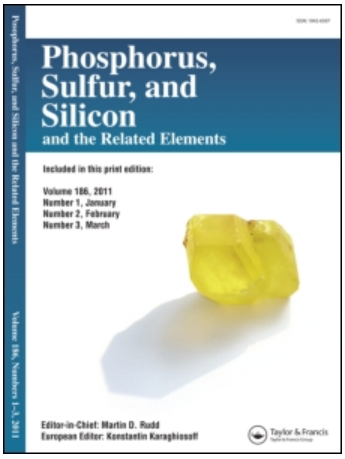

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New Asymmetric Synthesis of Tertiary Phosphines via Phosphinous Complexes

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NEW ASYMMETRIC SYNTHESIS OF TERTIARY PHOSPHINES VIA PHOSPHINOUS COMPLEXES

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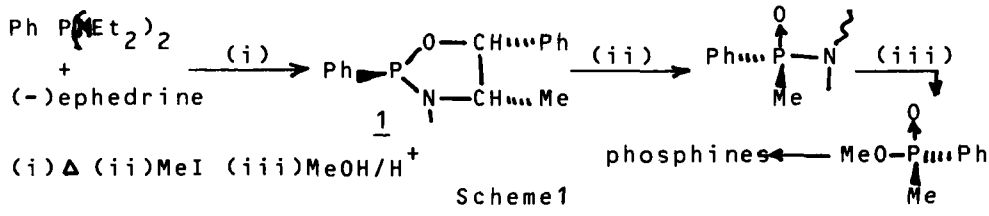
Abstract: Asymmetric syntheses of phosphinous complexes and tertiary phosphines were described by regioselective P—O bond cleavage of diastereomerically pure oxazaphospholidine $W(CO)_5$ or BH_3 complexes.

Chiral organophosphorus compounds with chirality on the phosphorus atom , have been an important subject of investigation over the last twenty years , due to the widespread study of these compounds for the comprehension of biochemical mechanisms and in asymmetric synthesis.

The spectacular asymmetric syntheses with C—H or C—C bond creation described up to now have shown the key importance of the trivalent organophosphorus ligands in homogenous catalysis. Several patented chiral phosphines prove the interest of the industrial world in the potential of catalytic reactions (1).

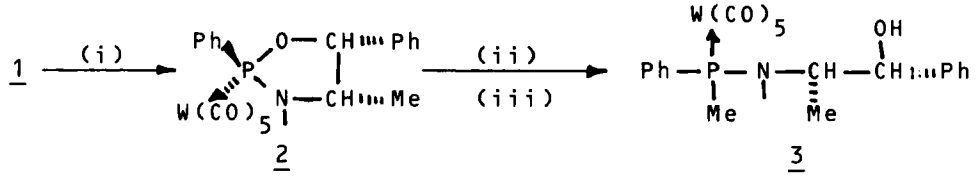
A few years ago ,we proposed a general method for asymmetric synthesis of phosphinates and phosphine oxides, using the Michaelis-Arbuzov rearrangement of chiral diheterophosphacycloalkanes (2)(Scheme1):



Scheme1

Yet, in spite of the progress in the preparation of phosphinates , chemical difficulties remain.

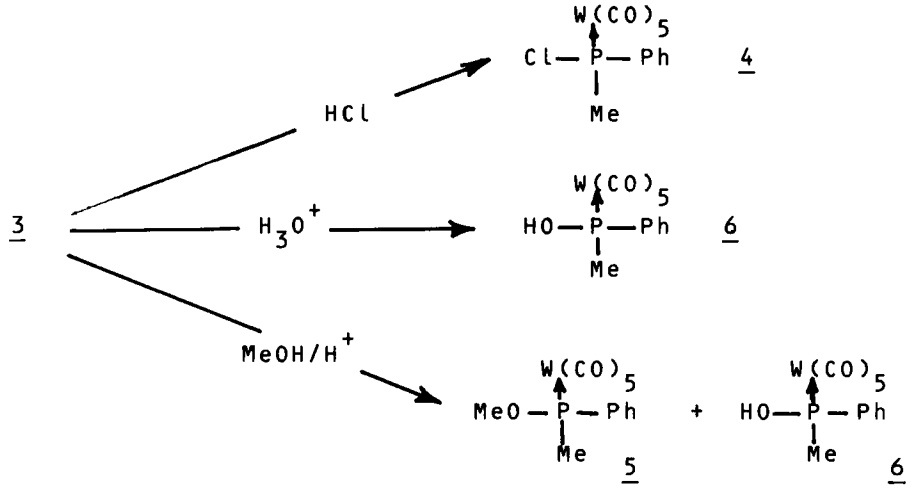
In our continuing program for the synthesis of chiral organophosphorus compounds from diheterophosphacycloalkanes we report here our results in complexed series.



(i) $W(CO)_5$.THF (ii) MeLi/-78°C (iii)H_2O

Scheme 2

Pentacarbonyl tungsten complex 2 was prepared diastereomerically pure from oxazaphospholidine 1 and $W(CO)_5$ with 80% yield (Scheme 2). The complex 2 give stereospecifically the compound 3 , by P—O bond cleavage ,which is stable and was used for synthetic applications (Scheme3):

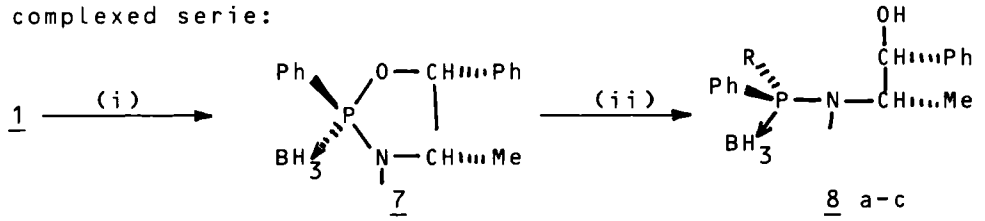


Scheme 3

HCl gas reacted with 3 in CH_2Cl_2 to give the optically active complex 4 which gave the salt of 6 by reaction with menthol and triethylamine. The acid methanolysis of 3 gave a mixture of 5 and 6 , and the inchanged ephedrine salt.The acid hydrolysis of 3 gave the phosphinous acid complex 6 with an optical rotation of +4,8° . The enantiomeric excess

of the methyl phenyl phosphinous acid complex 6 was determined by ^{31}P NMR of the (1:1) cinchoninium salt . A sample with $[\alpha]$ = +20° corresponds to 50 % ee which indicates a predominant racemisation during the alcoholysis, or the hydrolysis of the aminophosphine tungsten complex 3.

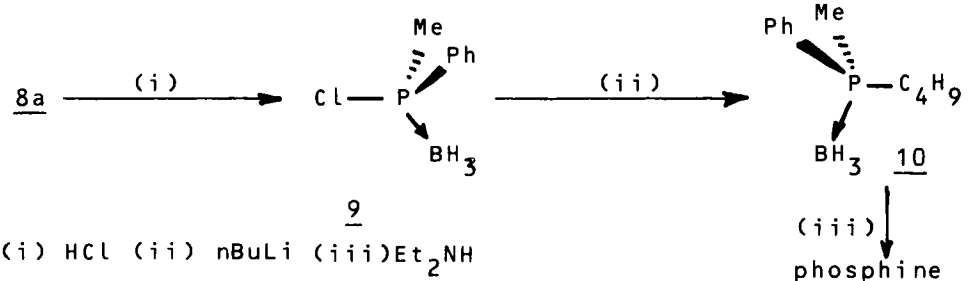
The synthetic approach was reexamined in borane complexed serie:



(i) BH_3.THF (ii) RM

Scheme 4

The borane complex 7 was prepared in one step from bis diethylamino phenyl phosphine , (-)-ephedrine and borane in 75 % yield (Scheme 4). The NMR analyses indicate the formation of only one diastereoisomer , and the X ray structure show a phenyl group in the opposite position with regard to the substituants of the ephedrine part. Alkyl and aryl organometallics reacted with 7 to give the corresponding aminophosphine borane 8, with a high stereoselectivity , and a good yield. The X ray structure of the methyl phenyl aminophosphine borane 8a indicates a retention of configuration at the phosphorus atom.



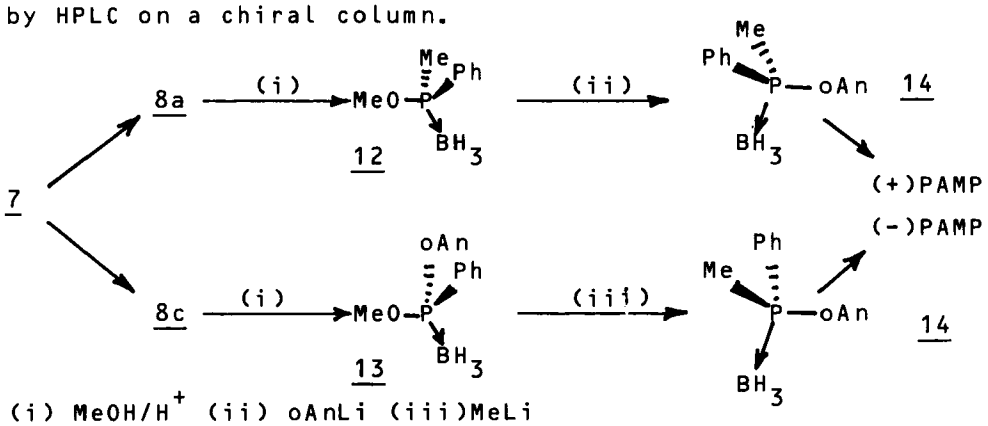
(i) HCl (ii) nBuLi (iii) Et_2NH

Scheme 5

HCl gas reacted with 8a in toluene to give the optically active chlorophosphine complex 9 which is directly used to prepare the butyl phosphine complex 10 (Scheme 5).

We found that the enantiomeric excess decreases with the HCl concentration .

More interestingly , the acid methanolysis of the aminophosphines borane 8a and 8c gave the corresponding phosphinites 12,13 which were used for the preparation of the two antipodal PAMP.BH_3 14 , with ee $>$ 95%, respectively by reaction with oAnisyl and methyl lithium (Scheme 6).The enantiomeric excess of the phosphines borane was determined by HPLC on a chiral column.



(i) $MeOH/H^+$ (ii) oAnLi (iii)MeLi

Scheme 6

The transformation of the phosphine borane 14 into PAMP and DIPAMP was recently described by T.IMAMOTO (3).

The results obtained in this work demonstrate the validity of the synthetic approach based on the two key steps:

- diastereoselectivity in the complex preparation
- regioselectivity in the ring opening due to the heterocycle dissymetry.

This very efficient synthesis of (+) and (-)-PAMP can be used on a large scale, and an extension of this methodology is under investigation in our laboratory , for the synthesis of various alkyl and aryl organophosphorus compounds.

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