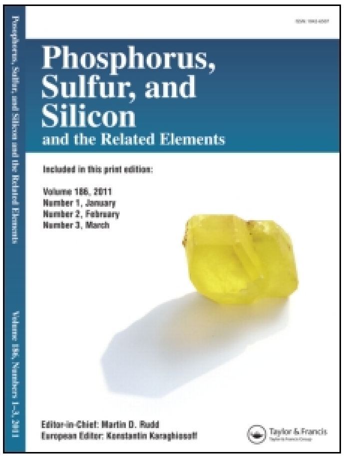

Phosphorus, Sulfur, and Silicon and the Related Elements

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P, B-Containing Heterocycles

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P,B-CONTAINING HETEROCYCLES

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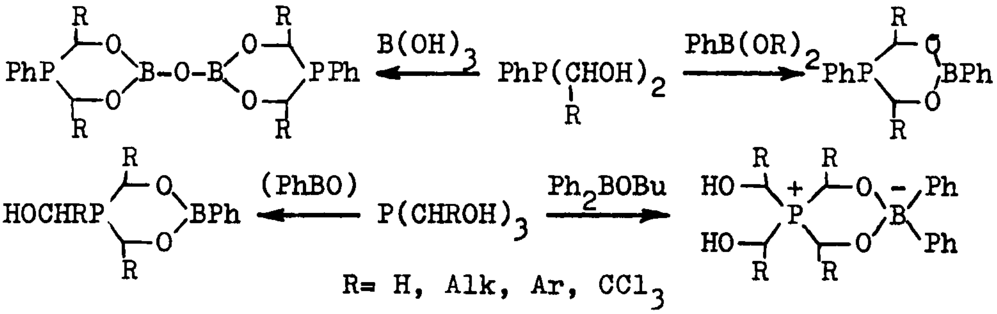
Abstract Synthetic methods and principal chemical properties of boroxyalkyl derivatives of phosphines are presented.

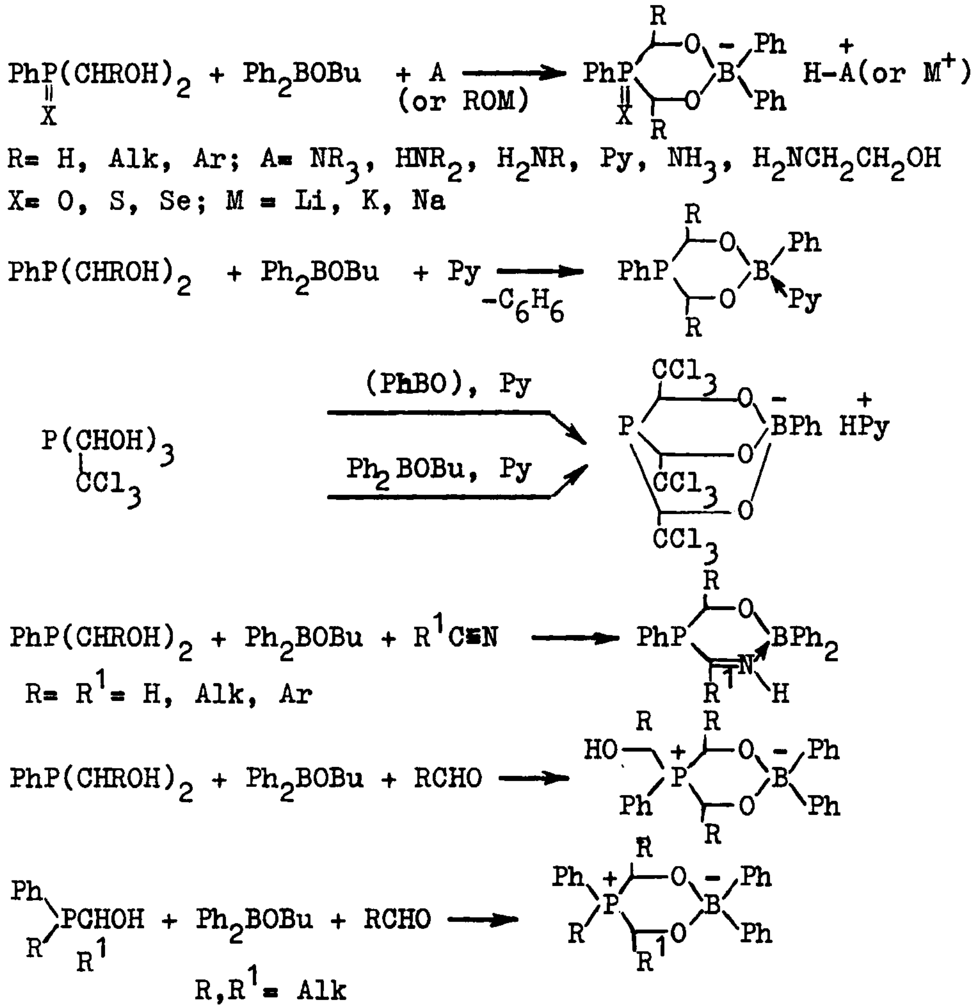
The synthesis of boroxyalkylphosphines appears to be extremely effective in the borylation of α-oxyalkylphosphines and their derivatives by ethers of boric acid with or without extra reagents. Mono-, bis- and tris-α-oxyalkylphosphines as well as their oxides, sulfides or selenides can be used as initial reagents. Borylation can be carried out by boric acid or its ethers and by ethers or anhydrides of diphenyl- and phenylboric acids. Depending on the number of oxyalkyl groups in a phosphine and the type of boric acid - acyclic, cyclic or bicyclic boryloxyalkylphosphines can be obtained.

$$\mathrm{Ph(R)PCHROH} + \mathrm{Ph_2BOBu} \longrightarrow \mathrm{Ph(R)PCHROBPh_2}$$



R= H, Alk, Ar, CCl_3

In boryloxyalkylphosphines phosphorus and boron atoms are in the three-coordinated state. At the same time their more stable state is known to be with the coordination number 4. By introducing extra reagents capable of reacting with three-coordinated phosphorus and boron atoms into the reaction of oxyalkylphosphines borylation it appears possible to obtain derivatives of boryloxyalkylphosphines with different valence state of phosphorus and boron atoms.



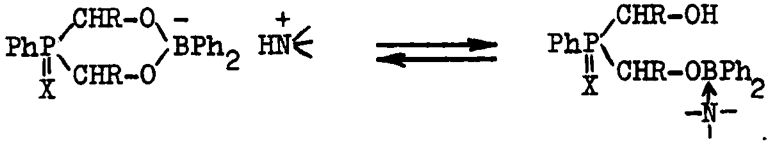
R= H, Alk, Ar; A= NR_3, HNR_2, H_2NR, Py, NH_3, $H_2NCH_2CH_2OH$

X= O, S, Se; M = Li, K, Na

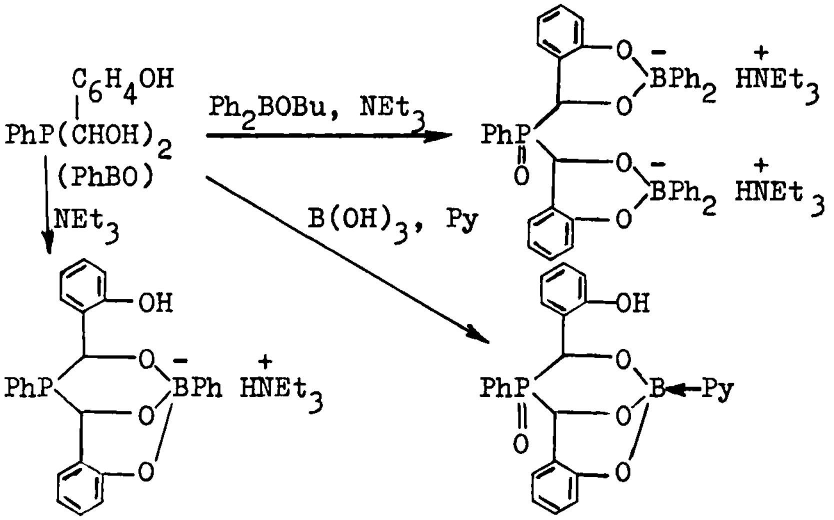
R= R^1= H, Alk, Ar

R,R^1= Alk

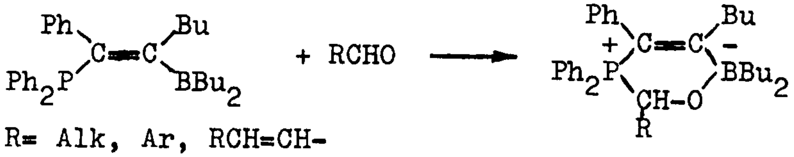
Ammonium 1,3,2,5-dioxaborataphosphorinanes and their bicyclic analogues possess ionic-complex tautomerism and can be in two isomeric forms in solution.



Comparable conditions for the synthesis of initial α-oxyalkylphosphines and the reaction of borylation enabled us to combine the stages of formation of α-oxyalkylphosphines and boron acid derivatives omitting the stages of isolation and purification of phosphoric alcohols. This essentially simplifies the methods of obtaining boroxyalkylphosphines. The reaction of bis(α-oxyalkyl)phosphines with functional substituents of carbon atoms opens new possibilites for synthesizing heterocycles.

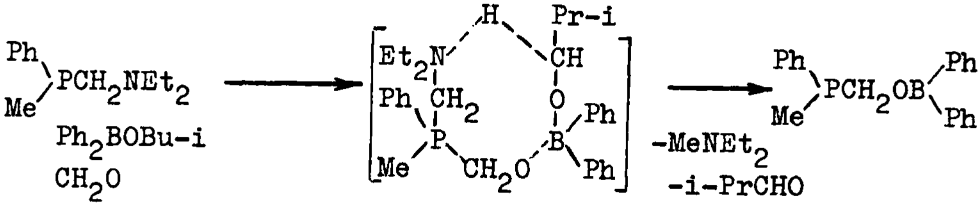


Heterocycles with a boroxyalkyl fragment can be obtained in the course of the interaction of 1-borate-4-phosphoniacyclobutane-2 with aldehydes,and six-membered betaines are formed in this case.

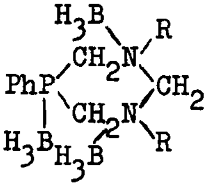


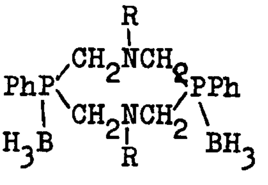
R= Alk, Ar, RCH=CH-

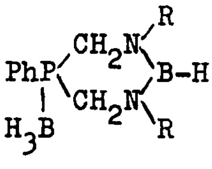
The synthesis of boroxyalkylphosphines can be performed with aminomethylphosphines.



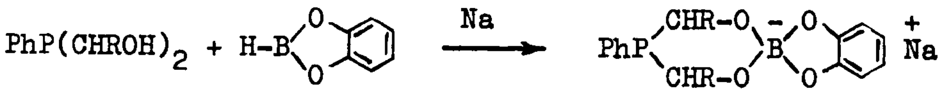
Not only boric acid ethers but also borohydrides can be used as borylation agents which makes it possible to synthesize new P,B-heterocycles. Hydroborylation of aminomethyl derivatives of phosphines results in the formation of the complexes of phosphines the structure of which is determined by the type of the cyclic phosphine and by the radicals of phosphorus and nitrogen atoms. Boron in hydrides is coordinated either in accordance with the phosphorus atom or with nitrogen atoms. Borylation of acyclic aminomethylphosphines by boranes produces new heterocycles containing borylaminomethylphosphine fragment.



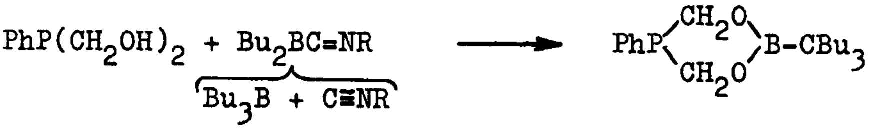




Interaction of bis(α-oxyalkyl)phosphines with catecholboranes gives spiro acids which react with metallic sodium yielding corresponding salts.



Bis(oxymethyl)phenylphosphine reacts with N-Ph-α-iminoalkyldibutylboranes as a protonodonor causing the migration of the butyl group from the boron atom to the neighbouring carbon atom. However the reaction does not stop and the migration of one more butyl group proceeds in the same conditions.



The procedures developed for the synthesis of P,B-containing heterocycles are simple enough, they are based on available raw materials and are of preparative character. Involvement of great variety of phosphorus and boron derivatives in these reactions makes the research area promising.