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Four- and Eight-Membered Phosphazanes with Five-Membered Fragments

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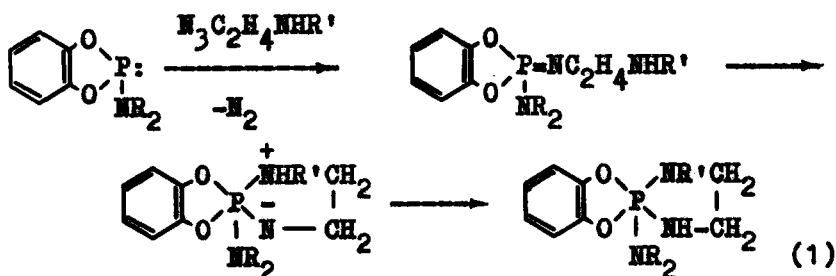
FOUR- AND EIGHT-MEMBERED PHOSPHAZANES WITH FIVE-MEMBERED FRAGMENTS

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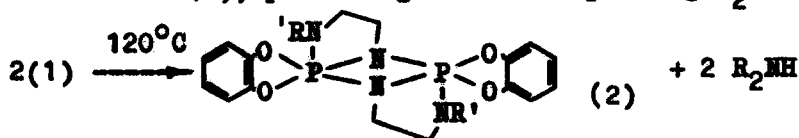
Abstract 4- and 8-membered phosphazanes with 5-membered cycles containing phosphorus have been synthesized by disamination of spiroposphoranes and phosphorylation of amineketones with primary amino group by means of PCl_3 . The structural investigation of the above mentioned phosphazanes was carried out.

DIAZADIPHOSPHETIDINES

Reaction of 2-azidoamines that contain an alkyl group at the amine N with cyclic phosphites yield the products (1) whose structure indicates that protonation of the imine N does ultimately occur despite the fact that the acid properties of the N-atom in secondary aliphatic amines are not high.

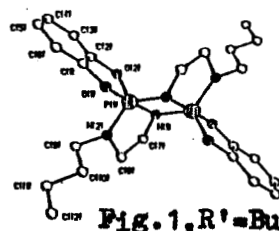


On heating spiroposphoranes (1) are converted with a good yield to dimer (2), producing the corresponding R_2NH



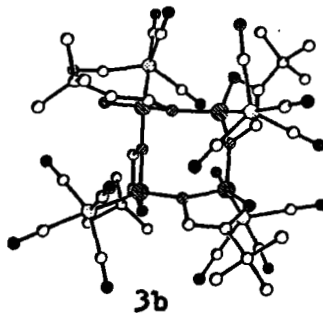
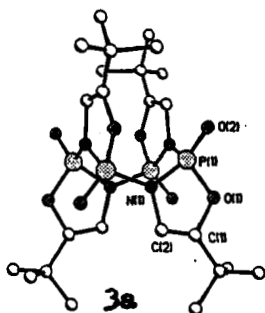
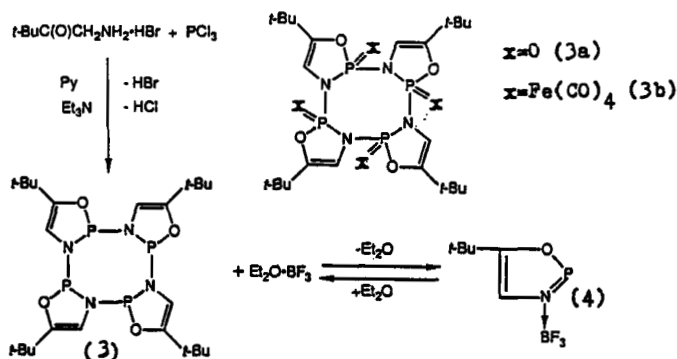
This conversion is probably the first observed instance

of formation of diazadiphosphetidines from spirophosphoranes through abstraction of the Alk_2NH elements from the neighbour P and N atoms. The structure of dimers (2) has been identified by X-Ray investigation (Fig.1)



POLYOXAZAPHOSPHOLES (3)

Interaction of PCl_3 with 1-amino-3,3-dimethyl-2-butanone hydrobromide in CHCl_3 under addition of Py and Et_3N leads to the polyoxazaphosphole (3) in 45% yield. On refluxing in C_6H_6 under O_2 it gives the derivative (3a). (3) reacts with $\text{Fe}(\text{CO})_5(\text{C}_6\text{H}_6, \text{h})$ forming adduct (3b). But in refluxing benzene in the presence of $\text{Et}_2\text{O} \cdot \text{BF}_3$ tetramer (3) decomposes to (4) which is isolated as stable trifluoroborate.



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