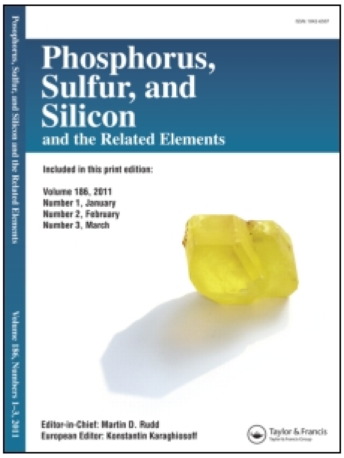

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Azaphospholes[1,2]: State and Advances

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To cite this Article Schmidpeter, A. , Bansal, R. K. , Karaghiosoff, K. , Steinmüller, F. and Spindler, C.(1990) 'Azaphospholes[1,2]: State and Advances', Phosphorus, Sulfur, and Silicon and the Related Elements, 49: 1, 349 — 354
To link to this Article: DOI: 10.1080/10426509008038977
URL: http://dx.doi.org/10.1080/10426509008038977

Phosphorus, Sulfur, and Silicon, 1990, Vols. 49/50, pp. 349-354
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AZAPHOSPHOLES[1,2]: STATE AND ADVANCES

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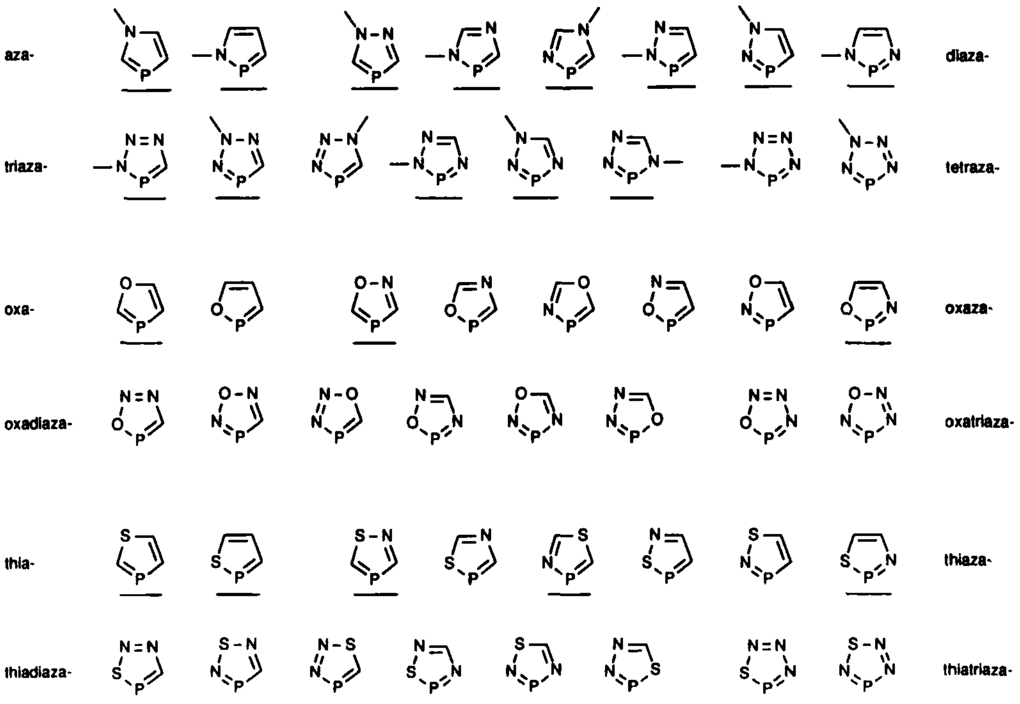
Heterophospholes[3] derive from the classical nitrogen, oxygen or/and sulfur containing five-membered 6π-heterocycles by replacing a CH unit by two-coordinate phosphorus as a member of the ring. Formally 48 systems seem possible this way. Of 21 of them representatives have been prepared so far[4].


POSSIBLE AND KNOWN HETEROPHOSPHOLES

Of the different routes developed for the synthesis of heterophospholes[5] four may be quoted as the more important ones:

(1) An unsaturated four-membered chain with replaceable

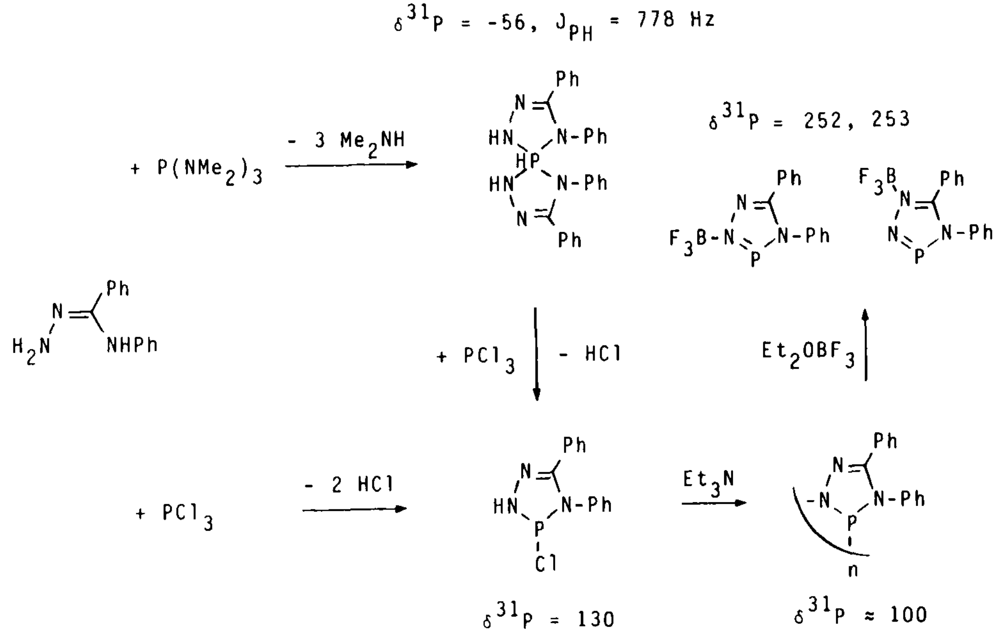
hydrogen at its ends is condensed with PCl_3 or $P(NMe_2)_3$. By this route 1,2,3-diazaphospholes were prepared in 1967 as the first examples (*Melnikov et al.*, *Schmidpeter et al.*). Moreover systems with two heteroatoms adjacent to phosphorus are readily accessible this way (*Schmidpeter et al.*, *Barrans et al.*, *Malavaud et al.*, *Gololobov et al.*, *Majoral et al.*).

(2) 2-Aminoethylphosphines or -phenylphosphines with a functional heteroatom group in 2-position are condensed with reactive carbonic acid derivatives to give 1,3-azaphospholes and benzo-1,3-heterophospholes (*Issleib et al.*, *Tzschach et al.*, *Heinicke*).

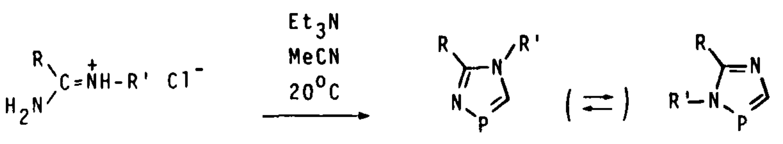
(3) 1,3-Aza- and 1,2,4-diazaphospholes are obtained from the condensation of $P(SiMe_3)_3$ to cationic carbon centers in a one-step (*Märkl et al.*) or two-step way (*Schmidpeter et al.*).

(4) 1,3-Dipolar cycloaddition of phosphaalkynes $RC{\equiv}P$ and phosphaalkenes $R(Me_3SiO)C{=}PSiMe_3$ (with loss of $(Me_3Si)_2O$) or $R(Me_3Si)C{=}PCl$ (with loss of Me_3SiCl) gives rise to various heterophospholes with none or one heteroatom adjacent to phosphorus (*Regitz et al.*, *Carrié et al.*, *Märkl et al.*).

Some of the heterophospholes are as stable and unreactive as familiar from the classical aromatic five-membered heterocycles. There are however considerable and characteristic differences in reactivity even among the isomers of the same ring system. While for example 1*H*- and 2*H*-1,2,4,3-triazaphospholes are long known, stable and easily accessible by route (1), no 4-substituted representative has yet been prepared. We find that the reaction of N^3-phenyl benzamidrazone with $P(NMe_2)_3$ even in excess gives a spirocyclic phosphorane. Its PCl_3 condensation yields oligomers of the triazaphosphole which - as experienced in other cases before - becomes monomeric as BF_3-complex.



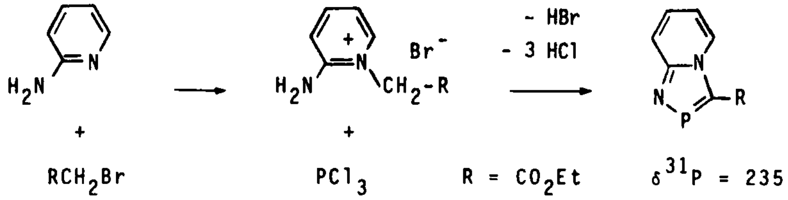
While 1,2,3-diazaphospholes are easily prepared by a condensation of type (1) this is normally not the case for 1,3,4-diazaphospholes; the methylene group at the end of the required four-membered chain is sufficiently reactive in a ketone hydrazone but looses this reactivity as the nitrogen changes its place in the chain as in an alkylamidine. The difficulty is overcome if an unsubstituted or primary amidine is used for condensation and the methylene group is introduced together with the phosphorus in the form of chloromethyl dichlorophosphine.



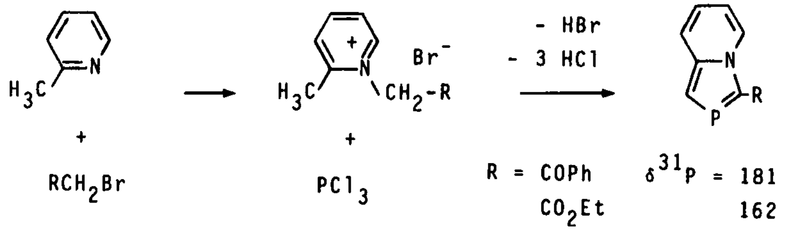
R = Me	R' = H	$\delta^{31}P$ = 199 (60%)	209 (40%)
Ph	H		185 (100%)
Ph	Ph	183 (85%)	212 (15%)
SMe	Me	183 (54%)	213 (46%)

The analogous condensation of 2-aminopyridine, 2- and 4-aminothiazole gives rise to 1,3,4-diazaphospholes with annellated rings. Likewise the condensation of thiobenzamide gives a 1,3,4-thiazaphosphole[5].

In an earlier synthesis of 5-substituted 1,3,4-thiazaphospholes we S-alkylated the thioamide at first and extended thus its chain by a methylene group with an electron withdrawing substituent to increase its reactivity. Under controlled conditions a PCl_3-condensation (1) was then successful again[6]. The same route now proved effective also for the synthesis of 1,3,4-diazaphospholo[1,2-a]pyridines and -[1,2-b]thiazoles.

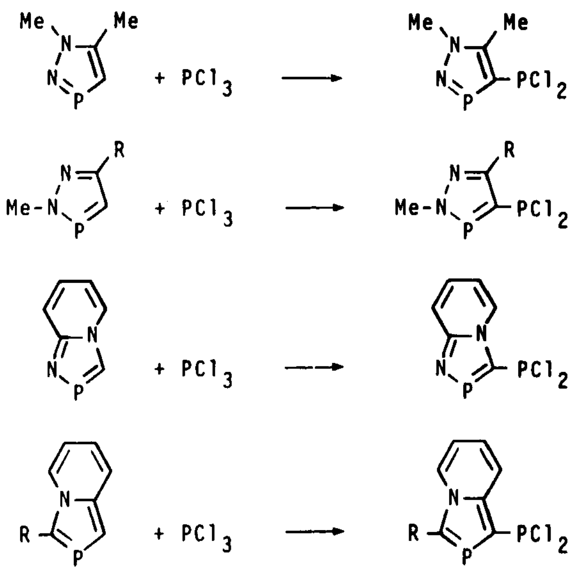


Heterophospholes with no heteroatom adjacent to phosphorus were so far accessible only by the relative expensive routes (2), (3) or (4). By further extending the above syntheses to 2-alkylpyridines even 2-phosphaindolizines (1,3-diazaphospholo[1,5-a]pyridines can be obtained by PCl_3-condensation.



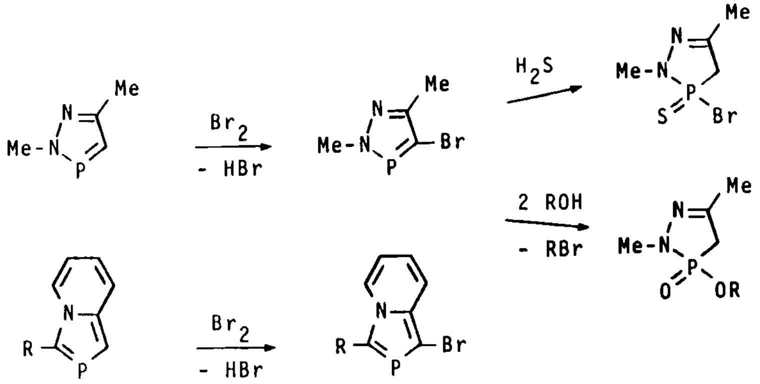
As compared to acyclic phosphaalkenes and iminophosphines heterophospholes show a lower phosphorus nucleophilicity and a reduced tendency to give 1,2-additions to the P=C or P=N bond. The two reactions tend to assist eachother however; their combination is found in complex formation and gives also rise to many derivatives with four- and five-coordinate phosphorus.

Azaphospholes with an unsubstituted carbon adjacent to phosphorus undergo electrophilic substitutions by a 1,2-addition/elimination sequence, for example with PCl_3.

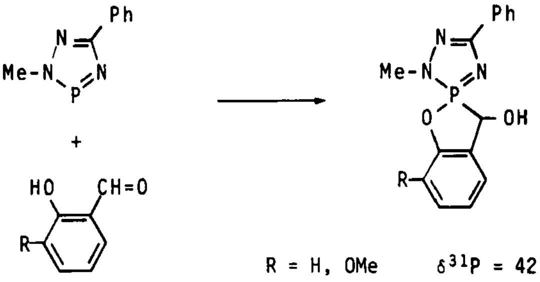


$\delta^{31}P$		J_{PCP} [Hz]	
231	157	52	
249	157	79	R = Me
248	157	61	Et
244	123	166	
180	161	159	R = CO_2Et
201	156	175	COPh

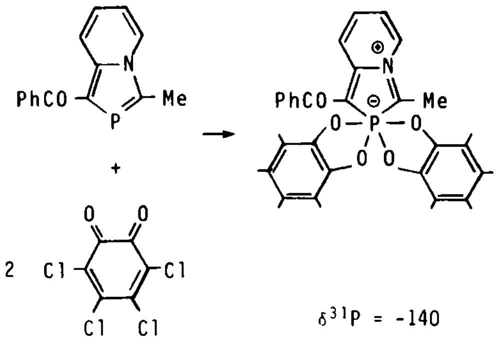
Brominations provide another example; protic reagents may subsequently cause an intramolecular redox reaction between the adjacent C and P members.

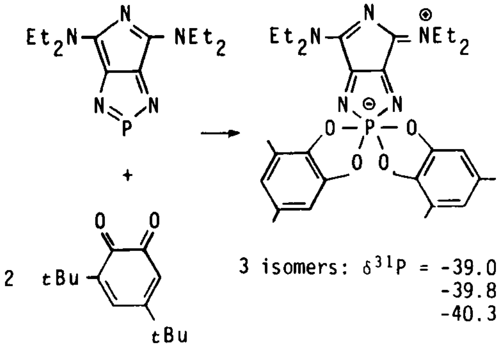


Many cycloaddition reactions of heterophospholes have been reported[7]. A new type is found in the reaction of salicylaldehyde and 2*H*-1,2,4,3-triazaphospholes. What looks like a [4+1]cycloaddition with a concomitant 1,5-shift of hydrogen most probably results from a combination of steps as mentioned above.



In some cases oxidizing heterodienes such as quinones give double 1,1-additions resulting in zwitterionic products.





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