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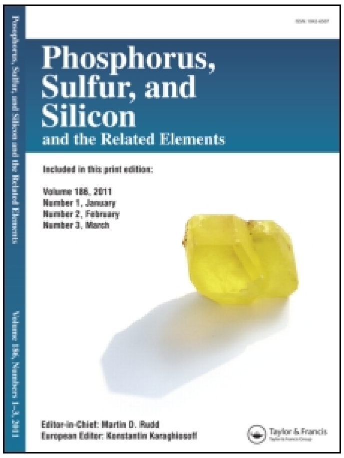

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STEREOSELECTIVE SYNTHESIS AND RESOLUTION OF P-CHIRAL PHOSPHINE CHALCOGENIDES.

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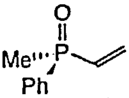
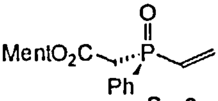
Abstract New synthetic methods and resolution procedures securing ready access to the resolved P-chiral phosphinoylethenes, phosphinoylacetates and secondary phosphine oxides of diversified structures have been developed. The methods are based on processes employing stereoselective nucleophilic displacement at phosphorus, asymmetric deprotonation, immolative vinyl and chirality transfer from sulfur to phosphorus, chemical and enzymatic kinetic resolution, resolution via covalent diastereoisomers, as well as direct resolution of racemates by classical resolving agents and by chromatography on chiral stationary phases.

Rapidly growing utility of resolved P-chiral phosphorus compounds stimulates interest in the development of convenient methods for their preparation.[1] In recent years enantiopure methylphenylvinylphosphine oxide (1), readily available from the spontaneously resolving menthyl phenylvinylphosphinoylacetate (2),[2] was shown to serve as an organophosphorus chiron whose resolved stereogenic P-center could be incorporated into a large diversity of chemical structures by virtue of the versatile chemistry of its pendant double bond functionality.[1,3]

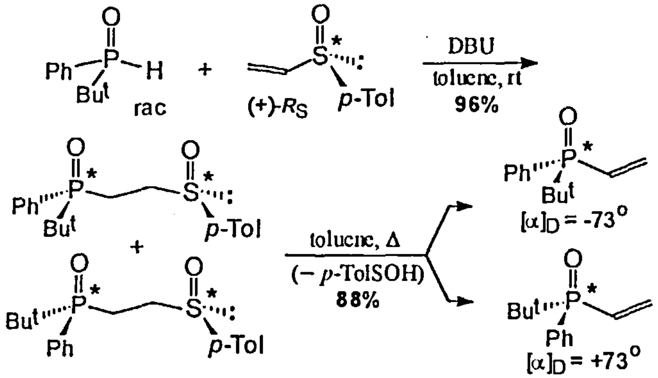


Sp-1

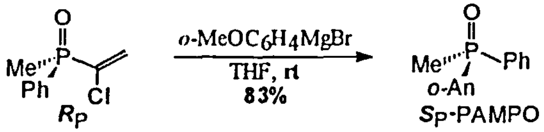


Sp-2

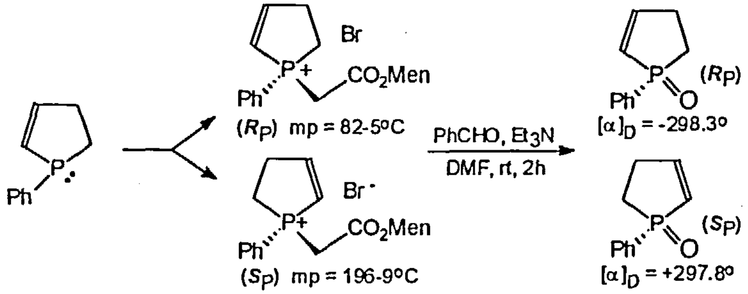
In an effort to further expand the synthetic potential of this approach we have focused our attention on the development of procedures allowing relatively easy access to enantiopure vinyl phosphine oxides of different structures including also the corresponding cyclic systems. One of such procedures has originated from the idea of employing sulfur instead of the conventional carbon as the chirality source. The developed procedure involves immolative vinyl and chirality transfer from enantiopure *p*-tolylvinylsulfoxide to nonsymmetrical secondary phosphine oxides and is illustrated below with the preparation of the two enantiomers of *t*-butylphenylvinylphosphine oxide.[4]



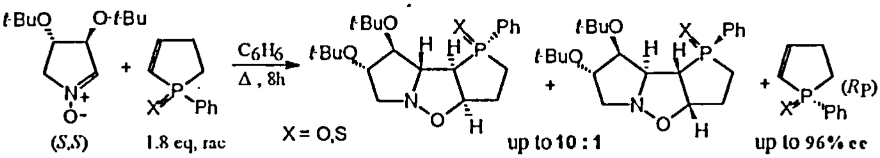
Pursuing further the fruitful combinations and parallelism of sulfur and phosphorus chemistry we have capitalized on the recent observation by Naso et al., that the α-chlorovinyl group at sulfur can be readily substituted by Grignard reagents with clean inversion of configuration at S.[5] In expected analogy, treatment of enantiopure α-chlorovinylmethylphenylphosphine oxide[6] with aryl and vinyl Grignard reagents led to substitution of the α-chlorovinyl group by an aryl or substituted vinyl group with 100% inversion of configuration at P.[7] The substitution process is very facile and accomodates easily ortho substituents in the entering aryl groups as demonstrated by the synthesis of the renowned (*S*p)-*o*-anisylmethylphenylphosphine oxide (PAMPO) in 83% yield.[7]



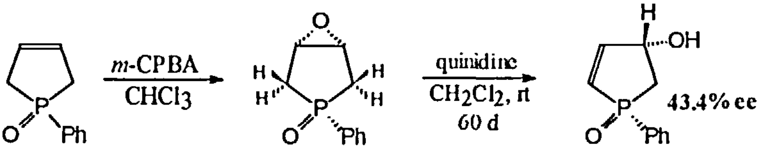
Larger quantities of PAMPO can be conveniently obtained by the menthyl phosphinoylacetate route developed earlier for the large scale preparation of **1**. The two P-epimeric menthyl *o*-anisylphenylphosphinoylacetates are expeditiously separable as in this particular case only one of them is crystalline at ambient temperature.[8] Analogously facile separations of P-epimeric (menthoxycarbonylmethyl)phosphonium bromides led



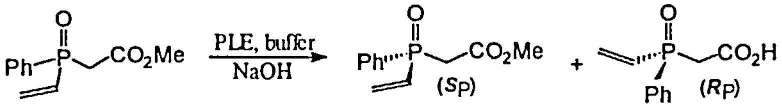
in turn to the development of an efficient synthetic route to enantiomers of 1-phenyl-2-phospholene 1-oxide, a cyclic congener of 1.[9] 1-Phenyl phospholene derivatives of high enantiomeric purity are also accessible by kinetic resolutions of the corresponding racemates subjected to the highly enantioselective (k_S/k_R ratio up to 14) cycloadditions with enantiopure nitrones derived from tartaric acid.[10]



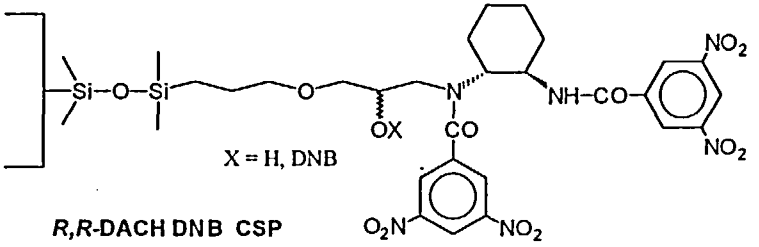
In a single case an asymmetric creation of the phosphorus stereogenic center within the phospholene framework by the action of a chiral base on an achiral phospholene epoxide has also been shown feasible.[9]



Finally, recent successful studies[11] on enzymatic resolutions of racemic P-chiral methyl phosphinoylacetates included among others also a P-vinyl model and provided access to still another acyclic unsaturated P-chiral system of virtually 100% enantiomeric purity.

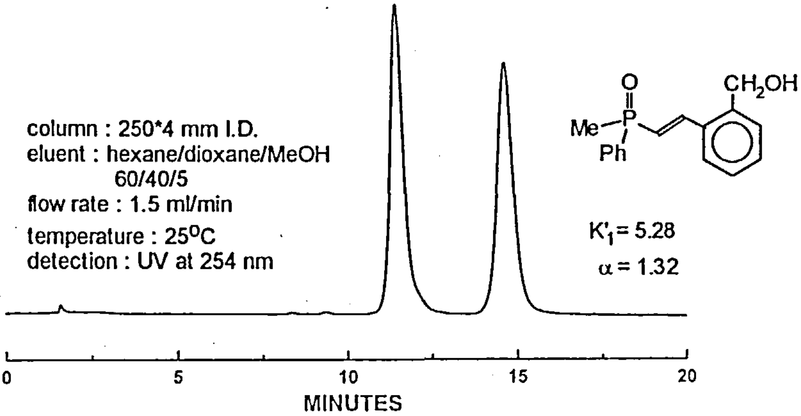


Effective recognition of phosphorus chirality by various chemical and enzymatic systems mentioned above finds its close parallel in similarly efficient enantiomeric recognition in chromatography. A totally synthetic chiral stationary phase based on *trans*-1,2-diaminocyclohexane as selector (DACH-DNB CSP) developed by Gasparrini et al.[12] emerged recently as the CSP of choice for analytical and preparative resolutions



***R,R*-DACH DNB CSP**

of P-chiral compounds. A wide range of P-chiral phosphinoylethenes including both unsubstituted and terminally substituted ones of either E or Z configuration, cyclic and acyclic, have been readily resolved by means of HPLC utilizing the DACH-DNB CSP.[13]



The DACH-DNB CSP is however best suited for the resolution of P-chiral secondary phosphine oxides which can now be promptly and completely resolved into enantiomers in a single preparative run on this phase.

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