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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.

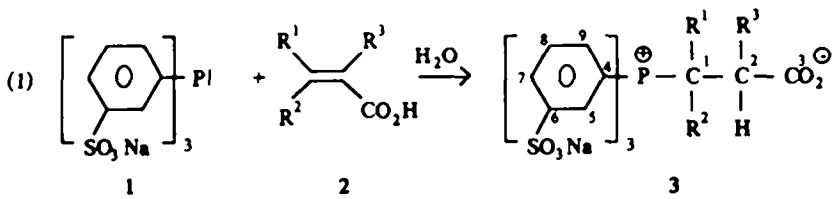
Organophosphorus chemistry has received considerable attention and phosphorus derivates are now commonly used in biology, in synthetic organic chemistry and in industrial processes. For instance, the versatile tervalent phosphorus compounds have been widely studied in organic solvents for their aptitudes to stabilize reactive intermediates and to coordinate transition metals. Recently, some emphasis has been put on water-soluble and hydrophilic phosphines, particularly in the field of organometallic chemistry, because such compounds are ligands which can accord water-solubility to coordination compounds and thus afford a means to separate easily catalysts from aqueous phases [2-6]. Our contributions to this field have led us to discover unusual behaviours of some water-soluble phosphines towards unsaturated organic molecules which are novel examples of organic chemistry in water. Effectively, for these reactions we take profit of the high polarity of water and of its acido-basic properties which allow for instance quantitative reactions by displacement of equilibria because reactive intermediates are instantaneously protonated.

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 D_2O 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.

Results and Discussion

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

The water-soluble phosphine 1 (TPPTS) reacts in water with the α, β -unsaturated carboxylic acids 2 to form the phosphonium salts 3 [equation (1)].

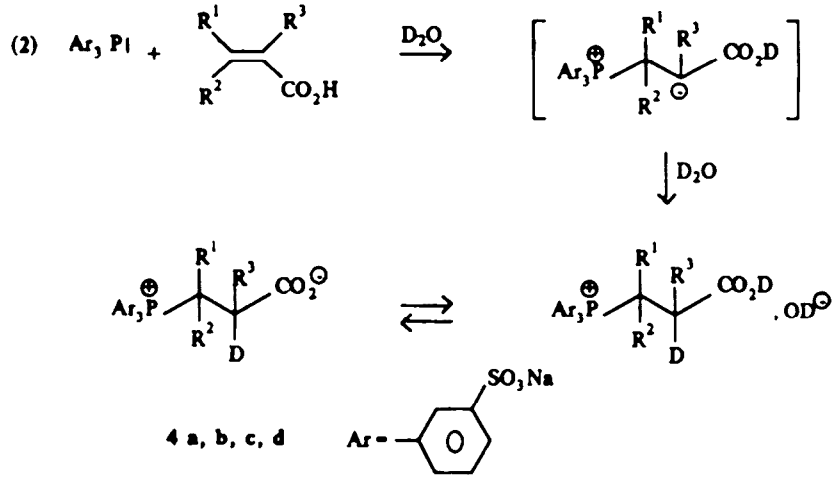


1 2 3

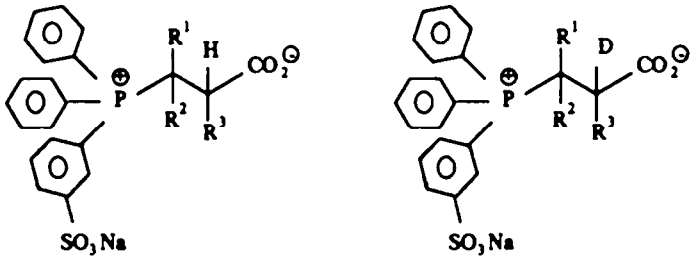
(a) R1 = R2 = R3 = H
(b) R1 = R2 = H, R3 = CH_3
(c) R1 = R2 = H, R3 = CH_2CO_2H
(d) R1 = CH_3, R2 = R3 = H

These reactions are readily monitored using ^{31}P NMR spectroscopy. By addition of a stoechiometric amount of 2 to an aqueous solution of 1, the singlet at δ = -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 (δ = 2.66 and 3.74 ppm) corresponding to the CH_2 protons with $^3J_{H-H}$ = 8 Hz, $^2J_{P-H}$ = 13.4 Hz and $^3J_{P-H}$ = 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] : δC_1 = 21.60 ppm, $^1J_{P-C_1}$ = 52 Hz, δC_2 = 31.96 ppm, $^2J_{P-C_2}$ = 3 Hz ; δC_4 = 121.26 ppm, $^1J_{P-C_4}$ = 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 described [9,10]. 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 (TPPMS = Ph_2PPhSO_3Na) 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 (δ = - 5.5 ppm for TPPTS and - 5.9 ppm for TPPMS) and of their oxides (δ = 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.

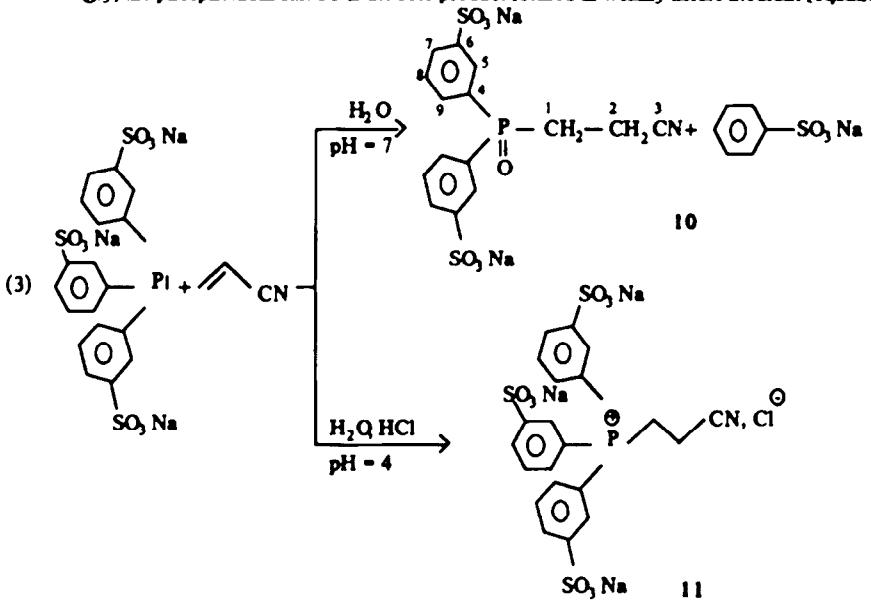
a) Reaction with acrylonitrile

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 C_4 bonded to phosphorus (δC_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 = $P(CH_3)(PhSO_3Na)_2$ (δ = 132.9 and 133.6 ppm, $^1J_{P-C}$ = 107 and 108 Hz respectively). The expected ^1H and ^{13}C 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.

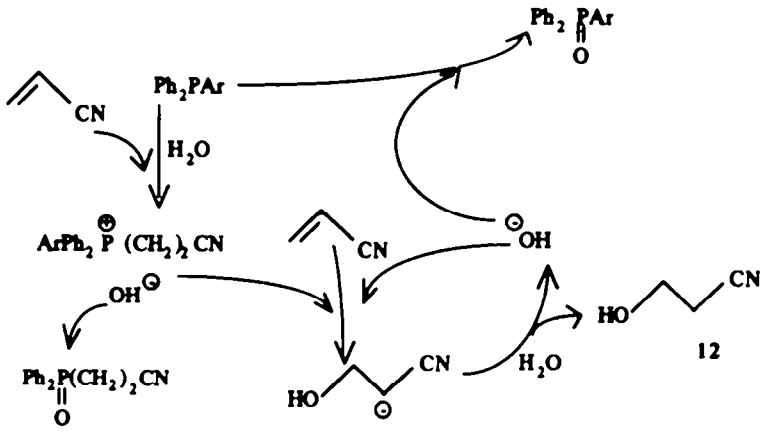
The hydrolysis of phosphonium salts in the presence of base is well known. In water, it occurs instantaneously with neutral olefins which cannot neutralize the hydroxide anion arising from the protonation of the carbanionic intermediate. Accordingly, the phosphonium salt 11 is the sole product formed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



The synthesis of the analogous phosphonium salt $[Ph_3P^+(CH_2)_2CN,X^-]$ requires strongly acidic conditions [12]. 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 ylid [12-15].

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 Michaël reaction between nitroalcanes and olefins [16].

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.



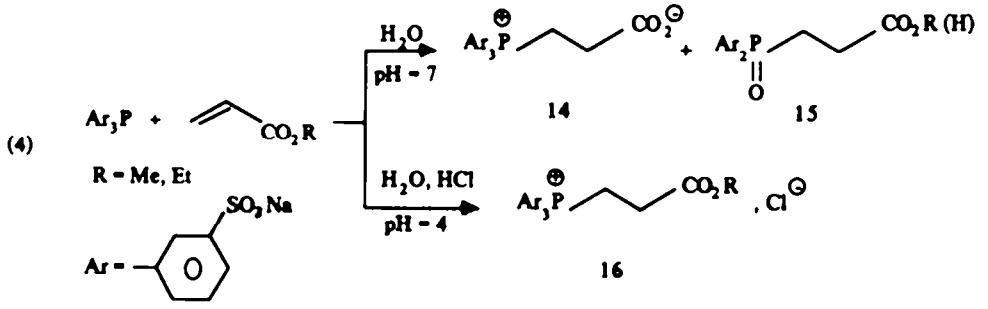
scheme 1

The amphiphilic properties of the monosulfonated phosphine 5 increase the solubility of acrylonitrile in water, and play a main role in the hydration process occuring 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 similary 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)].

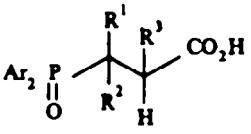
(5) $Ar_3P + RX \xrightarrow{H_2O} Ar_3\overset{\oplus}{P}-R,\ X^{\ominus}$

RX = CH_3I ; Br - CH_2CO_2Me 17 ; 18

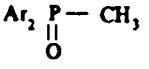
The reaction monitored by 31P NMR spectroscopy of the aqueous phase shows also quantitative transformation of TPPTS into phosphonium salts by reaction with allylbromide, benzylbromide and propargylbromide. In these biphasic systems water plays exclusively the role of solvent ; consequently the success 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 stoechiometric 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.



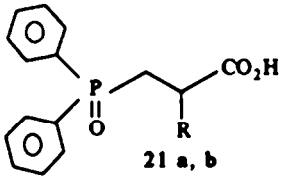
19 a, b, c, d



20

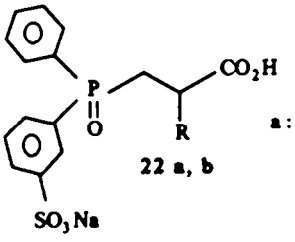
On the contrary, the reaction of OH^- with 18 leads to the triarylphosphine oxide 8 by removing of the alkyl group because an electron withdrawing fonction is located at the α carbon atom.

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.



21 a, b

and

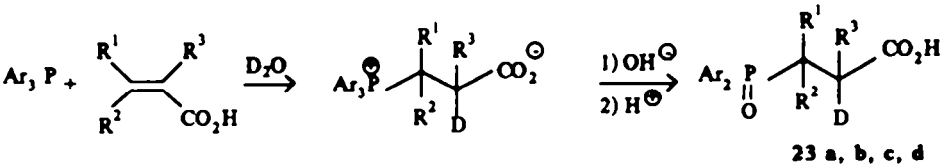


22 a, b

a : R = H, b : R = Me

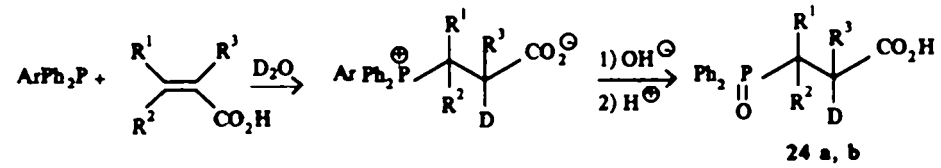
The lack of selectivity of this elimination process is consistent with the weak electron withdrawing effect of the sulfonate anion. These reactions afford a new and efficient synthetic pathway to prepare deuterated water-soluble phosphine oxides from 1 and organosoluble phosphine oxides from 5 [equations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

(6)



23 a, b, c, d

(7)



24 a, b

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 asymetric 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 controling 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 developped 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]. Unsatured 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 Brucker WP 80 MHz[18] (31P{1H}, 32.38 MHz, external reference H_3PO_4 85 %), a Brucker AM 300 MHz[18] [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 unsatured 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 precipated 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 $^{31}P\{^1H\}$ NMR, H_2O, δ ppm : 25.50, s. ^1H NMR, (D_2O), δ ppm : 2.66, $^3J_{H-H}$ = 8 Hz, $^3J_{P-H}$ = 13 Hz, doublet of triplets, CH_2 ; 3.74, $^3J_{H-H}$ = 8 Hz, $^2J_{P-H}$ = 13 Hz, doublet of triplets, CH_2 ; 7.72 - 8.30, multiplet, Ar-H. ^1H NMR with irradiation of phosphorus nucleus, δ ppm : 2.66, $^3J_{H-H}$ = 8 Hz, t, CH_2 ; 3.74, $^3J_{H-H}$ = 8 Hz, t, CH_2 ; 7.70 - 8.30, multiplet, Ar-H. ^{13}C NMR, D_2O, [(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 $^{31}P\{^1H\}$ NMR, H_2O, δ ppm : 24.80, s. ^1H NMR, (D_2O), δ ppm : 1.29, $^3J_{H-H}$ = 7 Hz, $^4J_{P-H}$ = 1 Hz, dd, CH_3 ; 2.78, broad multiplet, CH ; 3.56, $^3J_{H-H}$ = 6 Hz, $^1J_{H-H}$ = 16 Hz, $^2J_{P-H}$ = 13 Hz, septuplet, CH_2, H_a ; 3.88, $^3J_{H-H}$ = 9 Hz, $^1J_{H-H}$ = 16 Hz, $^2J_{P-H}$ = 13 Hz, octuplet, CH_2, 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, CH_3 ; 2.78, broad multiplet, CH ; 3.56, $^3J_{H-H}$ = 6 Hz, $^1J_{H-H}$ = 16 Hz, dd, CH_2, H_a ; 3.88, $^3J_{H-H}$ = 9 Hz, $^1J_{H-H}$ = 16 Hz, q, CH_2, H_b ; 7.30-8.21, multiplet, Ar-H.

3c $^{31}P\{^1H\}$ NMR, H_2O, δ ppm : 24.37, s. ^1H NMR, (D_2O), δ ppm : 2.83, $^3J_{H-H}$ = 6 Hz, d, CH_2 ; 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, CH_2, H_a ; 3.95, $^3J_{H-H}$ = 10 Hz, $^1J_{H-H}$ = 16 Hz, $^2J_{P-H}$ = 12 Hz, broad octuplet, CH_2, H_b ; 7.82-8.38, multiplet, Ar-H.

3d 31P {1H} NMR, H_2O, δ ppm : 30.85, s. 1H NMR, (D_2O), δ ppm : 1.45, $^3J_{H-H}$ = 7 Hz, $^3J_{P-H}$ = 19 Hz, dd, CH_3 ; 2.92, $^3J_{P-H}$ = 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 31P {1H} NMR, H_2O, δ ppm : 25.50, s. 1H NMR, (D_2O), δ ppm : 2.61, $^3J_{H-H}$ = 7 Hz, $^3J_{P-H}$ = 13 Hz, broad sextuplet, CH ; 3.65, $^3J_{H-H}$ = 7 Hz, $^2J_{P-H}$ = 13 Hz, q broad, CH_2 ; 7.65-8.35, multiplet, Ar-H. 13C 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, $^1J_{P-C}$ = 53 Hz, $^1J_{C-H}$ = 133 Hz [C(1), (i) d, (ii) dt] ; 31.25, $^2J_{P-C}$ = 3 Hz, $^1J_{C-D}$ = 17 Hz ; $^1J_{C-H}$ = 133 Hz [C(2), (i) dt, (ii) ddt].

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

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

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

Reaction of TPPMS with α , β unsatured carboxylic acids

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

7.10^{-4} mole of TPPMS 5 and 7.10^{-4} mole of 3a or 3 b 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) 31P {1H} NMR, H_2O, δ ppm : 24.03, s. 1H NMR, (D_2O), δ ppm : 2.55, $^3J_{H-H}$ = 7 Hz, $^3J_{P-H}$ = 13 Hz, sextuplet, CH_2 (CHD) ; 3.61, $^3J_{H-H}$ = 7 Hz, $^2J_{P-H}$ = 13 Hz, sextuplet (q), CH_2 ; 7.30-8.37, multiplet, Ar-H.

6a (7b) 31P {1H} NMR, H_2O, δ ppm : 23.30, s. 1H NMR, (D_2O), δ ppm : 1.22, $^3J_{H-H}$ = 7 Hz, d(s), CH_3 ; 2.69, broad multiplet (no signal) ; C-H ; 3.25, $^3J_{H-H}$ = 16 Hz, $^1J_{H-H}$ = 6 Hz, $^1J_{P-H}$ = 12 Hz, sextuplet (q), CH_2 : H_a ; 3.69, $^3J_{H-H}$ = 6 Hz, $^1J_{H-H}$ = 16 Hz, $^2J_{P-H}$ = 12 Hz, sextuplet (q), CH_2 : 4_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.

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

IR (KBr) : νS=O(cm-1) 1050 (strong) ; 1200 (strong, broad).

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

Remark : 8 can more easily by synthetized 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^{-2} mole) of acrylonitrile are added to an aqueous solution of 1 (1.14 g ; 1.9 10^{-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 31P 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 ≡ N ; 1050 (strong), 1200 (strong, broad) S = O.

$^{31}P\{^1H\}$ NMR (H_2O) δ ppm : 38.25 (s).

^1H NMR (H_2O) 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], CH_2 ; 2.90, $^3J_{H-H}$ = 7 Hz, $^3J_{P-H}$ = 11 Hz [(i) sextuplet (ii) t], CH_2 ; 7.62-8.25 (multiplet), ArH.

^{13}C NMR (D_2O) 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 ^{13}C NMR study of the reaction mixture (H_2O/D_2O) shows, in addition to the spectrum of **10** described above, the characteristic signals of $PhSO_3Na$.

- 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 ^{31}P NMR spectrum shows that all the phosphine has been transformed. Attempts to eliminate the remaining sodium chloride by repeated precipitations has been unsuccessfull ; 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 ≡ N ; 1050 (strong), 1200 (strong, broad) S = O.

$^{31}P\{^1H\}$ NMR (H_2O) δ ppm : 24.07 (s).

^1H NMR (D_2O) δ ppm : 1.90, $^3J_{H-H}$ = 7 Hz, $^2J_{P-H}$ = 13 Hz, sextuplet, CH_2 ; 2.84, $^3J_{H-H}$ = 7 Hz, $^3J_{P-H}$ = 12 Hz, sextuplet, CH_2 ; 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 H_2O or D_2O). 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 $Pb_2P(O)(CH_2)_2CN$ 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 ≡ N ; 3300 (strong, broad) O-H.

^1H NMR ($CDCl_3$) δ ppm : 3.82, $^3J_{H-H}$ = 7 Hz, t(d), CH_2 ; 3.55, s, OH ; 2.60, $^3J_{H-H}$ = 7 Hz, t(t), CH_2 (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**)

$^{31}P\{^1H\}$ NMR (H_2O) δ ppm : 26.11, s, 72 %, **14** ; 38.72, s, 17 %, **15**, R = Et ; 40.08, s, 11 %, **15**, R = H.

^1H NMR (H_2O) δ ppm : 1.15, $^3J_{H-H}$ = 7 Hz, t, CH_3 ; 1.20, $^3J_{H-H}$ = 7 Hz, t, CH_3 ; 2.79, $^3J_{H-H}$ = 7 Hz, $^3J_{P-H}$ = 12 Hz, sextuplet, CH_2, **14** ; 3.03, $^3J_{H-H}$ = 7 Hz, $^2J_{P-H}$ # $^3J_{P-H}$ # 13 Hz, multiplet, CH_2, **15**, R = H or Et ; 3.73, $^3J_{H-H}$ = 7 Hz, q, CH_2 (CO_2Et) ; 3.87, $^3J_{H-H}$ = 7 Hz, $^2J_{P-H}$ = 12 Hz, sextuplet, CH_2, **14** ; 4.13, $^3J_{H-H}$ = 7 Hz, q, CH_2 (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 ^{31}P NMR spectrum shows that the phosphine has been quantitavely transformed.

Spectroscopic data

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

^1H NMR (D_2O) δ ppm : 1.10, $^3J_{H-H}$ = 7 Hz, t, CH_3 ; 2.73, $^3J_{H-H}$ = 7 Hz, $^3J_{P-H}$ = 12 Hz, sextuplet, CH_2 ; 3.75, $^3J_{H-H}$ = 7 Hz, $^2J_{P-H}$ = 13 Hz, sextuplet, CH_2 ; 3.88 ; $^3J_{H-H}$ = 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 methylbromoacetate is added to an aqueous solution of 1 (200 mg ; 3.3 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 : $^{31}P\{^1H\}$ NMR (H_2O) δ ppm : 23.24, s.

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

18 : $^{31}P\{^1H\}$ 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, $^1J_{P-C}$ = 56 Hz, $^1J_{C-H}$ = 136 Hz [C(1) ; (i) d, (ii) dt] ; 168.52, $^2J_{P-C}$ = 4 Hz [C(2) (i) d, (ii) d] ; 56.53, $^1J_{C-H}$ = 149 Hz [C(3) (i) s ; (ii) q] ; 120.41, $^1J_{P-C}$ = 90 Hz, $^2J_{C-H}$ = 8 Hz [C(4) (i) d, (ii) dd] ; 134.35, $^2J_{P-C}$ = 13 Hz, $^1J_{C-H}$ = 169 Hz [C(5) (i) d, (ii) dd] ; 147.93, $^3J_{P-C}$ = 13 Hz, $^2J_{C-H}$ = 8 Hz [C(6) (i) d, (ii) q] ; 135.62, $^1J_{C-H}$ = 170 Hz, $^2J_{C-H}$ = 7 Hz [C(7) (i) s, (ii) dd] ; 133.44, $^2J_{P-C}$ = 12 Hz, $^1J_{C-H}$ = 168 Hz, $^2J_{C-H}$ = 6 Hz [C(8) (i) d, (ii) dq] ; 139.39, $^2J_{P-C}$ = 11 Hz, $^1J_{C-H}$ = 168 Hz, $^2J_{C-H}$ = 8 Hz [C(9) (i) d, (ii) dq].

- Reaction with other alkyl halides

The ^{31}P NMR spectra of aqueous solutions after reaction with $PhCH_2Br$, $CH_2=CH-CH_2Br$, $HC\equiv C-CH_2Br$ 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.

Stoechiometric 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 ajusted 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 recristallized in methanol.

Spectroscopic data

19a, b, c, d : $^{31}P\{^1H\}$ 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, $^3J_{H-H}$ = 7 Hz, $^3J_{P-H}$ = 13 Hz, sextuplet, CH_2 ; 2.92, $^3J_{H-H}$ = 7 Hz, $^2J_{P-H}$ = 12 Hz, sextuplet, CH_2 ; 7.57-8.45, multiplet, Ar-H. **19b** : 1.37, $^3J_{H-H}$ = 7 Hz, d, CH_3 ; 2.98, $^3J_{H-H}$ = 7 Hz, $^2J_{H-H}$ = 16 Hz, $^2J_{P-H}$ = 13 Hz, septuplet, CH_2 (H_a) ; 3.04, $^3J_{H-H}$ = 8 Hz, $^2J_{H-H}$ = 16 Hz, $^2J_{P-H}$ = 13 Hz, septuplet, CH_2 (H_a) ; 7.59-8.45, multiplet, Ar-H. **19c** : 2.95, $^3J_{H-H}$ = 7 Hz, d broad, CH_2 ; 3.20, multiplet broad, CH_2 ; 7.58-8.44, multiplet, Ar-H.

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

^1H NMR (D_2O), δ ppm : 2.08, $^2J_{P-H}$ = 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, $^1J_{P-C}$ = 75 Hz, $^1J_{C-H}$ = 130 Hz [C(1), (i) d, (ii) dq] ; 128.12, $^2J_{P-C}$ = 12 Hz, $^1J_{C-H}$ = 163 Hz, $^2J_{C-H}$ = 8 Hz [C(7), (i) d, (ii) dt] ; 132.57, $^1J_{C-H}$ = 166 Hz, $^2J_{C-H}$ = 8 Hz [C(5), (i) s, (ii) dd] ; 133.55, $^1J_{P-C}$ = 106 Hz, $^2J_{C-H}$ = 8 Hz [C(2), (i) d, (ii) dd] ; 134.25, $^3J_{P-C}$ = 12 Hz, $^1J_{C-H}$ = 162 Hz [C(6), (i) d, (ii) dq] ; 136.10, $^2J_{P-C}$ = 10 Hz, $^1J_{C-H}$ = 165 Hz [C(3), (i) d, (ii) dd] ; 146.28, $^3J_{P-C}$ = 11 Hz, $^2J_{C-H}$ = 8 Hz [C(4), (i) d, (ii) dt].

Reactivity of monosulfonated phosphonium salts in the presence of base.

Stoechiometric 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 ajusted to 1-2 by addition of concentrated hydrochloric acid. The resulting solution becomes turbid and is allowed to stand overnight at + 5°C to complete the precipitation. The white precipitate of 21 is filtrated and 21 is recristallized 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 vaccuo for 48 h. Yields : 21 : 65 %, 22 : 30 %. **21a** : mp = 138°C (litt. : 138 [9a]) ; **21b** : mp = 136°C (litt. 136 [9a]).

Spectroscopic data

21 : $^{31}P\{^1H\}$ 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, $^3J_{H-H}$ = 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, $^1J_{P-C}$ = 73 Hz, $^1J_{C-H}$ = 130 Hz [C(1), (i) d, (ii) dt] ; 26.53, $^2J_{P-C}$ = 4 Hz, $^1J_{C-H}$ = 130 Hz, [C(2), (i) d, (ii) dt] ; 128.89, $^2J_{P-C}$ = 12 Hz, $^1J_{C-H}$ = 163 Hz, $^2J_{C-H}$ = 7 Hz [C(5), (i) d, (ii) dt] ; 130.83, $^3J_{P-C}$ = 10 Hz, $^1J_{C-H}$ = 166 Hz, $^2J_{C-H}$ = 7 Hz [C(6), (i) d, (ii) dq] ; 131.14, $^1J_{P-C}$ = 101 Hz, $^2J_{C-H}$ = 7 Hz [C(4), (i) d, (ii) dt] ; 132.27, $^4J_{P-C}$ = 2 Hz, $^1J_{C-H}$ = 160 Hz, $^2J_{C-H}$ = 7 Hz [C(7), (i) d, (ii) dq] ; 174.09, $^3J_{P-C}$ = 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.

$^{31}P\{^1H\}$ 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, $^3J_{H-H}$ = 7 Hz, $^4J_{P-H}$ = 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 : $^{31}P\{^1H\}$ 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, $^3J_{H-H}$ = 7 Hz, $^3J_{P-H}$ = 13 Hz sextuplet, CH ; 2.90, $^3J_{H-H}$ = 7 Hz, $^2J_{P-H}$ = 12 Hz, dd, CH_2 ; 7.50-8.45, multiplet, Ar-H. **23b** : 1.25, s, CH_3 ; 3.00, $^2J_{H-H}$ = 16 Hz, $^2J_{P-H}$ = 13 Hz, dd, CH_2 (H_a) ; 3.11, $^2J_{H-H}$ = 16 Hz, $^2J_{P-H}$ = 13 Hz, dd, CH_2 (H_b) ; 7.45-8.40, multiplet, Ar-H. **23c** : 2.70 ; s, CH_2 ; 3.10, $^2J_{H-H}$ = 15 HZ, $^2J_{P-H}$ = 13 Hz, d, CH_2 (H_a) ; 3.21, $^2J_{H-H}$ = 15 Hz, $^2J_{P-H}$ = 15 Hz, $^2J_{P-H}$ = 13 Hz, d, CH_2 (H_b) ; 7.50-8.45, multiplet, Ar-H.

24 : $^{31}P\{^1H\}$ 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, $^1J_{P-C}$ = 73 Hz, $^1J_{C-H}$ = 130 Hz. [C(1), (i) d, (ii) dt] ; 26.05, $^2J_{P-C}$ = 4 Hz, $^1J_{C-H}$ = 130 Hz, $^1J_{C-D}$ = 19 Hz, [C(2), (i) dt, (ii) ddt] ; 128.86, $^2J_{P-C}$ = 12 Hz, $^1J_{C-H}$ = 163 Hz ; $^2J_{C-H}$ = 7 Hz [C(5), (i) d, (ii) dt] ; 130.80, $^3J_{P-C}$ = 10 Hz, $^1J_{C-H}$ = 163 Hz, $^2J_{C-H}$ = 7 Hz [C(6), (i) d, (ii) dq] ; 131.07, $^1J_{P-C}$ = 101 Hz, $^2J_{C-H}$ = 7 Hz [C(4), (i) d, (ii) dt] ; 132.25, $^4J_{P-C}$ = 2 Hz, $^1J_{C-H}$ = 160 Hz, $^2J_{C-H}$ = 7 Hz [C(7), (i) d, (ii) dq] ; 174.13, $^3J_{P-C}$ = 16 Hz, [C(3), (i) d, (ii) d].

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