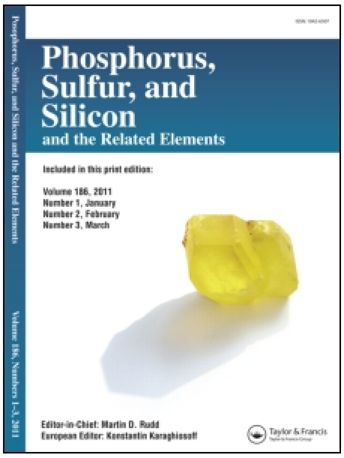

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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To cite this Article Michalski, Jan , Łopusinski, Andrzej and Łuczak, Lech(1990) 'P-Chiral Thioxaphosphoranesulphenyl Chlorides RR[1] P(S)SC1. A New Tool in Stereochemistry of Organophosphorus-Sulphur Compounds', Phosphorus, Sulfur, and Silicon and the Related Elements, 49: 1, 115 — 118

To link to this Article: DOI: 10.1080/10426509008038920

URL: http://dx.doi.org/10.1080/10426509008038920

Phosphorus, Sulfur, and Silicon, 1990, Vols. 49/50, pp. 115–118

Printed in the United Kingdom

P-CHIRAL THIOXAPHOSPHORANESULPHENYL CHLORIDES $RR^1P(S)SCl$. A NEW TOOL IN STEREOCHEMISTRY OF ORGANOPHOSPHORUS-SULPHUR COMPOUNDS

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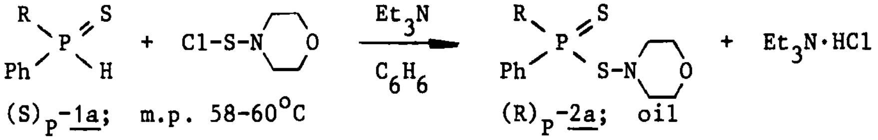
Phosphoranesulphenyl halides of the general formula RR'P(Y)SX and their selenium analogues RR'P(Y)SeX (X=Cl,Br; Y=O,S) have been shown to be useful intermediates for access to many new classes of compounds containing phosphorus, sulphur, or selenium centers.[1]
We want to demonstrate in this communication that important mechanistic information about the nature of bond breaking and bond formation at the dicoordinate sulphur can be disclosed using P-chiral thioxaphosphoranesulphenyl chlorides $RR^1P(S)SCl$ 3.

The achiral chlorides 3 ($R=R^1$) recently became readily available from the corresponding bromides via thioxaphosphoranealkylsulphenates $R_2P(S)SOR'$ in reaction with trimethylsilylchloride[2] or chlorination of mixed anhydrides of phosphorodithioic and carboxylic acids.[3] Neither of these methods was found suitable for the synthesis of their chiral analogues.

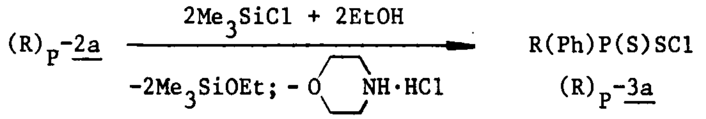
The diastereoisomeric P-chiral 3a (R=L-Menthoxy, R^1=Ph) was prepared by the following sequence of highly stereoselective reactions:

$$\text{L-Menthol} \xrightarrow[C_5H_5N]{PhPCl_2} R(Ph)PCl \xrightarrow[C_5H_5N]{H_2S} \underset{(R)_P,(S)_P\text{-}1a}{R(Ph)P(S)H}$$

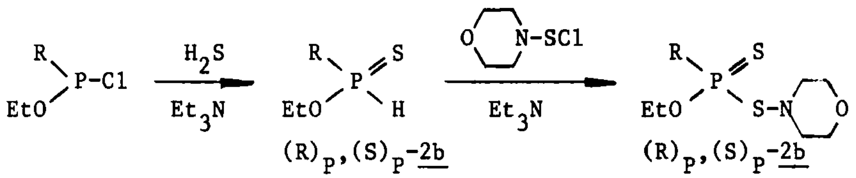
The hydrogenthiophosphonate $(R)_P,(S)_P$-1a was separated into the crystalline $(S)_P$-1a and an oily residue with $(R)_P$-1a as the main component. The $(R)_P$-1a isomer readily rearranges thermally or under influence of acids into the 1:1 mixture $(R)_P,(S)_P$-1a. This property allows full conversion of the reaction products into the single isomer $(S)_P$-1a. Absolute configuration at phosphorus atom and the high optical purity of $(S)_P$-1a were established by chemical correlations and ^{31}P NMR spectroscopy.[4] $(S)_P$-1a was allowed to react with morpholinesulphenyl chloride to yield the corresponding thioxaphosphoranesulphenyl morpholidate $(R)_P$-2a in almost quantitative yield and full stereoselectivity.



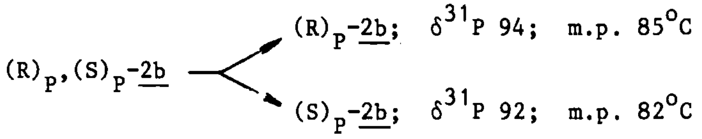
The crucial step in the synthesis of chiral $(R)_P$-3a is conversion of the morpholidate $(R)_P$-2a into the sulphenyl chloride $(R)_P$-3a, by action of hydrogen chloride. Although this type of reaction of an achiral system was described by Almasi,[5] the chlorides 3 have been obtained in excellent yield in this laboratory[6] only when sulphenamides of type 2 were allowed to react with hydrogen chloride produced in situ from trimethylsilyl chloride and ethanol.

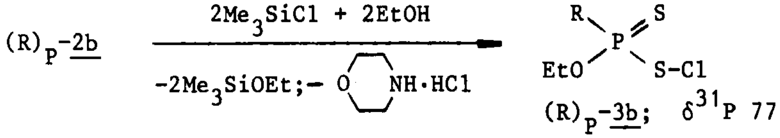


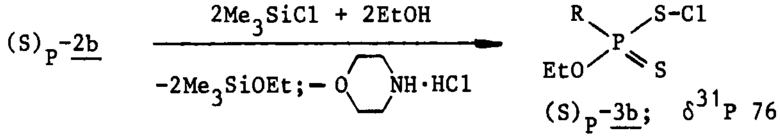
The high optical purity of $(R)_P$-3a was established by ^{31}P NMR spectroscopy and its reconversion into the sulphenamide $(R)_P$-2a. A similar strategy was employed for the stereoselective synthesis of the ethoxy-L-menthoxythioxaphosphoranesulphenyl chlorides $(R)_P$-3b and $(S)_P$-3b (R=L-Menthoxy, R^1=EtO).



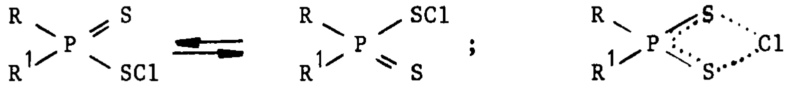
The morpholidate 2b, which is a 1:1 mixture of diastereoisomers $(R)_P$ and $(S)_P$, was readily separated by crystallization into pure components.







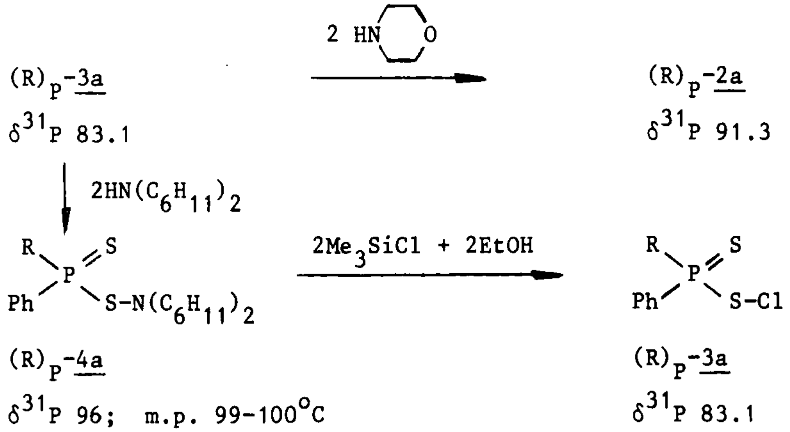
Successful stereoselective synthesis of configurationally stable sulphenyl chlorides 3a and 3b demonstrates an absence of halotropy; a symmetrical structure in which the chloride atom is bonded to both sulphur atoms is not involved since in this type of structure the phosphorus atom is achiral.

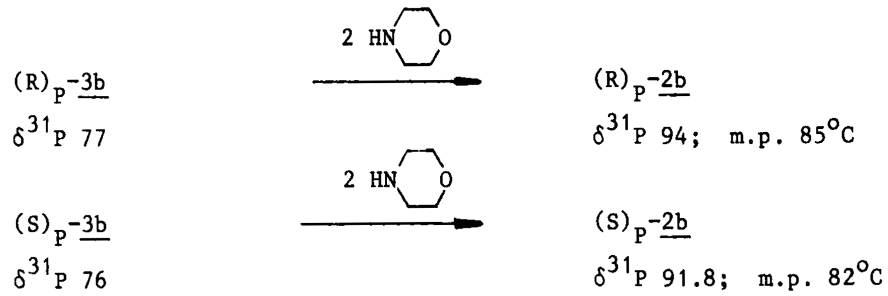


Sulphenyl chlorides of type 3 are very reactive towards C,N,O,S, and P nucleophiles.[1,2] Their chemical behaviour is similar to other compounds of dicoordinate sulphur of the general formula R-S-X where X is a good leaving group. Previous mechanistic studies on the nucleophilic displacement at a dicoordinate sulphur atom based on kinetics and free energy correlations have led to the general belief that such substitutions normally entail a trigonal bipyramidal intermediate (or transition state) in which the entering and leaving groups occupy two apical positions.[7]

P-chiral sulphenyl chlorides 3 serves as a stereochemical probe for displacement reactions occuring at dicoordinate sulphur in this type of compound. Only synchronous processes of bond breaking and bond formation at the S center will be accompanied by retention of configuration at the chiral P-center; in contrast, a dissociative process, either ionic or radical, should result in loss of the stereoselectivity in the course of nucleophilic displacement.

To illustrate this, the P-chiral chlorides 3 were allowed to react with secondary amines such as morpholine and dicyclohexylamine.





All these displacement reactions proceed with almost complete stereoselectivity at the phosphorus atom. These observations speak for a synchronous mechanism of bond breaking and bond formation during the nucleophilic displacement at the dicoordinate sulphur atom. This statement is also valid for the reaction of sulphenamides 2a, 2b and 4a with hydrogen chloride. Even though the achiral nature of dicoordinate sulphur precludes any direct investigations of the stereochemistry of nucleophilic substitution at sulphenyl sulphur our stereochemical results corroborates with mechanistic views derived from the kinetic studies.[7]

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