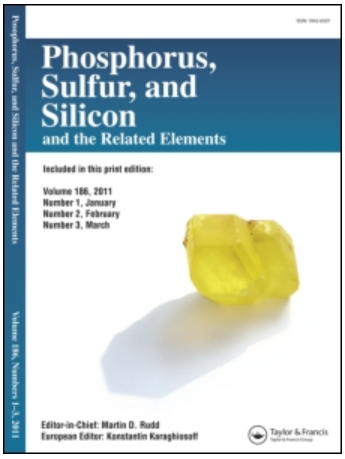

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The Chemistry of Fused Cyclotriazaphosphole - Synthesis, Reactions, Mechanism and Conformation

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THE CHEMISTRY OF FUSED CYCLOTRIAZAPHOSPHOLE - - SYNTHESIS, REACTIONS, MECHANISM AND CONFORMATION

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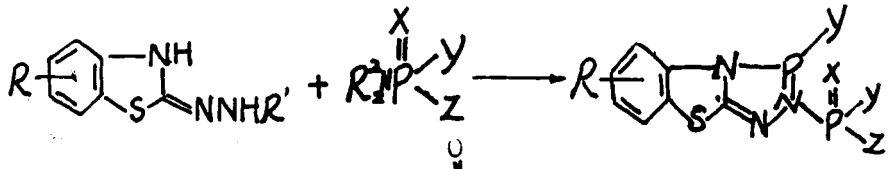
Fused tricyclotriazaphosphole was first synthesized in our laboratory. It is a very interesting series in phosphorus heterochemistry.

I. Synthesis

We can now directly prepare quite different derivatives of fused tricyclotriazaphosphole, such as that containing a tercoordinated and tetracoordinated phosphorus atoms in one molecule, containing NR_2 and OR group in one molecule and even on one phosphorus atom, in one step according to equation (1).

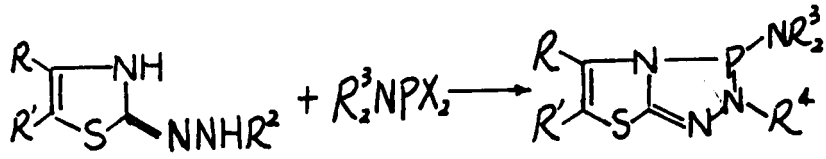


(1)

R=H, Me, Cl, R^1=H, Ar, CNHph, X=$P(OR)_2$.

X="..", O,S, Y,Z=NR^2, OR.

Except tricyclo triazaphosphole, derivatives of fused dicyclotriazaphosphole were synthesized as well according to the equation (2).



(2)

R=Me, Ph; R'=H,Me; R^2=H,Ac; R^3=Me, Et, n-Pr, n-Bu;

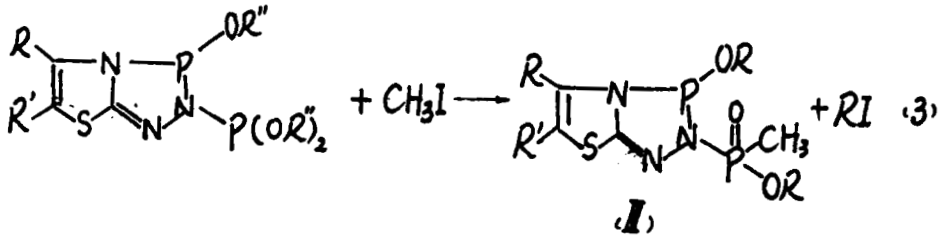
R^4=Ac, $P(NR^3_2)_2$; X=Cl, NR^3_2

2. Reactionary Selectivities

The properties of derivatives of fused cyclotriazaphosphole containing two phosphorus atoms in one molecule have been studied in detail and some interesting results were obtained.

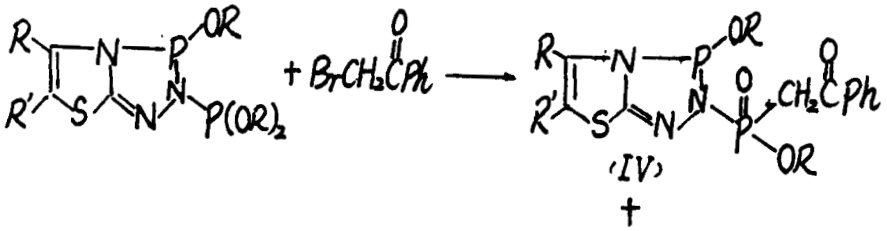
A typical Arbuzov reaction and Perkow reaction can occurred when compounds (I) and (II) are reacted with methyl iodide or α-bromoacetophenone.

Vinyl-phosphates, ketophosphonates and phosphonyl derivatives can be obtained from these reactions.



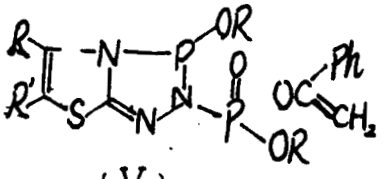
(3)

(I)



(IV)

+



(4)

(V)

R=R'=Me, R,R'=-CH=C(R)-CH=CH-; R''=n-Pr, R''=n-Bu, n-C_5H_{11}, i-C_5H_{11}

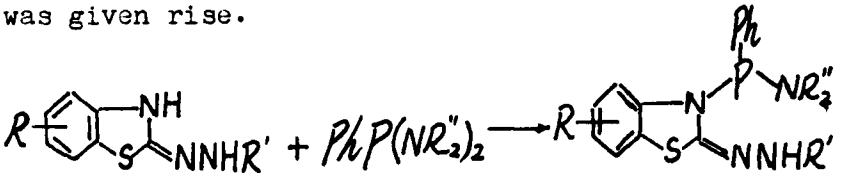
In these two reactions only acyclic phosphoruscontaining group takes place, the cyclic phosphorus remains unchanged at all. We found that the sulfurization of compounds (I) and (II) proceeds stepwisely, this is, the sulfur attacks the acyclic phosphorus atom at first and then the cyclic one. So compounds (I) and (II) are selective in their nucleophilic substitution reactions. But there is nonseletive for these compounds in their electrophilic substitution reactions, as alcoholysis.

3. Mechanism

As memtioned above the key effect on the cyclocondensation reaction(1,2) comes from to the groups attached on the phosphorus-containing reagents. Their reactive sequence is as following:

$$Cl_2PNR_2 > ClP(NR_2)_2 > P(NR_2)_3 > ROP(NR_2)_2 > PhP(NR_2)_2$$

When $PhP(NR_2)_2$ was taken as reagents in reaction (1), no cyclic compounds could be obtained, only an acyclic product was given rise.



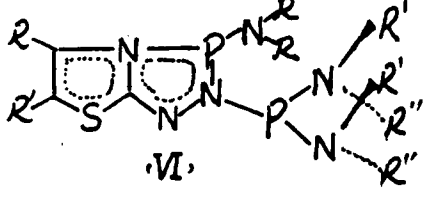
(5)

R=H, Me, Cl; R'=H, $\overset{O}{\overset{\|}{C}}CH_3$, R''=alkyl

Compounds(VI) is probably an intermediate of these reactions, the mechanism of these cyclocondensation has been suggested.

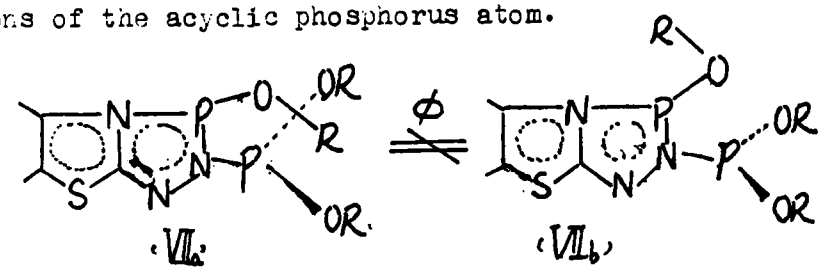
4. Conformation

The conformation of some compounds obtained was investigated on the basis of the data of IR, MS and ^1H, $^{13}C$and ^{31}P NMR spectra.



(VI)

Compounds (VI) prefers C_{2v} conformation and behaves some aromatic properties, P-N bonds outside the ring cannot rotate along the bond axis. R groups attached on nitrogens can be be divided to three classes. The R of acyclic phosphorus group are located at the cis-position to the lone pair electrons of the acyclic phosphorus atom.



(VIIa) (VIIb)

The alkoxy groups on acyclic phosphorus are not located at the same plane of the ring but orthogonal with the ring plane, and can be divided into two classes, associated to endo and exo position. (VIIa) and (VIIb) cannot convert each other at room temperature.

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