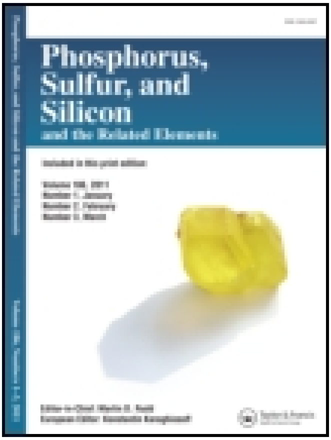

Phosphorus, Sulfur, and Silicon and the Related Elements

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Synthesis and Use of 6-, 7-and 8-Membered P-Heterocycles

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Synthesis and Use of 6-, 7-and 8-Membered P-Heterocycles

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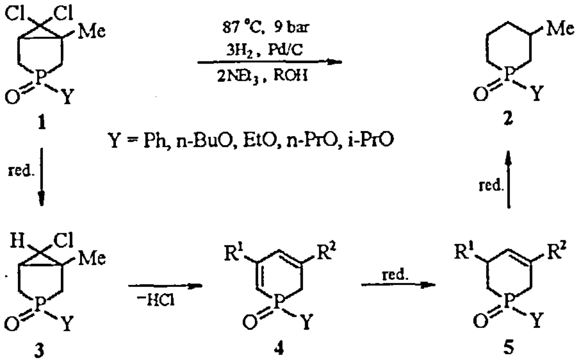
The synthesis of new families of P-heterocycles by reductive modifications, ring enlargement and Diels-Alder cycloaddition is described.

Keywords: P-heterocycles; ring enlargement; reductive methods; fragmentations

In this paper, the latest results of ours in P-heterocyclic chemistry are summarized.

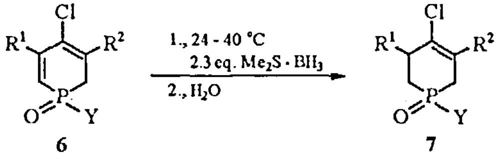
1. Synthesis of six-membered P-heterocycles by reductive modifications

It was observed that the catalytic hydrogenation of phosphabicyclohexanes 1 led to the diastereomers of hexahydrophosphinine oxides 2[1]. The formation of product 2 is the result of a consecutive series of reactions involving intermediates 3-5. Decreasing the activity of the catalyst, we could achieve that monochloro species 3 should be the main component[2].



	R^1	R^2
A	H	Me
B	Me	H

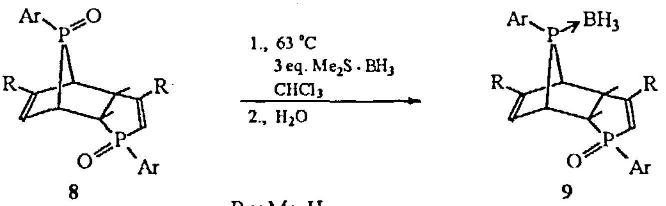
We found that double-bonds with electron-withdrawing substituents at one end can be easily reduced by the borane-dimethyl sulfide (BMS) reagent. Thus, the reaction of the 2,3-dihydro-1H-phosphole oxides with BMS followed by hydrolysis afforded the corresponding tetrahydrophosphole oxides. Similar reaction of the 1,2-dihydrophosphinine oxides (6) gave the 1,2,3,6-tetrahydrophosphinines (7) in a regioselective manner[3]. The reductions take place certainly through hydroboration. Both the steric and the electronic reasons stand for the enhanced reactivity of the α,β-double bond.



	R¹	R²
A	H	Me
B	Me	H

Y = Ph, MeO, EtO, i-PrO

It was interesting to observe that the reaction of the phosphole-oxide dimers (8) with BMS resulted in a change in the functionality of the bridging P-center rather than selective reduction of the double-bond in the 2,3-dihydrophosphole moiety.

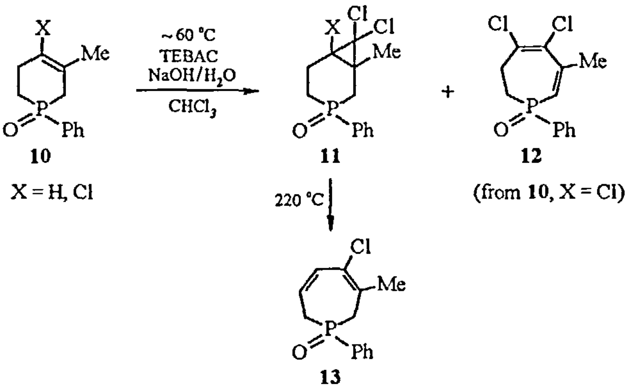


R = Me, H
Ar = Ph, 2,4,6-triMeC$_6$H$_2$
2,4,6-tri-i-PrC$_6$H$_2$

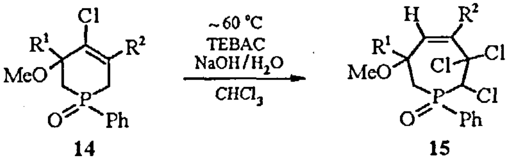
In the first step, the bridging phosphine oxide moiety in 8 is deoxygenated by the borane, then the phosphine so obtained is complexed by another unit of borane to give phosphine-borane 9.

2. Synthesis of seven-membered P-heterocycles by ring enlargement of tetrahydrophosphinine oxides

We wished to utilize the tetrahydrophosphinine oxides in the syntesis of seven-membered P-heterocycles. The reaction of tetrahydrophosphinine oxides 10 with dichlorocarbene afforded phosphabicycloheptanes 11. In the reaction of the 4-chloro derivative (10, X=Cl) ca. 30% of 2,3-dihydrophosphepine oxide 12 was also formed. The thermolysis of the dichlorocarbene adducts (**11**) led, in both cases, to the same 2,7-dihydrophosphepine oxide (**13**)[4].

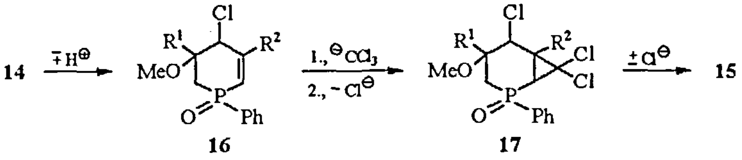


Applying the dichlorocarbene ring enlargement to 3-methoxy-tetrahydrophosphinines **14**, the reaction followed an unexpected route: 2,3,6,7-tetrahydrophosphepine oxides **15** could be isolated from the reaction mixture.



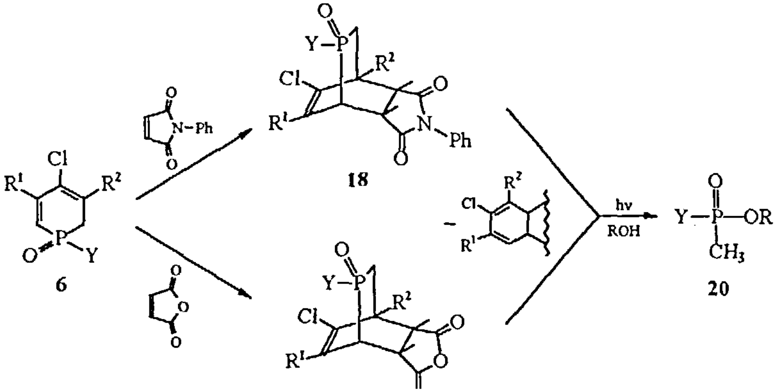
	R^1	R^2
A	H	Me
B	Me	H

The key-step for the formation of products **15** is the isomerisation of 1,2,3,6-tetrahydrophosphinines **14** to 1,2,3,4-tetrahydro derivatives **16**. The next step may involve Michael-type addition of a trichloromethyl anion at the end of the double-bond of **16** followed by cyclopropanation. Products **15** are formed by the opening of the cyclopropane ring in **17** by the effect of a chloride anion.



3. Synthesis of 2-phosphabicyclo[2.2.2]octene derivatives and their utilization in phosphorylations

We have synthesized Diels-Alder cycloadducts **18** and **19** to utilize them in the UV light-mediated phosphorylation of alcohols. The alcohols were added to the reaction mixture prior to irradiation.



6

18

19

20

	R¹	R²
A	H	Me
B	Me	H

Y = Ph, EtO
R = Me, Et, n-Pr, i-Pr, n-Bu

Phosphinic and phosphonic esters **20** were obtained in good yields. The mechanistic investigations suggest that beside the E-A pathway involving methylene phosphine oxide ($Y-P(O)(CH_2)$) as the intermediate, the A-E route is also realized. According to this, the alcohol is added to the phosphoryl group of the phosphabicyclooctene (**18** or **19**) to form an intermediate with a pentacoordinate phosphorus atom[5].

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