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A NEW ROUTE TO WATER-SOLUBLE SULFONATED PHOSPHINES.

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Among the water-soluble phosphines sulfonated arylphosphines have been widely studied, particularly in the field of organometallic chemistry and biphasic catalysis because such ligands accord water-solubility to coordination compounds and thus afford means to separate easily the organic components from the catalysts in the aqueous phase [1-3]. More recently, mono- and tri-sulfonated triphenylphosphine have found applications in organic synthesis for the preparation of specifically deuterated alkenes and more generally for nucleophilic additions in water [4-8]. Sulfonated triarylphosphines or alkyldiarylphosphines have been prepared by sulfonation with oleum of the corresponding phosphines on one or several aromatic nuclei [9-11]. The sulfonation leads usually to mixtures of compounds having various degrees of sulfonation and to oxidation at phosphorus which forces subsequent separations [11-12]. On the other hand this direct sulfonation method is not convenient for the synthesis of hydrophilic phosphines bearing functionalities on alkyl chains.

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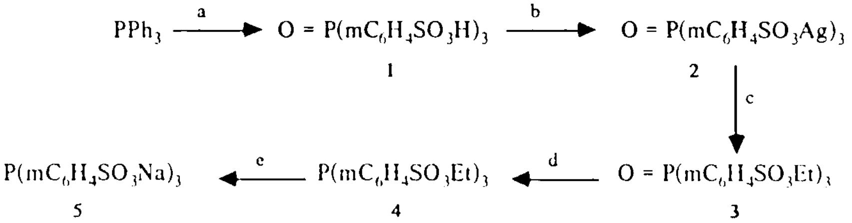
In this paper we describe a new multistep sequence leading to sulfonated phosphines which uses a protecting group methodology and can be applied for the preparation of mono-, di- or tri-sulfonated triaryl- or alkylarylphosphines.

The starting material is PPh_3 and the key step consists in the reduction of a phosphine oxide in which the sulfonate anions have been protected. The choice of the protecting agent is crucial because (i) it must accord a reasonable solubility in convenient organic solvents, (ii) it must not be reduced by trichlorosilane, (iii) the deprotection step must occur in neutral and non-oxidizing conditions. We have chosen sulfonic esters which fit perfectly well with the required conditions [13] and are readily hydrolyzed into sulfonate anions by action of sodium halides.

The above methodology has been successfully applied to the synthesis of pure $P(mC_6H_4SO_3Na)_3$ and $Me\text{-}P(mC_6H_4SO_3Na)_2$ which are respectively described in scheme I and scheme II.

Thus, sulfonation of PPh_3 with oleum affords the trisulfonic acid 1 in quantitative yield. The silver salt 2 is obtained by neutralization of 1 with silver carbonate in water. The neutralization rate is slow because Ag_2CO_3 is almost insoluble in water, the addition of a powerful wetting agent, aerosol OT, favors the dispersion of silver carbonate in water and greatly accelerates the reaction. The silver salt is isolated and put in reaction with iodoethane [14-18] in toluene to give the triethyl sulfonate ester 3. Phosphine 4 is obtained by reduction of the phosphine oxide 3 with trichlorosilane. The reduction step, monitored by thin layer chromatography, is selective and the sulfonic ester functions are not modified. Finally addition of stoechiometric amount of sodium bromide to a solution of 4 in a mixture of water and acetone afford pure trisulfonated triphenyl phosphine 5.

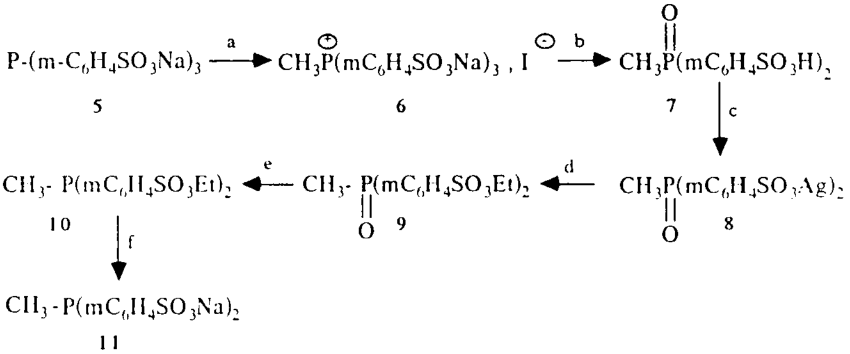
Following the same procedure the methyl-di[3-sulfophenyl]-phosphine 11 is obtained starting from the phosphine oxide 7 prepared quantitatively in one pot [6] from the phosphine 5 (scheme II).



$$\begin{tikzcd}
PPh_3 \arrow[r, "a"] & \underset{1}{O=P(mC_6H_4SO_3H)_3} \arrow[r, "b"] & \underset{2}{O=P(mC_6H_4SO_3Ag)_3} \arrow[d, "c"] \\
\underset{5}{P(mC_6H_4SO_3Na)_3} & \underset{4}{P(mC_6H_4SO_3Et)_3} \arrow[l, "e"'] & \underset{3}{O=P(mC_6H_4SO_3Et)_3} \arrow[l, "d"']
\end{tikzcd}$$

(a) H_2SO_4-SO_3 45 %, 50°C, 24 h ; (b) H_2O, Ag_2CO_3 3 eq., Aerosol OT 5 % w/w, 25°C, 24 h ; (c) EtI 10 eq., toluene, reflux, 24 h ; (d) $SiHCl_3$, toluene-THF, reflux, 22 h ; (e) NaBr 3 eq., water-acetone (1/80), 25°C, 48 h.

Scheme I



$$\begin{tikzcd}
\underset{5}{P\text{-}(m\text{-}C_6H_4SO_3Na)_3} \arrow[r, "a"] & \underset{6}{CH_3\overset{\oplus}{P}(mC_6H_4SO_3Na)_3 , I^{\ominus}} \arrow[r, "b"] & \underset{7}{CH_3\overset{O}{\overset{\|}{P}}(mC_6H_4SO_3H)_2} \arrow[d, "c"] \\
\underset{10}{CH_3\text{-}P(mC_6H_4SO_3Et)_2} \arrow[d, "f"] & \underset{9}{CH_3\text{-}\underset{O}{\underset{\|}{P}}(mC_6H_4SO_3Et)_2} \arrow[l, "e"'] & \underset{8}{CH_3\underset{O}{\underset{\|}{P}}(mC_6H_4SO_3Ag)_2} \arrow[l, "d"'] \\
\underset{11}{CH_3\text{-}P(mC_6H_4SO_3Na)_2} & &
\end{tikzcd}$$

(a) CH_3I 10 eq, H_2O, 25°C, overnight [6] ; (b) NaOH, reflux, 30 min then HCl ; (c) Ag_2CO_3 2 eq, H_2O, 25°C, 4 days ; (d) EtI 10 eq, CH_3CN, reflux, 20 h ; (e) $SiHCl_3$, toluene-THF, reflux, 18 h ; (f) NaBr 2 eq, Acetone-water, 25°C, 30 h.

Scheme II

The reduction of phosphine oxide 7 is performed like above after esterification of the sulfonic acid groups by reaction of silver sulfonates with iodoethane. Then, addition of sodium bromide to **10** affords the new water-soluble disulfonated phosphine **11**.

This methodology is currently being developed in our laboratory to prepare mono- or di-sulfonated phosphines (with chirality at the phosphorus atom or bearing functional groupings) starting from substituted alkyl- or vinyl- sulfophenyl phosphonium salts or phosphine oxides readily obtained by nucleophilic addition of water-soluble phosphines on activated alkenes or alkynes in water [4,5,6,8].

Experimental Section

NMR spectra were recorded on a Jeol FX90Q [^1H(89.55 MHz) and ^{13}C(22.50 MHz)] and a Brucker WP 80 MHz [^{31}P(32.38 MHz)]. The results of elemental analysis are not significant for salts **1**, **2**, **5**, **7**, **8**, **11** because the hydration number depends on the purification and drying procedures and also for phosphines **4** and **10** which are air sensitive. The silver salts (**2**, **8**)d and the sodium salts (**5**, **11**) melt above 300°C.

Tris (3-sulfonatophenyl) phosphine oxide, triacid : 1

97 ml of 65 % oleum was added dropwise under nitrogen to a cooled solution of PPh_3 (20 g) in 43 ml of concentrated sulfuric acid. The temperature of the reaction mixture was maintained below 50°C during the addition. The solution was then heated under N_2 at 40-50°C for 24 h. After cooling the reaction mixture was poured on 500 g of ice and the resulting acidic aqueous solution was carefully neutralized by addition of concentrated NaOH. The aqueous solution was allowed to stand at room temperature for 48 h and filtrated to remove sodium sulfate. Further precipitation of sodium sulfate was obtained by addition of an equal volume of ethanol. The mixture obtained after filtration was concentrated under vacuum to a volume of 150 ml. Concentrated hydrochloric acid (150 ml) was then added and the acidic solution was allowed to stand at room temperature for 2 h. The solvent was removed under vacuum. The viscous residue was treated with 250 ml of hot absolute alcohol and, after filtration of the insoluble, the acid 1 (34 g, 100 % yield) was isolated by removing ethanol under vacuum. TLC : Rf = 0.6 (MeOH) ; $^{31}P\{^1H\}$ NMR, D_2O, δ ppm : 33.82 (s) ; $^{13}C\{^1H\}$ NMR, D_2O, δ ppm :

111.83 (d, J_{P-C} = 9 Hz), 113.17 (d, $^1J_{P-C}$ = 106 Hz, C ipso), 113.4 (d, J_{P-C} = 12 Hz), 113.68 (broad s, C_4), 117.64 (d, J_{P-C} = 11 Hz), 127.19 (d, $^3J_{P-C}$ = 13 Hz, C-SO_3H).

Silver salt : 2

1.8 g (6.53 mmol) of silver carbonate were added to 50 ml of an aqueous solution of aerosol OT (5 % w/w). The resulting mixture was magnetically stirred for 30 min to ensure a good dispersion. After addition of 2 g (3.86 mmol) of **1** the suspension was allowed to stir in the dark for 24 h until TLC control showed complete transformation of **1**. The turbid mixture was filtered on a 0.45 µm micropore and concentrated to dryness under vacuum. The brown solid residue was stirred overnight with light petroleum (50 ml) to solubilize the aerosol OT and the insoluble brown solid **2**, separated by filtration, was dried in a desicator in vacuo (2.6 g, 80 % yield). $^{31}P\{^1H\}$ NMR, D_2O, δ ppm : 34.17 (s) ; $^{13}C\{^1H\}$ NMR, D_2O, δ ppm : 110.68 (d, J_{P-C} = 11 Hz), 111.92 (d, $^1J_{P-C}$ = 106 Hz, C ipso), 112.02 (d, J_{P-C} = 13 Hz), 112.30 (broad s, C_4), 116.5 (d, $^2J_{P-C}$ = 11 Hz), 125.59 (d, $^3J_{P-C}$ = 13 Hz, C-SO_3Ag) ; IR (HCB, cm^{-1}) : 1180 (S=O), 1110 (P=O).

Tris (3-ethyl phenyl sulfonate) phosphine oxide : 3

3 g (3.6 10^{-2} mol) of **2**, 300 ml of toluene and 3 ml (3.8 10^{-1} mol) of iodoethane were refluxed under magnetic stirring for 24 h. The precipitation of silver iodide was removed by filtration of the hot reaction mixture and the filtrate concentrated under vacuum to a volume of 50 ml. The white solid **3** cristallized upon cooling at - 10°C (1.6 g, 75 % yield). F(°C) = 104-106 ; TLC Rf = 0.7 (ether-methanol 50/50) ; $^{31}P\{^1H\}$ NMR, $CDCl_3$, δ ppm : 24.36 (s) ; ^1H NMR, $CDCl_3$, δ ppm : 1.33 (t, 3H, $^3J_{H-H}$ = 7 Hz, CH_3), 4.17 (q, 2H, $^3J_{H-H}$ = 7 Hz, CH_2), 7.66 to 8.24 (m, 4H, ArH) ; IR (HCB, cm^{-1}) : 1360, 1180 (S=O), 1130 (P=O). Elemental analysis found 47.6 % C, 4.4 % H ; calculated 47.8 % C ; 4.5 % H. Mass spectrometry $M^{+\bullet}$ 602.04933 (found) ; $M^{+\bullet}$ 602.05039 (calculated).

Tris (3-ethyl phenyl sulfonate) phosphine : 4

5 ml of trichlorosilane were added dropwise under nitrogen to a cooled mixture (ice bath) of **3** (1.5 g, 2.5 mmol), THF (30 ml) and toluene (120 ml). After refluxing for

22 h under N_2 the cooled reaction mixture was poored in 200 ml water and the white precipitate of silica removed by filtration. The filtrate was washed twice with brine and dried over magnesium sulfate. Removal of the solvent afforded crude 4 which was purified by column chromatography (ether, Rf = 0.5) (viscous oil, 1.3 g, 89 % yield). $^{31}P\{^1H\}$ NMR, $CDCl_3$, δ ppm : -5.05 (s) ; ^1H NMR, $CDCl_3$, δ ppm : 1.31 (t, 3H, $^3J_{H\text{-}H}$ = 7 Hz), 4.12 (q, 2H, $^3J_{H\text{-}H}$ = 7 Hz), 7.53 to 7.86 (m, 4H, ArH) ; IR (neat, cm^{-1}) : 1360, 1180 (S=O).

Tris (3-sulfonatophenyl) phosphine, trisodium salt : 5

A solution of sodium bromide (1.58 g, 1.5 mmol) in 5 ml of water was added to a solution of 4 (3 g, 5.1 mmol) in 400 ml of acetone. The reaction was allowed to stir at room temperature under N_2 for 48 h. The white precipitate of 5 was separated by filtration and dried in an exsiccator in vaccuo for 24 h (2 g, 66 % yield). TLC : Rf = 0.7 (MeOH) ; $^{31}P\{^1H\}$ NMR, D_2O, δ ppm : -5,76 (s) ; $^{13}C\{^1H\}$ NMR, D_2O, δ ppm : 128.99 (broad s, C_4), 131.98 (d, $J_{P\text{-}C}$ = 7 Hz), 132.36 (d, $J_{P\text{-}C}$ = 19 Hz), 138.70 (d, $J_{P\text{-}C}$ = 14 Hz), 145.65 (d, $^3J_{P\text{-}C}$ = 6 Hz, C-SO_3Na). IR (HCB, cm^{-1}) : 1200 (broad), 1050 (S=O).

Methyl di (3-sulfonatophenyl) phosphine oxide, diacid : 7

The phosphonium salt 6 was prepared following the procedure already described [6] by treatment of 5 (4 g, 7 mmol) in water (30 ml) with an excess of iodomethane (4 ml) at room temperature overnight. The aqueous phase was washed with dichloromethane to remove the excess of CH_3I and 10 ml of concentrated sodium hydroxide were added to the aqueous solution of 6 and the resulting solution was refluxed for 30 mn. After cooling the aqueous solution was acidified by addition of 12 ml of concentrated hydrochloric acid and then concentrated to dryness under vacuum. The residue was dissolved in 100 ml of hot absolute alcohol and the insoluble was removed by filtration. Removal of ethanol under vacuum afforded crude 7 as a yellow viscous oil (3.6 g). $^{31}P\{^1H\}$ NMR, D_2O, δ ppm : 38.65 (s) ; ^1H NMR, D_2O, δ ppm : 2.26 (d, 3H, $^2J_{P\text{-}H}$ = 14 Hz), 7.50 to 8.25 (m, 8H, ArH) ; TLC Rf = 0.51 (MeOH).

Silver salt : 8

Silver carbonate (2.7 g, 10 mmol) was added to a solution of 7 (3.6 g, 9.6 mmol) in 50 ml of water. The suspension was allowed to stir at room temperature in the dark for

4 days. 8 was isolated as a grey solid after filtration and concentration of the aqueous filtrate to dryness (4.4 g). ^{1}H NMR, D_2O, δ ppm : 2.26 (d, 3H, $^2J_{P\text{-}H}$ = 14 Hz), 7.58 to 8.22 (m, 8H, ArH).

Methyl di-(3-ethyl phenyl sulfonate)phosphine oxide : 9

A mixture of 8 (1 g, 1.7 mmol), acetonitrile (50 ml) and iodoethane (1 ml) was heated at 70°C for 20 h. After cooling the reaction mixture was filtrated to remove silver iodide and concentrated under vacuum. The residue was solubilized in dichloromethane and washed twice with water. Crude 9 was purified by column chromatography (eluent CH_2Cl_2-MeOH). 9 : viscous oil, 0.45 g, 66 % overall yield from 5. TLC Rf = 0.84 (CH_2Cl_2-MeOH, 60/40) ; $^{31}P\{^1H\}$ NMR, $CDCl_3$, δ ppm : 29.93 (s) ; ^{1}H NMR, $CDCl_3$, δ ppm : 1.32 (t, 6H, $^3J_{H\text{-}H}$ = 7 Hz, CH_3), 2.17 (d, 3H, $^2J_{P\text{-}H}$ = 14 Hz, CH_3), 4.17 (q, 4H, $^3J_{H\text{-}H}$ = 7 Hz, CH_2), 7.50 to 8.20 (m, 8H, ArH). Elemental analysis found 47.0 % C, 4.7 % H ; calculated 47.2 % C, 4.9 % H. IR (HCB, cm^{-1}) : 1360, 1180 (S=O), 1110 (P=O).

Methyl di-[3-ethyl phenyl sulfonate] phosphine : 10

2 ml of trichlorosilane were added dropwise under nitrogen to a cooled mixture of 9 (510 mg, 1.18 mmol), toluene (20 ml) and THF (5 ml). After refluxing under N_2 for 18 h, the reaction mixture was cooled and poored in 50 ml of ice water. The precipitate was removed by filtration and the organic phase, washed twice with water, was dried over $MgSO_4$. Concentration to dryness afforded crude 10 which was purified by column chromatography (eluent : ether, Rf = 0.53). (300 mg, 61 % yield). $^{31}P\{^1H\}$ NMR, $CDCl_3$, δ ppm : -23.74 (s) ; ^{1}H NMR, $CDCl_3$, δ ppm : 1.31 (t, 3H, $^3J_{H\text{-}H}$ = 7 Hz, CH_3), 1.72 (d, 3H, $^2J_{P\text{-}H}$ = 4 Hz, CH_3), 4.12 (q, 2H, $^3J_{H\text{-}H}$ = 7 Hz, CH_2), 7.40 to 8.10 (m, 8H, ArH). IR (HCB, cm^{-1}) : 1360, 1180 (S=O).

Methyl di-(3-sulfonatophenyl)phosphine, disodium salt 11

Sodium bromide (90 mg, 0.87 mmol) in 0.5 ml of H_2O was added under N_2 to a solution of 10 (180 mg, 0.43 mmol) in acetone (25 ml). The reaction mixture was allowed to stand at room temperature under N_2 for 30 h. The white precipitate of 11 was filtrated, washed with acetone and dried in a desicator (130 mg, 75 % yield). $^{31}P\{^1H\}$ NMR, D_2O, δ ppm : -24.73 (s) ; ^{1}H NMR, D_2O, δ ppm : 1.73 (d, $^2J_{P\text{-}H}$ = 2 Hz, 3H, CH_3), 7.45 to 8.25 (m, 8H, ArH). IR (Nujol, cm^{-1}) : 1200 (large), 1060 (S=O).

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