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1,3,5-Triaza-2-phosphapentalenes

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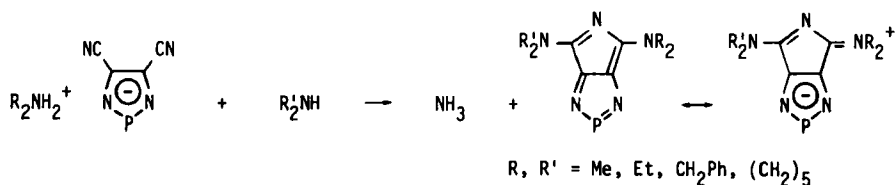
1,3,5-Triaza-2-phosphapentalenes

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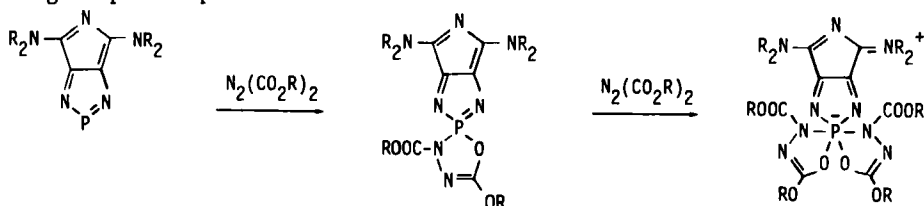
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Refluxing a dialkylammonium 4,5-dicyano-1,3,2-diazaphospholate¹ with a dialkylamine in chloroform gives a 4,6-bis(dialkylamino)-1,3,5-triaza-2-phosphapentane¹ in good yield as the only reaction product. Unsymmetrically substituted representatives are accessible this way too.



The diamino-phosphapentalenes are stable, deep red crystalline solids. They represent the first known $(4n)\pi$ heterophospholes. As in the case of the corresponding carbocyclic pentalenes² the 8π system is stabilized by the two amino substituents. According to the second mesomeric formula the diaminopentalenes can be regarded as zwitterions, consisting of an anionic 1,3,2-diazaphospholyl and a cationic 2-azaallyl part. The molecular structure, as obtained from an X-ray analysis, strongly supports this view. The colour of the diamino phosphapentalenes is due to an intramolecular charge transfer. The results are in good agreement with MNDO-calculations.

The chemical reactivity of the phosphapentalenes is also in accord with their zwitterionic character and compares to that of the 1,3,2-diazaphospholate anion. Under simultaneous oxidation by sulfur or selenium alcohols add to the $\text{P}=\text{N}$ bond yielding deep blue products.



Azodicarboxylic esters give two successive $[4+1]$ additions to the phosphorus yielding purple and colourless products, respectively. The latter provides the first example of a hexacoordinate phosphorus with an N_4O_2 surrounding.

¹ A. Schmidpeter and K. Karaghiosoff, Nachr. Chem. Tech. Lab. 33 (1985) 793 and references cited therein.

² K. Hafner, K. F. Bangert and V. Orfanos, Angew. Chem. 79 (1967) 414; Angew. Chem. Int. Ed. Engl. 6 (1967) 451.