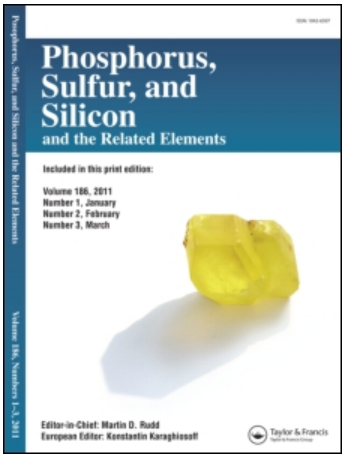

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ADDITIONS OF NUCLEOPHILES TO VINYL PHOSPHONIUM SALTS. A USEFUL WAY TO OBTAIN NEW SYNTHONS

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ADDITIONS OF NUCLEOPHILES TO VINYL PHOSPHONIUM SALTS. A USEFUL WAY TO OBTAIN NEW SYNTHONS

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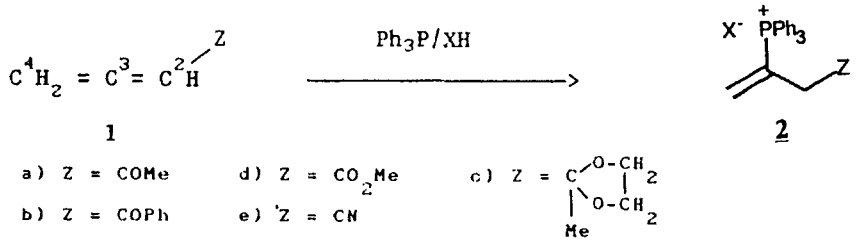
The vinylphosphonium salts **2.** obtained from allenyl compounds **1.** are phosphorus synthetic equivalents of γ functionalized allylic carbocations. Nucleophilic addition reactions give polyfunctional phosphonium salts, useful starting materials for further investigations. As a function of the basicity of the nucleophile, the addition reaction is in competition with elimination of the phosphorus group in **2**, leading to reformation of the allenic starting material **1**.

Key words: Vinylphosphonium salts; inversion of polarity; umpolung; allenyl compounds, nucleophilic additions.

INTRODUCTION

In two previous articles,[1,2] we have described the addition a^3, $a^{4,3}$ of a nucleophilic group such as an alcoholate (RO^-) or an amine (RNH_2) to the γ-carbon atom (C^4) of the activated allene la (Z = COMe). This was accomplished by introduction of a phosphonio group, by normal nucleophilic 1,4-addition of triphenylphosphine in an acidic medium, to methyl allenyl ketone (**la**). This implies the inversion of the polarity of the carbon atom C^4 in the allenic system.

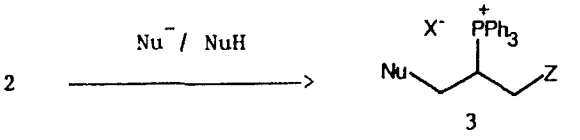


1 **2**

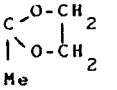
a) Z = COMe d) Z = CO_2Me c) Z =

b) Z = COPh e) Z = CN

In connection with this, we here report the results of our investigations on the comparative reactivity of compounds **2a–2e** towards different kinds of nucleophile (Table I).



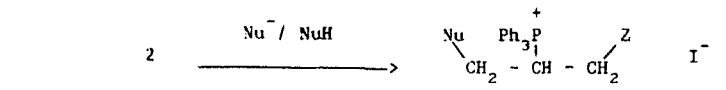
2 **3**

a) Z = COMe d) Z = CO_2Me c) Z = 

b) Z = COPh e) Z = CN

TABLE I

Reactions of vinylphosphonium salts **2** with different nucleophilic reactives



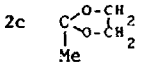
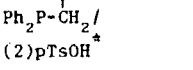
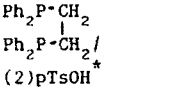
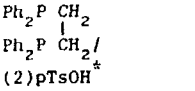
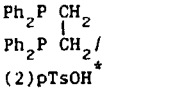
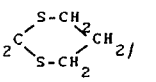
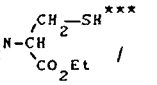
Salt 2 n°	Z	Nucleophile NuH/(n.eq.) Activating compound	[NuH]/[2]	Yield (%) [React.Temp./Time]	obtained compound
2a	CO Me	Ph_3P/ (1) pTsOH	5	72 [25°C/126h]	4a
2b	CO Ph	Ph_3P/ (1) pTsOH	5	66 [25°C/240h]	4b
2c		Ph_3P/ (1) pTsOH	5	48 [25°C/216h	4c
2d	CO_2Me	Ph_3P/ (1) pTsOH	1	32 [25°C/240h]	4d
2d	CO_2Me	Ph_3P/ (1) pTsOH	3	67 [25°C/168h]	4d
2d	CO_2Me	Ph_3P/ (1) pTsOH	5	77 [25°C/216h]	4d
2e	CN	Ph_3P/ (1) pTsOH	1	86 [25°C/24h]	4e
** 1a	CO Me	 (2)pTsOH*	1	70 [25°C/96h]	5a
** 1b	CO Ph	 (2)pTsOH*	1	63 [25°C/96h]	5b
** 1d	CO_2Me	 (2)pTsOH*	1	75 [25°C/96h]	5d
** 1e	CN	 (2)pTsOH*	1	91 [25°C/96h]	5e

TABLE I (*continued*)

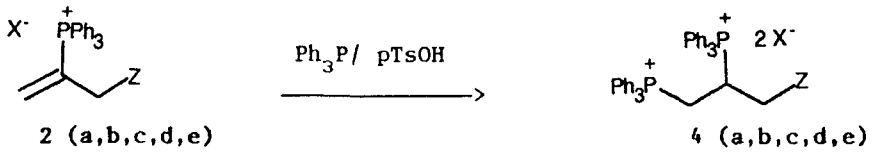
2c		$(EtO)_2P(O)H$/ (0.1) HNa	3	76 [25°C/4h]	6c
2d	CO_2Me	$(EtO)_2P(O)H$/ (0.1) HNa	3	84 [25°C/4h]	6d
2c		EtSH/ (1) HNa	1	76 [25°C/24h]	7c
2d	CO_2Me	EtSH	1	61 [25°C/4h]	7d
2e	CO_2Me	EtSH	1	67 [25°C/4h]	7e
2c		$CH_3CH_2NO_2$/ (1) HNa	1	87 [25°C/24h]	8c
2c		 (1) nBuLi	1	86 [25°C/24h]	9c
2c		 (1) HNa	1	75 [25°C/24h]	11

* pTsOH means anhydrous p-toluenesulfonic acid
** The corresponding allene 1 is the starting material
*** As the chlorhydrate

RESULTS

I. Addition a[A] to Vinyl Phosphonium Salts 2

The addition reaction with triphenylphosphine (Nu) in the presence of *p*-toluene sulfonic acid gave the corresponding diphosphonium salt **4** with good yields. We observed that the ratio Nu^-/**2** required depends on the nature of Z in **2** (Table I).



2 (a,b,c,d,e) **4 (a,b,c,d,e)**

TABLE II

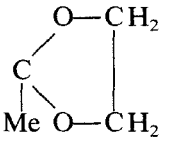
Characteristic data of newly prepared phosphonium salts

Compound	M.P. °C	Formula M.W.	Analysis % Calcd./ Found C	H	P	I	^{31}P-NMR (δ ppm, J=Hz)
4a	183.9	$C_{41}H_{38}O\,P_2I_2,CH_3OH$	56.41	4.69	6.92	28.38	23.54 (d, J=43.9)
		894.19	56.08	4.42	6.90	27.90	35.70 (d, J=43.9)
4b	193.5	$C_{46}H_{40}O\,P_2I_2,CH_3OH$	59.03	4.60	6.47	26.54	23.22 (d, J=45.3)
		956.25	58.82	4.46	6.33	26.39	35.96 (d, J=45.3)
4c	250.8	$C_{43}H_{42}O_2P_2I_2,CH_3OH$	56.32	4.90	6.60	27.05	23.48 (d, J=43.8)
		938.22	55,97	4.75	6.58	26.90	35.65 (d, J=43.8)
4d	192.6	$C_{41}H_{38}O_2P_2I_2,CH_3OH$	55.44	4.61	6.80	27.89	23.90 (d, J=44.5)
		909.78	55 26	4.27	6.83	27.62	35.80 (d, J=44.5)
4e	239.7	$C_{40}H_{35}NP_2I_2,CH_3OH$	56.14	4.44	7.06	28.93	20.34 (d, J=50.6)
		877.18	55.90	4.27	6.93	28.22	32.17 (d, J=50.6)
5a	217.0	$C_{31}H_{32}OP_2I_2$	50.54	4.34	8.42	34.51	16.11 (d, J=25.5)
		736.32	50.32	4.34	8.10	34.10	22.60 (d, J=25.5)
5b	>300.0	$C_{36}H_{34}OP_2I_2$	54.13	4.26	7.76	31.82	15.80 (d, J=25.5)
		798.38	54.15	4.21	7.77	31.09	22.50 (d, J=25.5)
5d	215.8	$C_{31}H_{32}O_2P_2I_2,1/2\ CH_3OH$	49.26	4.42	8.06	33.04	16.00 (d, J=27.1)
		768.08	49.07	4.23	8.17	32.64	22.10 (d, J=27.1)
5e	235.0	$C_{30}H_{29}NP_2I_2,CH_3OH$	49.70	4.09	8.24	33.04	15.20 (d, J=22.0)
		751.07	49.45	4.01	8.17	32.78	20.30 (d, J=22.0)
6a	oil	$C_{27}H_{33}O_4P_2I$	53.15	5.40	10.15	20.79	22.10 (d, J=25.8)
		610.14	53.01	5.37	10.10	20.70	32.80 (d, J=25.8)
6c	172.2	$C_{29}H_{37}O_5P_2I$	53.24	5.65	9.46	19.39	26.60 (d, J=22.0)
		654.16	52.90	5.83	9.03	19.16	32.90 (d, J=22.0)
6d	122.3	$C_{27}H_{33}O_5P_2I$	51.79	5.27	9.89	20.26	24.60 (d, J=63.8)
		626.14	51.75	5.30	9.91	19.72	31.30 (d, J=63.8)
7c	130.0	$C_{27}H_{32}O_2SPI$	56.09	5.53	5.35	21.94	31.60 (s.)
		578.17	55.99	5.57	5.38	21.81	
7d	124.5	$C_{25}H_{28}O_2SPI$	54.58	5.08	5.63	23.06	31.60 (s.)
		550.14	54.20	5.10	5.49	22.83	
7e	119.0	$C_{24}H_{25}NSPI$	55.70	4.82	5.99	24.50	27.60 (s.)
		517.13	55.53	4.93	5.79	23.90	

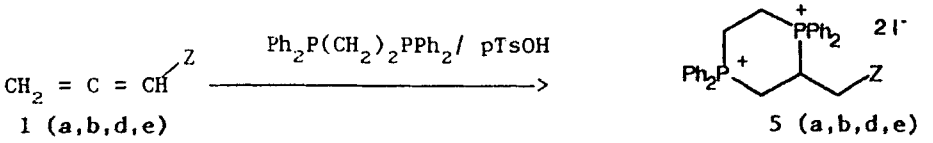
TABLE II (*continued*)

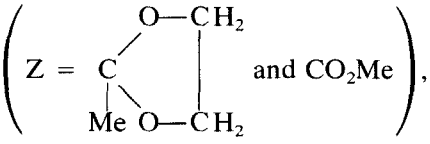
8a	132.1	$C_{25}H_{27}O_3NPI$	54.85	4.97	5.65	23.18	34.10 (s.)
		547.34	54.62	4.91	5.48	23.02	
8c	143.0	$C_{27}H_{31}O_4NPI$	54.84	5.24	5.23	21.46	34.10 (s.)
		591.17	54.59	5.37	5.25	21.27	
9a	136.3	$C_{27}H_{30}OS_2PI$	54.72	5.06	5.20	21.40	30.60 (s.)
		565.31	54.45	4.97	4.91	21.50	
9c	147.1	$C_{29}H_{34}O_2S_2PI$	54.71	5.34	4.87	19.96	29.30 (s.)
		636.40	54.76	5.24	4.74	19.65	
10	112.2	$C_{26}H_{28}O_3PI$	57.11	5.12	5.67	23.25	31.50 (s.)
		546.30	55.06	5.08	5.54	22.99	
11	112.2	$C_{26}H_{28}O_3PI$	57.11	5.12	5.67	23.25	33.40 (s.)
		546.30	55.06	5.08	5.54	22.99	

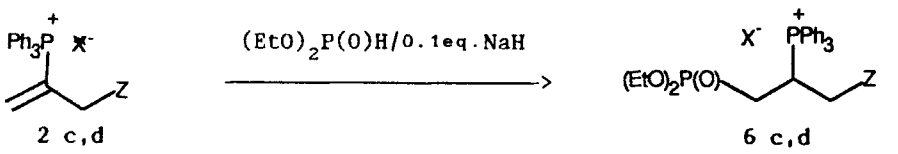
The rates of such reactions increase as a function of the group Z as follows:

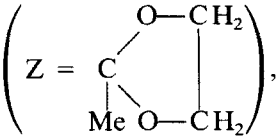
$$Z = CN >> CO_2Me > CO{-}Me > CO{-}Ph > \text{  }$$

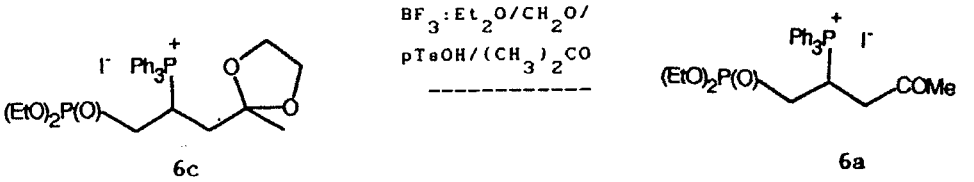
Starting from the allenes, **1(a,b,d,e)** we obtained directly the corresponding cyclic diphosphonium salts, **5** by consecutive a^3, a^4-diaddition[3] of bis(diphenyl phosphonio) 1,2-ethane (Nu). As a result of the more favorable entropy change for such annelations, an equimolecular amount of nucleophilic reagent was sufficient.



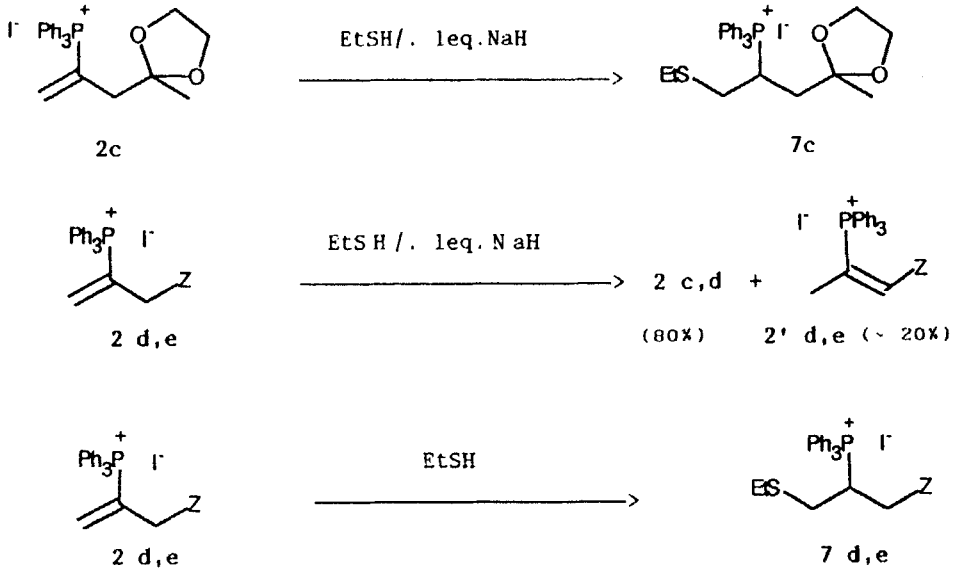
In the same manner, the phosphite $(EtO)_2P(O)H$, activated by a catalytic amount of NaH, reacted with salts **2c** and **2d**  , to give high yields (Table I) of compounds of type **6** bearing three functional groups: Z, Ph_3P^+ and $(EtO)_2P(O)$.

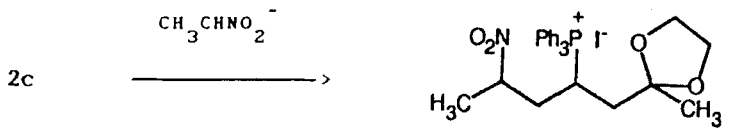


The salts, **2 a, b,** and **e** (with Z = COMe, COPh, and CN) gave, instead of the compounds expected, as a result of nucleophilic addition of $(EtO)_2P(O)^-$, a mixture of starting material, **2** accompanied by its isomer **2a'**,[4] (with the double bond conjugated to the carbonyl function). However the derivative **6a** (Z = COMe) could be prepared starting from compound **6c** (Z = ), by cleavage of its acetal function. This deprotection was accomplished in acetone solution in the presence of BF_3:Et_2O/CH_2O/pTsOH.[5]

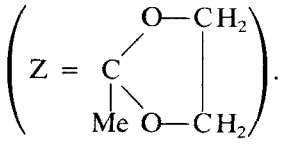


Similar results were obtained in reactions of the thiolate anion (Nu = EtS^-) and the vinyl salts, **2c**, **d**, and **e**. Only regiospecific addition of the thiolate anion



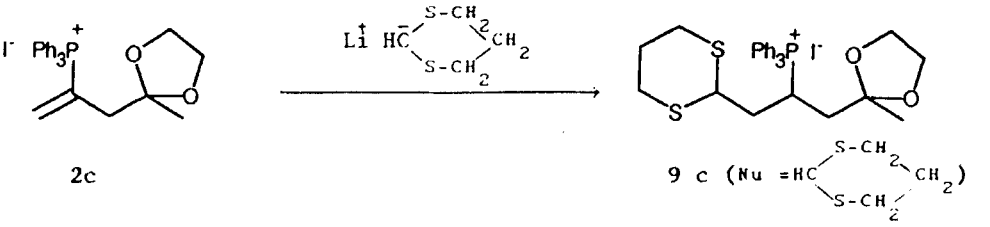


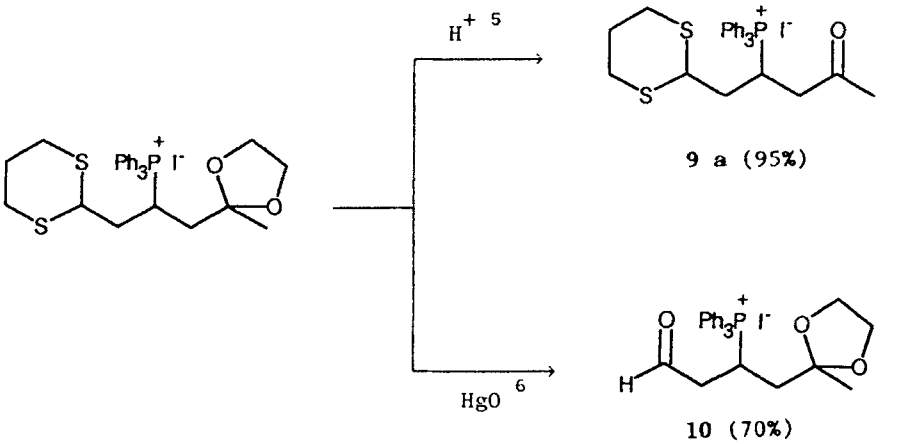
8 c

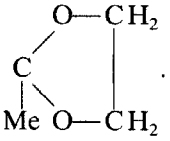
to the activated double bond of **2c** occurs and leads to the β-ethylthiophosphonium salt, **8c** (Z = ). For all the others a mixture of the corresponding starting salt **2**, and of its isomer, **2′** was obtained.

8 a

The β-ethylthiophosphonium salts, **7d** and **7e** (Z = CO_2Me, and Z = CN) were obtained in good yields from the corresponding salts, **2d** and **2e** using ethane thiol as nucleophile, without hydride ion activation.



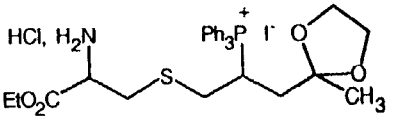


The addition of the α-nitro ethyl anion was only investigated in the case of the vinyl phosphonium salt, **2c** with Z =  . The expected salt, **8c** was obtained.

The salt **8a** was generated from the salt **8c**, by deprotection of the ketone function.

In the same way salt **9c** was obtained by nucleophilic addition of 2-lithio-1,3-dithiane to the salt **2c**. Subsequent appropriate hydrolysis of **9c** gave the ketonic phosphonium salt **9a** or the aldehydic phosphonium salt **10**.

As expected, the vinylic phosphonium salt **2c** reacts with 1-cysteine ethyl ester hydrochloride hydrate to give the corresponding saturated salt **11**.



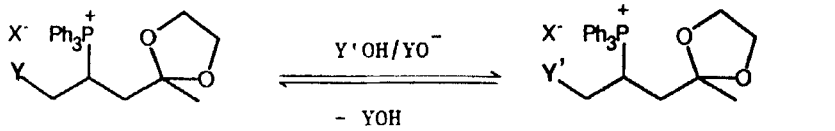
11

All phosphonium salts **5–11**, are new compounds. Satisfactory elemental analyses and spectral data were obtained. Some typical spectral data are given in Table II.

DISCUSSION

I. Reversibility of Nucleophilic Addition to the Vinylphosphonium Salts **2**

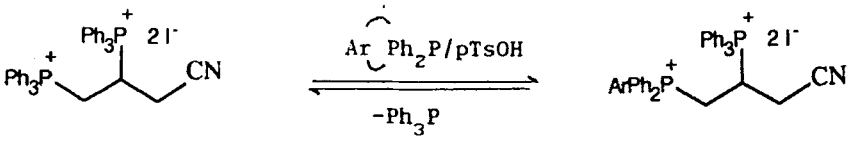
Many examples of nucleophilic addition to vinylphosphonium salts have been reported,[6–9] and the reaction has been extensively studied in our laboratory.[10] We have shown that for β-substituted phosphonium salts such as **12c** exchange of the heteroatomic group Y occurs and gives substantial amounts of salt **12'c** through base-catalyzed elimination-addition.



12c (Y = OMe) **12'c (Y' = OEt)**

We have confirmed the reversibility of the acid-catalyzed addition of triphenylphosphine to the vinylphosphonium salt **2a**. Using the same experimental conditions as in the synthesis of the disalts **4**, the salt **4e** was allowed to react with one equivalent of p-anisyldiphenylphosphine. After 24 h, a mixture of the diphosphonium salts **4e** and **4'e** was obtained in the proportion of 88 to 12%, respectively.

We also studied, always with the same conditions, the kinetic variations in the yields of disalt, **4a** using as starting material one equivalent of the vinylic salt **2a** and excess three and five equivalents of triphenylphosphine. With 3 equivalent



4e 4'e (Ar = *p*-$OMeC_6H_4$)

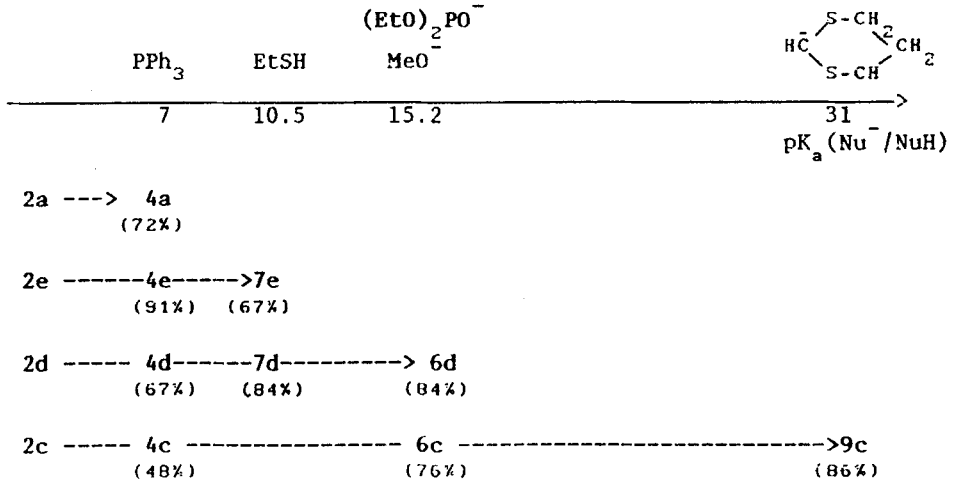
after 4 days the maximum yield obtained was 47% whereas with 5 equivalent the maximum yield reached 80% in 5 days.

II. Competition between Nucleophilic Addition, and β-elimination of the Triphenylphosphonio Group in the Salts **2**, *as a Function of the Nature of the Nucleophile NuH Used*

The results obtained appear to be influenced by both the nucleophilicity and basicity of groups NuH.

In the salt **2** the acidity of the methylene protons in the β-position with respect to group Z depends on the nature of Z. The results show that for each salt **2** only nucleophiles which fall within a given range of pKa will undergo the addition reaction with that salt. The more acidic are the methylene protons in **2** the higher is their reactivity with basic nucleophiles. In such reactions, the nucleophile acting as a base gives, by β-elimination of the Hofmann type of the triphenylphosphonio group, the corresponding allene **1**, so addition does not occur.

This is illustrated in the following diagram. The salts **2a**, **2c**, and **2d**, are ordered as expected, in terms of the decreasing acidity of their methylene protons, and so in terms of enhanced aptitude to nucleophilic addition, but the salt **2e** is out of order. As is known,[11] the difference ΔpKa = [pka(CH_2CO_2R)—pKa(CH_2CN)] of methylene protons in the α-position with respect to an ester or a nitrile function, is only about one unit.



It is possible that the anomalous behaviour of salt **2e** is related to some feature of its structure. The ^1H NMR spectra of salts **2** in $CDCl_3$ (Table II), are in agreement with the general structure of this type of compound. However the methylene proton signals at δ 3.77–4.70 ppm for salts **2a**, **2b**, **2d**, and **2e**, and at δ 2.90 ppm for **2c** are doublets. These methylene protons appear in all cases as equivalent and the values of the $^3J_{PH}$ coupling constants are about 16 Hz except for **2e** for which $^3J_{PH}$ = 10 Hz. In acyclic compounds it is hazardous to deduce structural correlations from $^3J_{PH}$ values. More information might be obtained by variable temperature ^1H NMR studies.

In conclusion, we have shown that by using the Michael addition of a protonated nucleophilic group to vinylphosphonium salts **2** we obtain saturated trifunctional phosphonium salts **3**. In a future publication we will detail the synthetic potential of these salts as well as the possibility of converting them into phosphonium ylides.

EXPERIMENTAL

All melting points are uncorrected. The IR spectra were recorded, on KBr pellets, using Perkin-Elmer Infracord Spectrometer 377 G. The ^1H NMR spectra were recorded on a Varian spectrometer EM 360 at 60 MHZ or a Bruker spectrometer AC 250 at 250 MHZ using TMS as an internal reference. ^{31}P RMN spectra were recorded on the instrument Brûker WP80 DS (80 MHZ) with irradiation of the protons.

The appropriate precautions in handling moisture-sensitive compounds were observed. Solvents were dried by standard techniques. *Starting materials:* The allenyl compounds were prepared as reported: the allenyl methyl ketone,[12] the allenyl phenyl ketone,[13] the methyl α-allenyl carboxylate,[13] and the α-allenyl nitrile.[13] The vinylphosphonium salts **2** were prepared following the published method.[1]

General procedure for nucleophilic a[4]-addition to vinylphosphonium salt **2** using the typical published[1] procedure with some modifications. Details on the amount of reactants, reaction time of contact, and the yields of phosphonium salts **5–11** are given in Table I. Characteristic data for the salts **5–11** prepared are listed in Table II.

General preparation of diphosphonium diiodides **4a**, **4b**, **4c**, **4d**, *and* **4e:** To a (100 ml) solution of equimolecular quantities of *para*-toluene sulfonic acid and vinylphosphonium salt **2** (0.1 mmol) in anhydrous chloroform, at room temperature and under a nitrogen atmosphere, was added dropwise a solution (20 mL) of the equimolecular quantity of Ph_3P in the same solvent. After stirring during a given time (Table I), water (50 ml) was added, the layers separated, the organic phase was twice washed with (50 mL) aqueous solution of NaI (0.1 mmol), dried (anhydrous Na_2SO_4), concentrated to 7 ml and added dropwise to ether (500 ml). The precipitated crude salt **4** was recrystallized from a mixture of CH_2Cl_2/CH_3OH/THF (1/0.5/5).

General preparation of cyclic diphosphonium diiodides **5a**, **5b**, **5d**, *and* **5e:** To a (100 ml) solution of *para*-toluene sulfonic acid (0.2 mmol, 2 equiv.) and allene **1** (0.1 mmol, 1 equiv.) in anhydrous chloroform, at room temperature and under a nitrogen atmosphere, was added dropwise a solution (20 mL) of the equimolar quantity of $Ph_2P—(CH_2)_2—Ph_2P$ (0.1 mmol) in the same solvent. After stirring during a given time (Table I), water (50 ml) was added, the layers were separated, and the organic phase was twice washed with an aqueous solution (50 mL) of NaI (0.1 mmol, 1 equiv.), dried (anhydrous Na_2SO_4), concentrated to 7 ml and added dropwise to ether (500 ml). The precipitated crude salt **5** was recrystallized from a mixture of CH_2Cl_2/CH_3OH/THF/**1**/0.5/5.

General preparation of phosphonium iodides **6c**, **6d:** To a (100 ml) solution of diethylphosphite (1.9 mg, 14.10 mmol, 2 equiv.) and sodium hydride (33.6 mg, 1.41 mmol, 0.1 equiv.) in anhydrous acetonitrile, at room temperature and under a nitrogen atmosphere, was added dropwise a solution (20 mL) of vinyl triphenyl phosphonium iodide **2** (1.8 g, 7.05 mmol, 1 equiv.) in the same solvent. After stirring during a given time (Table I), water (50 ml) was added, the layers separated, the organic phase was dried (anhydrous Na_2SO_4), concentrated to 7 ml and added dropwise to ether (500 ml). The precipitated crude salt **6** was recrystallized from a mixture of $CH_2Cl_2/CH_3CO_2C_2H_5$(1/5).

Preparation of phosphonium iodide **6a:** A (50 ml) solution of diethylphosphite **6c** (5.0 g, 7.60 mmol, 1 equiv.), of *p*-toluenesulfonic acid (0.14 g, 0.76 mmol, 0.1 equiv.), of boron trifluoride etherate (1.2

g, 8.52 mmol, 1.12 equiv.) and aqueous 37% formaldehyde solution (5.7 ml, 76.0 mmol, 10 equiv.) in anhydrous acetone was left at room temperature under a nitrogen atmosphere and stirred during two days. Then the reaction mixture was neutralized by adding dropwise 0.1 N $NaHCO_3$-aqueous solution. Brine (50 ml) and CHCl (100 mL) were added, the layers separated, and the organic phase was twice washed with an aqueous solution (50 mL) of NaI (1 equiv.), dried (anhydrous Na_2SO_4), concentrated to 7 ml and added dropwise to ether (500 ml). The precipitated crude salt **6a** (Z = COMe) was recrystallized from a mixture of $CH_2Cl_2/CH_3CO_2C_2H_5$ (1/5).

Preparation of phosphonium iodide **7c:** To a (40 ml) solution of vinyl phosphonium iodide **2c** (9.0 g, 17.40 mmol, 1 equiv.) in anhydrous ethanethiol, at room temperature and under a nitrogen atmosphere, was added dropwise a solution (20 mL) of sodium hydride (1.27 mg, 1.72 mmol, 0.1 equiv.) in the same solvent. After stirring during a given time (Table I), water (50 ml) was added, the layers separated, the organic phase was dried (anhydrous Na_2SO_4), concentrated to 7 ml and added dropwise to ether (500 ml). The precipitated crude idodide **7c** was recrystallized from a mixture of $CH_2Cl_2/CH_3CO_2C_2H_5$ (1/5).

General preparation of phosphonium iodides **7d, 7e:** A (100 mL) solution of vinyl phosphonium salt **2d**, or **2e**, (17.00 mmol, 1 equiv.) in anhydrous ethanethiol, at room temperature and under a nitrogen atmosphere, was stirred during a given time (Table I), water (50 ml) was added, the layers separated, the organic phase was dried (anhydrous Na_2SO_4), concentrated to 7 ml and added dropwise to ether (500 ml). The precipitated crude iodide **7d**, or **7e** was recrystallized from a mixture of $H_2Cl_2/CH_3CO_2CH_3$ (1/3).

Preparation of phosphonium iodide **8c:** To a (80 ml) solution of nitroethane (0.8 mL, 8.50 mmol, 1.10 equiv.) in anhydrous tetrahydrofuran, at room temperature, anhydrous sodium hydride (0.20 g, 8.37 mmol, 1.00 equiv.) was added. Then, a (6 mL) solution of vinylphosphonium iodide **2c** (4.00 g, 8.50 mmol, 1 equiv.) in dichloromethane was added to the reaction mixture. After stirring at room temperature during a given time (Table I), 0.1 N aqueous HCl (5 mL) and also water (50 ml) were added, the layers separated, the organic phase was dried (anhydrous Na_2SO_4), concentrated to 7 ml and added dropwise to ether (500 ml). The precipitated crude iodide **8c** was isolated, and recrystallized from CH_2Cl_2/CH_3—$CO_2C_2H_5$ (1/5).

Preparation of phosphonium iodide **8a:** A (180 ml) solution of nitrophosphonium salt **8c** (10.0 g, 16.0 mmol, 1 equiv.), of *p*-toluenesulfonic acid (0.50 g, 1.6 mmol, 0.1 equiv.), of boron trifluoride etherate (13 ml, 16.0 mmol, 1.0 equiv.) and aqueous 37% formaldehyde solution (4.8 ml, 32.0 mmol, 2 equiv.) in anhydrous acetone was left at room temperature under a nitrogen atmosphere and stirred during two days. Then the reaction mixture was neutralized adding dropwise 0.1 N $NaHCO_3$-aqueous solution. Brine (50 ml) and $CHCl_3$ (100 mL) were added, the layers separated, and the organic phase was twice washed with an aqueous solution (50 mL) of NaI (1 equiv.), dried (anhydrous Na_2SO_4), concentrated to 7 ml and added dropwise to ether (500 ml). The precipitated crude salt **8a** (Z = COMe) was recrystallized from a mixture of $CH_2Cl_2/CH_3CO_2C_2H_5$ (1/5).

Preparation of phosphonium iodide **9c:** To a (100 ml) solution of 2-lithio 2,3-dithiane[14] (930.0 mg, 7.70 mmol) in anhydrous tetrahydrofuran, at room temperature, vinylphosphonium iodide **2c** (4.00 g, 7.70 mmol) was added. After stirring at room temperature during 90 min, the red solution was neutralized by adding 0.1 N HCl (5 mL). Water (50 ml) was added, and the layers separated. The organic phase was dried (anhydrous Na_2SO_4), concentrated to 7 ml and added dropwise to ether (500 ml). The precipitated crude iodide **9c** was isolated, and recrystallized from CH_2Cl_2/CH_3—$CO_2C_2H_5$ (1/2.5).

Preparation of phosphonium iodide **9a:** A (50 ml) solution of phosphonium salt **9c** (4.0 g, 6.20 mmol), of *p*-toluenesulfonic acid (0.10 g, 0.62 mmol, 0.1 equiv.), of boron trifluoride etherate (3.5 ml, 12.4 mmol, 2 equiv.) and aqueous 37% formaldehyde solution (1.2 ml, 12.4 mmol, 2 equiv.) in anhydrous acetone was left at room temperature under a nitrogen atmosphere and stirred during two days. Then the reaction mixture was neutralized adding dropwise 0.1 N $NaHCO_3$-aqueous solution. Brine (50 ml) and $CHCl_3$ (100 mL) were added, the layers separated, and the organic phase was twice washed with an aqueous solution (50 mL) of NaI (1 equiv.), dried (anhydrous Na_2SO_4), concentrated to 7 ml and added dropwise to ether (500 ml). The precipitated crude salt **9a** (Z = COMe) was recrystallized from a mixture of $CH_2Cl_2/CH_3CO_2C_2H_5$ (1/5).

Preparation of phosphonium iodide **10:** A (50 ml) solution of phosphonium salt **9c** (2.0 g, 3.10 mmol), of mercury (II) oxyde (600 mg, 4.65 mmol) in acetonitrile/water (4/1) was left at room temperature under a nitrogen atmosphere and stirred during two days. Then, the filtered solution was diluted by adding chloroform (100 ml). The layers separated, the aqueous solution was extracted using chloroform

(2 × 30 ml). The organic phases were combined, dried (anhydrous Na_2SO_4), concentrated to 7 ml and added dropwise to ether (500 ml). The precipitated crude iodide **10** was isolated, and recrystallized from $CH_2Cl_2/CH_3—CO_2C_2H_5$ (1/5).

Preparation of phosphonium iodide **11:** A (100 mL) solution of vinyl phosphonium salt **2c** (4.00 g, 7.70 mmol, 1 equiv.) and L-cysteine ethyl ester hydrochloride in acetonitrile/water (80/20) at room temperature was stirred during 24 h. Then water (50 ml) was added, the layers separated, the aqueous solution was extracted using chloroform (2 × 30 ml). The organic phases were combined, dried (anhydrous Na_2SO_4), concentrated to 7 ml and added dropwise to ether (500 ml). The precipitated crude iodide **11** was recrystallized from a mixture of $H_2CC1_2/CH_3CO_2CH_3$ (1/3).

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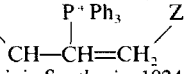
4. Isomer **2'** is: I^- 
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