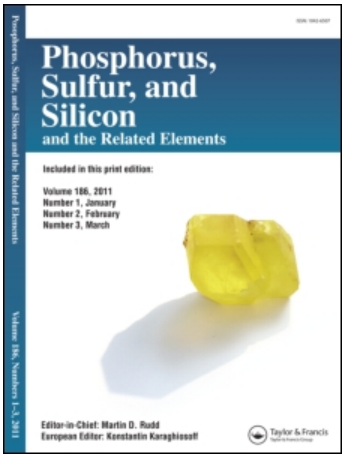


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# Synthesis of Phosphinines and its Saturated Devivatives:DI-, Tetra-and Hexahydrophosphinine Oxides

György Keglevich[a]; László Tóke[a]; Attila Kovács[a]; Kálmán Újszászy[a]; Gábor Tóth[a]
[a] Department of Organic Chmical Technology, Technical University of Budapest, Budapest, HUNGARY

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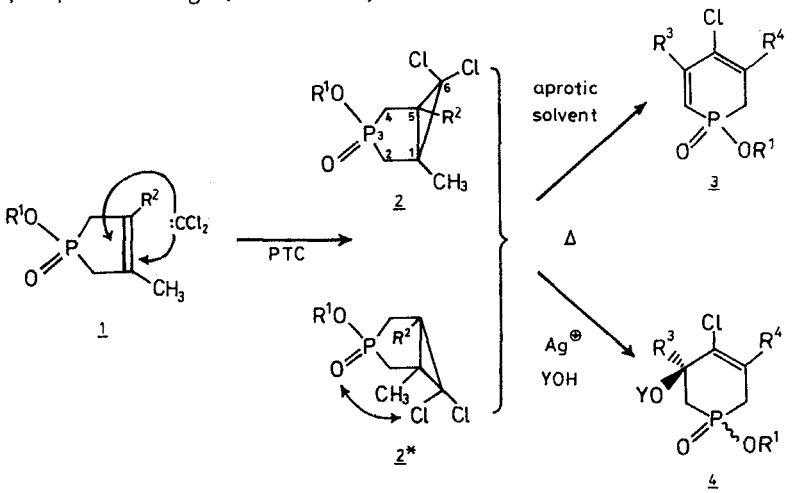
# SYNTHESIS OF PHOSPHININES AND ITS SATURATED DERIVATIVES: DI-, TETRA- AND HEXAHYDROPHOSPHININE OXIDES

GYÖRGY KEGLEVICH, LÁSZLÓ TŐKE, ATTILA KOVÁCS, KÁLMÁN ÚJSZÁSZY, GÁBOR TÓTH
Department of Organic Chemical Technology, Technical University of Budapest, 1521 Budapest, HUNGARY

Our ring enlargement procedure[1] 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 (3[2] or 4) by the opening of the cyclopropane ring (Scheme I).



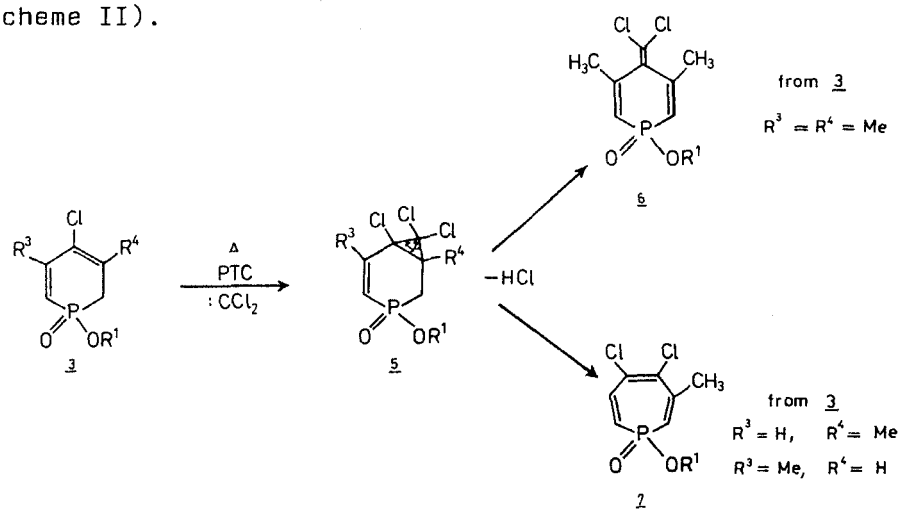

Scheme I

Depending on the structure of the starting material ($R^2$ 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.

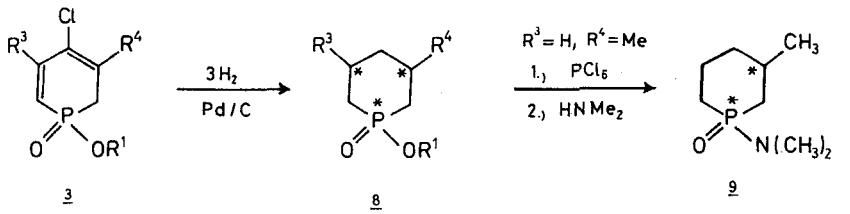
The dihydrophosphinine oxide (3) gives adduct 5 on reaction with a second unit of dichlorocarbene to result 4-dichloromethylene-1,4-dihydrophosphinine oxide 6 or phosphepine oxide 7 by the opening of the cyclopropane ring (Scheme II).




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).

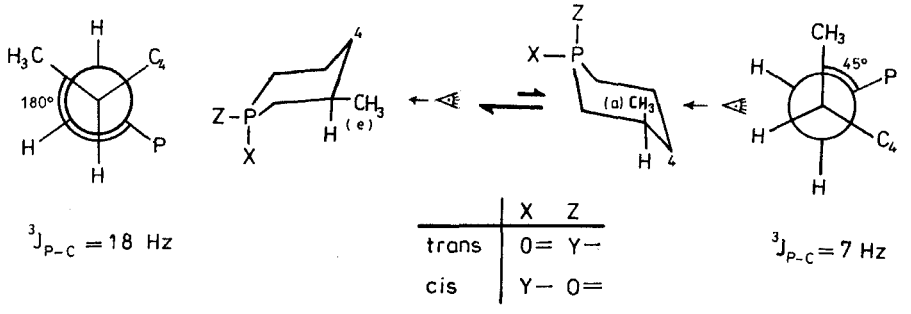
The 1,2-dihydrophsphinine oxides (3) are also useful in the synthesis of other phosphinine derivatives. E.g. hexahydrophosphinine oxide 8 is formed from 3 on reaction with three equivalents of hydrogen. The resulting phosphinic acid ester (8, $R^3$=H, $R^4$=Me) can then be transformed to the amide (9)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




3 8 9

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 ($R^3$=H, $R^4$=Me) and 9 can be imagined as the equilibria of two pairs of conformers, the measured values for the $^3J(P-C)$ coupling constants[3] show the equilibria to be strongly biased toward the form with equatorial skeletal methyl group (Scheme IV).



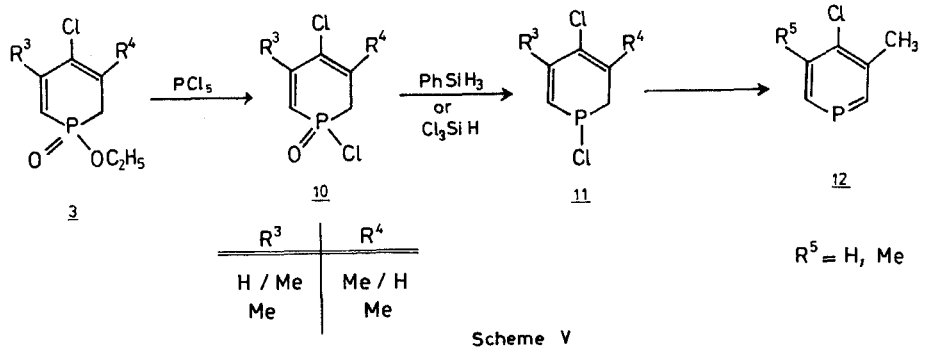

| | X | Z |
|---|---|---|
| trans | O= | Y— |
| cis | Y— | O= |

Y = $OR^1$ ( 8, $R^3$ = H, $R^4$ = Me ), $NMe_2$ ( 9 )

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, $R^5$=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 $^{1}H$, $^{13}C$ and $^{31}P$ NMR and mass spectroscopy.

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



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