

Organic Chemistry in water (part II)¹

NUCLEOPHILIC ADDITION OF WATER-SOLUBLE PHOSPHINES ON ACTIVATED OLEFINS

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SUMMARY

Triphenylphosphine m-trisulfonate $P(PhSO_3Na)_3$ = TPPTS and triphenylphosphine m-monosulfonate Ph_2PPhSO_3Na = TPPMS react in water with α,β unsaturated acids affording hydrosoluble phosphonium salts. The conversion is quantitative because water readily protonates the carbanionic intermediate thus displacing the equilibrium towards the right. This nucleophilic addition of hydrosoluble phosphines has been extended to non water miscible activated olefins in biphasic media ; depending on the pH, phosphine oxides or phosphonium salts are obtained. When the reactions are carried out in D_2O , the addition products are specifically deuterated.

RESUME

La triphenylphosphine m-trisulfonate $P(PhSO_3Na)_3$ = TPPTS et la triphenylphosphine m-monosulfonate Ph_2PPhSO_3Na = TPPMS réagissent dans l'eau avec les acides α,β insaturés pour donner des sels de phosphonium hydrosolubles. Ces réactions sont quantitatives car la protonation par l'eau du carbanion intermédiaire déplace l'équilibre vers la droite. Ces additions nucléophiles de phosphines hydrosolubles ont été généralisées à des oléfines activées non miscibles à l'eau en milieu biphasique ; en fonction du pH des sels de phosphonium ou des oxydes de phosphines sont obtenus. Lorsque les réactions sont réalisées dans D_2O , les produits d'addition sont spécifiquement deutériés en β du phosphore.

In this paper we describe the addition of TPPTS (Triphenyl Phosphine-meta Tri-Sulfonate) and TPPMS (Triphenyl Phosphine meta-Mono-Sulfonate) to various activated olefins. In the presence of water, we obtain new families of phosphonium salts and phosphine oxides which can be regioselectively deuterated when D₂O is used. The differences found between the reactivities of TPPTS and TPPMS are not the result of a change in the nucleophilic properties of the phosphines but the consequence of the modification of their water-solubility and consequently of their amphiphilic character.

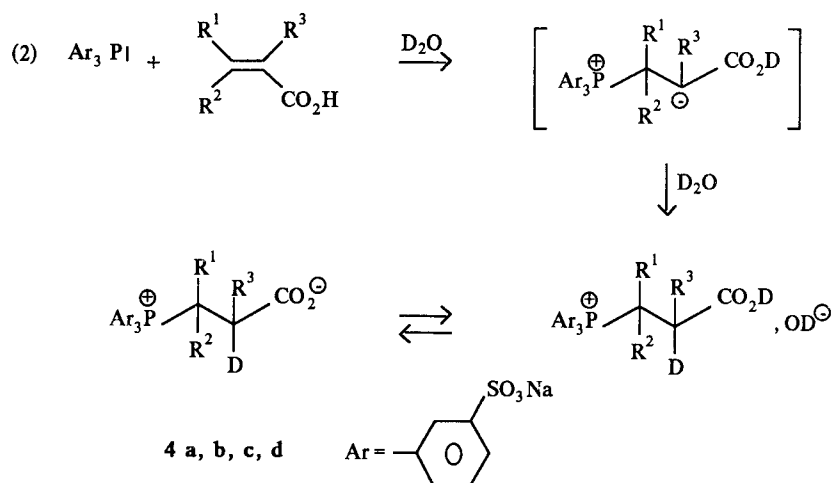
- Nucleophilic addition of water-soluble phosphines on α , β - unsaturated carboxylic acids.

$$(1) \quad \left[\text{C}_6\text{H}_4(\text{SO}_3\text{Na}) \right]_3 \text{P} + \begin{array}{c} \text{R}^1 \quad \text{R}^3 \\ \diagdown \quad \diagup \\ \text{C} = \text{C} \\ \diagup \quad \diagdown \\ \text{R}^2 \quad \text{CO}_2\text{H} \end{array} \xrightarrow{\text{H}_2\text{O}} \left[\text{C}_6\text{H}_4(\text{SO}_3\text{Na}) \right]_3 \text{P}^+ - \begin{array}{c} \text{R}^1 \quad \text{R}^3 \\ | \quad | \\ \text{C} - \text{C} \\ | \quad | \\ \text{R}^2 \quad \text{H} \end{array} \text{CO}_2^-$$

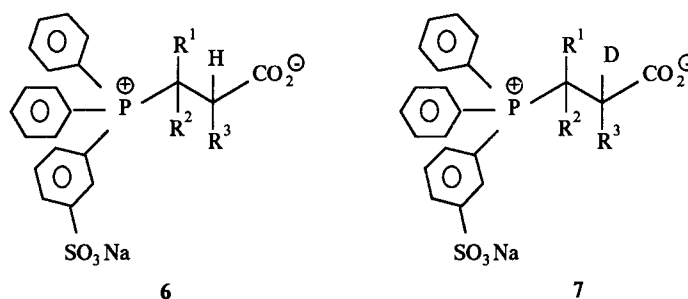
- (a) $R_1 = R_2 = R_3 = H$
 (b) $R_1 = R_2 = H, R_3 = CH_3$
 (c) $R_1 = R_2 = H, R_3 = CH_2CO_2H$
 (d) $R_1 = CH_3, R_2 = R_3 = H$

These reactions are readily monitored using ^{31}P NMR spectroscopy. By addition of a stoichiometric amount of **2** to an aqueous solution of **1**, the singlet at $\delta = -5.5$ ppm characteristic of the phosphine is removed while a new signal, attributed to the phosphonium salt **3** appears at lower field (+ 25 to 30 ppm). The chemical shift depends on the nature of the substituents R^1 , R^2 and R^3 . For instance, the ^1H NMR spectrum of **3a** shows two doublets of triplets ($\delta = 2.66$ and 3.74 ppm) corresponding to the CH_2 protons with $^3\text{J}_{\text{H-H}} = 8$ Hz, $^2\text{J}_{\text{P-H}} = 13.4$ Hz and $^3\text{J}_{\text{P-H}} = 12.8$ Hz. Selective irradiation of the phosphorus nucleus proves that a phosphorus-carbon bond has been formed. The ^{13}C NMR data are consistent with those already described for phosphonium salts ⁷⁻⁸: $\delta\text{C}_1 = 21.60$ ppm, $^1\text{J}_{\text{P-C}_1} = 52$ Hz, $\delta\text{C}_2 = 31.96$ ppm, $^2\text{J}_{\text{P-C}_2} = 3$ Hz; $\delta\text{C}_4 = 121.26$ ppm, $^1\text{J}_{\text{P-C}_4} = 87$ Hz. Similarly, the ^1H and ^{13}C NMR spectra of **3b**, **c**, **d** confirm their structure. In all these cases, the ^{31}P NMR spectroscopy, easily carried out in water, is a very efficient technique for monitoring the reactivity of water-soluble phosphines. The reaction rate is influenced by steric factors: the phosphine reacts instantaneously and quantitatively with the activated terminal olefins **2a**, **b**, **c** but the rate of the reaction is much slower with the β substituted crotonic acid **2d** and in that case a slight heating is required. These results show that the nucleophilic addition of a hydrophilic phosphine on activated olefins readily occurs in water. Similar nucleophilic reactions of classical

tertiary phosphines (especially PPh_3) with α, β unsaturated carboxylic acids have already been described⁹⁻¹⁰. In aprotic solvents, the addition is reversible and phosphonium salts can only be obtained when the reaction is carried out in highly acidic media (concentrated HCl or HBr). In our case, the acidity of the solvent is not strong enough to protonate the phosphine but water protonates instantaneously the strongly basic carbanionic intermediate thus making the reaction quantitative by driving the equilibrium towards the right. The intervention of water is demonstrated by using D_2O . In these conditions specifically deuterated phosphonium salts **4** are obtained [equation (2)].



The monosulfonated triphenylphosphine **5** ($\text{TPPMS} = \text{Ph}_2\text{PPhSO}_3\text{Na}$) also reacts with α, β -unsaturated carboxylic acids leading respectively to the phosphonium salts **6** and **7** when the reaction is carried out in H_2O or D_2O .



Nevertheless, we notice a significant decrease in the reaction rate. This can be explained by the dilution of the reaction medium rather than by the weaker nucleophilicity of the phosphine because the ^{31}P chemical shifts of the phosphines ($\delta = -5.5$ ppm for TPPTS and -5.9 ppm for TPPMS) and of their oxides ($\delta = 33.4$ and 33.9 ppm respectively for TPPTS and TPPMS oxides **8** and **9**) are very close^{9,11}.

- Reaction of water-soluble phosphines with activated olefins in biphasic system.

An aqueous solution of TPPTS also reacts with hydrophobic olefins such as acrylonitrile and acrylic esters. The reaction is carried out in biphasic system without phase transfer reagent by stirring the aqueous phase in the presence of olefin at room temperature. Like before, the nucleophilic addition can be monitored by ^{31}P NMR spectroscopy of the aqueous solution.

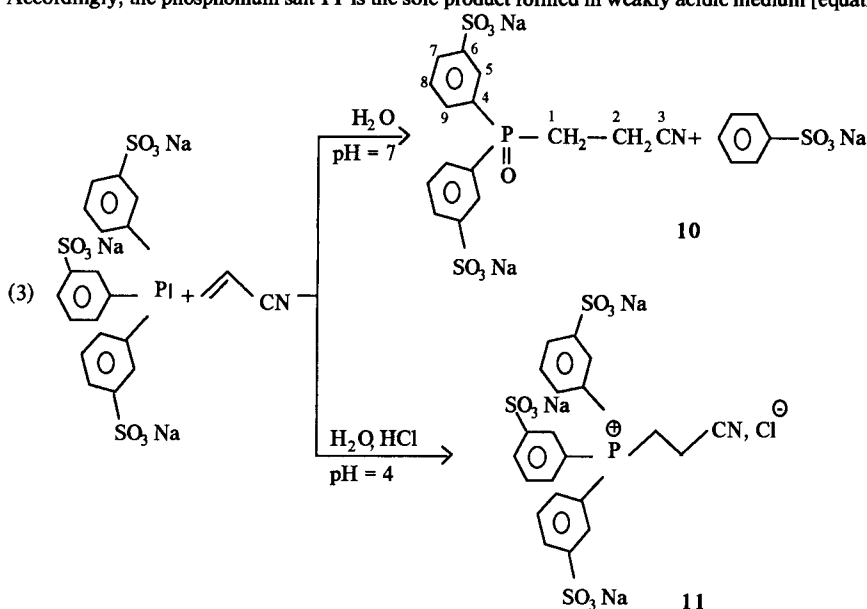
a) Reaction with acrylonitrile

After 10 h of reaction a single resonance corresponding to the phosphine oxide **10** is observed at 38.2 ppm [equation (3)]. The proton decoupled ^{13}C NMR spectrum shows the signals of aromatic nucleus linked to phosphorus and

additionnal peaks corresponding to the free benzenesulfonate ring removed from phosphorus. The chemical shift and coupling constant values for the aromatic carbon C₄ bonded to phosphorus ($\delta_{C_4} = 132.6$ ppm, $1J_{P-C_4} = 106$ Hz) are very close to those obtained for $O = P(PhSO_3Na)_3$ **8** and $O = P(CH_3)(PhSO_3Na)_2$ ($\delta = 132.9$ and 133.6 ppm, $1J_{P-C} = 107$ and 108 Hz respectively). The expected ¹H and ¹³C NMR spectroscopic data are obtained for the aliphatic chain.

The phosphine oxide formation is the result of a nucleophilic attack of the hydroxide anion (generated in situ) on the phosphonium with elimination of a phenylsulfonate group.

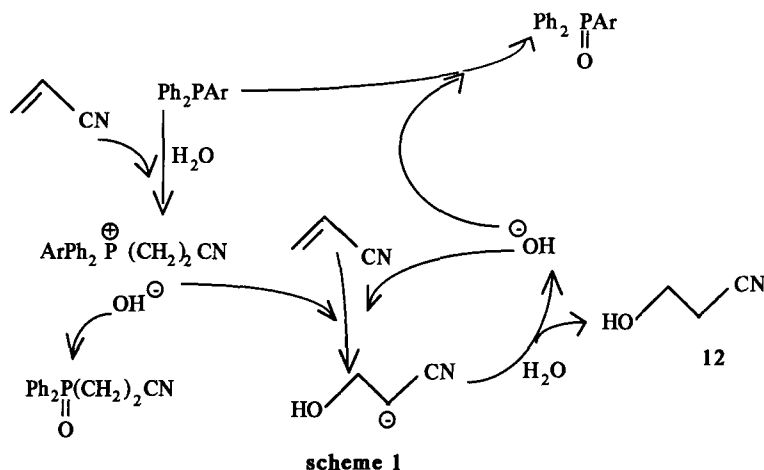
The hydrolysis of phosphonium salts in the presence of base is well known. In water, it occurs instantaneously with neutral olefins which cannot neutralize the hydroxide anion arising from the protonation of the carbanionic intermediate. Accordingly, the phosphonium salt **11** is the sole product formed in weakly acidic medium [equation (3)].



The synthesis of the analogous phosphonium salt $[Ph_3P^+(CH_2)_2CN, X^-]$ requires strongly acidic conditions¹². In protic solvents such as alcohols, the nucleophilic addition of PPh_3 on acrylonitrile is used to initiate its anionic oligomerization or to perform Wittig reactions via the phosphorus ylid¹²⁻¹⁵.

The reaction of the monosulfonated phosphine **5** is also governed by the amphoteric properties of water. The hydration of acrylonitrile occurs readily and is accompanied by a pH increase which induces the oxidation of the phosphine. Further studies show that small amounts of phosphine catalyze the production of hydroxy-3 propionitrile **12**. The nucleophilic addition of the phosphine on acrylonitrile produces hydroxide anions which can either react with the phosphonium or add to the activated double bond. As shown in scheme 1, the hydration of acrylonitrile is catalytic because it produces hydroxide anions. The formation of very small amounts of $Ph_2P(O)(CH_2)_2CN$ at the beginning of the reaction demonstrates that hydroxide anions initiate the hydration process (scheme 1). In organic solvents, tertiary phosphines have also been used to catalyze the Michael reaction between nitroalkanes and olefins¹⁶.

This reaction, carried out in D_2O , affords an efficient pathway to synthesize the monodeuterated hydroxypropionitrile $OH-CH_2-CHD-CN$ **13**. In the absence of TPPMS higher concentrations of sodium hydroxide are required to achieve the same hydration reaction but in these conditions partial hydrolysis of the nitrile is observed.

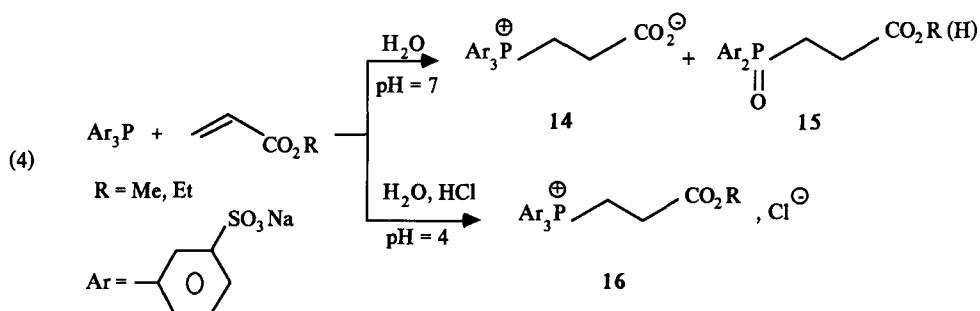


The amphiphilic properties of the monosulfonated phosphine **5** increase the solubility of acrylonitrile in water, and play a main role in the hydration process occurring in the aqueous phase. On the contrary, with the highly hydrophilic trisulfonated phosphine **1**, the phosphorus atom, which can be considered as the lipophilic head of the molecule, probably adds on acrylonitrile at the interface and leads to **10**. Thus, the behaviour of acrylonitrile is strongly dependent on the amphiphilic properties of the phosphine and these types of reactions can only be observed in an amphoteric solvent such as water.

b) Reaction with acrylic esters

In the same way, the reactions of TPPTS **1** with methyl or ethylacrylate produce a mixture of phosphonium salts **14** and phosphines oxides **15** [equation (4)].

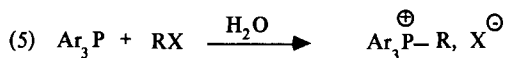
In this case the hydroxide anion resulting from the protonation of the carbanionic intermediate can either react with the phosphonium or hydrolyze the ester grouping. Like before, the phosphonium salts **16** are the unique products obtained in weakly acidic medium [equation (4)].



The monosulfonated phosphine TPPMS **5** reacts similarly and the catalytic hydration of acrylic esters is not observed because the ester group is more sensitive than the nitrile to hydrolysis in weakly basic medium.

- Reaction of TPPTS with alkyl halides in biphasic system.

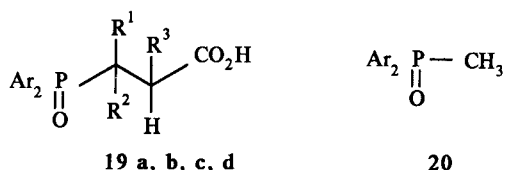
The reactivity of the highly water-soluble TPPTS **1** is not limited to nucleophilic addition on activated olefins and we have also found that phosphonium salts are readily formed by reaction on alkyl halides without added phase transfer reagent or co-solvent. For instance, the phosphonium salts **17**, **18** are obtained when an aqueous solution of **1** and an excess of the corresponding alkyl halide are stirred together overnight at room temperature [equation (5)].



The reaction monitored by ^{31}P NMR spectroscopy of the aqueous phase shows also quantitative transformation of TPPTS into phosphonium salts by reaction with allylbromide, benzylbromide and propargylbromide. In these biphasic systems water plays exclusively the role of solvent; consequently the success of these substitution reactions in biphasic systems confirms that the nucleophilicity of the phosphorus is not affected by the presence of sulfonate groups. This is in agreement with previously described NMR data 4a.

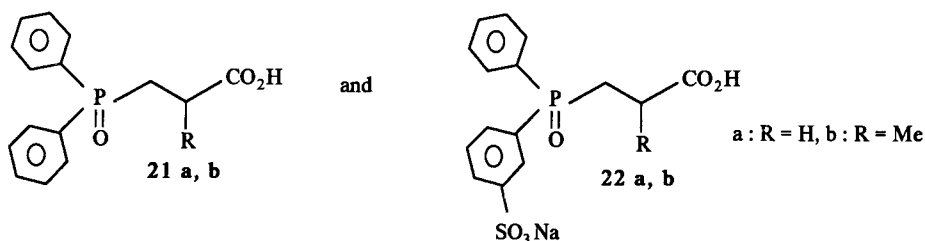
- Reactivity of phosphonium salts in the presence of base.

As shown above, the addition of stoichiometric amounts of sodium hydroxide to aqueous solutions of phosphonium salts instantaneously produces phosphine oxides with elimination of a benzene sulfonate or of the alkyl chain. For instance, the zwitterionic phosphonium salts 3 and the iodide 17 give the expected oxides 19 and 20.

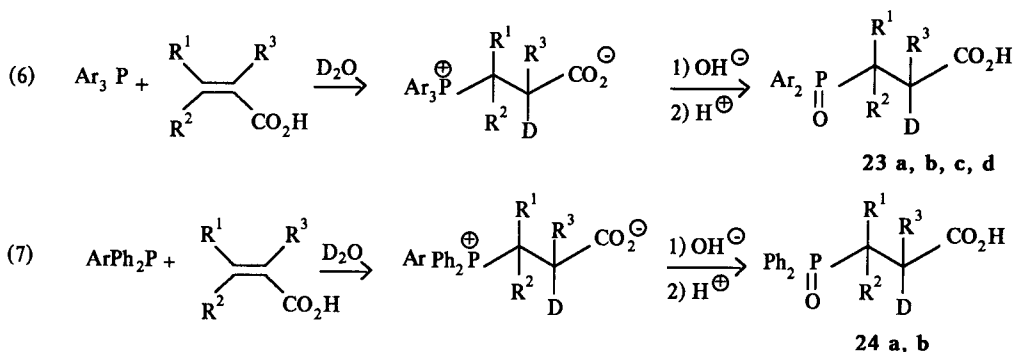


On the contrary, the reaction of OH^- with 18 leads to the triarylphosphine oxide 8 by removing of the alkyl group because an electron withdrawing function is located at the α carbon atom.

In basic media, the monosulfonated phosphonium salts 6 are transformed into the phosphine oxides 21 and 22 arising respectively from the elimination of PhSO_3^- or of a benzene nucleus.



The lack of selectivity of this elimination process is consistent with the weak electron withdrawing effect of the sulfonate anion. These reactions afford a new and efficient synthetic pathway to prepare deuterated water-soluble phosphine oxides from 1 and organosoluble phosphine oxides from 5 [equations (6, 7)].



All these results show that the sequential use of nucleophilic addition of TPPMS on olefins or on alkyl halides followed by elimination of an aromatic nucleus after addition of OH⁻ lead to chiral phosphine oxides water-soluble or not. These aspects are being developed with alkyldiaryl phosphines in order to obtain easily chiral compounds suitable for the synthesis of water-soluble transition metal compounds and to study possible asymmetric deuteration on convenient activated olefins.

CONCLUSION

This first study on the nucleophilic addition of water-soluble phosphines towards organic molecules has shed light on several important aspects of phosphorus chemistry in water. Thus a great variety of new phosphonium salts and phosphine oxides can be obtained at will by controlling the pH of water. Furthermore, one deuterium atom can be specifically introduced at the carbon β to phosphorus. The substrates may not be hydrosoluble and we have shown that nucleophilic additions occur efficiently in biphasic conditions. Further studies are currently being developed to find other applications in organic synthesis.

ACKNOWLEDGEMENT : Valuable suggestions made by a referee are gratefully acknowledged.

EXPERIMENTAL SECTION

TPPTS 1 and TPPMS 5 have been prepared using previously described procedures ^{6a,17}. Unsaturated compounds and alkylhalides are of commercial origin and used without further purification. NMR spectra were respectively recorded on a Varian EM 360 (1H 60 MHz), a Bruker WP 80 MHz¹⁸ (³¹P{1H}, 32.38 MHz, external reference H₃PO₄ 85 %), a Bruker AM 300 MHz¹⁸ [¹³C (75.47 MHz), 1H (300 MHz)], external reference TMS]. Water was distilled before use. The numbering starts with the aliphatic chain and continues on the aromatic ring (see formula 10 for an example). The results of elemental analysis are not significant because the hydration number depends on the purification and drying procedures.

Reaction of TPPTS with α , β unsaturated carboxylic acids

- Preparation of 3a, 3b, 3c

7.10⁻⁴ mole of TPPTS and 7.10⁻⁴ mole of 2a, 2b or 2c are dissolved in 3 ml of water. After removal of water under vacuum, the white product is washed with acetone and dichloromethane. The yields are quantitative. (The phosphonium salts can also be precipitated from the aqueous solution by adding a mixture of ethanol and acetone 80/20 but the yields are lower and the products contain small amounts of ethanol). These hygroscopic phosphonium salts are then dried at 50°C for 2 days under vacuum and stored in an exsiccator.

- Preparation of 3d

420 mg of 1 and 60 mg of 2d are dissolved in 3 ml of water and the mixture is heated at 50°C overnight.

Spectroscopic data

3a ³¹P{1H} NMR, H₂O, δ ppm : 25.50, s. 1H NMR, (D₂O), δ ppm : 2.66, ³J_{H-H} = 8 Hz, ³J_{P-H} = 13 Hz, doublet of triplets, CH₂ ; 3.74, ³J_{H-H} = 8 Hz, ²J_{P-H} = 13 Hz, doublet of triplets, CH₂ ; 7.72 - 8.30, multiplet, Ar-H. 1H NMR with irradiation of phosphorus nucleus, δ ppm : 2.66, ³J_{H-H} = 8 Hz, t, CH₂ ; 3.74, ³J_{H-H} = 8 Hz, t, CH₂ ; 7.70 - 8.30, multiplet, Ar-H. ¹³C NMR, D₂O, [(i) with 1H decoupling, (ii) without decoupling], δ ppm : 21.60, ¹J_{P-C} = 52 Hz, ¹J_{C-H} = 135 Hz [C(1), (i) d, (ii) dt] ; 31.96, ²J_{P-C} = 3 Hz, ¹J_{C-H} = 133 Hz [C(2), (i) d, (ii) dt] ; 121.26, ¹J_{P-C} = 87 Hz, ²J_{C-H} = 8 Hz [C(4), (i) d, (ii) dd] ; 133.13, ²J_{P-C} = 14 Hz, ¹J_{C-H} = 162 Hz, ²J_{C-H} = 8 Hz [C(9), (i) d, (ii) dq] ; 134.18, ²J_{P-C} = 13 Hz, ¹J_{C-H} = 169 Hz, ²J_{C-H} = 8 Hz, [C(5), (i) d, (ii) dd] ; 135.20, ¹J_{C-H} = 161 Hz, ²J_{C-H} = 8 Hz, [C(7), (i) s, (ii) dd] ; 139.03, ³J_{P-C} = 10 Hz, ¹J_{C-H} = 167 Hz, ²J_{C-H} = 8 Hz [C(8), (i) d, (ii) dq] ; 147.73, ³J_{P-C} = 12 Hz, ²J_{C-H} = 8 Hz [C(6), (i)d, (ii)dt] ; 179.77, ³J_{P-C} = 13 Hz [C(3), (i)d, (ii)d].

3b ³¹P{1H} NMR, H₂O, δ ppm : 24.80, s. 1H NMR, (D₂O), δ ppm : 1.29, ³J_{H-H} = 7 Hz, ⁴J_{P-H} = 1 Hz, dd, CH₃ ; 2.78, broad multiplet, CH ; 3.56, ³J_{H-H} = 6 Hz, ¹J_{H-H} = 16 Hz, ²J_{P-H} = 13 Hz, septuplet, CH₂, H_a ; 3.88, ³J_{H-H} = 9 Hz, ¹J_{H-H} = 16 Hz, ²J_{P-H} = 13 Hz, octuplet, CH₂, H_b ; 7.31-8.22, multiplet, Ar-H. 1H NMR with irradiation of the phosphorus nucleus : 1.29, ³J_{H-H} = 7 Hz, d, CH₃ ; 2.78, broad multiplet, CH ; 3.56, ³J_{H-H} = 6 Hz, ¹J_{H-H} = 16 Hz, dd, CH₂, H_a ; 3.88, ³J_{H-H} = 9 Hz, ¹J_{H-H} = 16 Hz, q, CH₂, H_b ; 7.30-8.21, multiplet, Ar-H.

3c ³¹P{1H} NMR, H₂O, δ ppm : 24.37, s. 1H NMR, (D₂O), δ ppm : 2.83, ³J_{H-H} = 6 Hz, d, CH₂ ; 3.23, ³J_{H-H} = 7 Hz, ³J_{P-H} = 13 Hz, broad octuplet, CH ; 3.71, ³J_{H-H} = 6 Hz, ¹J_{H-H} = 16 Hz, ²J_{P-H} = 12 Hz, broad septuplet, CH₂, H_a ; 3.95, ³J_{H-H} = 10 Hz, ¹J_{H-H} = 16 Hz, ²J_{P-H} = 12 Hz, broad octuplet, CH₂, H_b ; 7.82-8.38, multiplet, Ar-H.

3d ^{31}P { ^1H } NMR, H_2O , δ ppm : 30.85, s. ^1H NMR, (D_2O), δ ppm : 1.45, $^3\text{J}_{\text{H-H}} = 7$ Hz, $^3\text{J}_{\text{P-H}} = 19$ Hz, dd, CH_3 ; 2.92, $^3\text{J}_{\text{P-H}} = 14$ Hz, broad multiplet, CH_2 ; 7.30-8.35, multiplet Ar-H.

- Preparation of **4a**, **4b**, **4c**, **4d**

4a, **4b**, **4c** and **4d** are prepared in D_2O following the experimental procedure described above for **3a**, **3b**, **3c**, **3d**.

Spectroscopic data :

4a ^{31}P { ^1H } NMR, H_2O , δ ppm : 25.50, s. ^1H NMR, (D_2O), δ ppm : 2.61, $^3\text{J}_{\text{H-H}} = 7$ Hz, $^3\text{J}_{\text{P-H}} = 13$ Hz, broad sextuplet, CH ; 3.65, $^3\text{J}_{\text{H-H}} = 7$ Hz, $^2\text{J}_{\text{P-H}} = 13$ Hz, q broad, CH_2 ; 7.65-8.35, multiplet, Ar-H. ^{13}C NMR, D_2O , [(i) with ^1H decoupling, (ii) without decoupling] δ ppm aliphatic carbon nucleus (the chemical shifts and coupling constants of aromatic carbon nuclei are not modified by the incorporation of deuterium) : 21.62, $^1\text{J}_{\text{P-C}} = 53$ Hz, $^1\text{J}_{\text{C-H}} = 133$ Hz [C(1), (i) d, (ii) dt] ; 31.25, $^2\text{J}_{\text{P-C}} = 3$ Hz, $^1\text{J}_{\text{C-D}} = 17$ Hz ; $^1\text{J}_{\text{C-H}} = 133$ Hz [C(2), (i) dt, (ii) ddt].

4b ^{31}P { ^1H } NMR, H_2O , δ ppm : 24.85, s. ^1H NMR, (D_2O), δ ppm : 1.39, $^4\text{J}_{\text{P-H}} = 1$ Hz, d, CH_3 ; 3.67, $^1\text{J}_{\text{H-H}} = 17$ Hz, $^2\text{J}_{\text{P-H}} = 13$ Hz, q, CH_2 , H_a ; 3.89, $^1\text{J}_{\text{H-H}} = 17$ Hz, $^2\text{J}_{\text{P-H}} = 13$ Hz, q, CH_2 , H_b ; 7.77-8.35, multiplet, Ar-H.

4c ^{31}P { ^1H } NMR, H_2O , δ ppm : 24.41, s. ^1H NMR, (D_2O), δ ppm : 2.81, s, CH_2 ; 3.79, $^1\text{J}_{\text{H-H}} = 16$ Hz, $^2\text{J}_{\text{P-H}} = 13$ Hz, q, CH_2 , H_a ; 4.02, $^1\text{J}_{\text{H-H}} = 16$ Hz, $^2\text{J}_{\text{P-H}} = 13$ Hz, q, CH_2 , H_b ; 7.87-8.39, multiplet Ar-H.

4d ^{31}P { ^1H } NMR, H_2O , δ ppm : 30.81, s. ^1H NMR, (D_2O), δ ppm : 1.40, $^3\text{J}_{\text{H-H}} = 7$ Hz, $^3\text{J}_{\text{P-H}} = 19$ Hz, dd, CH_3 ; 2.85, $^3\text{J}_{\text{P-H}} = 14$ Hz, d broad, C-H ; 7.25-8.35, multiplet, Ar-H.

Reaction of TPPMS with α , β unsaturated carboxylic acids

- Preparation of **6a** (**7a**), **6b** (**7b**).

7.10 $\cdot$ 4 mole of TPPMS **5** and 7.10 $\cdot$ 4 mole of **3a** or **3b** are dissolved in 10 ml of water (or D_2O). After removal of water under vacuum, the crude product is washed with acetone and ethanol. The yields are quantitative. The phosphonium salts are then dried at 50°C for 2 days under vacuum and stored in an exsiccator.

Spectroscopic data (a)

6a (**7a**) ^{31}P { ^1H } NMR, H_2O , δ ppm : 24.03, s. ^1H NMR, (D_2O), δ ppm : 2.55, $^3\text{J}_{\text{H-H}} = 7$ Hz, $^3\text{J}_{\text{P-H}} = 13$ Hz, sextuplet, CH_2 (CHD) ; 3.61, $^3\text{J}_{\text{H-H}} = 7$ Hz, $^2\text{J}_{\text{P-H}} = 13$ Hz, sextuplet (q), CH_2 ; 7.30-8.37, multiplet, Ar-H.

6a (**7b**) ^{31}P { ^1H } NMR, H_2O , δ ppm : 23.30, s. ^1H NMR, (D_2O), δ ppm : 1.22, $^3\text{J}_{\text{H-H}} = 7$ Hz, d(s), CH_3 ; 2.69, broad multiplet (no signal) ; C-H ; 3.25, $^3\text{J}_{\text{H-H}} = 16$ Hz, $^1\text{J}_{\text{H-H}} = 6$ Hz, $^1\text{J}_{\text{P-H}} = 12$ Hz, sextuplet (q), CH_2 : H_a ; 3.69, $^3\text{J}_{\text{H-H}} = 6$ Hz, $^1\text{J}_{\text{H-H}} = 16$ Hz, $^2\text{J}_{\text{P-H}} = 12$ Hz, sextuplet (q), CH_2 : H_b ; 7.40-8.15, multiplet, Ar-H.

Preparation of the phosphine oxides OTPPTS **8 and OTPPMS **9**.**

8 and **9** are prepared respectively from **1** and **5** by using H_2O_2 as oxidant. 600 mg of **1** or **5** are dissolved in 90 ml of hydrogen peroxide (10 % in water) and the solution is heated to reflux overnight. After removal of water the crude product is dried under vacuum for 24 h. The yields are quantitative.

^{31}P { ^1H } NMR, δ ppm : 34.3 for **8** ; 34.8 for **9**.

IR (KBr) : $\nu_{\text{S=O}}$ (cm $^{-1}$) 1050 (strong) ; 1200 (strong, broad).

^{13}C NMR, D_2O , [(i) with ^1H decoupling, (ii) without decoupling], δ ppm, **8** : 131.49, $^2\text{J}_{\text{P-C}} = 11$ Hz, $^1\text{J}_{\text{C-H}} = 167$ Hz, $^2\text{J}_{\text{C-H}} = 8$ Hz [C(2) ; (i)d ; (ii)dt] ; 132.93, $^1\text{J}_{\text{P-C}} = 107$ Hz, $^2\text{J}_{\text{C-H}} = 6$ Hz [C(1) ; (i)d ; (ii)dt] ; 133.12, $^2\text{J}_{\text{P-C}} = 11$ Hz ; $^1\text{J}_{\text{C-H}} = 166$ Hz ; $^2\text{J}_{\text{C-H}} = 7$ Hz [C(6) ; (i)d ; (ii)dt] ; 133.22, $^1\text{J}_{\text{C-H}} = 167$ Hz, $^2\text{J}_{\text{C-H}} = 9$ Hz [C(4) ; (i)s ; (ii)dd] ; 137.55, $^3\text{J}_{\text{P-C}} = 11$ Hz, $^1\text{J}_{\text{C-H}} = 166$ Hz, $^2\text{J}_{\text{C-H}} = 8$ Hz [C(5) ; (i)d ; (ii)dq] ; 146.66, $^3\text{J}_{\text{P-C}} = 7$ Hz, $^2\text{J}_{\text{C-H}} = 6$ Hz [C(3) ; (i)d ; (ii)q].

Remark : **8** can more easily be synthesized by sulfonation of PPh_3 in oleum (65 % in sulfuric acid) at room temperature for 24 h.

Reaction of TPPTS **1 and TPPMS **5** on activated olefins in biphasic system.**

- Reaction of **1** with acrylonitrile in neutral medium.

6 ml (9.2 10 $\cdot$ 2 mole) of acrylonitrile are added to an aqueous solution of **1** (1.14 g ; 1.9 10 $\cdot$ 3 mole in 4 ml of water). The two phase mixture is stirred magnetically overnight at room temperature. The mixture is then decanted and the aqueous layer washed with dichloromethane. The ^{31}P NMR spectrum shows that all the phosphine has been transformed. 2 ml of the

(a) in brackets indications for the deuterated compounds **7a** and **7b**.

aqueous solution is used to perform the NMR spectroscopic studies. **10** is precipitated from the remaining 2 ml of solution by addition of a mixture of ethanol and acetone, filtrated washed with dichloromethane and dried under vacuum.

Spectroscopic data

10 : IR (KBr) ν cm⁻¹ : 2240 (weak), C $\equiv$ N ; 1050 (strong), 1200 (strong, broad) S = O.

³¹P {¹H} NMR (H₂O) δ ppm : 38.25 (s).

¹H NMR (H₂O) δ ppm [(i) without decoupling, (ii) with phosphorus decoupling] : 2.78, ³J_{H-H} = 7 Hz, ²J_{P-H} = 13 Hz [(i) sextuplet (ii) t], CH₂ ; 2.90, ³J_{H-H} = 7 Hz, ³J_{P-H} = 11 Hz [(i) sextuplet (ii) t], CH₂ ; 7.62-8.25 (multiplet), ArH.

¹³C NMR (D₂O) δ ppm [(i) with ¹H decoupling, (ii) without decoupling] : 26.68, ¹J_{P-C} = 73 Hz, ¹J_{C-H} = 134 Hz, [C(1), (i) d (ii) dt] ; 12.61, ²J_{P-C} = 3 Hz, ¹J_{C-H} = 139 Hz [C(2), (i) d (ii) dt] ; 122.36, ³J_{P-C} = 3 Hz [C(3), (i) (ii) d] ; 132.68, ¹J_{P-C} = 106 Hz, ²J_{C-H} = 6 Hz [C(4), (i) d ; (ii) dd] ; 134.72, ²J_{P-C} = 14 Hz, ¹J_{C-H} = 167 Hz, ²J_{C-H} = 7 Hz [C(5), (i) d ; (ii) dd] ; 147.07, ³J_{P-C} = 12 Hz ; ²J_{C-H} = 8 Hz [C(6), (i) d ; (ii) dt] ; 134.32, ¹J_{C-H} = 162 Hz, ²J_{C-H} = 7 Hz [C(7) (i) s, (ii) dt] ; 138.6, ³J_{P-C} = 10 Hz, ¹J_{C-H} = 166 Hz, ²J_{C-H} = 7 Hz [C(8) (i) d ; (ii) dq] ; 133.25, ²J_{P-C} = 13 Hz, ¹J_{C-H} = 163 Hz, ²J_{C-H} = 8 Hz [C(9) (i) d, (ii) dq].

The ¹³C NMR study of the reaction mixture (H₂O/D₂O) shows, in addition to the spectrum of **10** described above, the characteristic signals of PhSO₃Na.

- Reaction of 1 with acrylonitrile in acidic medium.

6 ml (9.2 10⁻² mole) of acrylonitrile are added to an aqueous acidic solution of **1** (1.14 g, 1.9 10⁻³ mole in 4 ml of dilute hydrochloric acid, pH = 4). The two phases mixture is stirred overnight at room temperature and then decanted. The separated aqueous layer is carefully neutralized with sodium bicarbonate and washed with dichloromethane. The ³¹P NMR spectrum shows that all the phosphine has been transformed. Attempts to eliminate the remaining sodium chloride by repeated precipitations has been unsuccessful ; the spectroscopic data were therefore obtained without further purification after removal of water under vacuum.

Spectroscopic data

11 : IR (KBr) ν cm⁻¹ : 2240 (weak) C $\equiv$ N ; 1050 (strong), 1200 (strong, broad) S = O.

³¹P {¹H} NMR (H₂O) δ ppm : 24.07 (s).

¹H NMR (D₂O) δ ppm : 1.90, ³J_{H-H} = 7 Hz, ²J_{P-H} = 13 Hz, sextuplet, CH₂ ; 2.84, ³J_{H-H} = 7 Hz, ³J_{P-H} = 12 Hz, sextuplet, CH₂ ; 7.63-8.32, multiplet, Ar-H.

- Reaction of 5 with acrylonitrile in neutral medium.

8 ml (1.2 10⁻¹ mole) of acrylonitrile are added to an aqueous solution of **5** (1g ; 2.5 10⁻³ mole in 20 ml of H₂O or D₂O). After stirring overnight at room temperature, the reaction mixture becomes homogeneous. The resulting basic solution (pH = 9-10) is neutralized with diluted hydrochloric acid. The organic products are extrated with dichloromethane and the organic layer dried with magnesium sulfate is then concentrated under vacuum. **12** (**13**) is separated by chromatography on a silica gel column (eluant : methanol) after previous elution of Ph₂P(O)(CH₂)₂CN and excess of acrylonitrile with chloroform. The removal of methanol under vacuum yields 3.2 g (4.5 10⁻² mole) of **12** (**13**).

Spectroscopic data

12 (**13**) : IR (liquid) ν cm⁻¹ : 2230 (weak), C $\equiv$ N ; 3300 (strong, broad) O-H.

¹H NMR (CDCl₃) δ ppm : 3.82, ³J_{H-H} = 7 Hz, t(d), CH₂ ; 3.55, s, OH ; 2.60, ³J_{H-H} = 7 Hz, t(t), CH₂ (CHD).

- Reaction of 1 with acrylic esters in neutral medium.

Ethylacrylate (1 ml) is added to an aqueous solution of TPPTS (7.10⁻⁴ mole, 423 mg in 5 ml of water) and the two phases mixture is stirred overnight at room temperature. The aqueous layer is washed with ether. The spectroscopic studies were performed directly on this aqueous solution.

Spectroscopic studies (14 + 15)

³¹P {¹H} NMR (H₂O) δ ppm : 26.11, s, 72 %, **14** ; 38.72, s, 17 %, **15**, R = Et ; 40.08, s, 11 %, **15**, R = H.

¹H NMR (H₂O) δ ppm : 1.15, ³J_{H-H} = 7 Hz, t, CH₃ ; 1.20, ³J_{H-H} = 7 Hz, t, CH₃ ; 2.79, ³J_{H-H} = 7 Hz, ³J_{P-H} = 12 Hz, sextuplet, CH₂, **14** ; 3.03, ³J_{H-H} = 7 Hz, ²J_{P-H} # ³J_{P-H} # 13 Hz, multiplet, CH₂, **15**, R = H or Et ; 3.73, ³J_{H-H} = 7 Hz, q, CH₂ (CO₂Et) ; 3.87, ³J_{H-H} = 7 Hz, ²J_{P-H} = 12 Hz, sextuplet, CH₂, **14** ; 4.13, ³J_{H-H} = 7 Hz, q, CH₂ (EtOH) ; 7.70-8.42, multiplet, ArH, **14** and **15**.

- Reaction of 1 with acrylic esters in acidic medium.

Ethylacrylate (1 ml) is added to a solution of TPPTS (7.10⁻⁴ mole, 423 mg) in 5 ml of diluted hydrochloric acid (pH = 4) and the two phases mixture is stirred overnight at room temperature. The aqueous layer is washed with ether and then concentrated to dryness affording **16**. The ³¹P NMR spectrum shows that the phosphine has been quantitatively transformed.

Spectroscopic data

16 : $^{31}\text{P}\{^1\text{H}\}$ NMR (H_2O) δ ppm : 24.75, s.

^1H NMR (D_2O) δ ppm : 1.10, $^3\text{J}_{\text{H-H}} = 7$ Hz, t, CH_3 ; 2.73, $^3\text{J}_{\text{H-H}} = 7$ Hz, $^3\text{J}_{\text{P-H}} = 12$ Hz, sextuplet, CH_2 ; 3.75, $^3\text{J}_{\text{H-H}} = 7$ Hz, $^2\text{J}_{\text{P-H}} = 13$ Hz, sextuplet, CH_2 ; 3.88; $^3\text{J}_{\text{H-H}} = 7$ Hz, q, CH_2 ; 7.50-8.35, multiplet, Ar-H.

- Reaction of 1 with alkyl halides in biphasic system.

Synthesis of 17 and 18

1 ml of methyl iodide or methylbromacetate is added to an aqueous solution of 1 (200 mg; $3.3 \cdot 10^{-4}$ mole in 2 ml of water). The mixture is stirred overnight at room temperature and then decanted. The aqueous layer is washed with dichloromethane. The ^{31}P NMR spectra demonstrate that all the phosphine has been transformed. 17 and 18 are isolated after removal of the water under vacuum.

Spectroscopic data

17 : $^{31}\text{P}\{^1\text{H}\}$ NMR (H_2O) δ ppm : 23.24, s.

^1H NMR (D_2O) δ ppm : 3.05, $^2\text{J}_{\text{P-H}} = 14$ Hz, d, CH_3 ; 7.60-8.30, multiplet, Ar-H.

18 : $^{31}\text{P}\{^1\text{H}\}$ NMR (H_2O) δ ppm : 21.43, s.

^1H NMR (D_2O) δ ppm : 3.50, s, CH_3 ; 7.63-8.42, multiplet, Ar-H. The signal of the CH_2 protons is masked by the HOD signal.

^{13}C NMR (D_2O) δ ppm [(i) with ^1H decoupling; (ii) without decoupling] : 33.61, $^1\text{J}_{\text{P-C}} = 56$ Hz, $^1\text{J}_{\text{C-H}} = 136$ Hz [C(1); (i) d, (ii) dt]; 168.52, $^2\text{J}_{\text{P-C}} = 4$ Hz [C(2) (i) d, (ii) d]; 56.53, $^1\text{J}_{\text{C-H}} = 149$ Hz [C(3) (i) s; (ii) q]; 120.41, $^1\text{J}_{\text{P-C}} = 90$ Hz, $^2\text{J}_{\text{C-H}} = 8$ Hz [C(4) (i) d, (ii) dd]; 134.35, $^2\text{J}_{\text{P-C}} = 13$ Hz, $^1\text{J}_{\text{C-H}} = 169$ Hz [C(5) (i) d, (ii) dd]; 147.93, $^3\text{J}_{\text{P-C}} = 13$ Hz, $^2\text{J}_{\text{C-H}} = 8$ Hz [C(6) (i) d, (ii) q]; 135.62, $^1\text{J}_{\text{C-H}} = 170$ Hz, $^2\text{J}_{\text{C-H}} = 7$ Hz [C(7) (i) s, (ii) dd]; 133.44, $^2\text{J}_{\text{P-C}} = 12$ Hz, $^1\text{J}_{\text{C-H}} = 168$ Hz, $^2\text{J}_{\text{C-H}} = 6$ Hz [C(8) (i) d, (ii) dq]; 139.39, $^2\text{J}_{\text{P-C}} = 11$ Hz, $^1\text{J}_{\text{C-H}} = 168$ Hz, $^2\text{J}_{\text{C-H}} = 8$ Hz [C(9) (i) d, (ii) dq].

- Reaction with other alkyl halides

The ^{31}P NMR spectra of aqueous solutions after reaction with PhCH_2Br , $\text{CH}_2=\text{CH-CH}_2\text{Br}$, $\text{HC} \equiv \text{C-CH}_2\text{Br}$ show also a quantitative conversion of 1 leading to the corresponding phosphonium salts. Their chemical shifts (ppm) are respectively : 23.31 ; 25.19 ; 22.26.

- Reactivity of trisulfonated phosphonium salts in the presence of base.

Stoichiometric amounts of sodium hydroxide are added to an aqueous solution of phosphonium salt. The starting colourless solution becomes instantaneously slight yellow. The reaction mixture is allowed to stand at room temperature for 15 mn. The pH is then measured and adjusted to 3-4 by adding diluted hydrochloric acid. The ^{31}P NMR spectra show in all cases a quantitative transformation of the phosphonium salts. The crude phosphine oxides are isolated after removal of water under vacuum and recrystallized in methanol.

Spectroscopic data

19a, b, c, d : $^{31}\text{P}\{^1\text{H}\}$ NMR (H_2O) δ ppm : 40.50, s, 19a ; 39.10, s, 19b ; 37.94, s, 19c ; 43.89, s, 19d.

^1H NMR, (D_2O), δ ppm, 19a : 2.60, $^3\text{J}_{\text{H-H}} = 7$ Hz, $^3\text{J}_{\text{P-H}} = 13$ Hz, sextuplet, CH_2 ; 2.92, $^3\text{J}_{\text{H-H}} = 7$ Hz, $^2\text{J}_{\text{P-H}} = 12$ Hz, sextuplet, CH_2 ; 7.57-8.45, multiplet, Ar-H. 19b : 1.37, $^3\text{J}_{\text{H-H}} = 7$ Hz, d, CH_3 ; 2.98, $^3\text{J}_{\text{H-H}} = 7$ Hz, $^2\text{J}_{\text{H-H}} = 16$ Hz, $^2\text{J}_{\text{P-H}} = 13$ Hz, septuplet, CH_2 (H_a); 3.04, $^3\text{J}_{\text{H-H}} = 8$ Hz, $^2\text{J}_{\text{H-H}} = 16$ Hz, $^2\text{J}_{\text{P-H}} = 13$ Hz, septuplet, CH_2 (H_b); 7.59-8.45, multiplet, Ar-H. 19c : 2.95, $^3\text{J}_{\text{H-H}} = 7$ Hz, d broad, CH_2 ; 3.20, multiplet broad, CH_2 ; 7.58-8.44, multiplet, Ar-H.

20 : $^{31}\text{P}\{^1\text{H}\}$ NMR, (H_2O), δ ppm : 38.69, s.

^1H NMR (D_2O), δ ppm : 2.08, $^2\text{J}_{\text{P-H}} = 13$ Hz, d, CH_3 ; 7.40-8.35, multiplet, Ar-H.

^{13}C NMR (D_2O) [(i) with ^1H decoupling, (ii) without decoupling] δ ppm : 17.27, $^1\text{J}_{\text{P-C}} = 75$ Hz, $^1\text{J}_{\text{C-H}} = 130$ Hz [C(1), (i) d, (ii) dq]; 128.12, $^2\text{J}_{\text{P-C}} = 12$ Hz, $^1\text{J}_{\text{C-H}} = 163$ Hz, $^2\text{J}_{\text{C-H}} = 8$ Hz [C(7), (i) d, (ii) dt]; 132.57, $^1\text{J}_{\text{C-H}} = 166$ Hz, $^2\text{J}_{\text{C-H}} = 8$ Hz [C(5), (i) s, (ii) dd]; 133.55, $^1\text{J}_{\text{P-C}} = 106$ Hz, $^2\text{J}_{\text{C-H}} = 8$ Hz [C(2), (i) d, (ii) dd]; 134.25, $^3\text{J}_{\text{P-C}} = 12$ Hz, $^1\text{J}_{\text{C-H}} = 162$ Hz [C(6), (i) d, (ii) dq]; 136.10, $^2\text{J}_{\text{P-C}} = 10$ Hz, $^1\text{J}_{\text{C-H}} = 165$ Hz [C(3), (i) d, (ii) dd]; 146.28, $^3\text{J}_{\text{P-C}} = 11$ Hz, $^2\text{J}_{\text{C-H}} = 8$ Hz [C(4), (i) d, (ii) dt].

Reactivity of monosulfonated phosphonium salts in the presence of base.

Stoichiometric amounts of sodium hydroxide are added to a concentrated aqueous solution of phosphonium salt. The reaction mixture is allowed to stand at room temperature for 15 mn while it turns slight yellow. The pH is then adjusted to 1-2 by addition of concentrated hydrochloric acid. The resulting solution becomes turbid and is allowed to stand overnight at $+5^\circ\text{C}$ to complete the precipitation. The white precipitate of 21 is filtrated and 21 is recrystallized in acetone. The filtrate containing 22 is concentrated under vacuum and the resulting crude material is dissolved in methanol. 22 which precipitates upon dropwise addition of ethanol is then filtrated and dried at 50°C in vacuo for 48 h. Yields : 21 : 65 %, 22 : 30 %. 21a : mp = 138°C (litt. : 138°C); 21b : mp = 136°C (litt. 136°C).

Spectroscopic data

21 : $^{31}\text{P}\{^1\text{H}\}$ NMR (CHCl_3) δ ppm : 36.33, s, **21a** ; 35.95, s, **21b**

^1H NMR, δ ppm, **21a** (CDCl_3) : 2.65, multiplet, CH_2 ; 7.27-7.75, multiplet Ar-H ; 10.49, s broad, CO_2H . **21b** (CD_2Cl_2) : 1.22, $^3\text{J}_{\text{H-H}} = 7$ Hz, d, CH_3 ; 2.39, multiplet, CH ; 2.90, multiplet, CH_2 ; 7.26-8.16, multiplet, Ar-H ; 12.26, s, CO_2H .

^{13}C NMR [CDCl_3 , (i) with ^1H decoupling, (ii) without decoupling] δ ppm, **21a** : 24.71, $^1\text{J}_{\text{P-C}} = 73$ Hz, $^1\text{J}_{\text{C-H}} = 130$ Hz [C(1), (i) d, (ii) dt] ; 26.53, $^2\text{J}_{\text{P-C}} = 4$ Hz, $^1\text{J}_{\text{C-H}} = 130$ Hz, [C(2), (i) d, (ii) dt] ; 128.89, $^2\text{J}_{\text{P-C}} = 12$ Hz, $^1\text{J}_{\text{C-H}} = 163$ Hz, $^2\text{J}_{\text{C-H}} = 7$ Hz [C(5), (i) d, (ii) dt] ; 130.83, $^3\text{J}_{\text{P-C}} = 10$ Hz, $^1\text{J}_{\text{C-H}} = 166$ Hz, $^2\text{J}_{\text{C-H}} = 7$ Hz [C(6), (i) d, (ii) dq] ; 131.14, $^1\text{J}_{\text{P-C}} = 101$ Hz, $^2\text{J}_{\text{C-H}} = 7$ Hz [C(4), (i) d, (ii) dt] ; 132.27, $^4\text{J}_{\text{P-C}} = 2$ Hz, $^1\text{J}_{\text{C-H}} = 160$ Hz, $^2\text{J}_{\text{C-H}} = 7$ Hz [C(7), (i) d, (ii) dq] ; 174.09, $^3\text{J}_{\text{P-C}} = 15$ Hz, [C(3), (i) d, (ii) d].

22 : IR ν (cm^{-1}) : 1050 (strong), 1200 (strong, broad) S = O ; 1715 (strong broad), C = O ; 3600 (strong broad), OH.

$^{31}\text{P}\{^1\text{H}\}$ NMR, (H_2O), δ ppm : 39.82, s, **22a** ; 39.23, s, **22b**.

^1H NMR, (D_2O), δ ppm, **22a** : 2.57, broad multiplet, CH_2 ; 7.40-8.15, multiplet, Ar-H. **22b** : 1.38, $^3\text{J}_{\text{H-H}} = 7$ Hz, $^4\text{J}_{\text{P-H}} = 1$ Hz, dd, CH_3 ; 2.95, broad multiplet, CH_2 ; 7.57-8.10, multiplet, Ar-H.

Synthesis of deuterated phosphine oxides 23, 24

They are obtained by the experimental procedure described above using D_2O instead of H_2O .

Spectroscopic data

23 : $^{31}\text{P}\{^1\text{H}\}$ NMR, (H_2O), δ ppm : 40.50, s, **23a** ; 39.10, s, **23b** ; 37.94, s, **23c** ; 43.89, s, **23d**.

^1H NMR, (D_2O), δ ppm, **23a** : 2.55, $^3\text{J}_{\text{H-H}} = 7$ Hz, $^3\text{J}_{\text{P-H}} = 13$ Hz sextuplet, CH ; 2.90, $^3\text{J}_{\text{H-H}} = 7$ Hz, $^2\text{J}_{\text{P-H}} = 12$ Hz, dd, CH_2 ; 7.50-8.45, multiplet, Ar-H. **23b** : 1.25, s, CH_3 ; 3.00, $^2\text{J}_{\text{H-H}} = 16$ Hz, $^2\text{J}_{\text{P-H}} = 13$ Hz, dd, CH_2 (H_a) ; 3.11, $^2\text{J}_{\text{H-H}} = 16$ Hz, $^2\text{J}_{\text{P-H}} = 13$ Hz, dd, CH_2 (H_b) ; 7.45-8.40, multiplet, Ar-H. **23c** : 2.70 ; s, CH_2 ; 3.10, $^2\text{J}_{\text{H-H}} = 15$ Hz, $^2\text{J}_{\text{P-H}} = 13$ Hz, d, CH_2 (H_a) ; 3.21, $^2\text{J}_{\text{H-H}} = 15$ Hz, $^2\text{J}_{\text{P-H}} = 15$ Hz, $^2\text{J}_{\text{P-H}} = 13$ Hz, d, CH_2 (H_b) ; 7.50-8.45, multiplet, Ar-H.

24 : $^{31}\text{P}\{^1\text{H}\}$ NMR, (CDCl_3), δ ppm : 36.30, s, **24a** ; 35.95, s, **24b**.

^1H NMR, (CDCl_3), δ ppm, **24a** : 2.62, multiplet, CH_2 and CH ; 7.31-7.75, multiplet, Ar-H ; 10.50, s broad, CO_2H . **24b** : 1.20, s, CH_3 ; 2.85, multiplet, CH_2 ; 7.26-8.16, multiplet, Ar-H ; 12.10, s, CO_2H .

^{13}C NMR, [CDCl_3 , (i) with ^1H decoupling, (ii) without decoupling], δ ppm, **24a** : 24.62, $^1\text{J}_{\text{P-C}} = 73$ Hz, $^1\text{J}_{\text{C-H}} = 130$ Hz, [C(1), (i) d, (ii) dt] ; 26.05, $^2\text{J}_{\text{P-C}} = 4$ Hz, $^1\text{J}_{\text{C-H}} = 130$ Hz, $^1\text{J}_{\text{C-D}} = 19$ Hz, [C(2), (i) dt, (ii) ddt] ; 128.86, $^2\text{J}_{\text{P-C}} = 12$ Hz, $^1\text{J}_{\text{C-H}} = 163$ Hz ; $^2\text{J}_{\text{C-H}} = 7$ Hz [C(5), (i) d, (ii) dt] ; 130.80, $^3\text{J}_{\text{P-C}} = 10$ Hz, $^1\text{J}_{\text{C-H}} = 163$ Hz, $^2\text{J}_{\text{C-H}} = 7$ Hz [C(6), (i) d, (ii) dq] ; 131.07, $^1\text{J}_{\text{P-C}} = 101$ Hz, $^2\text{J}_{\text{C-H}} = 7$ Hz [C(4), (i) d, (ii) dt] ; 132.25, $^4\text{J}_{\text{P-C}} = 2$ Hz, $^1\text{J}_{\text{C-H}} = 160$ Hz, $^2\text{J}_{\text{C-H}} = 7$ Hz [C(7), (i) d, (ii) dq] ; 174.13, $^3\text{J}_{\text{P-C}} = 16$ Hz, [C(3), (i) d, (ii) d].

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