Synthesis, Molecular Structure, and Spectroscopical Properties of Alkenylphosphonic Derivatives. 1. Vinyl-, Propenyl-, (Bromoalkenyl)-, and (Cyanoalkenyl)phosphonic Compounds

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Several vinyl-, propenyl-, (bromoalkenyl)-, and (cyanoalkenyl)phosphonate derivatives have been synthesized. The (2-cyanovinyl)phosphonates have been obtained with an important improvement in the yield (40% versus 6%). The separation of the *E* and *Z* isomers of the cyano derivatives and their hydrolysis to the corresponding phosphonic acids have been studied. The bromination and dehydrobromination of some alkenylphosphonic derivatives have also been studied. Spectroscopical studies from UV, IR, Raman, and ^{1}H, ^{13}C, and ^{31}P NMR have been performed in most of these derivatives. The C=C/P=O π conjugation exists but it is weak in all these compounds. Dipole moments and C=C/P=O conformational populations have been calculated theoretically by *ab initio* methods. The effect of the solvent polarity on the conformational population has been observed by IR spectroscopy disclosing two C=C/P=O conformers. Experimental and theoretical results have been compared, a high level of agreement has been found.

Introduction

Phosphonates are compounds of broad use and interest in chemistry, pharmacology, and industry, such as Wittig–Horner–Emmons reactives, as analogues of natural phosphates,[1] drugs,[2–4] and herbicides,[5] polymer additives,[6] selective extractants of metal,[7] flame retards,[8] etc. In nature, some phosphonates have been isolated from a certain number of microorganisms.[1] However, there are very few references about molecular structure and spectroscopical properties of these compounds.

In earlier papers, preliminary studies about the structure of alkenylphosphonic derivatives have been performed by means of NMR, IR, and UV spectroscopy and *ab initio* calculations.[9–11] These compounds are presented as very polar, especially as far as the phosphoryl bond is concerned. This bond is a partially polarized triple bond.[12] Around the rotation of the C–P bond, two conformers *s-cis* and *s-trans-gauche* and two low internal rotation barriers were found, *s-cis* being the most stable in vinyl and *trans*-propenyl derivatives. In the case of *cis*-propenylphosphonic compounds the conformers are *s-cis* and *s-trans* with higher internal rotation barriers.[13]

Synthesis of phosphonates can be performed following two different main pathways: (i) An haloalkenyl compound reacts with an alkyl phosphite yielding directly the alkenylphosphonate (Michaelis–Arbuzov's reaction), and (ii) the alkylphosphonate is obtained previously by Arbuzov's procedure and the alkenyl moiety is obtained by the usual methods of dehydrogenation, reduction, dehydrohalogenation, Wittig's reactions, etc. The second procedure gives higher yields, but a mixture of *E* and *Z* isomers is obtained. The hydrolysis of the phosphonates yields the corresponding phosphonic acids. On the other hand, in some of these compounds no reference on the *Z*/*E* rate study and separation yield of these *E*/*Z* isomers has been found in the bibliography. In a previous paper the synthesis procedure of the vinylphosphonic acid has been improved, increasing the yield to up to 90%,[12] by means of the formation of diethyl vinylphosphonate by Arbuzov's reaction and the hydrolysis of this phosphonate by the McKenna *et al.* method[14] modified by us.

The interest and applications of the phosphonates have prompted us to study the synthesis methods with the aim of improving them and obtaining better yields, *Z*/*E* ratios, and isomer separations. With these compounds, a structural study by means of NMR, UV, IR, and Raman spectroscopy and *ab initio* calculations has been performed with the purpose to gain a better insight into the molecular structures and elucidate their physicochemical properties and applications. Twenty-three vinyl-, pro-

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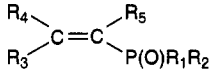
Table 1. Alkenylphosphonic Derivatives



compd	R_1	R_2	R_3	R_4	R_5
I	OH	OH	H	H	H
II	OEt	OEt	H	H	H
III	OMe	OMe	H	Me	H
IV	OEt	OEt	H	Me	H
V	OH	OH	H	Me	H
VI	OH	OH	Me	H	H
VII	OEt	OEt	Me	H	H
VIII	O^{t}But	O^{t}But	Me	H	H
IX	O^{t}But	O^{t}But	H	Me	H
X	Cl	Cl	Me	H	H
XI	OMe	OMe	H	CN	H
XII	OMe	OMe	CN	H	H
XIII	OH	OH	H	CN	H
XIV	O$^-$	O$^-$	H	CN	H
XV	O^{t}But	O^{t}But	H	CH_2Br	H
XVI	OH	OH	H	Me	Br
XVII	OH	OH	Me	H	Br
XVIII	OEt	OEt	H	H	Br
XIX	Cl	Cl	H	Me	H
XX	O^{t}But	O^{t}But	$CH_2=C=$		H
XXI	OEt	OEt	ethylphosphonate		
XXII	OEt	OEt	2-propenylphosphonate		
XXIII	OH	OH	2-propenylphosphonic acid		

penyl-, (bromoalkenyl)-, and (cyanoalkenyl)phosphonates and phosphonic acids with different substituents in the alkenyl group are studied in this work.[15] They are shown and labeled in Table 1.

Results and Discussion

Five substituent groups have been considered in the vinylphosphonic structure (Table 1): R_1 and R_2 on the phosphonic moiety and R_3 to R_5 on the vinyl group. R_1 and R_2 may be OH, *O*-alkyl (alkyl = methyl, ethyl, *tert*-butyl), Cl, or the anion O^- (ammonium salt). R_3–R_5 may be hydrogen, methyl, cyano, bromo, and bromomethyl. Besides, allenyl-, ethyl-, and 2-propenylphosphonates and 2-propenylphosphonic acid have also been included.

Synthesis and Reactivity Studies. In order to perform the spectroscopical studies, the phosphonic derivatives studied (Table 1) have been synthesized either by using known methods or by new synthesis procedures. The alkenylphosphonates have mainly been synthesized from their precursor phosphonates, which were prepared by Michaelis–Arbuzov's reaction, except **XI** and **XII** (see below). These precursors have been transformed to their corresponding alkenylphosphonates either by dehydrohalogenation (**II**, **XVI**–**XVIII**, **XXII**) or by isomerization (**III**, **IV**, **IX**, **XV**). The phosphonic acids have been obtained from the corresponding phosphonates either by hydrolysis catalyzed by acids (**I**, **V**, **XXIII**), by thermolysis (**VI**), or by silanization and hydrolysis of the silanyl derivative (**XIII**). The phosphoryl dichlorides were prepared by means of known methods of P-chlorination of the corresponding phosphonates. Only the most remarkable improvements obtained in the synthesis of these compounds will be described below.

Cyano Derivatives. The synthesis of the (*E*)- and (*Z*)-(2-cyanovinyl)phosphonates **XI** and **XII** was performed by a Michaelis–Arbuzov reaction directly from α-bromoacrylonitrile. An exhaustive search in the literature showed us that there was no previous reference about

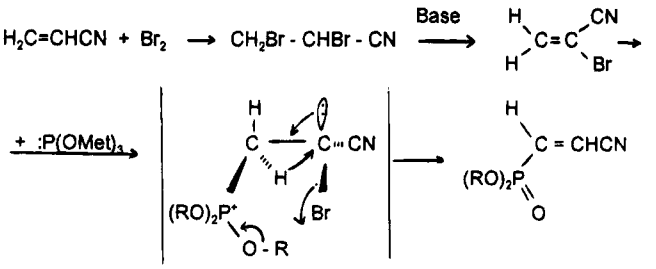


Figure 1. Formation of (2-cyanovinyl)phosphonates.

Table 2. Synthesis of Dimethyl (*E*/*Z*) (2-Cyanovinyl)phosphonates (XI/XII)

T (°C)	t (h)	yield (%)	E/Z[a]
0	40	<20[b]	*c*
20	10	40	66/34
40	4	45	62/38
60	4	<20[d]	*c*

[a] Isolated products. [b] Dimethyl methylphosphonate as subproduct. [c] Not determined. [d] Partial polymerization.

either the ratio *E*/*Z* in the synthesis of these compounds by this method or the isolation of these isomers. Pudovik *et al.*[16] yielded a 25% yield of a mixture of isomers by using polymerization inhibitors such as hydroquinone. In the present work, this reaction has been studied at different conditions, in order to optimize the yield and the *E*/*Z* ratio (Table 2). At low temperatures, where the polymerization of the reactive 2-bromoacrylonitrile is minimal, the yields are very low (<20%) even with a double excess of trimethyl phosphite. Besides, the methyl bromide (potent carcinogen) formed in this reaction gives a secondary reaction with another molecule of phosphite, yielding the dimethyl methylphosphonate (it was detected and isolated in all cases). However, at temperatures higher than 40 °C the 2-bromoacrylonitrile polymerizes and the yield falls drastically. So, the temperature of the reaction must be compromised in order to avoid the polymerization of the reactive 2-bromoacrylonitrile and to quickly remove the methyl bromide formed in the reaction by distillation. The optimum temperature is 40 °C according to yield and highest proportion of *Z* isomer. At milder conditions the ratio of *E* isomer is slightly higher, probably because this isomer is thermodynamically more stable than the *Z* isomer. *Ab initio* calculations at STO-3G* basis set have shown that the minimal energy conformer of *E* isomer is 2.1 kcal/mol more stable than the *Z* isomer. For the first time, a yield of 45% of (2-cyanovinyl)phosphonate and an *E*/*Z* ratio of 62/38 for compounds **XI** and **XII** are described by means of Michaelis–Arbuzov's reaction without using polymerization inhibitors. The mechanism of this reaction is described in Figure 1. In this reaction a hydrogen atom, in position β with respect to the cyano group, suffers a Whitmore 1,2-transposition to the position α, leaving out the bromide atom, which forms an alkyl halide with one alkyl group of the phosphite moiety.

On the other hand, the isolation of both isomers is quite difficult even by chromatographic methods, at preparative and analytical scale, due to their similar physicochemical properties. However, we have isolated both isomers with a yield of 89% by a method of short column liquid chromatography at medium pressure and subsequent distillation (see the Experimental Section).

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An important key to obtain these results is the quality of the 2-bromoacrylonitrile. This product polymerizes very easily, and it is necessary to prepare it with a high purity, in order to obtain the phosphonates **XI** and **XII** with high yields. The previously described methods gave us very low yields (24%) of 2-bromoacrylonitrile by using AcONa as base[17] in the dehydrohalogenation of 2,3-dibromopropionitrile. Several conditions of this reaction have been studied, and the following conclusions can be drawn: (i) The best yields are obtained by using Quinolein as base. (ii) The purity of the 2,3-dibromopropionitrile must be higher than 90%. (iii) The addition of the base is exothermic, and it should be very slow, because the temperature must not be higher than 0 °C to avoid the polymerization of the product, the 2-bromoacrylonitrile. (iv) This process should be achieved under inert atmosphere and in the presence of a polymerization inhibitor (only in this first step). (v) The boiler temperature in the rectification of 2-bromoacrylonitrile should be lower than 30 °C to avoid its polymerization.

Taking into account these conclusions, the 2-bromoacrylonitrile has been prepared with a yield of 87% with respect to the 2,3-dibromopropionitrile, a yield considerably higher than that previously described.

With respect to the hydrolysis of (cyanovinyl)phosphonates **XI** and **XII**, Kreutzkamp *et al.*[18] found that the cyano group was hydrolyzed completely, obtaining (carboxyvinyl)phosphonic acids. However, we have found that **XI** can be partially hydrolyzed, maintaining the cyano group inalterated by means of a silanization with trimethylchlorosilane and a mild hydrolysis of the silanyl derivative intermediate. The *Z* isomer **XII** was much more reactive than the *E* isomer **XI**, and it was not possible to get the cyano group unchanged even under mild conditions, because of the intramolecular assistance of the cyano group to the phosphonate hydrolysis when both groups are in the cis position. On the contrary, the hydrolysis of the *E* isomer **XI** was much slower, the cyano group remained stable, and it was even possible to detect the monohydrolyzed phosphonate at low temperature.

Bromination/Dehydrobromination. The (bromoalkenyl)phosphonic compounds have been obtained by dehydrobromination of the 1,2-dibromoalkyl derivatives, which were previously prepared by bromination of the corresponding alkenyl derivatives. The only product obtained was the 1-bromovinyl derivative in all cases, in acid or basic catalysis (Figure 2). The same results have been found even by using bases of large molecular size, such as quinolein and potassium 2,6-di-*tert*-butyl-4-methylphenolate. This could be explained by the electron-withdrawing effect of the phosphonic group. With basic catalysis, the hydrogen in position α with respect to the phosphonic moiety is more acidic than the another one in the β position, and so it will be captured more easily even with large size bases (which could exert steric hindrance with respect to the phosphonic group), leaving the Br atom out of the β position and yielding the 1-bromovinyl derivative. With acid catalysis, the carbocation in the β position is more stable than in the α position, and the bromine of this β carbon will go away more easily than that of the α carbon, yielding also the 1-bromovinyl derivative (Figure 2). A similar fact is

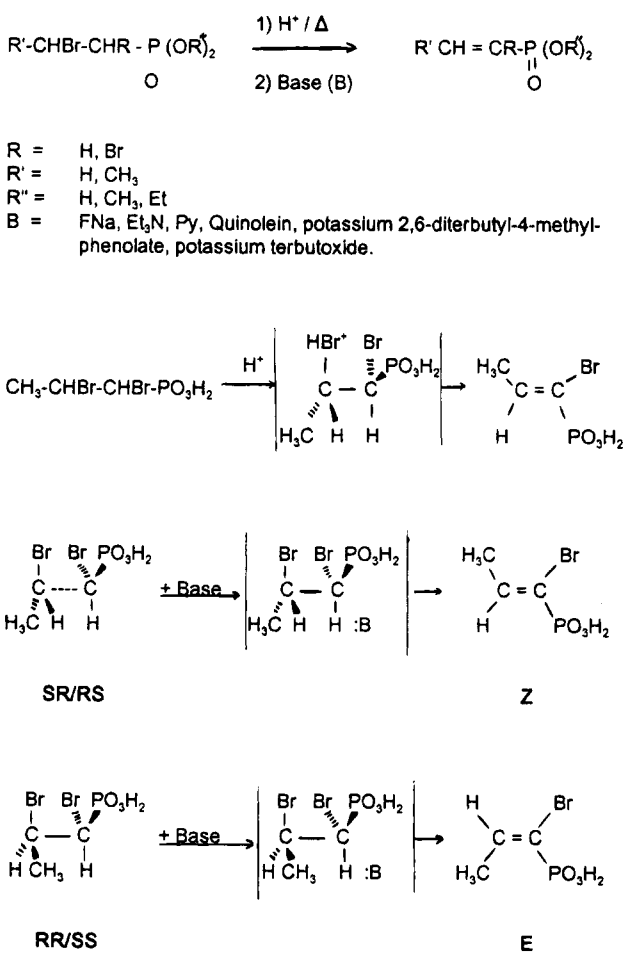

Figure 2. Dehydrobromination of (1,2-dihydroalkyl)phosphonic derivatives.

known in the vinylcarboxylic derivatives (for instance, in the dehydrobromination of methyl 2,3-dibromopropanoate, see Experimental Section).

According to the regioselectivity of this reaction, the bromination and dehydrobromination of the *cis*-1-propenylphosphonic acid (**VI**) yielded only the *Z* isomer of (1-bromo-1-propenyl)phosphonic acid (**XVI**), and the *trans*-1-propenylphosphonic acid (**V**) yielded a mixture of the *Z* (**XVI**) and *E* (**XVII**) isomers.

On the other hand, it is remarkable that the brominations of the *Z* (**VIII**) and *E* (**IX**) isomers of 1-propenylphosphonate with radicals (*N*-bromosuccinimide (NBS)/peroxides) yield the same product, the trans γ-bromo derivative **XV**, due to the isomerization of the C=C double bond to the trans isomer (thermodynamically more stable) in the radical intermediate, before the bromination step (Figure 3). This fact has been corroborated by the isolation of the trans isomer **IX** in the NBS-bromination of the cis isomer **VIII**.

Molecular Structure. Conformational analysis, geometry, and electronic structure for vinylphosphonic acid, vinylphosphoryl dichloride, vinylphosphine oxide,[12] and a certain number of alkenylphosphonic derivatives have been studied by means of *ab initio* calculations.[13] However, a general and comparative study of NMR, UV, IR, and Raman spectroscopy and theoretical calculations are missing in these compounds, and this is one of the main targets of this work. Theoretical calculations to determine dipole moments are also included.

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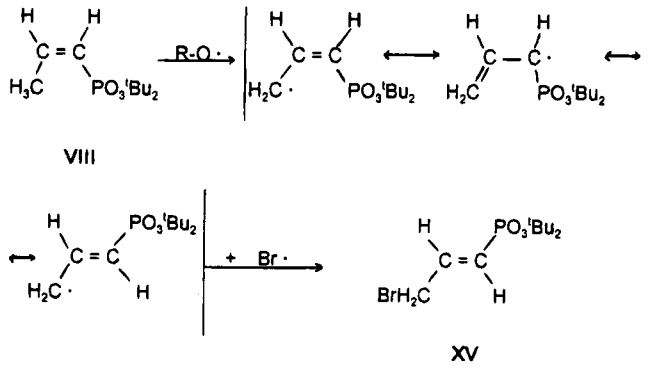

Figure 3. Formation of **XV** from bromination of **VIII** with *N*-bromosuccinimide (NBS).

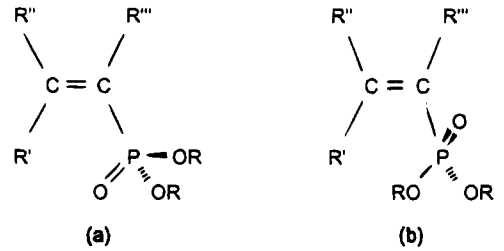

Figure 4. C=C/P=O conformers of alkenylphosphonic derivatives. (a) *s-cis* $^{-}$(C=C/P=O) $\approx$ 0°. (b) *s-trans-gauche* $^{-}$(C=C/P=O) $\approx$ 115–130°.

Theoretical Studies. The *ab initio* theoretical calculations were performed by using MONSTERGAUSS[19] and GAUSSIAN 90[20] programs. The molecular geometries of the compounds studied in this work were obtained previously in our laboratory with full optimizations at different basis sets[13] (Figure 4). The minimization methods are described elsewhere.[12,13]

The dipole moments (μ) and the conformational populations of the C=C/P=O conformers have been calculated. Conformer population in each molecule at a given temperature may be approximated by the following equation

$$\frac{N_i}{N_t} = \frac{e^{-\Delta E_i/RT}}{\sum_{n=1-i} e^{-\Delta E_i/RT}}$$

where N_i is the population of the conformer "i", N_t is the total population of all "n" possible conformers, and ΔE is the energy difference with respect to the most stable conformer. A temperature of 30 °C and no intermolecular effects were considered.

Dipole moments of the different conformers around the C–P bond of **I**–**III**, **V**–**VII**, and **X**–**XII** compounds have been calculated at the STO-3G* basis set and in the critical points of the rotational potential energy hypersurface of the C–P bond. They are represented in Table 3 along with the conformer populations. Polarization functions are very important to describe electronic structure and conformational properties in these molecules.

Table 3. Conformational Populations and Dipolar Moments of Phosphonic Derivatives[a]

	M1			M2				
compd	confgn	%[b]	μ[c]	confgn	%[b]	μ[c]	ΔE[d]	rotat barrier[e]
I	s-cis	87	1.26	s-trans-gauche	13	1.31	1.13	2.70
II	s-cis	87	1.54	s-trans-gauche	13	1.70	1.16	2.04
III	s-cis	73	1.11	s-trans-gauche	27	1.60	0.59	1.46
V	s-cis	66	0.66	s-trans-gauche	34	1.20	0.37	1.09
VI	s-cis	98	0.74	s-trans	2	1.43	1.39	1.50
VII	s-cis	95	1.33	s-trans	5	2.00	1.36	3.31
X	s-cis	99	2.96	s-trans	<1	3.46	2.81	5.90
XI	s-cis	84	3.51	s-trans-gauche	16	4.43	1.09	1.99
XII	s-cis	48	4.16	s-trans	33	4.24	0.22	0.85

[a] At STO-3G* basis set. [b] Conformational populations. [c] Dipolar moments in Debyes. [d] Interconformational energy difference $\Delta E = E(\text{M1}) - E(\text{M2})$, kcal/mol.[13] [e] Rotational barrier between both conformers, kcal/mol.[13]

Furthermore, the STO-3G* basis set yields results essentially similar to those obtained with the split valence basis set plus polarization functions in vinylphosphonic acid, vinylphosphoryl dichloride, and vinylphosphine oxide.[12] Therefore, we can expect than the rest of the members of the series present the same behavior at least for qualitative comparisons inside the series.[13] In the *cis*-1-alkenyl derivatives (**VI**, **VII**, **X**, and **XII**), the secondary conformer is the *s-trans*, due to the interactions between the phosphonate moiety and the group which is in the cis position. In all cases, the secondary conformer *s-trans-gauche* or *s-trans* are more polar than the planar *s-cis*. Taking into account that the most stable conformer is the *s-cis*, an increase of the dipole moment with the C=C/P=O conformational angle is observed (taking the *s-cis* configuration as the origin of the internal rotation coordinate). The phosphonic esters have a higher μ than the phosphonic acids. In the phosphoryl dichloride **X** and the cyano derivatives **XI** and **XII** a considerably higher μ is observed. The molecule **X** shows the most difference of interconformational energy and the highest internal rotation barrier among both conformers, existing practically only the conformer *s-cis*. This can be explained by a higher interaction between the Cl and CH_3 groups in this molecule than in the homologous phosphonate, due to the higher size of the chlorine atom in front of the oxygen.

NMR Results. Proton NMR chemical shifts of the title compounds are shown in Table 4. In the derivative **II**, the cis-vicinal proton (H_X) chemical shift appears at a significatively lower field that the other olefinic protons, due to the anisotropic effect of the phosphoryl group. Williamson *et al.*[21a] found similar results from a solution of **II** in carbon tetrachloride (10%) (the values shown in Table 4 are from a solution of **II** in deuterated chloroform at 4%), except in the case of the proton H_X chemical shift (6.19 ppm). However, as a neat liquid, they found that all olefinic protons showed similar chemical shifts (H_X = 6.17 ppm, H_Y = 6.14 ppm, H_Z = 6.15 ppm). These chemical shift variations with the solvent are already known[21] and can be explained by solvent and intermolecular effects. Furthermore, the conformation of the phosphoryl group with respect to the C=C double bond can also contribute to these variations. In the vapor

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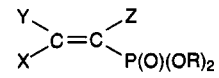
Table 4. ^{1}H-NMR Chemical Shifts and Coupling Constants of Alkenylphosphonic Derivatives (δ = ppm, J = Hz)



no.	solvent[a]	H_X	H_Y	H_Z	H[b]	J_{XY}	J_{XZ}	J_{YZ}	J_{XP}	J_{YP}	J_{ZP}	^3J[c]	^4J[d]
II	C	6.31	6.05	6.02		4.5	16.2	11.2	20.5	51.3	20.0		
III	C	6.79		5.63	1.90		16.9		21.4		21.0	6.4	2.3
IV	C	6.75		5.63	1.90		16.6		21.4		21.0	6.7	2.3
V	M	6.64		5.77	1.90		17.0		21.0		21.4	6.5	2.2
VI	M		6.45	5.70	2.03			13.2		51.6	21.4	6.9	3.6
VIII	C		6.33	5.62	2.05			13.0		52.3	19.3	7.1	3.5
IX	C	6.28		5.70	1.85		17.4				20.4	6.3	2.2
X	C		7.75	6.11	2.18			12.4		74.8	39.0	7.2	3.8
XI	C	6.37		6.75			17.8		21.0		15.4		
XII	C		6.26	6.65				13.8		43.7	14.0		
XIII	D	6.21		7.04			17.8		20.3		15.4		
XIV	M	6.07		6.91			18.0		19.2		13.5		
XV	C	6.63		5.91	4.0[e]		16.5		20.0		17.2	7.0	1.1
XVI	M	7.00			1.90				13.5			6.8	3.2
XVII	M		6.80		2.03					36.0		7.0	3.0
XVIII	C	6.90	6.45			2.0			15.6	35.7			

[a] C = $CDCl_3$, M = CD_3OD, D = D_2O. [b] H of CH_3 allylic. [c] On ^3J(H,H(R')), R' = sustituent of C=C. [d] With respect to ^4J(P,H(R')). [e] From CH_2Br.

state, the most stable C=C/P=O conformation of this molecule is the *s-cis*. With nonpolar solvents and at low concentrations, this conformation will present the highest population and the anisotropic effect will be maximal, because the phosphoryl group is appointed toward the cis-vicinal hydrogen. At higher concentrations or in more polar solvents, the interactions with the solvent or with other similar molecules can cause the population of other more polar conformers, such as *s-trans-gauche*, to increase, and therefore, the anisotropic effect should decrease. This phenomenon will be discussed later.

In the 1-propenylphosphonate derivatives (**III**–**X**), the geminal proton (H_Z) has lower chemical shifts than in the vinyl derivative **II**, possibly due to the hyperconjugative effect of the methyl group. Effectively, this effect has also been found previously by *ab initio* theoretical studies.[13] A higher Mulliken net atomic charge was found on the C_1 carbon atom in the 1-propenyl derivatives [it ranges from (−0.161) to (−0.167) at STO-3G* level] with respect to the vinyl derivative **II** (−0.151 at the STO-3G* level). This fact can be explained by an electron flow from the methyl group toward C_1 caused probably by the hyperconjugative effect and predicting the experimental results. On the other hand, the vicinal protons with respect to the phosphonic moiety (H_X and H_Y) show higher chemical shifts than in the vinyl derivative **II**. This could be explained by the γ-cis steric effect. The anisotropic effect of the phosphoryl group on the cis-vicinal proton (H_X) can also be observed. However, in the di-*tert*-butyl ester **IX** this anisotropic effect is very small and the H_X chemical shift is the lowest of these vinyl and propenyl derivatives. In this molecule the steric effect of the *tert*-butyl groups is so strong that the population of the C=C/P=O conformation *s-cis* can decrease significatively and the phosphoryl group would not mainly be appointed towards the vicinal proton. In the same way, Berkova *et al.*[22] found in the styrenylphosphonates that the population of the *s-transoid* conformation increases quickly when the steric effect between the phosphoryl group and the cis-substituent enlarges.

Notice the effect of the phosphoryl dichloride group in the compound **X**, where the olefinic hydrogens appear at considerably lower field than in the above derivatives. On the other hand, the π conjugative effect of the cyano group is clearly shown in the derivatives **XI**–**XIV**, where the geminal proton with respect to the phosphonic group (H_Z) appears at lower field than the other olefinic protons, contrary to the case of the vinyl and propenyl derivatives.

With respect to the methyl protons in allylic position, their chemical shifts are lower when they occupy the cis position with respect to the phosphonic group. This could be explained by a γ effect of the phosphoryl group, as it happens in analogous carboxylic compounds.[23]

The proton NMR coupling constants are also shown in Table 4. In the phosphoryl dichloride **X**, ^3J(H,P) (J_{YP}) and ^2J(H,P) (J_{ZP}) are clearly higher that in the other derivatives. Vafina *et al.*[24] found this fact in other phosphoryl dichlorides. On the other hand, when the electron-withdrawing effect of the C=C substituents increases (Me < H < CH_2Br < CN), the ^2J(H,P) (J_{ZP}) decreases slightly. Besides, when the substituents are in the cis position with respect to the phosphoryl group, ^2J(H,P) is lower than when they are in trans position. This fact could be connected with the bond angle "H–C–P". The "s" character of the bonding molecular orbitals increases when the HCP bond angle enlarges, and therefore the ^2J(H,P) also increases, as it will be seen later.

The ^3J(H,P) is considerably higher when both nuclei are in the trans-position (J_{YP}) than when they are in cis (J_{XP}). This is explained because the vicinal couplings H–C–C–P have an angular relation analogous to the Karplus one in H–C–C–H couplings.[25] With respect to the ^2J(H,H) (J_{XY}), it decreases when the volume of the substituent in Cα (R_5) increases, probably because the HCH angle decreases due to steric interactions.

Table 5 shows the ^{13}C-NMR chemical shifts. In the vinyl derivatives **I** and **II**, the δC_2 value appears at significatively lower field than δC_1. However, this difference of chemical shifts is not so strong as in the acrylic

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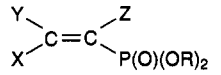
Table 5. ^{13}C-NMR Chemical Shifts and Coupling Constants of Alkenylphosphonic Derivatives (δ = ppm, J = Hz)



no.	C_1[a]	C_2[a]	$C(CH_3)$[b]	CN	$^1J_{C_1P}$	$^2J_{C_2P}$	$^3J_{CP}$	$^1J_{C_1H_1}$	$^1J_{C_2H_2}$	$^3J_{C_3H_1}$	$^3J_{C(CN)P}$
I	129.6	136.7			177			166	166		
II	126.3	135.3			184	2		161	162		
III	117.8	149.6	20.0		189	5	24	153	151	7.5	
V	121.6	150.3	21.7		184	4	24	163	155	8.0	
VI	121.3	151.4	19.6		178	3.2	10.5	159	159	10.5	
VIII	123.4	144.2	16.2		188.6	3.9	8.5	157	155	10.0	
X	125.6	151.3	16.8		143.4	2.0	10.5				
XI	138.5	117.2		115.2	184.6	10.4					32.7
XII	138.1	115.0		114.5	182.6	4.0					6.0
XIII	146.6	113.5		118.3	172.5	9.6					31.7

[a] With respect to the phosphoryl group. [b] C=C−CH_3.

derivatives,[23,26] where a strong C=C/C=O π conjugation is observed. This difference in the chemical shifts is higher in the propenylphosphonic derivatives due to the hyperconjugative effect of the methyl group which has been discussed above. On the other hand, the chemical shift of C_2 is lower in di-*tert*-butyl ester **VIII** than in the other propenylphosphonics. This could be justified by a decreased hyperconjugative effect of the methyl group owing to the steric interactions of the phosphoryl moiety. The π conjugative effect of the cyano group is clearly revealed in compounds **XI**–**XIII**, where C_1 appears at lower field than C_2.

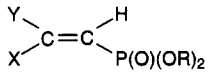
Concerning the allylic methyl groups, their δC values appear at lower field when they are in the cis position with respect to the phosphoryl group. This could be justified by the "γ-cis" effect of the voluminous phosphoryl group.

The ^{13}C-NMR coupling constants are also shown in Table 5. The phosphoryl dichloride **X** presents a very low ^1J(C,P). This could be explained by the lower electronegativity of the chlorine with respect to the oxygen, in agreement with the rule: "When the electronegativity of the phosphoryl group substituents increases, ^1J(C,P) also increases".[27] In general, ^2J(C,P) is higher in the trans isomers than in the cis. In the case of the carbons joined to C_2, ^3J(C,P) is also higher in the trans isomers. This could indicate a Karplus-like relationship in these systems.

The ^{13}C-NMR chemical shifts can be compared with the Mulliken net charges, calculated at the STO-3G* level of these compounds.[13] A reasonable agreement is found in the vinyl- and 1-propenylphosphonic derivatives. When the negative net charge of an olefinic carbon becomes higher, the chemical shift of this carbon decreases. This is also observed in the methyl carbons joined to C_2. However, this correlation does not work with substituents conjugated to the C=C double bond as in the case of cyano derivatives **XI** and **XII**.

When the theoretical data[13] are compared with the NMR coupling constants, interesting observations can be obtained. So, the ^2J(H,P) (J_{ZP}) decreases with electron-withdrawing substituents at the C=C group. Effectively, in the cyano compounds **XI**–**XIV**, the ^2J(H,P) is lower and the positive net charge of the phosphorus atom is higher than in the vinyl- and propenylphosphonates. On the other hand the ^2J(H,P) is higher in the trans isomer **XI** than in the cis **XII**; however, in these compounds the positive net charge of the phosphorus is also higher in the trans isomer. Consequently, another effect should operate on this coupling constant. Comparing some NMR data with some geometrical features calculated at STO-3G* level[13] for these compounds, a direct relationship between ^2J(H,P) and the "H−C−P" bond angle can be observed. This could be explained by the s character of the bonding molecular orbitals. With a higher HCP bond angle, there will be a higher s character and therefore a higher ^2J(H,P). We could conclude that both effects, the HCP angle and the charge of the phosphorus atom, affect ^2J(H,P).

Table 6. ^{31}P-NMR Chemical Shifts of Alkenylphosphonic Derivatives



no.	X	Y	R	solvent	δ (ppm)
I	H	H	H	D_2O	17.3
II	H	H	Et	$CDCl_3$	17.8
III	H	CH_3	CH_3	$CDCl_3$	21.5
V	H	CH_3	H	D_2O	18.5
VI	CH_3	H	H	D_2O	17.0
VIII	CH_3	H	^{t}Bu	$CDCl_3$	8.9

Concerning $^2J(C_2,P)$, this is higher in the trans isomers than in the cis in all cases and the C=C−P bond angle is smaller in the trans isomers than in the cis.[13] Then, this geometric parameter could influence on the $^2J(C_2,P)$ value.

The ^{31} P-NMR chemical shifts are shown in Table 6. The low chemical shift of **VIII** is remarkable. This fact is not observed in the homologous acid **VI**. This could be explained by the steric effect of the *tert*-butyl groups, increasing the value of the bond angle (R)O−P−O(R) and consequently the phosphorus atom will be more shielded. Crutchfield *et al.*[28] found the same effect in trialkyl phosphates.

UV Spectroscopy. The wavelengths (λ) and the molar extinction coefficients (ϵ) of nine phosphonic derivatives are presented in Table 7. These compounds show an absorption band at 215–200 nm. Important differences in the ϵ values can be observed.

The smallest values of ϵ are detected in **XXII** and **XXIII**. The vinylphosphonate **II** shows an absorption higher than that from its homologous allylphosphonate **XXII**, where the C=C double bond is not joined directly to the phosphoryl group. However, this difference is

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Table 7. UV Spectroscopical Data of Alkenylphosphonic Derivatives (in MeOH)

no.	λ (max) nm	ε
I	206	179
II[a]	210	89
III	208	2048
V	206	1000
VIII[b]	212	598
XI	214	11861
XII	214	9935
XXII	208	34
XXIII	205	30

[a] ε = 100 (in CF_3CH_2OH), 157 (in $CNCH_3$), 143 (in hexane). [b] ε = 1215 (in $CNCH_3$), 701 (in hexane).

small, showing a π conjugation between the vinyl electronic system and the phosphoryl bond but in a weak extension, in comparison with the conjugation of the C=C/C=O system of the acrylic derivatives (ε = 13804 in H_2C=CH−COOR).[29] This fact confirms our previous results that a weak π conjugation in C=C/P=O system have been found in these compounds by means of *ab initio* calculations.[12,13] It is also in agreement with our next IR results in the following sections.

In the propenylphosphonates, the absorption ε is higher than in the vinyl derivatives. This fact could be explained by the hyperconjugative effect of the methyl group, as said above. The low absorption of the di-*tert*-butyl phosphonate **VIII** with respect to the dimethyl derivative **III** is possibly due to steric interactions between the methyl and phosphoryl groups, which can produce a decline of this hyperconjugative effect. This phenomenon has also been observed above in the ^{13}C-NMR data. Similar results have also been observed in propenoic acids and propenylmethylketones.[30] On the other hand, the 2-cyano derivatives **XI** and **XII** show the highest absorption values, due to the strong conjugative effect of the cyano group on the C=C double bond. This absorption is slightly lower in **XII** than in **XI**, due to a possible interaction between the cyano and phosphoryl groups, both in cis position.

With respect to the solvent effect on the absorption, it is not very important in the vinyl derivative **II**. The low values of ε in MeOH and CF_3CH_2OH could be due to interactions between the phosphoryl bond and the solvent molecules (probably intermolecular H-bonding). Nevertheless a slight increase of ε is observed with the polarity of solvent (157 ($CNCH_3$) vs 143 (hexane) or 100 (CF_3CH_2-OH) vs 89 (MeOH)). In the di-*tert*-butyl derivative **VIII** this effect is much higher than in **II**.

Vibrational Studies. The IR and Raman data from the most of these compounds are shown in Table 8. In all compounds studied, the stretching vibration ν(P=O) gives very intense IR bands and weak Raman bands. Differences about the frequency of ν(P=O) are appreciated between vinyl and propadienyl and vinyl- and allylphosphonate derivatives. In the alkenylphosphoryl dichlorides **X** and **XIX**, ν(P=O) appears at higher frequencies than in the other derivatives, as it has been found in other phosphoryl dichlorides.[31,32] In some cases, two ν(P=O) bands are observed which we attribute to the existence of C=C/P=O rotational isomers, as will be discussed later.

In the phosphonic acids **I** and **V**, ν(P=O) gives a broad band probably due to intermolecular associations through this group and to the presence of the δ(OH) band. The ν(P=O) appears at lower frequency than in the phosphonates, probably due to the mentioned interactions (Table 8).

The ν(C=C) IR bands present a very weak intensity, while the corresponding Raman bands are very strong. In the 1-propenyl derivatives, the ν(C=C) band appears at higher frequency (1629−1642 cm^{-1}) than in the vinyl derivatives (1610−1614 cm^{-1}). This difference is more remarkable in the trans isomers (1635 cm^{-1} in **IV**, for instance) than in the cis (1629 cm^{-1} in **VIII**). On the other hand, in the 2-cyano derivatives **XI** and **XII**, this band appears at the lowest frequency, owing to the conjugative effect C=C/CN already mentioned above.

In the 1-propenyl phosphonate **IV** the ν(C=C) appears at slightly lower frequency than the 2-propenyl homologous **XXII**. However, no difference is observed in ν(P=O). Gillis *et al.*[33] found the same effect in these compounds. This can be explained by the weak conjugative effect of the phosphoryl group with the C=C double bond. This effect would be too weak to be observed in ν(P=O). On the other hand, no C=C/P=O rotational isomery can be clearly detected from these ν(C=C) bands.

As is expected, in the *cis*-1-propenylphosphoryl dichloride **X**, the asymmetric ν(P−Cl) vibration bands are more intense in IR spectra than in the Raman, and on the contrary the symmetric vibration bands are more intense in Raman than in IR spectra. The ν(P−Cl) asymmetric bands appear at 545(vs) in IR and 553(vw) cm^{-1} in Raman spectra, while the symmetric bands appear at 475(s) in IR and 475(vs) cm^{-1} in Raman spectra.

The 1,2-propadienylphosphonate **XX** presents two IR bands at 1965 and 1942 cm^{-1} assigned to the ν(C=C=C) asymmetric vibration and one IR band at 1070 cm^{-1} assigned to the ν(C=C=C) symmetric vibration (very strong Raman band). The other ν_s(C=C=C) band cannot be observed probably due to the overlapping with other bands. Two ν(P=O) bands are also detected, which we attribute to the existence of C=C/P=O conformers. This fact was also observed by other authors[31,34] in similar allenes.

Other interesting vibrational bands of these compounds are also included in Table 8. In addition to the ν(P=O) and ν(C=C) bands, the most characteristic bands of the alkenylphosphonates are the ν(P−O−C) bands, which appear as two groups at 1056−970 and 840−714 cm^{-1}. Each group corresponds to the *out of phase* and *in phase* stretching vibrations, respectively. Previous references assign the first group to the *out of phase* vibrations; nevertheless, some discrepancies exist.[31,33,34] We have labeled the first group as ν(P−O−C) [(C−O)] bands and the second one as ν(P−O−C) [(P−O)] bands. The two bands of the first group are intense in IR and very weak in Raman. The bands of the second group present weak intensity, and there are also two bands, which are assigned to symmetrical and asymmetrical vibrations, according to the relative intensities of the IR and Raman bands. In the *tert*-butyl esters **VIII** and **XX**

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Table 8. Vibrational Bands of Alkenylphosphonic Derivatives[a,b]

compd	ν(P=O	ν(C=C)	ϱ(CH_3) (−OR) (rocking)	ν(POC) [(CO)] sym	ν(POC) [(CO)] asym	ν(POC) [(PO)] asym	ν(POC) [(PO)] sym
II	1245s (1245w)	1610vw (1613s)	1160w (1165vw)	1051s	1024vs (1029vw)	783m (790w)	714vw (721s)
III	1270sh 1240s (1237w)	1633m (1636s)	1185w	1056s	1033vs	832s (831w)	763w (768s)
IV	1255s 1240s	1635w	1165w	1056s	1030vs	828m	798w
VIII	1263s (1262sh) 1250sh-s (1248m)	1629m (1630vs)	1173m (1174w)	1006s (1008vw)	982vs (970vw)		
X	1272s (1268m)	1616m (1618s)					
XIX	1278vs	1640m					
XI	1258s (1258w)	1590vw (1600s)	1182w	1048sh	1028vs	840m	
XII	1260s (1267w)	1600vw (1602s)	1182w	1050s	1030vs	840m	798m
XX	1265s (1271w) 1250sh (1252w)	1965w[c] 1942m[c] 1070w[d] (1073vs[d,e])	1162m	1000s	985vs		
XXII	1255s	1640m (1641s)	1165w	1055s	1030vs		
I	1130m[f]	1614vw (1614vs)					
V[g]	1185m	1642s (1643vs)					

[a] Liquid state, ν in cm^{-1} and intensity: vs = very strong, s = strong, m = medium, w = weak, vw = very weak, sh = shoulder. [b] The frequencies in brackets correspond to the Raman bands. [c] ν_{as}(C=C=C). [d] ν_s(C=C=C). [e] Partially polarized. [f] Broad band. [g] In KBr (IR) or in solid state (Raman).

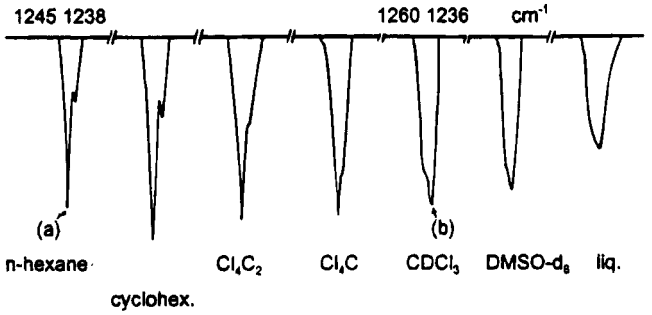

Figure 5. Vibrational ν(P=O) bands of the phosphonate **III** in different solvents: (a) *s-cis* conformer; (b) *s-trans-gauche* conformer.

the ν(P−O−C) [(C−O)] bands appear at lower frequencies than in the methyl and ethyl esters (**II**−**IV**, **XI**, **XII**, and **XXII**).

The ϱ(CH_3) appears in the 1185−1160 cm^{-1} region. This band is characteristic of the alkoxy groups joined to the phosphoryl bond[33] and shows a medium-weak intensity in IR, but is very weak in Raman. In Table 8, we can observe a difference of 15−20 cm^{-1} between the ethyl (lower) and methyl (higher) esters.

Conformational Analysis, C=C/P=O. As said before and in previous papers the C=C/P=O conformational analysis has been carried out.[12,13] Two main conformers have been found with low rotational barrier between them, the *s-cis* being the most stable (see Table 5). The dipole moment of these molecules changes with the C−P bond rotation, as said above. The conformational population found by means of *ab initio* calculations corresponds to the vapor state. The equilibrium of rotational isomery can be altered by the interactions with the medium. When the medium polarity increases, the population of the more polar conformers also increases.[32] The presence of rotational isomery is detected clearly in the ν(P=O) IR bands. In some cases, small changes are also observed in the ν(C=C) bands. In Table 9, the ν(P=O) bands of several compounds in solution are presented (same absorption coefficient for the ν(P=O) bands of the rotational isomers has been assumed). In general, two ν(P=O) bands can be observed, and the relative intensity of these bands changes with the polarity of the solvent (see Figure 5, for instance). We have assigned the band of higher frequency to the least polar C=C/P=O conformer, the *s-cis*. In nonpolar solvents, the higher frequency ν(P=O) band is considerably more intense than the other one, indicating that a C=C/P=O *s-cis* conformer is clearly predominant. Moreover, as the polarity of the medium increases, the intensity of the lower frequency ν(P=O) band also increases, and in $CDCl_3$ this band is the strongest. This shows that the population of the most polar C=C/P=O conformer has increased with the solvent polarity, as could be expected. This is in agreement with the theoretical results[12,13] where, without intermolecular effects, the most stable conformer is the *s-cis* and this is the least polar (Table 5). As is said above, the C=C/P=O rotational barriers are very low and the intermolecular effects can be strong enough to change the conformational population, increasing that of the conformer with higher dipole moment.

In the *cis*-propenylphosphonate **VIII**, the *s-cis* conformer is also the predominant in polar media. Theoretical conformational analysis shows a high rotational barrier, which can be hard to overcome by the solvent effect. In the phosphoryl dichloride **X**, only one ν(P=O) band is observed and attributed to the *s-cis* conformer. No change is detected with the solvent polarity. Effectively, theoretical results show a high rotational barrier (6 kcal/mol), the energy differences between the conformers are also high, and the dipole moments of this compound are much higher than in the other propenylphosphonic derivatives. These factors can justify the constant predominance of *s-cis* conformer of **X** in different media. In the cyano derivatives **XI** and **XII** only one ν(P=O) band is also observed in all media. Theoretical results show that, without intermolecular effects, the predominant conformer is the *s-cis*. However, these compounds have a extremely high polarity and the solvent effect could be considered weaker.

Conclusions

A series of alkenylphosphonic derivatives has been synthesized.

The (2-cyanovinyl)phosphonates were synthesized without polymerization inhibitors and with greater yield than that acquired by other authors (40% versus 6% from 2,3-dibromopropionitrile). The *E* and *Z* isomer separation

Table 9. IR ν(P=O) Bands of Alkenylphosphonic Derivatives in Different Solvents[a]

no.	hexane	cyclohex	Cl_4C	C_2Cl_4	$CDCl_3$	liquid	DMSO-d_6
II	1263s, 1248w		1252s, 1240sh	1252s, 1242sh	1235s[b]	1245s[b]	1244s[b]
III	1265s, 1238w	1265s, 1240w	1260s, 1236sh	1260s, 1242sh	1260sh, 1236s	1270sh, 1240s	1245s[b]
VIII			1262s, 1250sh-w		1260s, 1250sh-w	1263s, 1250sh-s	1259vs, 1248sh-s
X			1275s		1268s	1272s	
XI			1270s		1264s[c]	1258s	
XII			1264s		1260s[c]	1260s	

[a] Liquid state, ν in cm^{-1} and intensity: vs = very strong, s = strong, m = medium, w = weak, vw = very weak, sh = shoulder. [b] Broad band. [c] Asymmetry toward lower ν.

has not been described until now for these compounds. An *E/Z* ratio of 62/38 was achieved, and both isomers were separated with high yields. The phosphonate group has been hydrolized, maintaining the cyano moiety unaltered, and the (*E*)-2-cyano-1-vinylphosphonic acid has been obtained.

From the dehydrobromination of 1,2-dibromoalkylphosphonic derivatives, an electron-withdrawing effect of the phosphonic group can be deduced.

The spectroscopical results reveal a weak C=C/P=O π conjugation and the existence of two C=C/P=O conformers. The most stable conformer has the smallest dipole moment, and it can be assigned to a *s-cis* conformer with the aid of *ab initio* calculations. The secondary conformer is attributed to *s-trans-gauche* or *s-trans*. The populations of both conformers change with the solvent polarity. All these results are in good agreement with the *ab initio* theoretical calculations.

Experimental Section

High purity solvents have been used in all spectroscopic studies. UV spectra have been recorded using either a Beckman 24 or a Perkin-Elmer-Coleman 570 double beam spectrometer with 1 cm quartz cells. A Perkin-Elmer 599B spectrophotometer has been used to obtain IR spectra. The solid samples have been studied in KBr pellets and the liquid samples between NaCl and CsBr plates. The samples in solution have been prepared in 0.03–0.08 M concentrations with 0.5–0.1 mm NaCl cells. Raman spectra have been measured with a Jobin-Yvon U 1000 spectrometer using a laser of argon (5145 Å).

^{1}H-NMR spectra were measured either at 90 MHz with a Varian EM-390 spectrometer or at 200 MHz with a Varian VXR 200, using TMS (in $CDCl_3$ and CD_3OD) or DSS (in D_2O) as internal reference. ^{13}C-NMR spectra were recorded either at 22.6 MHz with a Brucker HX-90E or at 20 MHz with a Varian-FT80 or at 50.3 MHz with a Varian VXR 200 spectrometer, using TMS (in $CDCl_3$), CD_3OD (in CD_3OD), or TPS (in D_2O) as internal reference. ^{31}P-NMR spectra were determined either at 32.2 MHz with a Varian FT-80A or at 111 MHz with a Brucker WP 250SY spectrometer, using trimethyl phosphite as internal reference and phosphoric acid (85%) as external reference. In NMR studies, some ABX and ABCX spin systems have been analyzed with the LAOCOON-3 program.[35] In order to study the ABCX spin system of the diethyl vinylphosphonate (**II**), a wholly coupled ^{31}P-NMR spectrum was carried out (see supplementary material).

In the GLC analytical studies a Hewlett-Packard 5730A chromatograph has been used with a flame ionization detector and OV-17 column. The preparative column liquid chromatography of medium pressure was carried out with Merck 60-G silica gel and pressure of 0.2 kg/cm^2. The TLC analysis were conducted on 0.2 mm E. Merck silica gel plates (60F-254) using UV light (254 nm) and iodine or Cl_3Fe/EtOH (1%) plus sulfosalicylic acid/EtOH (0.1%) (for phosphonic acids) as developing agents. All preparative chromatographic separations and the following of the reactions were checked by GLC and TLC.

The compounds vinylphosphonic acid (**I**),[12] diethyl vinylphosphonate (**II**),[36] diethyl 2-propenylphosphonate (**XXII**),[37] *trans*-1-propenylphosphonic acid (**V**)[14,38] and dimethyl ester (**III**),[37b,38] *cis*-1-propenylphosphonic acid (**VI**),[39] *cis*-1-propenylphosphoryl dichloride (**X**), and trans isomer (**XIX**)[40] were obtained by known methods.[15] The acid **VI** was purified by recrystallization of its phenethylamine salt and recovery with ion exchange resins. Technical grade samples of di-*tert*-butyl *cis*-1-propenylphosphonate (**VIII**) and the di-*tert*-butyl 1-allenylphosphonate (**XX**) were donated by the pharmaceutical laboratories FYSE S.A., and two fractional distillations under reduced pressure were necessary to purify each product. All of these compounds have been obtained chromatographically (GLC, TLC) and spectroscopically pure. The main ^{1}H-NMR, ^{13}C-NMR, ^{31}P-NMR, UV, IR, and Raman spectral data of these compounds are described in Tables 4, 5, 6, 7, and 8, respectively.[15]

Dimethyl (*E/Z*)-(2-Cyano-1-vinyl)phosphonate (XI/XII). 2-Bromoacrylonitrile. A previous method[17] was modified. A solution of bromine (96 g, 0.8 mol) in dry $CHCl_3$ (360 mL) was added very slowly (3 days) to a solution of acrylonitrile (32 g, 0.6 mol) in dry $CHCl_3$ (200 mL) at 0 °C under indirect solar light. After the addition, the mixture decolored in 6 h at 0 °C and under direct solar light. The reaction mixture was fractionally distillated yielding 119 g (93%) of 2,3-dibromopropionitrile, bp = 46–48 °C/0.25 mmHg. *Caution: fumes highly irritable for skin and eyes.* ^{1}H-NMR ($CDCl_3$) δ (ppm): 3.76 (d, 2H, ^3J(H,H) = 7.8 Hz, CH_2Br), 4.55 (t, 1H, ^3J(H,H) = 7.8 Hz, –CHBr–). Recently dried (KOH) and distillated quinolein (31.7 g, 0.251 mol) was added slowly (2 h) to this freshly prepared 2,3-dibromopropionitrile (52 g, 0.246 mol) in the presence of hydroquinone (150 mg) at 0 °C under argon atmosphere and darkness. The mixture was fractionally distilled yielding 28 g (87%) of 2-bromoacrylonitrile, bp = 18 °C/20 mmHg. ^{1}H-NMR ($CDCl_3$) δ (ppm): 6.36 (d, 1H, ^2J(H,H) = 2.5 Hz, HC=CBr cis), 6.67 (d, 1H, ^2J(H,H) = 2.5 Hz, HC=CBr trans).

(Cyanovinyl)phosphonates (XI/XII). Trimethyl phosphite (28.4 g, 0.23 mol) was added slowly (1 h) to this freshly prepared 2-bromoacrylonitrile (27 g, 0,20 mol) gently stirred at 0 °C (exothermic reaction) under argon atm. The mixture was warmed slowly (1 h) until it reached 40 °C for 3 h (*caution: toxic and carcinogenic gases are produced and exhausted along with the inert gas*[41]) and fractionally distilled yielding mainly a first fraction of dimethyl methylphosphonate and 2-bromoacrylonitrile and a second fraction of a mixture of **XI** and **XII** (14.6 g, 45%) (bp = 50–85 °C/0.025–0.030 mmHg). These isomers were separated by short column liquid chromatography of medium pressure, with a yield of 89% and a ratio *E/Z* = 62/38. Each isomer was redistillated (bp = 55–58 °C/0.03 mmHg (*E*), 76–80 °C/0.025 mmHg (*Z*)). **XI** (*E*). IR ν_{max} (liq) cm^{-1}: 2220vw ν(CN), 1594vw, 1258s, 1182w, 1048sh,

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1028vs, 967w, 840m. ^{1}H-NMR ($CDCl_3$) δ (ppm): 3.8 (d, 6H, ^3J(H,P) = 11.2 Hz, CH_3OP), 6.37 (dd, 1H, ^3J(H,H) = 17.8 Hz, ^3J(H,P) = 21.0 Hz, HC=CP cis), 6.75 (dd, 1H, ^3J(H,H) = 17.8 Hz, ^2J(H,P) = 15.4 Hz, C=CHP *gem*). ^{13}C-NMR ($CDCl_3$) δ (ppm): 53.3, 115.2, 117.2, 138.5. **XII** (*Z*). IR ν_{max} (liq) cm^{-1}: 2228vw ν(CN), 1600vw, 1260s, 1182w, 1050sh, 1030vs, 840m, 798m. ^{1}H-NMR ($CDCl_3$) δ (ppm): 3.87 (d, 6H, ^3J(H,P) = 11.4 Hz, CH_3-OP), 6.26 (dd, 1H, ^3J(H,H) = 13.8 Hz, ^3J(H,P) = 43.7 Hz, HC=CP trans), 6.65 (dd, 1H, ^3J(H,H) = 13.8 Hz, ^2J(H,P) = 14.0 Hz, C=CHP gem). ^{13}C-NMR ($CDCl_3$) δ (ppm): 53.4, 114.5, 115.0, 138.1. (UV data in Table 7).

(*E*)-(2-Cyanovinyl)phosphonic Acid (XIII). A solution of **XI** (2.8 g, 0.017 mol) in $ClSiMe_3$ (10 mL) was deoxygenated with argon, hermetically closed, and stirred magnetically at 80 °C during 69 h (*caution: toxic gases are produced*[41]). The reaction mixture was concentrated, treated with water (15 mL) for 1 h at room temperature, washed with ethyl ether and $CHCl_3$, and dried. A white solid was obtained and identified (TLC, ^{1}H-NMR) as the acid **XIII**. ^{1}H-NMR (D_2O) δ (ppm): 6.21 (dd, 1H, ^3J(H,H) = 17.8 Hz, ^3J(H,P) = 20.3 Hz, HC=CP cis), 7.04 (dd, 1H, ^3J(H,H) = 17.8 Hz, ^2J(H,P) = 15.4 Hz, C=CHP *gem*). ^{13}C-NMR (D_2O) δ (ppm): 113.5, 118.3, 146.6. A small amount (5%) of the monomethyl ester was detected. This acid was purified as phenylammonium salt **XIV**, mp = 163 °C (acetone). ^{1}H-NMR (CD_3OD) δ (ppm): 6.07 (dd, 1H, ^3J(H,H) = 18.0 Hz, ^3J(H,P) = 19.2 Hz, HC=CP cis), 6.91 (dd, 1H, ^3J(H,H) = 18.0 Hz, ^2J(H,P) = 13.5 Hz, C=CHP gem).

Bromination/Dehydrobromination of Diethyl Vinylphosphonate, II. A solution of bromine (8 mmol) in CCl_4 (2 mL) was dropped into **II** (7.9 mmol) dissolved in dry $CHCl_3$ (10 mL) at room temperature under solar light. The mixture was stirred until decoloring (1 h). The concentrated mixture yielded 2.38 g of diethyl (1,2-dibromoethyl)phosphonate (**XXIV**). ^{1}H-NMR ($CDCl_3$) δ (ppm): 1.35 (t, 6H, ^3J(H,H) = 7 Hz, CH_3–), 3.4–3.85 (m, 2H, $-CH_2Br$), 3.9–4.5 (m, 1H + 4H, –CHBr– + $-CH_2O-$). A solution of this compound **XXIV** (1.5 mmol) in ethyleneglycol (1.5 mL) was added to NaF (1.67 mmol) dissolved in ethyleneglycol (2 mL) at 100–120 °C. After 1 h, water (10 mL) was added and the mixture was extracted with $CHCl_3$ (4 × 10 mL). The organic phase was concentrated and purified by TLC, yielding 210 mg of a colorless liquid of diethyl (1-bromovinyl)phosphonate (**XVIII**). ^{1}H-NMR ($CDCl_3$) δ (ppm): 1.35 (t, 6H, ^3J(H,H) = 7.5 Hz, CH_3C), 3.95–4.35 (m, 4H, CH_2O), 6.45 (dd, 1H, ^2J(H,H) = 2 Hz, ^3J(H,P) = 35.7 Hz, HC=CP trans), 6.9 (dd, 1H, ^2J(H,H) = 2 Hz, ^3J(H,P) = 15.6 Hz, HC=CP cis).

Bromination/Dehydrobromination of *cis*-1-Propenylphosphonic Acid (VI). A solution of bromine (0.01 mol) in CCl_4 was dropped slowly (1.5 h) into **VI** (0.01 mol) dispersed in $CHCl_3$ (10 mL) at 64–70 °C and illuminated with 4 × 250 W visible light lamps. The discolored mixture (after about 1 h) was concentrated yielding the (1,2-dibromopropyl)phosphonic acid (**XXV**). ^{1}H-NMR (CD_3CD) δ (ppm): 1.81 (dd, 3H, ^3J(H,H) = 6.6 Hz, ^4J(H,H) = 0.8 Hz, CH_3–), 4.32 (dd, 1H, ^2J(H,P) = 14.7 Hz, ^3J(H,H) = 2.4 Hz, CHBrP), 4.6–4.9 (m, 1H, CHBrC). This acid **XXV** (1 g) was heated at 180 °C for 2 h, obtaining the (*Z*)-1-bromo-1-propenylphosphonic acid (**XVI**). ^{1}H-NMR (CD_3OD) δ (ppm): 1.9 (dd, 3H, ^3J(H,H) = 6.75 Hz, ^4J(H,P) = 3.15 Hz, CH_3-CH), 6.83–7.2 (dq, 1H, ^3J(H,H) = 6.75 Hz, ^3J(H,P) = 13.5 Hz, HC=CPcis).

Bromination/Dehydrobromination of *trans*-1-Propenylphosphonic Acid (V). The acid **V** (0.035 mol) dispersed in $CHCl_3$ (56 mL) was treated with bromine (0.035 mol) as in the previous example obtaining **XXV**. **Acid Dehydrobromination.** This compound (1 g) was stirred at 140 °C for 7 h, obtaining a mixture of **XVI** and (*E*)-(1-bromo-1-propenyl)-phosphonic acid (**XVII**). ^{1}H-NMR (CD_3OD) of **XVII** δ (ppm): 2.03 (dd, 3H, ^3J(H,H) = 7 Hz., ^4J(H,P) = 3 Hz, CH_3), 6.8 (dq, 1H, ^3J(H,H) = 7 Hz, ^3J(H,P) = 36 Hz, HC=CP trans). Basic Dehydrobromination. A mixture of **XXV** (3.5 mmol) and freshly distillated quinolein (3.7 mmol) was gently stirred at 80 °C for 40 h. The mixture was concentrated under reduced pressure obtaining also a mixture of **XVI** and **XVII**.

Basic Dehydrobromination of Methyl 2,3-Dibromopropanoate. This compound, freshly obtained from methyl acrylate, was treated with quinolein as in the previous example, at 30–50 °C for 5 min. The mixture was rectified obtaining **methyl 2-bromoacrylate** (bp = 30–40 °C/1–2 mmHg). ^{1}H-NMR ($CDCl_3$) of methyl 2,3-dibromopropanoate δ (ppm): 3.7 (dd, 1H, ^3J(H,H) = 4.8 Hz, ^2J(H,H) = 10.1 Hz, *H*CHBr-C*), 3.8 (s, 3H, OCH_3), 3.95 (dd, 1H, ^2J(H,H) = 10.1 Hz, ^3J(H,H) = 10.6 Hz., HC*H*Br-C*), 4.5 (dd, 1H, ^3J(H,H) = 4.8, 10.6 Hz, –CHBr). **Methyl 2-bromoacrylate.** ^{1}H-NMR δ (ppm): 3.9 (s, 3H, $-OCH_3$), 6.3 (d, 1H, ^2J(H,H) = 1.8 Hz, HC=CBr trans), 6.95 (d, 1H, ^2J(H,H) = 1.8 Hz, HC=CBr cis).

Allylic Bromination of Di-*tert*-butyl *cis*-1-Propenylphosphonate (VIII). A mixture of **VIII** (4.27 mmol), NBS (4.3 mol), and benzoyl peroxide (50 mg) dissolved in CCl_4 (10 mL) was refluxed for 3 h. The mixture was filtered, concentrated, and purified by preparative TLC, yielding the di-*tert*-butyl (*E*)-3-bromo-1-propenylphosphonate (**XV**). ^{1}H-NMR ($CDCl_3$) δ (ppm): 1.5 (s, 18H, CH_3–), 3.95 (dt, 2H, ^3J(H,H) = 7 Hz, ^4J(H,H) = 1.2 Hz, ^4J(H,P) = 1.2 Hz, $-CH_2Br$), 5.9 (tt, 1H, ^3J(H,H) = 17 Hz, ^2J(H,P) = 17 Hz, ^4J(H,H) = 1.2 Hz, PCH=C), 6.65 (ddt, 1H, ^3J(H,H) = 7 Hz, ^3J(H,H) = 17 Hz, ^3J(H,P) = 20 Hz, CH=CP). A small amount of di-*tert*-butyl *trans*-propenylphosphonate (**IX**) was also isolated as a subproduct.

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Supplementary Material Available: ^{1}H- and ^{13}C-NMR spectra of **XI–XIII** and the ^{1}H-NMR spectra of **XIV–XVIII** are available. The ABCX spin system data and a wholly coupled ^{31}P-NMR spectrum of **II** is also available (16 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(41) The outlet gases should be passed through a double cool trap (−10 °C) and a NaOH aqueous solution.