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ORGANIC CHEMISTRY IN WATER (PART V)

NUCLEOPHILIC ADDITION OF WATER-SOLUBLE PHOSPHINES ON ACTIVATED ALKYNES : AN EFFICIENT SYNTHESIS OF NEW VINYLPHOSPHONIUM SALTS AND OF SPECIFICALLY DEUTERATED OLEFINS.

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Abstract : Triphenylphosphine m-trisulfonate [$P(mC_6H_4SO_3Na)_3$ = TPPTS] **1** and triphenylphosphine m-monosulfonate [$Ph_2P(mC_6H_4SO_3Na)$ = TPPMS] **2** react in water with activated alkynes R - C ≡ C - A (A = CO_2H, CO_2R^1, COR^2, CHO) affording new vinylphosphonium salts or vinylphosphine oxides or alkenes depending on the pH of the aqueous solution and on the nature of the substituent R. The reactions of **1** or **2** with alkynes bearing an electron-acceptor substituent R give rise to the corresponding *trans* disubstituted olefins. Specifically mono or dideuterated alkenes are thus obtained in good yields by sequential use of H_2O-D_2O. When R = H or Alkyl, vinylphosphonium salts or vinylphosphine oxides are quantitatively produced respectively in acidic or in neutral medium.

Résumé : La triphénylphosphine m-trisulfonate [$P(mC_6H_4SO_3Na)_3$ = TPPTS] **1** et la triphénylphosphine m-monosulfonate [$Ph_2P(mC_6H_4SO_3Na)$ = TPPMS] **2** réagissent dans l'eau avec des alcynes activés R - C ≡ C - A (A = CO_2H, CO_2R^1, COR^2, CHO) pour donner des nouveaux sels de vinylphosphonium ou des oxydes de vinylphosphines ou des alcènes en fonction du pH de la solution aqueuse et de la nature du substituant R. Quelle que soit la nature du groupement électro-attracteur A, les réactions des phosphines **1** et **2** sur les alcynes portant un substituent R électro-accepteur conduisent aux olefines *trans* disubstituées correspondantes. Des alcènes spécifiquement mono ou dideutériés sont obtenus avec de bons rendements en utilisant H_2O et/ou D_2O. Lorsque R = H ou Alkyl, des sels de vinylphosphonium ou des oxydes de vinylphosphines sont formés quantitativement selon que la réaction est réalisée en solution acide ou neutre.

Introduction

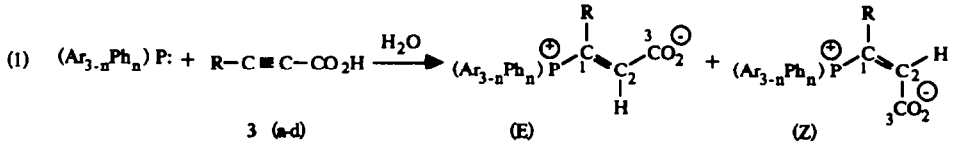
Recently, emphasis has been put on hydrophilic phosphines, particularly in Organometallic Chemistry, because these ligands can accord water solubility to coordination compounds and thus afford a means to separate easily catalysts from aqueous phases [1-5]. Our contributions to this field have led us to discover unusual behaviours of some water-soluble phosphines towards unsaturated organic molecules which represent novel examples of organic chemistry in water [6-8]. For these reactions we take profit of the high polarity of water and of its acido-basic properties to perform quantitative reactions by displacement of equilibria because the reactive intermediates are instantaneously protonated. Recently, we have described the reaction of TPPTS **1** (triphenylphosphine meta tri-sulfonate) [5] and TPPMS **2** (triphenylphosphine meta mono-sulfonate) [9] with activated olefins [6,7] giving new families of phosphonium salts and phosphine oxides which are regioselectively deuterated in D_2O.

In this paper, we describe the nucleophilic additions of the sulfonated phosphines 1 and 2 to activated acetylenic compounds which lead to vinylphosphonium salts or vinylphosphine oxides. Depending on the substitution of the vinylic group, vinylphosphonium salts release an aromatic ring or the olefinic group upon addition of hydroxide anion. The sequential use of H_2O and D_2O affords therefore a new and efficient pathway to prepare specifically mono or dideuterated alkenes.

Results and Discussion

- Nucleophilic addition of water-soluble phosphines on α-alkynic acids.

The water soluble phosphines 1 and 2 react in water with α-alkynic acids 3 to form a mixture of Z and E vinylphosphonium salts 4 and 5 [equation (1)]



(1)

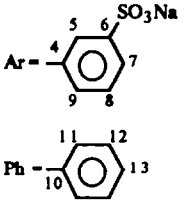
3 (a-d) (E) (Z)

1 : n = 0 a : R = n - C_5H_9 4 (a-d) : n = 0

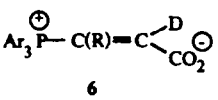
2 : n = 2 b : R = H 5 (a-d) : n = 2

c : R = Ph

d : R = CO_2H



The reaction rates are monitored by ^{31}P NMR spectroscopy. After addition of stoechiometric amounts of alkynic acid 3 to an aqueous solution of 1 or 2, the singlet characteristic of the phosphine ($\delta \equiv$ - 5.5 to - 6 ppm) is removed. Two new singlets appear at lower field (in the range 15 - 28 ppm). They are attributed to the E and Z isomers of the vinylphosphonium salts 4 or 5 [equation (1)]. The reaction rate markedly depends on the electron-withdrawing power and the bulk of the R substituent rather than on the nature of the phosphine (Table 1). Unsubstituted or electron deficient triple bonds of acetylenic acids 3b and 3d are the most reactive. Nevertheless, the reaction carried out at room temperature, is always rapid and quantitative. These results show that nucleophilic additions of hydrophilic phosphines on alkynes occur readily in water because the carbanionic intermediate is instantaneously protonated. The hydroxide anion produced is neutralized by the carboxylic acid function leading to a zwitterionic salt. The role of water is demonstrated by the formation of vinylphosphonium salts 6 and 7 specifically deuterated at the β-carbon when the reaction is carried out in D_2O.



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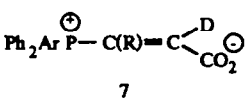

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Vinylphosphonium salts have been obtained before by nucleophilic addition of PPh_3 in concentrated HBr or HCl and of PPh_3, HBr in organic solvents [10,11]. When triphenylphosphine is added to alkynes in protic or aqueous

Table 1 : Reaction of phosphines 1 and 2 with α-alkynic acids.
$^{31}P\{^1H\}$NMR study.

R—C≡CO_2H		Phosphine	Reaction time	Vinylphosphonium salts		
					% Z (δ ppm) [a]	% E (δ ppm)
R = nC_5H_9	3a	1	10 h	4a	75 % (23.5)	25 % (26.9)
		2	12 h	5a	80 % (22.5)	20 % (26.1)
R = H	3b	1	10 mn	4b	70 % (17.1)	30 % (19.9)
		2	20 mn	5b	80 % (16.0)	20 % (18.9)
R = Ph	3c	1	1 h	4c	85 % (23.5)	15 % (25.1)
		2	1 h	5c	70 % (23.2)	30 % (24.7)
R = CO_2H	3d	1	5 mn	4d	20 % (26.6)	80 % (28.0)
		2	5 mn	5d	25 % (24.5)	75 % (25.4)

(a) $^{31}P\{^1H\}$ NMR chemical shift (H_2O, 36°C, 32.38 MHz).

Table 2 : Vinylphosphonium salts 4 and 5
^1H NMR Data [(a)] (D_2O, 90 MHz)

Compound	Z isomer		E isomer	
	δ H_2(ppm)	$^3J_{P\text{-}H}$ (Hz)	δ H_2(ppm)	$^3J_{P\text{-}H}$ (Hz)
4a	d 7.45	36	d 7.03	25
5a	half doublet [(b)] 7.23	-	d 6.94	25
4b	dd 7.37	37 ($^3J_{H\text{-}H}$ = 9 Hz)	dd 6.97	22 ($^3J_{H\text{-}H}$ = 17 Hz)
5b [(c)]	dd 7.02	36 ($^3J_{H\text{-}H}$ = 9 Hz)	dd 6.54	22 ($^3J_{H\text{-}H}$ = 17 Hz)

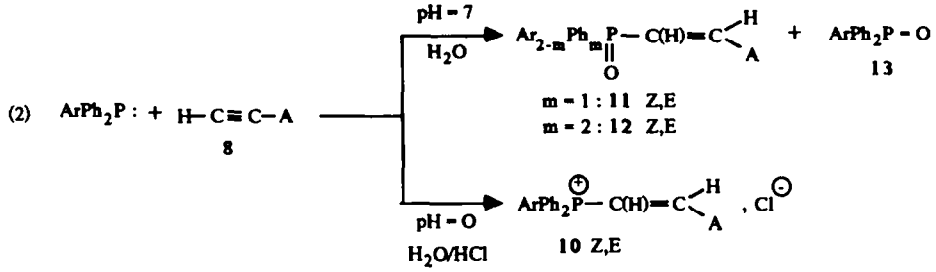
(a) For the high field ethylenic proton H_2 ; (b) Only one branch of the doublet is observed, the other is masked by the aromatic multiple ; (c) Spectrum registred at 300 MHz.

solvents [12,13], vinylphosphonium salts have been identified or postulated as transient species but they readily decompose, by alcoholysis, into alkoxyphosphonium ylids, vinylethers or alkenes. In our case, water acts as an acidic solvent and makes the reaction quantitative. The zwitterionic vinylphosphonium salts are stable (excepted for **4d** and **5d**, see below) and can be fully characterized. Compounds **4** and **5** are both water-soluble although the monosulfonated salts **5** can solubilize in organic solvents such as chlorinated solvents or alcohols. Thus, the proper choice of the phosphine **1** or **2** allows to isolate vinylphosphonium salts in water or in organic solvents for further synthetic purposes.

The structures of Z and E isomers are proved by ^1H NMR data. The ^1H NMR spectra of compounds **4a,b** and **5a,b** show two signals (a doublet for R = nPentyl and a double doublet for R = H) in the region 6.5 - 7.2 ppm attributed to the ethylenic protons H_2 at the β carbon which is in agreement with the $^3J_{P-H}$ and chemical shifts values previously reported for related compounds [14,15] (Table 2). These signals are effectively not observed for deuterated compounds **6** and **7**. In order to ascribe the ^{31}P NMR chemical shifts, selective irradiations of the phosphorus nuclei have been performed on the vinylphosphonium salts **4b** and **5b**. For **5b** the selective irradiation of the phosphorus nucleus at 16 ppm does not modify the ^1H NMR signal at 6.54 ppm but the signal at 7.02 ppm is transformed into a doublet with $^3J_{H-H}$ cis = 9 Hz because the ^{31}P - ^1H coupling is suppressed. Consequently the higher field ^{31}P resonance can be assessed to the Z isomer. As expected, irradiation of the phosphorus at 19 ppm (E isomer) transforms the double doublet into a doublet with $^3J_{H-H}$ trans = 17 Hz. The order of ^{31}P NMR chemical shift $\delta Z < \delta E$ is in agreement with data obtained for vinylphosphine oxides [14] and vinylphosphonates [15]. When R = Ph or CO_2H the ^1H NMR signal of the ethylenic proton is shifted at lower field and masked by the aromatic multiplet. However the ^{13}C NMR data are consistent with a mixture of E and Z isomers and for instance, the carboxylic carbon signals always appear as two doublets with $^3J_{P-C}$ cis = 6 Hz and $^3J_{P-C}$ trans = 21 Hz. The steric hindrance of the substituents on the triple bond does not affect significantly the E/Z ratio and in every cases the Z isomers always predominate. In agreement with the widely studied stereochemistry and mechanism of the nucleophilic additions to activated triple bonds [16,17], these results can be explained by assuming that external protonation of the carbanion trans to the phosphorus atom is more rapid than interconversion of the double bond. A stabilisation by chelation between the phosphonium and the carboxylate is also possible (see below). For compounds **4d** and **5d**, energetically favorable interactions between the carboxylate and the carboxylic acid in the cis-carbanionic intermediate as well as in the final product may be invoked to explain the predominant obtention of the E isomer.

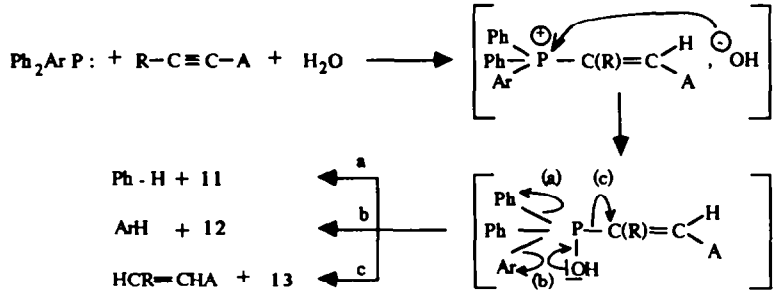
- Reaction of water-soluble phosphines with activated alkynes in biphasic system.

The sulfonated phosphines **1** and **2** also react quantitatively with hydrophobic alkynes like unsubstituted derivatives **8** or phenyl propargylaldehyde **9** in biphasic conditions without phase transfer reagent. The nucleophilic addition can again be monitored by ^{31}P NMR spectroscopy of the aqueous phase. These substrates having no ability to neutralize the hydroxide anion produced by the protonation of the carbanionic intermediate, the nature of the products dramatically depends on the acidity of the aqueous phase. Nevertheless, whatever the pH values in the range 1-7 the addition is always instantaneous and quantitative thus demonstrating the predominant role of water acting as a proton source. For instance, the reaction of TPPMS **2** with compounds **8** in aqueous HCl 1N gives selectively vinylphosphonium salts **10**. The same reaction performed at pH = 7 produces vinyldiarylphosphine oxides **11** and **12** and triarylphosphine oxide **13** [table 3, equation (2)].



a : A = $COCH_3$, b : A = CO_2Me, c : A = CO_2Et, d : A = CO_2iPr, e : A = CO_2nPent.

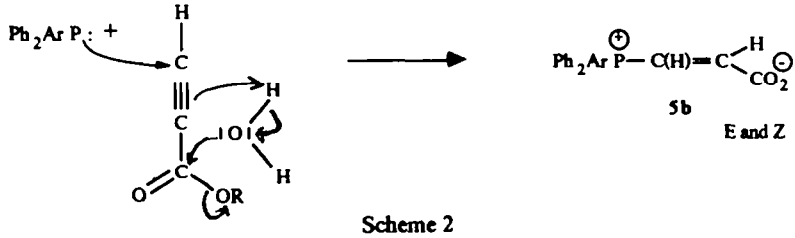
In distilled water, the production of phosphines oxides results from a nucleophilic attack of the hydroxide anion (generated in situ) on the phosphonium with elimination of a phenyl or a phenylsulfonate group (for 11 and 12) or of the vinylgroup for 13 (scheme 1) [6-8, 11,18,19]. The same mixtures of oxides (characterized by their ^{31}P NMR data (38 and 39 ppm for 11 and 12 ; 34 ppm for 13) are effectively obtained by addition of OH^- to vinylphosphonium salts 10.



Scheme 1

The formation of vinylphosphine oxides 11 et 12 or arylphosphine oxide 13 is greatly dependent on the nature of the substituent R [8,11,18]. When R = H, the elimination of an aromatic group is predominant affording a mixture of 11 and 12. For R = Ph, trans cinnamaldehyde and 13 are selectively obtained (see below).

The reaction of TPPMS 2 with propiolic esters 8b-e at neutral pH is much more complicated because hydrolysis of the carboxylic ester becomes competitive. In this case, the hydroxide anion generated in situ preferentially reacts on the carboxylic function affording zwitterionic vinylphosphonium salts 5b (scheme 2). ^{31}P NMR monitoring of



Scheme 2

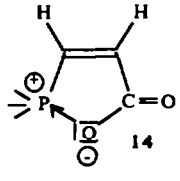
the reaction shows that the formation of the zwitterion is instantaneous thus demonstrating that hydrolysis of the ester group is rapid and predominant. Moreover, the amount of phosphine oxides produced is low (table 3).

Table 3 : Reaction of 2 with activated alkynes in biphasic system

Compound	pH (b)	Composition of the reaction mixture (a)	
		Vinylphosphonium salts E	Z	Phosphines oxides
H—C≡C—$COCH_3$ **8a**	0	**10a** E (6 %)	**10a** Z (70 %)	**13** (6 %)
	7	**10a** E (11 %)	**10a** Z (3 %)	**11** and **12** (70 %) ; **13** (15 %)
H—C≡C—CO_2CH_3 **8b**	0	**10b** E (17 %)	**10b** Z (78 %)	**11** and **12** (1 %)
	7	**10b** E (5 %) **5b** E (8 %)	**10b** Z (35 %) **14** (45 %)	**11** and **12** (5 %) ; **13** (2 %)
H—C≡C—CO_2Et **8c**	0	**10c** E (19 %) **5b** E (5 %)	**10c** Z (55 %)	**11** and **12** (12 %) ; **13** (3 %)
	7	**10c** E (6 %) **5b** E (12 %)	**10c** Z (30 %) **14** (33 %)	**11** and **12** (9 %) ; **13** (9 %)
H—C≡C—CO_2iPr **8d**	0	**10d** E (33 %)	**10d** Z (52 %)	**11** and **12** (4 %) ; **13** (3 %)
	7	**10d** E (4 %) **5b** E (6 %)	**10d** Z (30 %) **14** (42 %)	**11** and **12** (13 %) ; **13** (3 %)
H—C≡C—CO_2Pent **8e**	0	**10e** E (25 %)	**10e** Z (49 %)	**11** and **12** (2 %) ; **13** (10 %)
	7	**10e** E (2 %)	**10e** Z (6 %) **14** (18 %)	**11** and **12** (57 %) ; **13** (12 %)
Ph—C≡C—CHO **9**	0	**10f** E (40 %)	**10f** Z (60 %)	**11** and **12** (0 %) ; **13** (0 %)
	7	**10f** E (0 %)	**10f** Z (0 %)	**11** and **12** (0 %) ; **13** (100 %)

(a) Estimated from the ^{31}P NMR spectrum (32.38 MHz, H_2O), the reaction is quantitative ; (b) pH of water before adding 2 and 8 or 9 ; pH = 0 (HCl IN) ; pH = 7 (distilled water).

Both E and Z isomers of **5b** are obtained and were identified using ^{31}P NMR spectroscopy by addition of authentic samples. Nevertheless, the ^{31}P NMR spectra show a new singlet at 15 ppm which is transformed, upon addition of dilute hydrochloric acid or silver salt, into the Z isomer **5b**. This signal might correspond to the phosphorus nucleus of the chelate **14** formed during the hydrolysis of the ester group.



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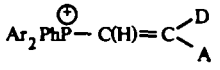
In acidic medium, the addition of TPPMS 2 on activated alkynes 8 and 9 affords selectively the vinylphosphonium salts 10. Stoechiometric amounts of H^+ in the reaction media inhibit the formation of phosphine oxides as well as the hydrolysis of carboxylic esters. The vinylphosphonium salts 10 (mixture of Z and E isomers) are water-soluble and can be solubilized in polar organic solvents (chloroform, dichloromethane, alcohols). They have been fully characterized by their ^{31}P, ^{1}H and ^{13}C NMR spectra. The ^{31}P NMR signals of the two isomers Z and E have been attributed by ^{1}H NMR with selective irradiation of the phosphorus nuclei. For instance the ^{1}H NMR spectrum of 8a (Z and E) allows to distinguish two singlets corresponding to the methyl group (respectively 2.16 and 2.52 ppm) and two double doublets for the β-ethylenic proton. The first one at δ = 6.66 ppm with $^{3}J_{P\text{-}H}$ = 16 Hz and $^{3}J_{H\text{-}H}$ (trans) = 17 Hz corresponds to the E isomer, the second at δ = 7.31 ppm with $^{3}J_{P\text{-}H}$ = 22 Hz and $^{3}J_{H\text{-}H}$ (cis) = 12 Hz for the Z isomer. Selective irradiation of the phosphorus nucleus at 21 ppm causes the disappearence of the P-H coupling at 6.66 ppm. Similarly, irradiation of the phosphorus nucleus at 18 ppm transforms the signal at 7.31 ppm. Therefore, the ^{31}P NMR signals at 21 and 18 ppm have been attributed respectively to the E and Z isomers. Similar experiments, performed on vinylphosphonium salts 10b-e, demonstrate that whatever the β substituent, the E isomer always resonates at lower field which is consistent with data previously described [8,15].

When the reactions were carried out in D_2O-DCl specifically monodeuterated vinylphosphonium salts 15 have been obtained and characterized by NMR spectroscopy (see experimental section).



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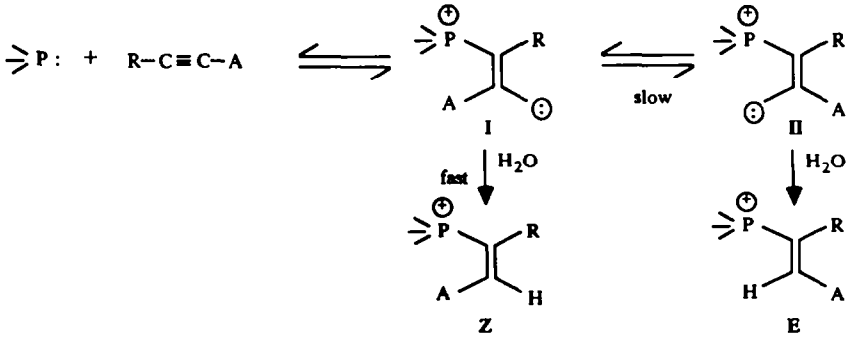
As already observed for α-alkynic acids 3, the nucleophilic additions of TPPMS 2 on compounds 8a-e and 9 preferentially give rise to Z vinylphosphonium salts (tables 2 and 3). The stereochemistry of the predominant isomer does not depend on the pH : experiments performed in acidic or neutral solutions lead predominantly to the Z isomer. The results obtained for a series of propiolic esters 8b-e show that the steric hindrance of the triple bond does not affect significantly the nature of the major isomer. Addition of nucleophiles such as amines or ammonium salts on activated acetylenics have already been described [16-17, 20-22] and in a recent paper Jung and Buszek [22] have reported that the reaction of trimethylammonium fluoroborate with propiolic esters in methanol lead to the production of E or Z isomer resulting respectively of reactions under thermodynamic or kinetic control. Thus in water, the obtention of larger amounts of Z isomer can be explained by a very rapid protonation of the kinetic trans carbanionic intermediate I. Protonation by water is faster than isomerization of the trans carbanion I into the thermodynamically more stable cis-carbanion II (scheme 3).



Scheme 3

Furthermore, under the reaction conditions no isomerization occurs between Z and E isomers. On the other hand, the E isomer is the sole product obtained after heating a mixture of Z and E isomers for 24 h at 60°C. Thus, the adduct of stereochemistries E and Z appear to be respectively the thermodynamic and the kinetic products.

- Reactivity of vinylphosphonium salts with hydroxide anions.

The reactivity and the stability of vinylphosphonium salts greatly depend on the nature of the substituent R at the β-carbon [8,11,18]. When R = H or alkyl, vinylphosphonium salts are very stable in water or in organic solvents ; upon addition of stoechiometric amounts of sodium hydroxide to the aqueous solution they are transformed into vinylphosphine oxides. Monosulfonated salts give a mixture of two vinylphosphine oxides **11** and **12** arising from the elimination of a benzene or a benzene sulfonate ring [equation (3)]. Trisulfonated vinylphosphonium salts afford the disulfonated vinylphosphine oxides **16** [equation (4)].

(3) $Ar_2PhP^{\oplus}-C(R)=C(H)A + NaOH \xrightarrow{H_2O} Ar(Ph)P(=O)-C(R)=C(H)A$ (**11** Z,E) + $Ph_2P(=O)-C(R)=C(H)A$ (**12** Z,E)

5a : R = nC_5H_9, A = $CO_2^{\ominus}$ — **11a, 12a** : R = nC_5H_9, A = $CO_2^{\ominus}$

5b : R = H, A = $CO_2^{\ominus}$ — **11b, 12b** : R = H, A = $CO_2^{\ominus}$

10a : R = H, A = $COCH_3$ — **11c, 12c** : R = H, A = $COCH_3$

10b-e : R = H, A = CO_2R'

(4) $Ar_3P^{\oplus}-C(R)=C(H)A + NaOH \xrightarrow{H_2O} Ar_2P(=O)-C(R)=C(H)A$ (**16** Z,E)

4a : R = nC_5H_9, A = $CO_2^{\ominus}$ — **16a** : R = nC_5H_9, A = $CO_2^{\ominus}$

4b : R = H, A = $CO_2^{\ominus}$ — **16b** : R = H, A = $CO_2^{\ominus}$

When R is electron acceptor (R = Ph or CO_2H) the stability of the vinylphosphonium salts depends on the degree of sulfonation. The monosulfonated salts are stable while the trisulfonated salts decompose into triarylphosphine oxide **18** and trans olefins **19** whatever the pH value [equation (5)]. The decomposition rate is fast when R = CO_2H and slow when R = Ph.

(5) $Ar_3P^{\oplus}-C(R)=C(H)A \xrightarrow{H_2O} Ar_3P=O$ (**18**) + $R(H)C=C(H)A$ (**19**)

4c : R = Ph, A = $CO_2^{\ominus}$ — **19a** : R = Ph, A = CO_2Na

4d : R = CO_2H, A = $CO_2^{\ominus}$ — **19b** : R = CO_2H, A = CO_2Na

18 : R = Ph, A = CHO — **19c** : R = Ph, A = CHO

The monosulfonated salts **5c-d, 10f** can be isolated. They are oxidized in H_2O upon addition of NaOH giving rise to the phosphine oxide **13** and the corresponding trans alkene **19** like their triphenylphosphonium analogs [11] [equation (6)].

(6) $ArPh_2\overset{\oplus}{P}-C(R)=C(H)(A) + NaOH \longrightarrow ArPh_2P=O + R(H)C=C(H)A$

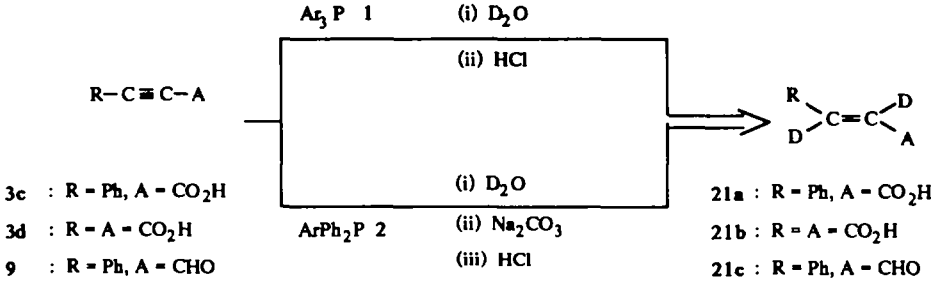
13 **19**

5c : R = Ph, A = $CO_2^{\ominus}$ **19a** : R = Ph, A = CO_2Na

5d : R = CO_2H, A = $CO_2^{\ominus}$ **19b** : R = CO_2H, A = CO_2Na

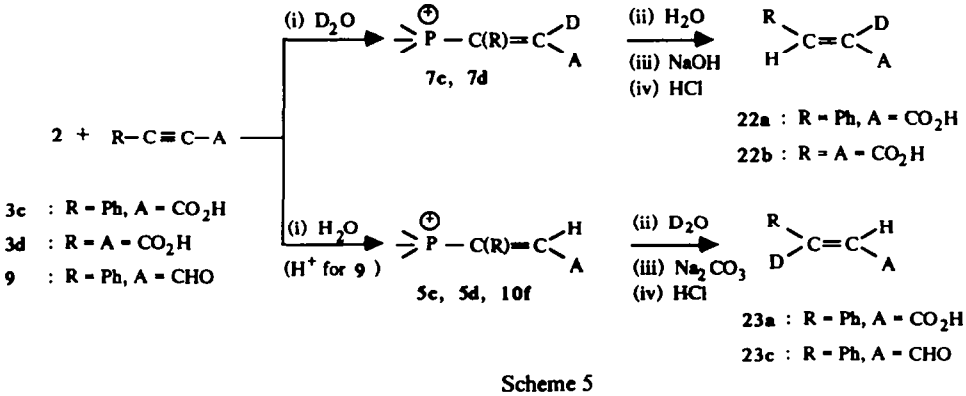
10f : R = Ph, A = CHO **19c** : R = Ph, A = CHO

Reactions (5) and (6) afford a new and efficient synthetic pathway to prepare trans-substituted alkenes from acetylenes the reaction products being quantitatively separated (by precipitation or extraction) after acidification. In D_2O, dideuterated trans-cinnamic acid **20a**, fumaric acid **20b** and trans-cinnamaldehyde **20c** are obtained starting either from TPPTS **1** or TPPMS **2** (scheme 4).



Scheme 4

Furthermore, with the monosulfonated phosphine **2**, specifically monodeuterated olefins **22** and **23** can be prepared by sequential use of H_2O and D_2O (scheme 5).



Scheme 5

Theses results shed light on some useful applications of water-soluble phosphines in organic synthesis. The preparation of specifically deuterated trans-alkenes illustrated in this paper by some examples may probably be extended to other olefins substituted by an electron withdrawing grouping. Furthermore, vinylphosphonium salts and vinylphosphine oxides are of interest to prepare for instance deuterated heterocycles (by nucleophilic addition followed by an internal Wittig reaction) or polyfunctionnal phosphorus compounds (by addition of dienes or nucleophiles). These aspects are currently being developed in our laboratory with monosulfonated derivatives in organic solvents and in water.

CONCLUSION

The nucleophilic addition of water-soluble phosphines on activated alkynes affords an useful synthetic pathway to new vinylphosphonium salts. By controling the pH and by a proper choice of the phosphine, vinylphosphonium salts or vinylphosphine oxides soluble in water or in organic solvents can be prepared at will. Water acts as an acido-basic solvent and increases the reaction rate by protonation of the carbanionic intermediate thus promoting a larger amount of the products of kinetic control (Z isomer). The reactivity and the stability of the vinylphosphonium salts are greatly dependent on the degree of sulfonation and on the nature of the substituent at the carbon α to the phosphorus. Salts bearing electron-acceptor groups lead to trans substituted alkenes which can be specifically mono or dideuterated by sequential reactions in H_2O and D_2O. Further studies are currently being developed to find other applications in organic synthesis.

EXPERIMENTAL SECTION

TPPTS 1 and TPPMS 2 have been prepared using previously described procedures [5, 9] (TPPMS is also available from SPECS). Alkynic acids 3, 3-butyn-2-one **8a** and phenylpropargylaldehyde 9 are of commercial origin and used without further purification. Propiolic esters **8b-e** have been prepared by esterification of propiolic acid in the presence of boron trifluoride etherate and purified by distillation [22]. Water was distilled before use, NMR spectra were recorded on a Brucker WP 80 MHz ^{23}[^{31}P{^{1}H}, 32.38 MHz, external reference H_3PO_4 85 %], a Brucker AM 300 MHz ^{23}[^{13}C(75.47 MHz), ^{1}H (300 MHz), ^{31}P(112.9 MHz), ^{2}H (46.1 MHz)] and a Jeol FX90Q 90 [^{1}H(89.55 MHz), external reference TMS]. The percentages of deuterium incorporation have been obtained by mass spectrometry using a Varian MAT 311 spectrometer [23]. The results of sulfonated vinylphosphonium salts and phosphine oxides elemental analysis are not significant because the hydration number depends on the purification and drying procedures. Sulfonated compounds (phosphonium salts and phosphine oxides) melt above 300°C.

- Reaction of TPPTS 1 and TPPMS 2 with α-alkynic acids

$5.5.10^{-4}$ mole of **3a-d** are added to an aqueous solution of 1 or 2 ($5.5.10^{-4}$ mole in 2 ml of H_2O or D_2O). The reaction rate is monitored by ^{31}P NMR spectroscopy. The conversion is complete after time given in table 1. After removal of water under vacuum, the phosphonium salts are dried at 50°C for 2 days in vaccuo and stored in an exsiccator.

- *[1-(carboxymethylene)hexyl]tris(3-sulfophenyl)phosphonium inner salt, trisodium salt : (Z,E)* : **4a** (390 mg, 95 %) ; $^{31}P\{^{1}H\}$ NMR, H_2O, δ ppm : 23.5 (s, Z, 75 %), 26.9 (s, E, 25 %) ; ^{1}H NMR, D_2O, δ ppm : 0.70 (t, CH_3), 0.90-1.10 (m, CH_2), 2.30 (m, CH_2-C=), 7.03 (d, $^{3}J_{P-H}$ = 25 Hz, H_2, E), 7.45 (d, $^{3}J_{P-H}$ = 36 Hz, H_2, Z), 7.5-8.4 (m, ArH).

- *[1-(carboxymethylene)hexyl]diphenyl(3-sulfophenyl)phosphonium inner salt, sodium salt (Z,E)* : **5a** (268 mg, 97 %) ; $^{31}P\{^{1}H\}$ NMR, H_2O, δ ppm : 22.5 (s, Z, 80 %), 26.1 (s, E, 20 %) ; ^{1}H NMR, D_2O, δ ppm : 0.70 (t, CH_3), 0.90-1.20 (m, CH_2), 2.27 (m, CH_2-C=C), 6.94 (d, $^{3}J_{P-H}$ = 25 Hz, E), 7.23 (half doublet, Z), 7.45-8.40 (m, Ar-H) ; $^{13}C\{^{1}H\}$ NMR, D_2O, δ ppm : 14.04 (s, CH_3,E), 14.20 (s, CH_3, Z), 22.06 (s, CH_2, Z), 22.25 (s, CH_2, E), 29.61 (broad, CH_2, Z), 29.78 (broad, CH_2, E), 31.24 (s, CH_2, Z), 31.78 (s, CH_2, E), 35.38 (broad, CH_2, Z), 35.91 (broad, CH_2, Z), 115-137 (aromatic and ethylenic), 145.55 (d, $^{3}J_{P-C}$ = 13 Hz, C-SO_3Na, E), 146.45 (d, $^{3}J_{P-C}$ = 13 Hz, C-SO_3Na, Z), 169.33 (d, $^{3}J_{P-C}$ = 6 Hz, CO_2, Z), 171.36 (d, $^{3}J_{P-C}$ = 21 Hz, CO_2, E).

-*[2-carboxyethenyl)tris(3-sulfophenyl)phosphonium inner salt, trisodium salt (Z,E)* : **4b** (3542 mg, 95 %) ; $^{31}P\{^{1}H\}$ NMR, H_2O, δ ppm : 17.1 (s, Z, 70 %), 19.9 (s, E, 30 %) ; ^{1}H NMR, D_2O, δ ppm : 6.97 (dd, $^{3}J_{P-H}$ = 22 Hz, $^{3}J_{H-H}$ = 17 Hz, H_2, E), 7.37 (dd, $^{3}J_{P-H}$ = 37 Hz, $^{3}J_{H-H}$ = 8 Hz, H_2, Z), 7.40-8.45 (m, ArH).

- *(2-carboxyethenyl)diphenyl(3-sulfophenyl)phosphonium inner salt, sodium salt (Z,E)* : **5b** (233 mg, 96 %) ; $^{31}P\{^{1}H\}$ NMR, H_2O, δ ppm : 16.0 (s, Z, 80 %), 18.9 (s, E, 20 %) ; ^{1}H NMR (300 MHz), D_2O, δ ppm : 6.61 (dd, $^{3}J_{H-H}$ = 17 Hz, $^{3}J_{P-H}$ = 16 Hz, H_2, E ; d upon irradiation of phosphorus at 19 ppm), 7.33 (d, $^{3}J_{H-H}$ = 12 Hz, $^{3}J_{P-H}$ = 21 Hz, H_2, Z ; d upon irradiation of phosphorus at 16 ppm), 7.40-8.25 (m, ArH and H_1) ; ^{13}C-NMR, D_2O, δ ppm : 118.3 (dt, $^{1}J_{P-C}$ =92 Hz, $^{2}J_{C-H}$ = 7 Hz, C_4, Z), 120.8 (dt, $^{1}J_{P-C}$ = 91 Hz, $^{2}J_{C-H}$ = 7 Hz, C_4, E), 120.9 (dt, $^{1}J_{P-C}$ = 93 Hz, $^{2}J_{C-H}$ = 8 Hz, C_{10}, Z), 123.3 (dd, $^{1}J_{P-C}$ = 92 Hz, $^{2}J_{C-H}$ = 8 Hz, C_{10}, E), 126.0 (dd, $^{1}J_{C-H}$ = 175 Hz, $^{1}J_{P-C}$ = 82 Hz, C_1, Z), 127.1 (dd, $^{1}J_{C-H}$ = 173 Hz, C_1, E), 147.9 (dd, $^{3}J_{P-C}$ = 13 Hz, $^{2}J_{C-H}$ = 6 Hz, C_6, Z), 148.4 (dd, $^{3}J_{P-C}$ = 13 Hz, $^{2}J_{C-H}$ = 6 Hz, C_6, E), 148.9 (ddd, $^{1}J_{C-H}$ = 174 Hz, $^{2}J_{C-H}$ = 5 Hz, $^{2}J_{P-C}$ = 4 Hz, C_2, E), 149.5 (ddd, $^{1}J_{C-H}$ = 174 Hz, $^{2}J_{C-H}$ = 5 Hz, $^{2}J_{P-C}$ = 4 Hz), 168.1 (d, $^{3}J_{P-C}$ = 21 Hz, C_3, E), 168.2 (d, $^{3}J_{P-C}$ = 8 Hz, C_3, Z).

- *(2-carboxy-1-phenylethenyl)tris(3-sulfophenyl)phosphonium inner salt, trisodium salt (Z,E)* : **4c** (not isolated) ; $^{31}P\{^{1}H\}$ NMR, H_2O, δ ppm : 23.5 (s, Z, 85 %), 25.1 (s, E, 15 %) ; ^{1}H NMR, D_2O, δ ppm : 7.35-8.43 (m, ArH).

- *(2-carboxy-1-phenylethenyl)diphenyl(3-sulfophenyl)phosphonium inner salt, sodium salt (Z,E)* : **5c** (270 mg, 97 %) ; $^{31}P\{^{1}H\}$ NMR, H_2O, δ ppm : 23.2 (s, Z, 70 %), 24.7 (s, E, 30 %) ; ^{1}H NMR, D_2O, δ ppm : 7.30-8.45 (m, ArH) ; $^{13}C\{^{1}H\}$ NMR, D_2O, δ ppm : 112-134 (aromatics and ethylenics), 142.21 (d, $^{3}J_{P-C}$ = 12 Hz, C-SO_3Na, Z), 142.75 (d, $^{3}J_{P-C}$ = 12 Hz, C-SO_3Na, E), 166.45 (d, $^{3}J_{P-C}$ = 5 Hz, CO_2, Z), 168.60 (d, $^{3}J_{P-C}$ = 21 Hz, CO_2, E).

- *(1,2-dicarboxyethenyl)tris(3-sulfophenyl)phosphonium inner salt, trisodium salt (Z,E)* : **4d** (not isolated) ; $^{31}P\{^{1}H\}$ NMR, H_2O, δ ppm : 26.6 (s, Z, 20 %), 28.0 (s, E, 80 %).

- *(1,2-dicarboxyethenyl)diphenyl(3-sulfophenyl)phosphonium inner salt, sodium salt (Z,E)* : **5d** (230 mg, 87 %) ; $^{31}P\{^{1}H\}$ NMR, H_2O, δ ppm : 24.5 (s, Z, 25 %), 25.4 (s, E, 75 %) ; $^{13}C\{^{1}H\}$ NMR, D_2O, δ ppm : 116-140 (aromatics and ethylenics), 146.55 (d, $^{3}J_{P-C}$ = 13 Hz, C-SO_3Na, Z), 147.67 (d, $^{3}J_{P-C}$ = 13 Hz, C-SO_3Na, E), 170.93 (d, $^{3}J_{P-C}$ = 7 Hz, CO_2, Z), 171.94 (d, $^{3}J_{P-C}$ = 21 Hz, CO_2, E), 173.43 (broad, CO_2, E), 175.63 (broad, CO_2,Z).

- *[1-(carboxymethylene-d)hexyl]tris(3-sulfophenyl)phosphonium inner salt, trisodium salt (Z,E)* : **6a** (397 mg, 97 %) ; $^{31}P\{^{1}H\}$ NMR, D_2O, δ ppm : 23.4 (s, Z, 70 %), 26.8 (s, E, 30 %) ; ^{1}H NMR, D_2O, δ ppm : 0.72 (t, CH_3), 0.95-1.15 (m, CH_2), 2.30 (m, CH_2-C=C), 7.45-8.45 (m, ArH).

- *(2-carboxyethenyl-2-d)tris(3-sulfophenyl)phosphonium inner salt, trisodium salt (Z,E)* : **6b** (357 mg, 96 %) ; $^{31}P\{^{1}H\}$ NMR, D_2O, δ ppm : 17.0 (s, Z, 70 %), 19.9 (s, E, 30 %) ; ^{1}H NMR, D_2O, δ ppm : 7.40-8.45 (m, ArH) ; $^{2}H\{^{1}H\}$ NMR, H_2O, δ ppm : 6.74 (s broad, E), 7.55 (s broad, Z).

- *(2-carboxy-1-phenylethenyl-2-d)tris(3-sulfophenyl)phosphonium inner salt, trisodium salt (Z,E)* : **6c** (not isolated) ; $^{31}P\{^{1}H\}$ NMR, D_2O, δ ppm : 23.5 (s, Z, 80 %), 25.0 (s, E, 20 %).

- *(1,2- dicarboxyethenyl-2-d)tris(3-sulfophenyl)phosphonium inner salt, trisodium salt (Z,E)* : **6d** (not isolated) ; $^{31}P\{^{1}H\}$ NMP., D_2O, δ ppm : 26.6 (s, Z, 30 %), 27.9 (s, E, 70 %).

- *[1-(carboxymethylene-d)hexyl]diphenyl(3-sulfophenyl)phosphonium inner salt, sodium salt (Z,E)*: **7a** (265 mg, 96 %) ; $^{31}P\{^{1}H\}$ NMR, D_2O, δ ppm : 23.5 (s, Z, 70 %), 26.2 (s, E, 30 %) ; ^{1}H NMR, D_2O, δ ppm : 0.75 (t, CH_3), 0.81-1.30 (m, CH_2), 2.32 (m, CH_2-C=), 7.40-8.40 (m, ArH) ; $^{2}H\{^{1}H\}$ NMR, H_2O-CH_3COCH_3, δ ppm : 6.75 (s, broad, E), 7.55 (s, broad, Z).

- *(2-carboxyethenyl-2-d)diphenyl(3-sulfophenyl)phosphonium inner salt, sodium salt (Z,E)* : **7b** (230 mg, 95 %) ; $^{31}P\{^{1}H\}$ NMR, H_2O, δ ppm : 16.5 (s, Z, 65 %), 18.9 (s, E, 25 %) ; $^{2}H\{^{1}H\}$ NMR, H_2O-CH_3COCH_3, δ ppm : 6.67 (s, broad, E), 7.53 (s, broad, Z).

- *(2-carboxy-1-phenylethenyl-2-d)diphenyl(3-sulfophenyl)phosphonium inner salt, sodium salt (Z,E)*: **7c** (264 mg, 93 %) ; $^{31}P\{^{1}H\}$ NMR, D_2O, δ ppm : 23.2 (s, Z, 35 %), 24.8 (s, E, 65 %).

- *(1,2-dicarboxyethenyl-2-d)diphenyl(3-sulfophenyl)phosphonium inner salt, sodium salt (Z,E)*: **7d** (228 mg ; 86 %) ; $^{31}P\{^{1}H\}$ NMR, D_2O, δ ppm : 18.8 (s, Z, 40 %), 24.9 (s, E, 60 %).

The reaction of **1** and **2** with α-alkynic acids has been scaled up in some experiments to check the preparative usefulness of the method. For example the reaction of **2** ($2.7.10^{-3}$ mole, 985 mg) with **3a** (3.10^{-3} mole, 420 mg) and **3c** (3.10^{-3} mole, 440 mg) affords respectively **5a** (1.25 g, 92 %) and **5c** (1.30, 94 %).

Reaction of 2 with activated alkynes in biphasic system.

10^{-3} mole of **8a-e** or **9** are added to an aqueous solution of **2** ($5.5\ 10^{-4}$ mole in 2 ml of H_2O (D_2O), pH = 7, or H_2O-HCl (D_2O-DCl), pH = 0). The mixture is vigourously shaked for 2-3 mn (**8a-e**) or 16 h (**9**) at room temperature. The ^{31}P NMR spectra show that the reaction is complete. The aqueous phase is washed twice with ether in order to remove the excess of alkynes. The vinylphosphonium salts obtained in acidic medium can be extracted in $CHCl_3$ or CH_2Cl_2 by salting out. The organic layer is then dried over $MgSO_4$ and the solvent removed under vacuum. The vinylphosphonium salts can also be isolated from water after neutralisation and removal of water in vaccuo.

Vinylphosphonium salts **10a-e**, **17** (reactions performed in H_2O-HCl) :

- *(2-acetylethenyl)diphenyl(3-sulfophenyl)phosphonium chloride, sodium salt (Z,E)* : **10a** (350 mg isolated from water ; 134 mg, 52 % extracted in $CHCl_3$) ; $^{31}P\{^1H\}$ NMR, $CDCl_3$, δ ppm : 18.14 (s, Z, 78 %) ; 20.84 (s, E, 17 %) ; ^1H NMR, $CDCl_3$, δ ppm : 2.16 (s, CH_3, Z), 2.52 (s, CH_3, E), 6.66 (dd, $^3J_{H-H}$ = 17 Hz, $^3J_{P-H}$ = 16 Hz, H_2, E), 7.31 (dd, $^3J_{H-H}$ = 12 Hz, $^3J_{P-H}$ = 22 Hz, H_2, Z), 7.50-8.40 (m, ArH and H_1, Z and E). ^1H NMR with irradiation of the phosphorus nucleus at δ = 20.84 ppm, $CDCl_3$, δ ppm : 2.16 (s, CH_3, Z), 2.52 (s, CH_3, E), 6.66 (d, $^3J_{H-H}$ = 17 Hz, H_2, E), 7.30 (dd, broad, $^3J_{H-H}$ # 12 Hz, $^3J_{P-H}$ # 22 Hz, H_2, Z), 7.50-8.40 (m, ArH and H_1). ^1H NMR with irradiation of the phosphorus nucleus at δ = 18.14, $CDCl_3$, δ ppm : 2.16 (s, CH_3, Z), 2.52 (s, CH_3, E), 6.66 (dd broad, $^3J_{H-H}$ # 17 Hz, $^3J_{P-H}$ # 16 Hz, H_2, E), 7.31 (d, $^3J_{H-H}$ = 12 Hz, H_2, Z), 7.50-8.40 (m, ArH and H_1). ^{13}C NMR, $CDCl_3$, δ ppm : 28.5 (q, $^1J_{C-H}$ = 121 Hz, CH_3, E), 30.1 (q, $^1J_{C-H}$ = 121 Hz, CH_3, Z), 116.2 (d, $^1J_{P-C}$ = 92 Hz, C_4, E), 116.3 (d, $^1J_{P-C}$ = 92 Hz, C_4, Z), 119.2 (d, $^1J_{P-C}$ = 92 Hz, C_{10}, Z), 119.5 (d, $^1J_{P-C}$ = 92 Hz, C_{10}, E), 121.5 (dd, $^1J_{P-C}$ = 81 Hz, $^1J_{C-H}$ = 173 Hz, C_1, Z), 122.2 (dd, $^1J_{P-C}$ = 81 Hz, $^1J_{C-H}$ = 173 Hz, C_1, E), 149.1 (dd, $^3J_{P-C}$ = 12 Hz, $^2J_{C-H}$ = 6 Hz, C_6, Z), 149.6 (dd, $^3J_{P-C}$ = 13 Hz, $^2J_{C-H}$ = 12 Hz, C_6, E), 151.4 (d, $^1J_{C-H}$ = 168 Hz, C_2, Z), 151.6 (d, $^1J_{C-H}$ = 167 Hz, C_2, E), 195.9 (d, $^3J_{P-C}$ = 20 Hz, C_3, E), 196.6 (d, $^3J_{P-C}$ = 8 Hz, C_3, Z), 129-137 (C_5, C_7, C_8, C_9, C_{11}, C_{12}, C_{13}).

- *(2-carbomethoxyethenyl)diphenyl(3-sulfophenyl)phosphonium chloride, sodium salt (Z,E)* : **10b** (385 mg isolated from water ; 125 mg, 47 % extracted in $CHCl_3$) ; $^{31}P\{^1H\}$ NMR, $CDCl_3$, δ ppm : 17.17 (s, Z, 65 %) ; 19.86 (s, E, 35 %) ; ^1H NMR, $CDCl_3$, δ ppm : 3.35 (s, CH_3, Z), 3.81 (s, CH_3, E), 6.54 (dd, $^3J_{P-H}$ = 20 Hz, $^3J_{H-H}$ = 17 Hz, H_2, E), 8.04 (dd, $^2J_{P-H}$ = 20 Hz, $^3J_{H-H}$ = 17 Hz, H_1, E), 7.50-8.40 (m, Ar-H and H_1 and H_2 of Z isomer). ^1H NMR with irradiation of the phosphorus nucleus at δ = 19.86 ppm, $CDCl_3$, δ ppm : 3.35 (s, CH_3, Z), 3.81 (s, CH_3, E), 6.54 (d, $^3J_{H-H}$ = 17 Hz, H_2, E), 8.04 (d, $^3J_{H-H}$ = 17 Hz, H_1, E), 7.50-8.40 (m, Ar-H and H_1 and H_2 of the Z isomer). The irradiation of the phosphorus nucleus resonating at 17.17 ppm did not modify the ^1H NMR spectrum. ^{13}C NMR, $CDCl_3$, δ ppm : 52.9 (q, $^1J_{C-H}$ = 149 Hz, CH_3, Z), 53.3 (q, $^1J_{C-H}$ = 149 Hz, CH_3, E), 115.3 (d, $^1J_{P-C}$ = 91 Hz, C_4, E), 115.8 (d, $^1J_{P-C}$ = 91 Hz, C_{10}, E), 118.2 (d, $^1J_{P-C}$ = 92 Hz, C_4, Z), 118.3 (d, $^1J_{P-C}$ = 91 Hz, C_{10}, Z), 124.4 (dd, $^1J_{C-H}$ = 174 Hz, $^1J_{P-C}$ = 80 Hz, C_1, Z), 124.5 (dd, $^1J_{C-H}$ = 174 Hz, $^1J_{P-C}$ = 83 Hz, C_1, E), 145.2 (dt, $^2J_{P-C}$ = 4 Hz, $^1J_{C-H}$ = 170 Hz, $^2J_{C-H}$ = 4 Hz, C_2, E), 145.6 (dt, $^2J_{P-C}$ = 4 Hz, $^1J_{C-H}$ = 174 Hz, $^2J_{C-H}$ = 4 Hz, C_2, Z), 149.6 (dd, $^3J_{P-C}$ = 12 Hz, $^2J_{C-H}$ = 8 Hz, C_6, Z), 150.2 (dd, $^3J_{P-C}$ = 12 Hz, $^2J_{C-H}$

= 8 Hz, C_6, E), 162.6 (d, $^3J_{P-C}$ = 9 Hz, C_3, Z), 163.7 (d, $^3J_{P-C}$ = 24 Hz, C_3, E), 129-138 (C_5, C_7, C_8, C_9, C_{11}, C_{12}, C_{13}).

- *(2-carboethoxyethenyl)diphenyl(3-sulfophenyl)phosphonium chloride, sodium salt (Z,E)*: **10c** ; *(2-carbopropoxyethenyl)diphenyl(3-sulfophenyl)phosphonium chloride, sodium salt (Z,E)* : **10d** ; *(2-carbopentoxyethenyl)diphenyl(3-sulfophenyl)phosphonium chloride, sodium salt (Z,E)*: **10e** ; *(2-formyl-1-phenylethenyl)diphenyl(3-sulfophenyl)phosphonium chloride, sodium salt (Z,E)*: **10f** ; $^{31}P\{^1H\}$ NMR, H_2O-CD_3COCD_3, δ ppm ; **10c** : 16.7 (s, Z, 55 %), 19.2 (s, E, 19 %). **10d** : 16.7 (s, Z, 52 %), 19.1 (s, E, 33 %). **10e** : 15.9 (s, Z, 49 %), 18.6 (s, E, 25 %). **10f** : 21.05 (s, Z, 60 %), 23.99 (s, E, 40 %).

Remark : The pure E isomers have been isolated by heating the crude Z and E mixtures in aqueous solution for 24 h at 60°C. The spectroscopic data of the Z isomers have thus been obtained by comparison of the NMR spectra of the Z and E mixtures with those of the pure E isomers.

Monodeuterated vinylphosphonium salts (reactions performed in D_2O-DCl).

- *(2-acetylethenyl-2-d)diphenyl(3-sulfophenyl)phosphonium chloride, sodium salt (Z,E)*: **15a** (370 mg isolated from water ; 152 mg, 59 % extracted in $CHCl_3$) ; $^{31}P\{^1H\}$ NMR, $CDCl_3$, δ ppm : 18.32 (s, Z) ; 20.96 (s, E) ; ^1H NMR, $CDCl_3$, δ ppm : 2.17 (s, CH_3, Z), 2.54 (s, CH_3, E), 7.25-8.25 (m, Ar-H and H_1, Z and E). ^{13}C NMR, E isomer, $CDCl_3$, δ ppm : 28.5 (q, $^1J_{C-H}$ = 129 Hz, CH_3), 116.0 (d, $^1J_{P-C}$ = 91 Hz, C_4), 116.3 (d, $^1J_{P-C}$ = 91 Hz, C_{10}), 122.4 (dd, $^1J_{P-C}$ = 80 Hz, $^1J_{C-H}$ = 172 Hz, C_1), 149.6 (dd, $^3J_{P-C}$ = 12 Hz, $^2J_{C-H}$ = 11 Hz, C_6), 151.2 (t, $^1J_{C-D}$ = 18 Hz), 195.9 (d, $^3J_{P-C}$ = 20 Hz, C_3), 129-138 (C_5, C_7, C_8, C_9, C_{11}, C_{12}, C_{13}). $^2H\{^1H\}$NMR, H_2O-CH_3OH, δ ppm : 6.80 (s broad, E), 7.71 (s broad, Z).

- *(2-carbomethoxyethenyl-2-d)diphenyl(3-sulfophenyl)phosphonium chloride, sodium salt (Z,E)*: **15b** (390 mg isolated from water ; 140 mg, 52 % extracted in $CHCl_3$) ; $^{31}P\{^1H\}$ NMR, $CDCl_3$, δ ppm : 17.17 (s, Z) ; 19.89 (s, E) ; ^1H NMR, CD_2Cl_2, δ ppm : 3.36 (s, CH_3, Z), 3.82 (s, CH_3, E), 7.40-8.30 (m, Ar-H and H_1, Z and E). $^2H\{^1H\}$NMR, H_2O-CH_3OH, δ ppm : 6.97 (s broad, E), 7.85 (s broad, Z).

- *(2-formyl-1-phenylethenyl-2-d)diphenyl(3-sulfophenyl)phosphonium chloride, sodium salt (Z,E)*: **15f** ; 410 mg isolated from water ; 196 mg, 67 % extracted in $CHCl_3$) ; $^{31}P\{^1H\}$ NMR, H_2O-CD_3COCD_3, δ ppm : 21.30 (s, Z) ; 24.1 (s, E).

^{31}P NMR study of the reactions of 2 with 8a-e at neutral pH : ($^{31}P\{^1H\}$NMR, H_2O).

Reaction with **8a**, δ ppm : 34.25 (s, **13**, 21 %), 38.17 (s, **12a**, 13 %), 39.00 (s, **11a**, 47 %). Reaction with **8b**, δ ppm : 15.47 (s, **14**, 38 %), 16.60 (s, **10b** Z, 42 %), 18.94 (s, **5b** E, 7 %), 19.09 (s, **10b** E, 8 %), 33.04 (s, **13**, 2 %), 37.79 (s, **11b**, 3 %). 280 mg ($1.1.10^{-3}$ mole) of silver triflate were then added to the aqueous solution and the $^{31}P\{^1H\}$ NMR spectrum recorded immediately, δ ppm : 16.45 (s, **5b** Z, 37 %), 16.60 (s, **10b** Z, 43 %), 18.94 (s, **5b** E, 7 %), 19.09 (s, **10b** E, 8 %), 34.02 (s, **13**, 2 %), 37.87 (s, **11b**, 3 %). Reaction with **8c**, δ ppm : 15.47 (s

14, 33 %), 16.68 (s, **10c** Z, 30 %), 18.86 (s, **5b** E, 12 %), 19.09 (s, **10c** E, 6 %), 34.47 (s, **13**, 9 %), 37.60 (s, **12c**, 1 %), 38.02 (s, **11c**, 9 %). Reaction with **8d**, δ ppm : 15.47 (s, **14**, 42 %), 16.68 (s, **10d** Z, 30 %), 18.87 (s, **5b** E, 6 %), 19.09 (s, **10d** E, 4 %), 34.17 (s, **13**, 2 %), 37.40 (s, **12d**, 1 %), 37.79 (s, **11d**, 13 %). Reaction with **8e**, δ ppm : 15.55 (s, **14**, 18 %), 16.60 (s, **10e** Z, 6 %), 18.94 (s, **10e** E, 2 %), 24.32 (s, **13**, 12 %), 37.06 (s, **12e**, 11 %), 36.73 (s, **11e**, 20 %). Reaction with **9**, δ ppm : 34.70 (s, **13**, 95 %). In all these mixtures, the compound **5b** was identified by addition of small amounts of authentic sample **5b** prepared independently by an unambiguous procedure (vide supra).

- Reactivity of vinylphosphonium salts in the presence of base

24 mg (6.10^{-4} mole) of sodium hydroxide were added to an aqueous solution of vinylphosphonium salt ($5.5.10^{-4}$ mole in 2 ml of H_2O). The reaction mixture was allowed to stand at room temperature for 15 mn while it turns slight yellow. The ^{31}P NMR spectra showed in all cases a quantitative transformation of the vinylphosphonium salts.

- The disulfonated vinyl phosphine oxides **16a-b** obtained from **4a-b** were isolated after neutralisation of the aqueous solution and removal of water.

- *[1-(carboxymethylene)hexyl]di(3-sulfophenyl)phosphine oxide, disodium salt*: **16a** (310 mg, 97 %) ; ^{31}P {^1H} NMR, H_2O, δ ppm : 38.32 (s) ; ^1H NMR, D_2O, δ ppm : 0.81 (t, CH_3), 1-1.60 (m, CH_2), 2.32 (m, CH_2-C=), 6.70 (d, $^3J_{P-H}$ = 26 Hz, H_2), 7.65-8.50 (m, ArH).

- *(2-carboxyethenyl)di(3-sulfophenyl)phosphine oxide, disodium salt*: **16b** (275 mg, 98 %) ; ^{31}P {^1H} NMR, H_2O, δ ppm : 38.54 (s) ; ^1H NMR, D_2O, δ ppm : 6.95 (dd, $^3J_{P-H}$ = 29 Hz, $^3J_{H-H}$ = 12 Hz, H_2), 7.50-8.25 (m, ArH).

- The monosulfonated vinylphosphonium salts **5a-b** and **10a-f** gave a mixture of vinylphosphine oxides (**11**, **12**) and triarylphosphine oxide **13** upon addition of NaOH. The ^{31}P NMR spectra of the crude mixtures gave the following data (^{31}P {^1H} NMR, H_2O) : reaction with **5a**, δ ppm : 37.83 (s, **11a**, 60 %), 38.21 (s, **12a**, 40 %). Reaction with **5b** : 38.39 (s, **11b**, 70 %), 38.77 (s, **12b**, 30 %). Reaction with **10a** (Z,E) : 34.02 (s, **13**, 15 %), 37.94 (s, **11b**, 13 %), 38.62 (s, **12b**, 72 %). Reaction with **10b** (Z,E) : 33.27 (s, **13**, 14 %), 38.09 (s, 14 %), 38.39 (s, 16 %), 38.62 (s, 50 %) (**11b** and **12b**, Z and E). Reaction with **10c** (Z,E) : 34.77 (s, **13**, 5 %), 38.99 (s, 9 %), 39.45 (s, 16 %), 39.60 (s, 64 %) (**11b** and **12b**, Z and E). Reaction with **10e** (Z,E) : 33.79 (s, **13**, 38 %), 37.64 (s, 4 %), 38.85 (s, 4 %), 39.37 (s, 54 %) (**11b** and **12b**, Z and E). Reaction with **10f** (Z,E) : 34.70 (s, **13**, 90 %).

- Preparation of alkenes

- starting from 1

2.10^{-3} mole of acetylenic acid **3c** or **3d** were added to an aqueous solution of **1** (2.10^{-3} mole in 5 ml of H_2O or D_2O). The reaction mixture was stirred at room temperature for 2 h (**3c**) or 5 h (**3d**). Hydrochloric acid was then added to pH = 1.

The cinnamic acid **19a** (reaction performed in H_2O) and the dideuteriocinnamic acid **21a** (reaction performed in D_2O) were extracted from the aqueous phase with chloroform ; the organic layer was then dried over $MgSO_4$ and the solvent was removed under vacuum.

- *trans* -cinnamic acid **19a** : 281 mg, 95 % yield ; F (°C) = 132 (litt [24] : 135) ; ^1H NMR, $CDCl_3$, δ ppm : 6.43 (d, $^3J_{H-H}$ = 16 Hz, =CH), 7.20-7.60 (m, ArH), 7.75 (d, $^3J_{H-H}$ = 16 Hz, =CH), 9.80 (s broad, CO_2H) ; Mass spectrometry, $M^{+\cdot}$ ($C_9H_8O_2$) : 148.0525 (found), 148.05243 (calculated). Elemental analysis found : 72.6 % C, 5.6 % H ; calculated : 72.9 % C, 5.4 % H.

- *trans* -[αβ-$^2H_2$]cinnamic acid **21a** : 270 mg, 90 % yield after recristallisation ; F (°C) = 134 ; ^1H NMR, $CDCl_3$, δ ppm : 7.25-7.65 (m, Ar-H), 10.30 (s broad, CO_2H) ; Mass spectrometry, $M^{+\cdot}$ ($C_9H_6O_2D_2$) : 150.06448 (found), 150.06498 (calculated), isotopic purity : 95.5 %. Elemental analysis found : 71.8 % C, 4.1 % H ; calculated : 72 % C, 4 % H.

The fumaric acid **19b** (reaction performed in H_2O), and the dideuteriofumaric acid **21b** (reaction performed in D_2O) were obtained by using the following procedure. The reaction mixture was acidified to pH = 1 with hydrochloric acid and the solvent removed at 50°C under vacuum. The resulting crude solid is then added to 30 ml of absolute ethanol, the insoluble material is removed by filtration and the alcoholic solution is concentrated to dryness.

- Fumaric acid **19b** : 202 mg, 87 % yield ; F (°C) = 299 subl (litt [24] : 300) ; ^1H NMR, CD_3COCD_3, δ ppm : 6.79 (s, =CH), 10.86 (s broad, CO_2H) ; Mass spectrometry, $M^{+\cdot}$ ($C_4H_4O_4$) : 116.0108 (found), 116.01095 (calculated). Elemental analysis found : 41.2 % C, 3.5 % H ; calculated 41.4 % C, 3.4 % H.

-[αβ-$^2H_2$] fumaric acid **21b** : 207 mg, 89 % yield ; F(°C) = 300 (subl) ; ^1H NMR, CD_3COCD_3, δ ppm : 10.73 (s broad, CO_2H). Mass spectrometry, $M^{+\cdot}$ ($C_4HO_4D_3$) : 119.0295 (found), 119.02979 (calculated), isotopic purity 95.8 %. Elemental analysis found 40.2 % C, 0.9 % H ; calculated 40.3 % C, 0.8 % H.

2.10^{-3} mole of aldehyd **9** were added to an aqueous solution of **1** ($2.2.10^{-3}$ mole in 5 ml of H_2O or D_2O). The reaction mixture was stirred at room temperature overnight under N_2. The aqueous phase was then washed with ether, the organic layer was dried over $MgSO_4$ and the solvent removed under vacuum.

- *trans* -cinnamaldehyde **19c** (reaction performed in H_2O) : 260 mg, 98 % yield ; ^1H NMR, $CDCl_3$, δ ppm : 6.69 (dd, $^3J_{H-H}$ = 16 Hz, $^3J_{H-H}$ = 8 Hz, =CH), 7.36-7.63 (m, ArH and =CH), 9.69 (d, $^3J_{H-H}$ = 8 Hz, CHO). Elemental analysis found : 82 % C, 5.9 % H ; calculated : 81.7 % C, 6.0 % H.

- *trans* -[αβ-$^2H_2$]cinnamaldehyde **21c** (reaction performed in D_2O) : 255 mg, 96 % yield ; ^1H NMR, $CDCl_3$, δ ppm : 7.40-7.60 (m, ArH), 9.70 (s, CHO). $^2H\{^1H\}$ NMR, $CHCl_3$, δ ppm : 6.81 (s, =CD), 7.72 (s, =CD). Elemental analysis found 80.9 % C, 4.7 % H ; calculated 80.5 % C, 4.5 % H.

- **Starting from 2**

The vinylphosphonium salts **5c, 5d, 6c, 6d, 10f** were prepared as previously described in H_2O (HCl) or D_2O (DCl) for the deuterated products. To an aqueous solution of the suitable salt (1 g in 15 ml of H_2O or D_2O) was added 0.5 g of Na_2CO_3. The reaction mixture was allowed to stand at room temperature for 15 mn (the ^{31}P NMR spectra showed only the signal of **13**) and then acidified to pH = 1 by addition of hydrochloric acid. The alkenes were isolated as described above. **22a** and **22b** were obtained from **6c** and **6d** in H_2O.

- *trans*-[α-^{2}H]cinnamic acid **22a** : 260 mg, 88 % yield ; F(°C) = 134 ; ^{1}H NMR, $CDCl_3$, δ ppm : 7.20-7.60 (m, Ar-H), 7.72 (s, =CH), 10.1 (s broad, CO_2H) ; Mass spectrometry, $M^{+\cdot}$ ($C_9H_7O_2D$) : 149.0581 (found), 149.0587 (calculated), isotopic purity : 96.3 %. Elemental analysis found 72.6 %C, 4.8 % H ; calculated 72.4 % C, 4.7 % H.

-[α-^{2}H]fumaric acid **22b** : 200 mg, 85 % yield ; F(°C) = 298 (subl) ; ^{1}H NMR, CD_3COCD_3, δ ppm : 6.78 (s, =CH), 10.80 (s broad, CO_2H) ; Mass spectrometry, $M^{+\cdot}$ ($C_4H_3O_4D$) : 117.0168 (found), 117.01723 (calculated), isotopic purity : 93 %. Elemental analysis found 41.4 % C, 2.9 % H ; calculated 41.0 % C, 2.6 % H.

23a and **23c** were obtained from **5c** and **10f** in D_2O :

- *trans*-[β-^{2}H]cinnamic acid **23a** : 270 mg, 90 % yield ; F(°C) = 135 ; ^{1}H NMR, $CDCl_3$, δ ppm : 6.45 (s, =CH), 7.25-7.65 (m, ArH), 10.4 (s broad, CO_2H) ; Mass spectrometry, $M^{+\cdot}$ ($C_9H_7O_2D$) : 149.0589 (found), 149.0587 (calculated), isotopic purity : 95.5 %. Elemental analysis found 72.8 % C, 4.9 % H ; calculated 72.4 % C, 4.7 % H.

- *trans*-[β-^{2}H]cinnamaldehyde **23c** : 245 mg, 92 % yield ; ^{1}H NMR, $CDCl_3$, δ ppm : 6.69 (dt, $^3J_{H-H}$ = 7.7 Hz, $^3J_{H-D}$ = 2.5 Hz, = CH), 7.38-7.65 (m, ArH), 9.68 (d, $^3J_{H-H}$ = 8 Hz, CHO). Elemental analysis found 81.5 % C, 5.4 % H ; calculated 81.1 % C, 5.2 % H.

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