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A Novel Method for the Synthesis of Chiral Sulfonated Phosphines

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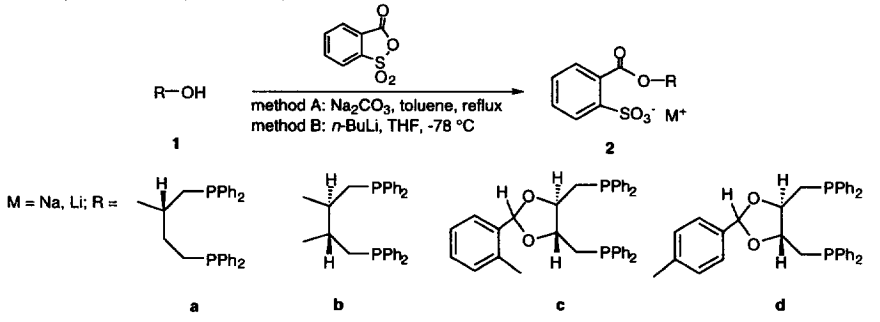
Abstract: The selective and smooth introduction of sulfonate groups in chiral diphosphines by the reaction of hydroxy diphosphines with *o*-sulfobenzoic anhydride in the presence of Na_2CO_3 or *n*-butyl lithium, respectively, is described.

Achiral and chiral sulfonated phosphines constitute a unique class of ligands in homogeneous metal catalysis owing hydrophilic properties which facilitate reactions in biphasic aqueous-organic media.[1] Several catalytic applications for sulfonated phosphines have been found, some of them got access into industrial processes.[2] For the introduction of a sulfonate group into alkyl- or arylphosphines different methodologies have been developed.[3] The most common approach consists in the direct aryl sulfonation of P-aryl phosphines with oleum followed by the treatment with a base. In phenylphosphines this method places the functional group in a position *meta* to the phosphorus.[4] If several aryl groups are present in the molecule, a mixture yields consisting of products with different degree of sulfonation. When chiral P-aryl phosphines were applied due to the chirality on the phosphorus, a mixture of epimers were formed which may cause varying enantioselectivities in consecutive catalytic reactions.[5] Clearly, the severe reaction conditions cannot be applied if sulfonation of phosphines, bearing acid sensitive functional groups is desired. More selective and smooth methods, hitherto preferentially used for the synthesis of achiral sulfonated phosphines, are e.g. the addition of phosphines on conjugated olefins bearing sulfonato groups,[6] reaction of alkali metal phosphides with sultones,[7] N-alkylation of pyridyl phosphines with sultones,[8] nucleophilic substitution of fluoroaromatics with phosphine in a superbasic medium,[9] substitution of halogen in alkylsulfonates by phosphide,[10] or Pd-catalyzed P-C cross coupling reactions between phosphines and functionalized aryl iodides.[11]

Herein, we wish to report a new and simple method for the selective preparation of enantiopure sulfonated phosphines. Our approach based on the acylation of chiral hydroxy phosphines with commercial *o*-sulfobenzoic anhydride (SBA) (Scheme).[12]



Scheme

Suitable chiral hydroxy phosphines serving as potential precursors possessing one or two HO-groups in distinguished positions in the chiral framework are available in a large variety.[13]

To demonstrate our method hydroxy diphosphines **1a-d** were chosen for the reaction with the anhydride. Thus, the mono- and disulfonated diphosphines **2a,b** could be obtained by treatment of the corresponding alcohols **1a**[14],**b**[15] with Na_2CO_3/SBA under reflux for approx. 2 h in toluene. The completion of the reaction was controlled by TLC (*n*-hexane/ethyl acetate). After evaporation of the solvent, the yielding sulfonate was dissolved in CH_2Cl_2 and filtrated in order to remove the excess of Na_2CO_3. However, this approach gave poor yields when the compounds **1c,d**[16] were tried. The acylation of these compounds with *n*-BuLi as a base in THF at -78 °C revealed to be more advantageous. In all cases the sulfonated diphosphines could be obtained in 70 - 90 % yield.[17]

To investigate the effect of the *o*-sulfobenzoate group on the complexation properties of the new ligands, the diphosphines were reacted with [Rh(COD)acac]. The subsequent addition of HBF_4 yielded the corresponding cationic rhodium complexes. The ^{31}P NMR spectra of the compounds obtained were comparable with those of related chelating 1,4-bis(diphenylphosphine)rhodium complexes.[18]

The behaviour of the new ligands and complexes in asymmetric catalytic reactions in organic solvents or water as well as in two-phase systems are now under investigation.

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References and Notes

1 Papadogianakis, G.; Sheldon, R. A. *New J. Chem.* **1996**, *20*, 175-185.

2 Cornils, B. *Angew. Chem.* **1995**, *107*, 1709-1711; *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1575. Wan, K. T.; Davis, M. E. *J. Catal.* **1994**, *148*, 1-8.

3 Herrmann, W. A.; Kohlpaitner, C. W. *Angew. Chem.* **1993**, *105*, 1588-1609; *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1524.

4 Lecomte, L.; Sinou, D. *Phosphorus, Sulfur, and Silicon* **1990**, *53*, 239-251. Amrani, Y.; Lecomte, L.; Sinou, D.; Bakos, J.; Toth, I.; Heil, B. *Organometallics* **1989**, *8*, 542-547.

5 Lensink, C.; de Vries, J. G. *Tetrahedron:Asymmetry* **1992**, *3*, 235-238. Bakos, J.; Orosz, À, Heil, B.; Laghmari, M.; Lhoste, P.; Sinou, D. *J. Chem. Soc., Chem. Commun.* **1991**, 1684-1685.

6 Lavenot, L.; Bortoletto, M. H.; Roucoux, A.; Larpent, C.; Patin, H. *J. Organomet. Chem.* **1996**, *509*, 9-14 and lit. cited therein.

7 Paetzold, E.; Kinting, A.; Oehme, G. *J. prakt. Chem.* **1987**, *329*, 725-731.

8 Fell, B.; Papadogianakis, G. *J. Mol. Catal.* **1991**, *66*, 143-154.

9 Bitterer, F.; Herd, O.; Hessler, A.; Kühnel, M.; Rettig, K.; Stelzer, O.; Sheldrick, W. S.; Nagel, S.; Rösch, N. *Inorg. Chem.* **1996**, *35*, 4103-4113 and lit. cited therein.

10 Ganguly, S.; Mague, J. T.; Roundhill, D. M. *Inorg. Chem.* **1992**, *31*, 3500-3501.

11 Herd, O.; Heßler, A.; Hingst, M.; Tepper, M.; Stelzer, O. *J. Organomet. Chem.* **1996**, *522*, 69-76.

12 *N*-Acylation of achiral amino phosphines with SBA and NEt_3 in THF has been described by: Nuzzo, R. G.; Feitler, D.; Whitesides, G. M. *J. Am. Chem. Soc.* **1979**, *101*, 3683-3685. Nuzzo, R. G.; Haynie, S. L.; Wilson, M. E.; Whitesides, G. M. *J. Org. Chem.* **1981**, *46*, 2861-2867.

13 See e.g.: Brunner, H.; Sicheneder, A. *Angew. Chem.* **1988**, *100*, 730-731; *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 718. Ward, J.; Börner, A.; Kagan, H. B. *Tetrahedron:Asymmetry* **1992**, *3*, 849-852. Börner, A.; Holz, J.; Ward, J. Kagan, H. B. *J. Org. Chem.* **1993**, *58*, 6814-6817. Börner, A.; Ward, J.; Ruth, W.; Holz, J.; Kless, A.; Heller, D.; Kagan, H. B. *Tetrahedron* **1994**, *50*, 10419-10430. Enders, D.; Berg, T. *Synlett* **1996**, 796-798.

14 Börner, A.; Kless, A.; Kempe, R.; Heller, D.; Holz, J.; Baumann, W. *Chem. Ber.* **1995**, *128*, 767-773.

15 Börner, A.; Ward, J.; Kortus, K.; Kagan, H. B. *Tetrahedron:Asymmetry* **1993**, *4*, 2219-2228.

16 Holz, J.; Börner, A.; Kless, A.; Borns, S.; Trinkhaus, S.; Selke, R.; Heller, D. *Tetrahedron:Asymmetry* **1995**, *6*, 1973-1988.

17 ^{31}P NMR ($CDCl_3$): **2a**: δ -14.7, -23.8; **2b**: δ -21.6; **2c**: δ -23.0, -23.9; **2d**: δ -20.3, -21.2.

18 ^{31}P NMR spectra (recorded in [d_8]-THF) of the [Rh(P-P)(COD)]BF_4-complexes based on: **2a**: δ 18.4 (dd, *J*=145.8, 37.3 Hz), 21.5 (dd, *J*=144.2 Hz); **2b**: δ 17.1 (dd, *J*=145.8 Hz); **2c**: δ 12.4 (dd, *J*=144.2, 35.6 Hz), 13.9 (dd, *J*=142.6 Hz); **2d**: δ 12.7 (dd, *J*=145.8, 35.6 Hz), 13.9 (dd, *J*=144.2 Hz).

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