Synthesis and structure elucidation of tetra- and hexahydrophosphinine oxides P-functionalized at position three

Ph.D. thesis

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Publications on the subject of the thesis


Other publications


Our aim was to introduce a phosphorus functional group into six-membered P-heterocycles at position three and the modification of the so obtained heterocycles. The most suitable way to introduce a P-functional group was the phospha-Michael addition reaction.

We examined the phospha-Michael addition with simple compounds to uncover the most suitable conditions for the addition of different \(\text{P(O)H}\) species onto electron deficient double bond. The addition of diethylphosphite to methylvinylketone was chosen to be the model reaction. We found that in the presence of sodium alcoholate or under phase transfer condition or in the presence of DBU 3-oxo-butylphosphonate as major product formed, although the later cases other minor products were also formed. In the presence of trimethyl aluminum α-hydroxy-phosphonate was formed as the major product. Upon microwave irradiation only the more reactive reagent, the diphenylphosphine oxide was able to do the addition onto methylvinylketone.

The phospha-Michael addition of cyclic P-compounds such as the H-phosphinic acid or the H-phosphonic acid onto methylvinylketone or cyclohex-2-enone could be performed in the presence of DBU or under microwave irradiation.
We found that the addition of diphenylphosphine oxide onto the electron deficient double bond of the 1,2-dihydrophosphinine oxide (18a) can not be performed under the same conditions sucessfully applied in case of the additions onto methylvinylketone. The reaction could be performed, as only under microwave irradiation in case of the synthesis of compound 19.

$$\text{Ph}_3\text{P(O)H} + \text{18a} \xrightarrow{\text{MW, N}_2, \text{toluene}} \begin{array}{c} \text{Ph}_3\text{P} \text{Ph} \end{array} \quad \text{19 (90%)}$$

We sucessfully performed the addition of dialkylphosphite, diphenylphosphine oxide, ethyl-phenyl-\textit{H}-phosphinate, as well as dibenzo-oxaphosphorine oxide (8) onto the double bond of 1-substituted dihydrophosphinine-oxides (18a-d) in the presence of trimethyl aluminum. Interestingly, all additions proceeded in a diastereoselective manner.

$$\begin{array}{c} \text{Z}_2\text{P(O)H} + \text{18a-d} \xrightarrow{1. \text{Me}_3\text{Al, CHCl}_3, 2. \text{H}_2\text{O}} \text{Z}_2\text{P} \text{19, 21-29} \end{array} \quad \text{Y= Ph, pMePh, Et, EtO} \quad \text{Z= Ph, MeO, EtO, BzO}$$

The synthesized 50 and 52 \textit{cis}-chelat complexes were tested as catalysts in the hydroformilation reaction of styrene. To accelerate the hydroformilation reaction 50 and 52 complexes were \textit{in situ} transformed into their trichloro-stannate derivatives.

In the presence of our catalysts (50 and 52) the hydroformilation reaction proceeded, in both cases, with high regioselectivity. In the presence of the unsaturated-ringed catalyst 50 the selectivity for the branched product was higher (85%) then in the presence of 52 saturated analogue (70%). Interestingly, the regioselectivity for the branched aldehyde was unexpectedly high, although platinum complexes usually show selectivity for the linear product.

We published 11 publications on the subject of my thesis in peer-viewed international journals [1-11].
The products (53 and 55) of the deoxygenation of the isomeric mixtures of 3-ethyl-phenylphosfinato tetra- és hexahydrophosphinine oxides (30 és 44) with phenylsilane were stabilized as borane complexes (54 and 56). Compounds 54 and 56 proved to be monoboran complexes.

The reaction of diphosphine (46) with dichlorodibenzonitrilo platinum(II) led to the cis-chelate complex (50).

The reduction of diphenylphosphinoxido-hexahydrophosphinine oxide (35) led to the corresponding diphosphine (51). The complexation of 51 with dichlorodibenzonitrilo platinum(II) resulted in, as before, the cis-chelate complex (52).

Quantum chemical calculations showed that the tetraphosphinine oxides substituted at position 3 (19, 21-29) exist in a twist-boat conformation.

Calculations also suggested a couple of intramolecular interactions had not been reported before. These interactions can be classified into four main groups. These H-bridge interactions are (i) between the oxygen of the exocyclic P=O group and one of the hydrogen of one of the methylene group of the heterocyclic ring in case of the P-Aryl substituted compounds (19, 21 and 22), (ii) between the oxygen of the endocyclic P=O group and one of the hydrogen of one of the methylene group of an exocyclic alkoxy group in case of the P-alkoxy substituted compounds (27 and 28), (iii) between the oxygen of the exocyclic P-alkoxy group and one of the hydrogen of one of the methylene group of the heterocyclic ring, and in case of the 27 and 28, a further interaction can be found between the phosphorus atom of the endocyclic P=O and the oxygen of the exocyclic POR group (iv).
The single crystal X-ray analysis of 3-diphenylphosphinoxido-1-phenyl-tetrahydrophosphonin oxide (19) showed that (i) compound 19 crystallized as a monohydrate, (ii) the conformation of the molecule twist-boat/cis, the oxygen of the P\textsuperscript{i}=O and the exocyclic P(O)Ph\textsubscript{2} group are in cis position, in the same side of the ring, and (iii) the intramolecular interaction between the oxygen of the exocyclic P=O and the hydrogen of the C\textsubscript{6} methylene group.

Quantum chemical calculations suggested that 3-P-functionalized hexahydrofosphinine oxides substituted with alkoxy groups at both phosphorus atoms exist in a chair conformation.

The deoxygenation of diphenylphosphinoxido-tetrahydrophosphinine oxide (19) with trichlorosilane or phenylsilane led to diphosphine (46), which was stabilized with borane (47), and therefore, could be stored for a longer period. From the borane complex the diphosphine (46) can be recovered by diethylamine.