalkynes[4] suprisingly the 1-chloro-1H-phosphirenes **7** can be isolated in yields up to 64% after work-up by destillation[5]. The phosphirenes are stable, coulorless oils which are however sensitive towards hydrolysis. The thermolysis temperature is governed by the decomposition temperature of the respectiv diazirine. We explain the above result as follows:

The carbenes initially formed by elimination of nitrogen from the diazirine undergo [2+1]-cycloaddition onto the triple bond of the phosphaalkyne yielding the 2H-phosphirenes **8**. These products however cannot be isolated since they isomerize by a rapid 1,3-chlorine shift to the 1H-isomers **7**. It is important for the stability of 1H-phosphirenes, that antiaromaticity is not operative here, since the phosphorus has a pyramidal configuration, which is evident from the crystal stucture of **7a**[6].



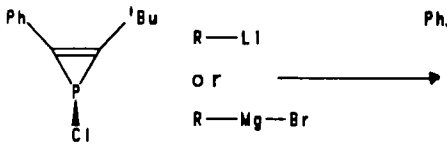
6 7 8

7, 8	R^1	R^2	%7	δ (^{31}P)
a	Ph	^{t}Bu	63	-73
b	^{t}Bu	^{t}Bu	33	-67
c	OMe	^{t}Bu	35	-36
d	Ph	1-Ad	24	-77
e	OPh	CMe_2Et	26	-29

When the 1-chloro-2-tert.-butyl-3-phenyl-1H-phosphirene is allowd to react with a series of nucleophiles substitution occurs in nearly quantitative or good yields.

So, organo lithium nucleophiles like tert.-butyl-lithium, lithium-tert.-butylacetylide, and lithium-diazo-(trimethylsilyl)-methane, lithium amides, alkoholates and phosphides or ethyl or vinyl grignard compounds furnish at -78° or -40° resp. the substitution products **9** when they are allowd to react with the chloro-phosphirene **7a**.

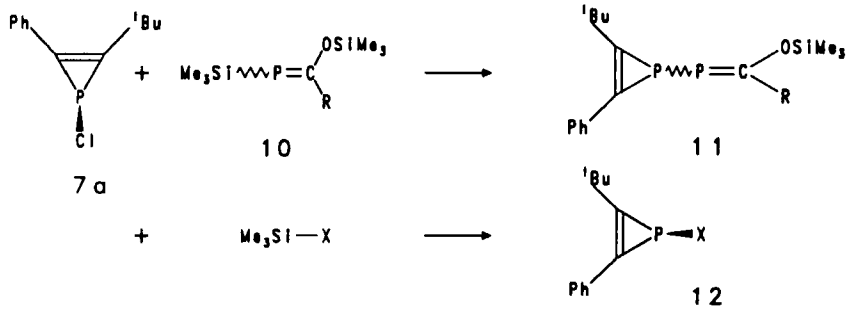
The resonances of the phosphorus atoms in three-membered ring depend very strongly onto the new introduced substituents whereby **9d** with -77 ppm and **9b** with -228 ppm exhibit extremly high and low limiting values. The phosphorus atoms in **9f** show the expected coupling constant from about 260 Hz.



7a 9

9	R	%9	$\delta(^{31}P)$
a	^tBu	67	-145
b	$^tBuC{\equiv}C$	35	-228
c	$Me_3SiC(=N_2)$	100	-179
d	OMe	71	-77
e	N^iPr_2	76	-127
f	$P(SiMe_3)_2$	23	-167
			-172
g	$H_2C{=}CH$	45	-185
h	H_3CH_2C	37	-175

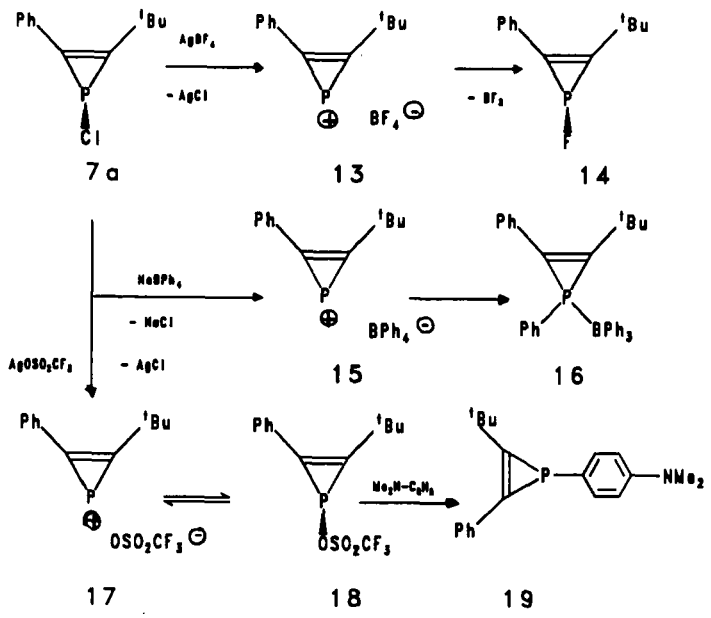
In a second variant of nucleophilic substitution processes at 1-chloro-1H-phosphinines, the nucleophiles are used in the form of their trimethylsilyl derivatives for example the trimethylsilyl-phosphaalkenes **10**. The resonances of the phosphorus atoms in the threee membered ring exhibit the expected values whereby the $\lambda^3\sigma^3$- and $\lambda^3\sigma^2$-phosphorus atoms in **11** show the expected large differences in their chemical shift values. The elimination of trimethylsilyl-chloride by the reaction of **7a** with silyl-compounds can be used for the exchange of the chlorine substituent at phosphorus towards other halogens or pseudohalogens. So the bromine, iodine, azido and cyano substituent can be introduced into the phosphirene ring system (formation of **12**). The phosphorus resonances exhibit the expected values but it is nothe-worthly, that in the cyano case the signal is shifted to comparable high field.



11	a	b	12	a	b	c	d
R	^tBu	1-Ad	X	Br	I	N_3	C≡N
%11	49	80	%12	100	100	100	95
$\delta(^{31}P)$	-179	-176	$\delta(^{31}P)$	-61	-64	-106	-233
	167	168					

One as yet unanswered question in the chemistry of low coordinated phosphorus compounds is that of the existance of the phosphirenylium cations. The above described 1-chloro-1H-phosphirenes **7** could contribute to the solution of this question should it ever become possible to detach the halogen ionically from the phosphorus atom.

Model reactions has only been carried out with **7a**. When this phosphirene is allowed to react with silver tetrafluoroborate in ether a chlorine fluorine exchange take place yielding the 1-fluoro-1H-phosphirene **14** in nearly quantitative yield. A plausible explanation for this result is that the phosphirenium cation **13** is formed initially and that this cation must be highly electrophil abstracting a fluorine atom from the tetrafluoroborate counterion to furnish **14** and boron trifluoride. When **1** is allowed to react with sodium tetraphenylborate instead of the fluorobarate, a comparable result is observed: the cation **15** extracts a phenyl group from the counterion to yield the 1-phenyl-1H-phosphirene **16** in form of its triphenylborane adduct. In a other experiment, **7a** was allowed to react with silver triflate. The product of this reaction was the phosphirene **18** which was isolatd in quantitative yield and could be purified by destillation. This observation clearly rule out a ionic form for **18** even though the phosphorus NMR signal appears at relative low field at -8.9 ppm. Further evidence of this assumption is provided by the electrophilic substitution reaction of N,N-dimethylaniline with **17** which proceeds in a electrophilic aromatic substitution manner to yield the 1-aryl-1H-phosphirene **19**.



1) Unusually coordinated phosphorus compounds; part 42. For part 41, see: M. Regitz, Chem. Rev. 1989, *89*, in press.
2) O. Wagner, G. Maas and M. Regitz, Angew. Chem. 1987, *99*, 1328; Angew. Chem. Int. Ed. Engl. 1987, *26*, 1257.
3) The P/C double bond lenght of the tungsten carbonyl complex is shortened to 1.634 A in comparison to other free or complexed phosphaalkenes.
4) M. Regitz and P. Binger, Angew. Chem 1988, *100*, 1541; Angew. Chem. Int Ed. Engl. 1988, *27*, 1484.
5) O. Wagner, M. Ehle and M. Regitz, Angew. Chem. 1989, 101, 227; Angew. Chem. Int. Ed. Engl. 1989, *28*, 225.
6) The angle between the phosphorus and the chlorine amounts about 70°. The phosphorus chlorine bond is lengthened to 2.166 A in comparison to normal phosphorus chlorine single bonds