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Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713618290>

Synthesis of Phosphinines and its Saturated Devivatives:DI-, Tetra-and Hexahydrophosphinine Oxides

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To cite this Article Keglevich, György , Tóke, László , Kovács, Attila , Újszászy, Kálmán and Tóth, Gábor(1993) 'Synthesis of Phosphinines and its Saturated Devivatives:DI-, Tetra-and Hexahydrophosphinine Oxides', Phosphorus, Sulfur, and Silicon and the Related Elements, 75: 1, 115 – 118

To link to this Article: DOI: 10.1080/10426509308037378

URL: <http://dx.doi.org/10.1080/10426509308037378>

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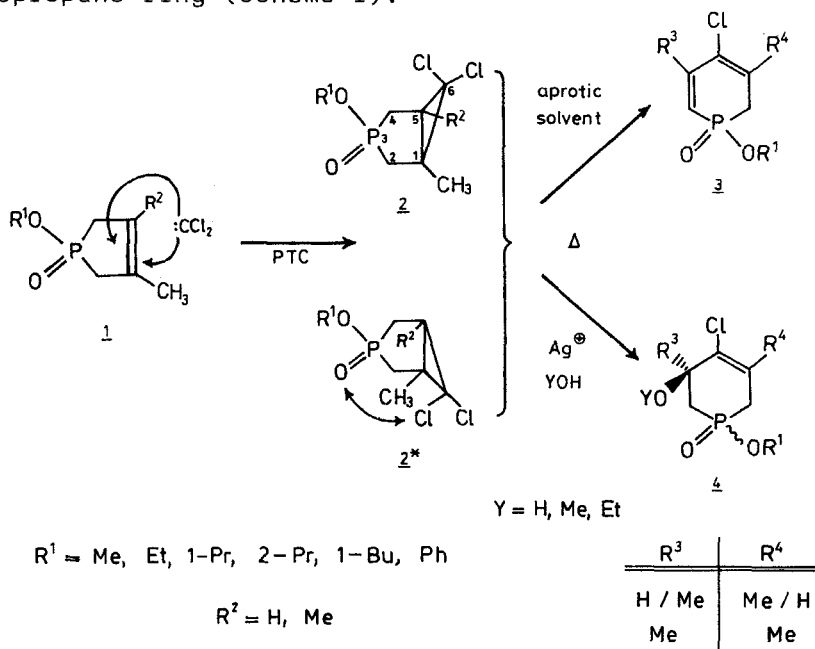
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SYNTHESIS OF PHOSPHININES AND ITS SATURATED DERIVATIVES: DI-, TETRA- AND HEXAHYDROPHOSPHININE OXIDES

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Our ring enlargement procedure¹ is extended to the synthesis of valuable 1,2-dihydrophosphinine oxides (3) and 1,2,3,6-tetrahydrophosphinine oxides (4) with alkoxy substituent on the P-atom. Dichlorocarbene is added to the double bond of dihydro-1H-phosphole oxide 1 in the first step. The diastereoisomeric adducts (2 and 2^{*}) so obtained afford the ring expanded products (3² or 4) by the opening of the cyclopropane ring (Scheme I).



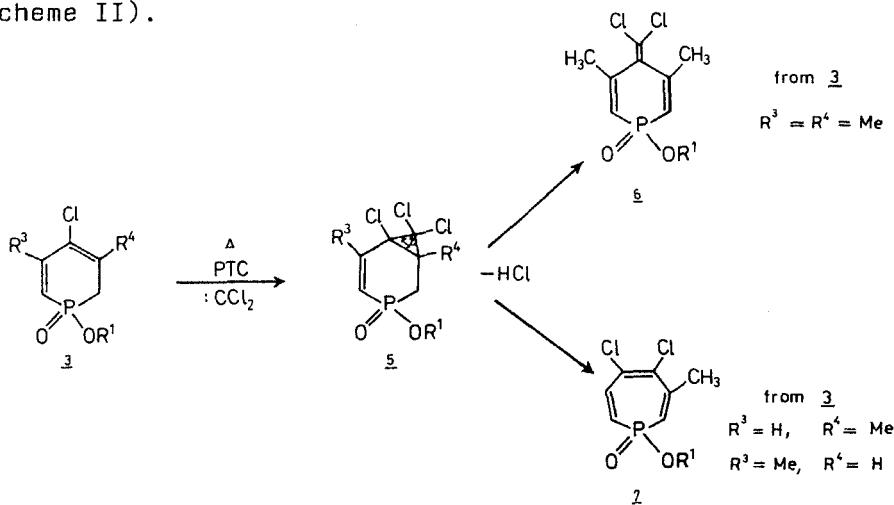
Scheme I

Depending on the structure of the starting material (R² may be Me or H in 1), 3 and 4 may be formed as a single product

($R^3=R^4=Me$), or as a mixture of two double bond isomers ($R^3=H, R^4=Me$ and $R^3=Me, R^4=H$).

Tetrahydrophosphinine oxide 4 may exist under the equilibrium of boat or half-chair conformers. The predominance of a boat conformer was substantiated for the 3,5-dimethyl-product, while the involvement of a half-chair conformer was pointed out in the case of the 3- and 5-methyl-derivatives.

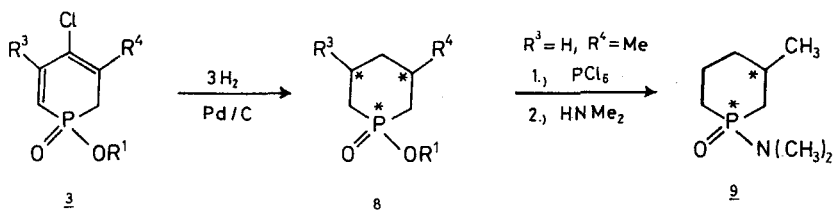
The dihydrophosphinine oxide (3) gives adduct 5 on reaction with a second unit of dichlorocarbene to result 4-dichloromethylene-1,4-dihydrophosphinine oxide 6 or phosphepine oxide 7 by the opening of the cyclopropane ring (Scheme II).



Scheme II

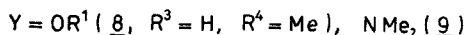
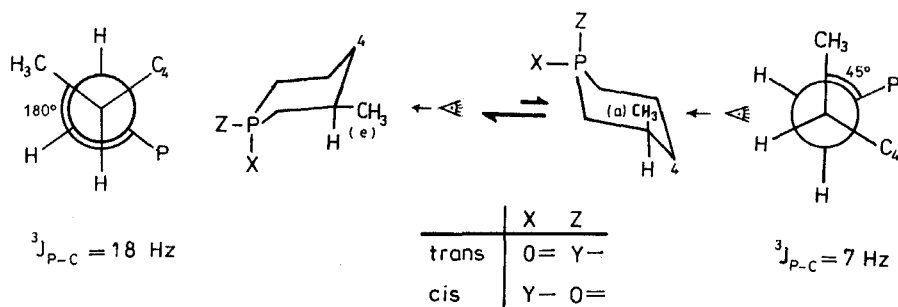
The outcome of the reaction depends on the number of the skeletal methyl groups in intermediate 5. 7 is formed by ring expansion (only one of R^3 and R^4 is Me), while 6 by the rather unusual opening of the cyclopropane ring (both R^3 and R^4 are Me).

The 1,2-dihydrophosphinine oxides (3) are also useful in the synthesis of other phosphinine derivatives. E.g. hexahydrophosphinine oxide 8 is formed from 3 on reaction with three equivalents of hydrogen. The resulting phosphinic acid ester (8, $R^3=H, R^4=Me$) can then be transformed to the amide (9) (Scheme III).



Scheme III

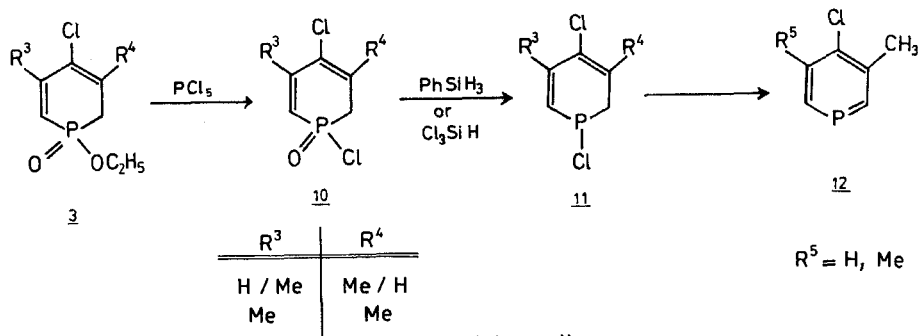
The 3-methyl-product is formed as the mixture of two diastereoisomers, while the 3,5-dimethyl-derivative as three isomers. Although the trans and cis diastereoisomers of 8 ($R^3 = \text{H}$, $R^4 = \text{Me}$) and 9 can be imagined as the equilibria of two pairs of conformers, the measured values for the $^3J(\text{P-C})$ coupling constants³ show the equilibria to be strongly biased toward the form with equatorial skeletal methyl group (Scheme IV).



Scheme IV

Fully unsaturated (aromatic) species, phosphinines (12) can also be obtained from the P-alkoxy-dihydrophosphinine oxides (3). Phosphinic chloride 10 is prepared in the first step to give the expected phosphinine (12, $R^5 = \text{H}$ or Me) after reduction and dehydrochlorination (Scheme V).

The formation of the dimethyl-phosphinine is accompanied by side reactions (decomposition or overreduction to 3,5-dimethylphosphinine).



Scheme V

Structure of the products (2-4, 6-9 and 12) was confirmed by ¹H, ¹³C and ³¹P NMR and mass spectroscopy.

The 1,2- and 1,4-dihydrophosphinine oxides (3 and 6) display interesting biological activity.

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