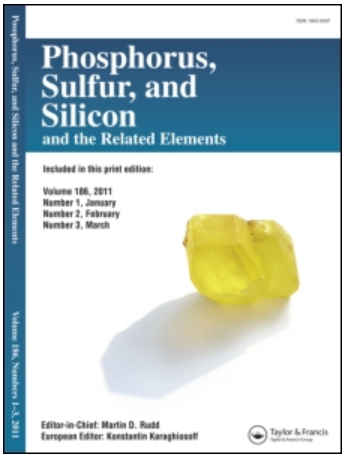

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Double Asymmetric Induction as Method for the Synthesis of Chiral Organophosphorus Compounds

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DOUBLE ASYMMETRIC INDUCTION AS METHOD FOR THE SYNTHESIS OF CHIRAL ORGANOPHOSPHORUS COMPOUNDS

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New examples of multistereoselective syntheses of organophosphorus compounds are described.

Keywords: Asymmetric Michael addidion; chiral aminophosphonic acids; chiral phosphoric acid esters; double asymmetric synthesis; multistereoselectivity

Multistereoselectivity is the reaction process proceeding under the control of several chiral auxiliaries effecting the asymmetric induction. Stereoselectivity of reagents can be estimated as a difference of reaction rates or activation energies leading to two opposite stereoisomers.[1,2]

The individual diastereofacial preferences of the two chiral reactants may reinforce one another (matched asymmetric synthesis (AS)), or, on the contrary, oppose one another (mismatched AS).

In the present work the following versions of multistereoselective syntheses have been studied:

- a chiral reagent reacts with a chiral substratum;
- a chiral reagent containing two chiral auxiliaries reacts with an achiral substratum; and
- AS of a chiral reagent in the presence of asymmetric catalyst.

Thus, the addition of chiral di-and trialkylphosphites (R*O = Menthyl, Bornyl, Gluco-*D*-furanosyl) to chiral C=N compounds is accompanied by double asymmetric induction at the α-carbon atom,

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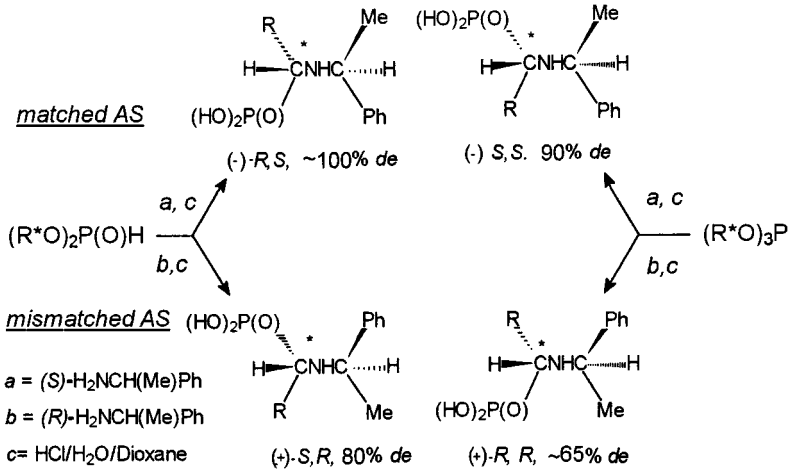


FIGURE 1

with formation of optically active aminophosphonic acid ethers of ~100% de in case of reagents having matched asymmetric induction and of 80% de in case of reagents possessing mismatched asymmetric induction. The reaction of di- and trimenthylphosphites gives aminophosphonic acids of opposite configuration, that allows to prepare all four possible diastereomers. The menthyl esters by acidic hydrolysis were converted to N-substituted aminophosphonic acids and then by catalytic hydrogenation under Pd/C to 1-aminobenzylphosphonic acids.[3,4]

Addition of chiral esters of trivalent phosphorus acids to chiral esters of crotonic or cinnamic acids proceeds more stereoselectively than in the case when only one of these reagents is chiral.[5] The reaction of dimenthyl phosphite with menthyl crotonoate proceeds with ~96–98% stereoselectivity.[2,5]

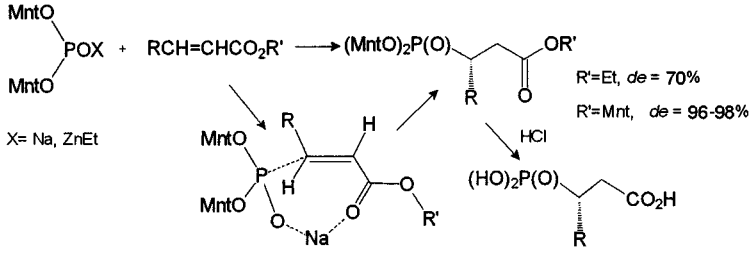
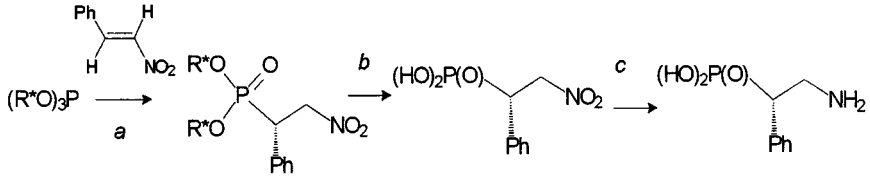


FIGURE 2



R* = *(1R,2S,5R)*-menth-2-yl *(+)-(R)*
a = BF_3 Et_2O; b = Me_3SiBr; H_2O; c H_2/Ni(Re)

FIGURE 3

The addition of nitrostyrene to trimenthylphosphite leads to the formation of optically active β-nitroalkylphosphonates and β-aminophoshonic acids 3,5.[2]

Reduction of dimenthyl acylphosphonate with $LiAlH_4$ or $NaBH_4$ affords a mixture of chiral (*R*)- and (*S*)-diastereomers in the ratio of ~3:1.[5] Meantime catalytic hydrogenation of the acylphosphonate by complex of lithium alumohydride with chiral ligand (A = cinchonin or cyclohexylidene 1,2-gluco-*D*-furanose) furnishs predominantly one diastereomer of dimenthyl 1-oxybenzylphosphonic acid.[5]

This diastereoface selectivity is explained by effect of menthyl group of the compounds which closes one of the sides of carbonyle group in such a manner that *Si*-side of ketone is shielded more than *Re*-party and lithium alumohydride attacks preferentially this side.

Chiral reagents containing two asymmetric auxiliaries in one molecule, increasing asymmetric induction, are especially interesting.[6] Thus, the lithium derivative of Schiff base, formed from (*R*)- camphor and diethyl aminomethanephosphonate, was allowed to react with alkyl and benzyl halides to yield the corresponding esters of (*S*)-α-aminoalkanephosphonic acids.

Acidolysis of the chiral di-alkylaminophosphines by formic acid leads in good yield to the formation of optically pure phosphonic acid amides.[7–9]

So multistereoselectivity represents effective methodology to increase the asymmetric synthesis of chiral organophosphorus compounds using in one reaction two or three asymmetric auxiliaries

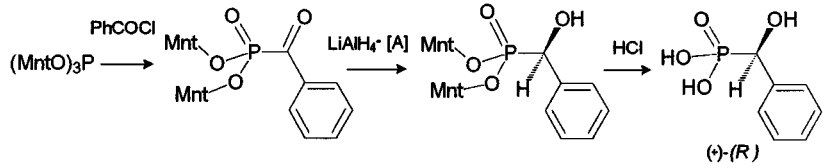


FIGURE 4

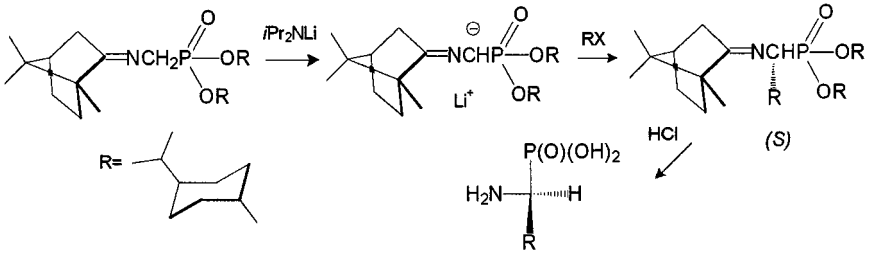
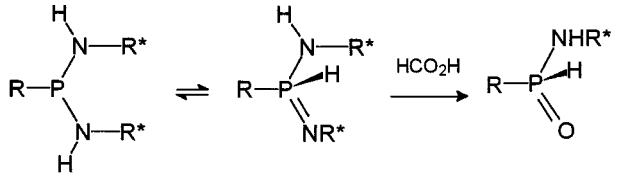


FIGURE 5



R*= *(S)*- or *(R)*-CH*(Me) Ph or *(R)*-CH*(Bu-*i*)CO_2Me

FIGURE 6

reinforcing one another. In some cases this methodology allows to increase the stereoselectivity of reactions up to 100% de.

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