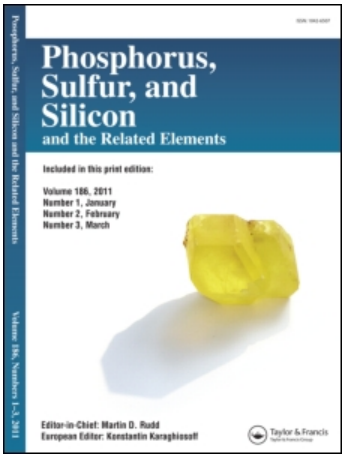

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Synthesis and Reactivity of Some Aromatic Sulfides Substituted by an Ortho-Phosphonyl Group

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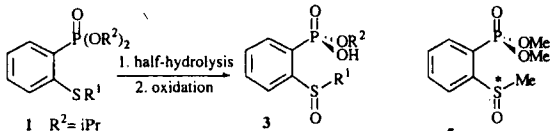
As phosphorus-based members of the biologically relevant thiosalicylic acid, monoesters of ortho-sulfinylated phenylphosphonic acids such as **3** and **4** (series **a**, R^1=Me; **b**, R^1=2-$C_6H_4CO_2H$) are of special interest. They might act both as potential sources of new anionic bidentate ligands for the synthesis of cisplatin analogues[1] and as suitable precursors of phosphorus-containing endocyclic sulfoximides and hypervalent organo-sulfur species. We have therefore undertaken the synthesis of these compounds. The starting phenylphosphonic acid diisopropyl esters **1** were formed by using a LDA-induced thiophosphate-mercaptophosphonate rearrangement[2] described earlier and converted into their dimethyl counterparts **2** by means of a trans-silylation procedure followed by alkylation. We have now performed the selective half-hydrolysis of phosphonic acid diesters **1**,**2** and sulfoxidation of the resulting monoesters.



1 R^2= iPr
2 R^2= Me

3

4

5

As a general trend, these phenylsulfides have been oxidized by $NaIO_4$ (**a**) and mCPBA or H_2O_2-cat.SeO_2(**b**) while diesters of phosphonic acids partially cleaved with NaN_3[3] (**1**) or NaOH (**2**). We have also achieved the optical resolution of sulfoxide **4a** with cinchonine and its conversion into enantiomerically pure **5** ($(\alpha)_D$=-150.7°).

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