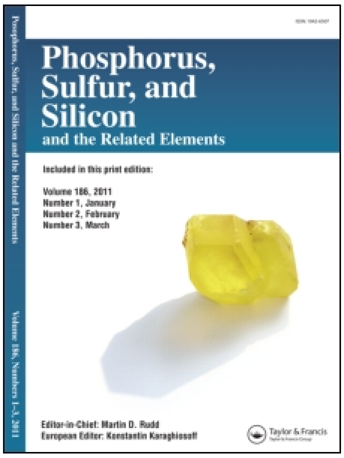

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SYNTHESIS OF FUNCTIONALIZED P-HETEROCYCLES INCLUDING PHOSPHINE-BORANE COMPLEXES

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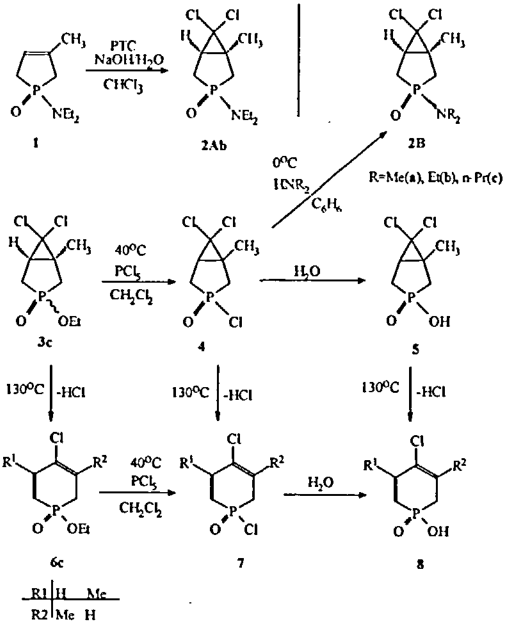
Abstract Preparation of phosphinic chlorides, amides, and sulfide derivatives, as well as phosphine-borane complexes of P-heterocycles is described.

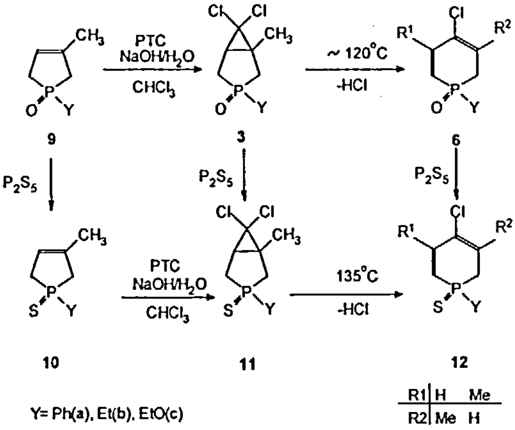
Synthesis of 3-phosphabicyclo[3.1.0]hexanes and 1,2-dihydrophosphinines having tertiary phosphine oxide or phosphinic ester functions has been described earlier.[1-3] In this paper, we show methods for the preparation of phosphinic chlorides, amides, acids, sulfide derivatives and phosphine-borane complexes.

P-amino phosphabicyclo[3.1.0]hexane oxides (2) were prepared by the addition of dichlorocarbene to the double bond of phospholene oxide 1, or by substitution at the phosphorus atom of phosphabicyclohexane 3c. The two approaches resulted in different diastereomers, isomer 2A or isomer 2B, respectively (Scheme I).[4] Phosphinic chloride 4, intermediate of the second method was also converted to phosphinic acid 5. Isomers of the P-hydroxy dihydrophosphinine oxide (8) were synthesised by the thermolysis of dichlorocyclopropane 5, or by substitution at the phosphorus atom of dihydrophosphinine 6c (Scheme I).[4]



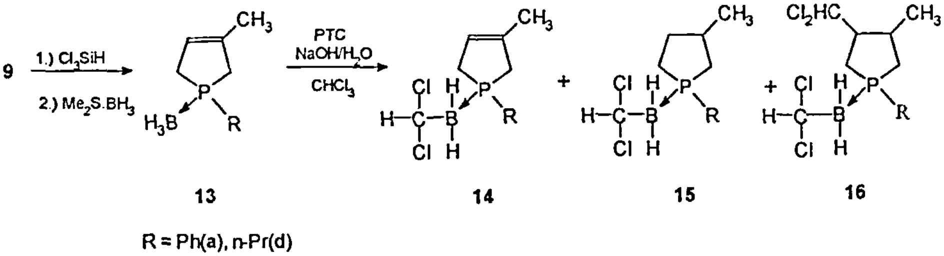
Scheme I

The P-sulfide derivatives of phosphabicyclohexanes (11) were prepared by the addition of dichlorocarbene to the double bond of phospholene sulfides (10), or by change in the functionality of the corresponding oxides (3) (Scheme II).[5] Isomers of the dihydrophosphinine sulfides (12) were obtained by the thermolysis of phosphabicyclohexane 11, or by thionation of oxide 6 by phosphorus pentasulfide (Scheme II).[5]



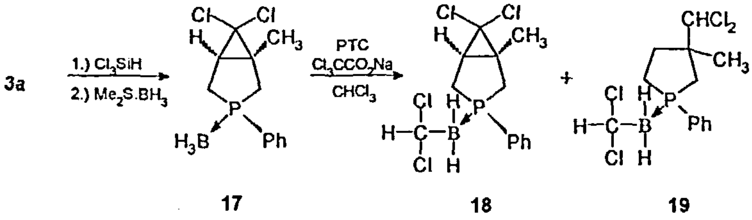
Scheme II

The 3-phospholene oxides (9) were deoxygenated by trichlorosilane and the phosphine intermediates so obtained reacted with dimethylsulfide-borane to afford phosphine-borane complexes (13). Reaction of 13 with dichlorocarbene did not give the expected phosphabicyclohexane (18), but resulted in a mixture containing phospholene 14, phospholane 15 and 3-dichloromethylphospholane 16 (Scheme III).



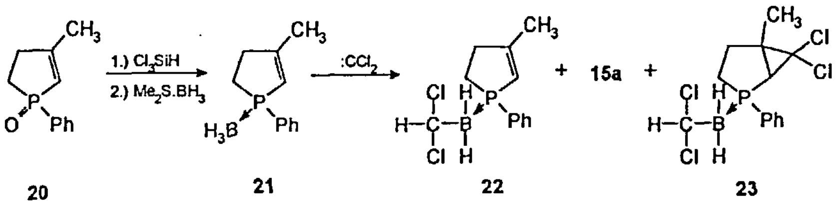
Scheme III

The phoshabicyclohexane-borane complex (17) could be prepared by change in the functionality of phosphine oxide 3a (Scheme IV). To prepare a more stable product, the dichloromethylborane derivative (18) was also synthesised (Scheme IV). Interestingly, a 3-dichloromethylphospholane (19) formed by the reductive type opening of the dichlorocyclopropane ring in 18 could also be isolated from the mixture (Scheme IV). This experience suggests that cyclopropane intermediates might be involved in the reaction resulting in the formation of 3-dichloromethylphospholanes 16. Reductions taking place during the work with phosphine-borane complexes are not unusual at all.[6]



Scheme IV

Due to the presence of the electron-withdrawing phosphoryl group, the double bond of 2-phospholene oxides failed to react with the electrophilic dichlorocarbene. To increase the reactivity of the double bond, phosphine oxide 20 was transformed to phosphine-borane complex 21. Reaction of 21 with dichlorocarbene gave the expected phosphabicyclohexane (23), but only in poor yields, as the main products were phospholene 22 and phospholene 15a (Scheme V). Forcing reaction conditions led to decomposition of the starting material (21) and the products (22, 15a and 23).



Scheme V

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