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Phosphonic Systems: 5. Prototropic Equilibria of Diethyl Alkenylphosphonates

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ABSTRACT

Base-catalyzed prototropic equilibria for nine pairs of diethyl 1- and 2-alkenylphosphonates have been determined. The results, together with those reported elsewhere for three other pairs, demonstrated that the diethoxyphosphoryl group PO_3Et_2 has only a very weakly stabilizing effect on the adjacent carbon–carbon double bond. The decisive factors are the number of carbon atoms attached to the double bond and the number of hydrogen atoms available for hyperconjugation.

INTRODUCTION

The free energy change for the double-bond migration in a 1,3-disubstituted propenyl system (Equation 1) is related to the effect of substituents X and Y on the stability of the alkene function. This subject has been extensively studied by Hine and coworkers, who derived the "double-bond stabilization parameter" as a quantitative measure of that effect [1].

$$\underset{\mathbf{1}}{XCH_2{-}CH{=}CH{-}Y} \rightleftharpoons \underset{\mathbf{2}}{X{-}CH{=}CH{-}CH_2Y} \qquad (1)$$

An analysis of a large number of equilibria (1) showed that practically all common substituents studied have a stabilizing effect (relative to that of hydrogen) on the adjacent olefinic bond, with the alkylsulfonyl group being the only possible exception [2]. A review of the literature on the substituent effects on the prototropic equilibrium (1) revealed a conspicuous absence of any data on the effect of phosphorus-containing functional groups and their relation to other typical substituents. For the dialkyl alkenylphosphonic esters [**1**, **2**; X = P(O)$(OR)_2$], a few available data indicate that the equilibrium (1) depends on the nature of substituent Y. For example, when Y = H, 1-propenylphosphonate **2** is reported to be the exclusive product in the equilibrium mixture [3]; whereas for Y = Pr the allylic (2-pentenyl) phosphonate **1** represents the thermodynamic product [4].

Because of our interest in the synthetic applications of alkenylphosphonates [5], we decided to investigate, in more detail, the effect of the diethoxyphosphoryl group [X = P(O)$(OEt)_2$] on the location of the double bond in Equation (1) by means of the prototropic equilibria of the corresponding unsaturated phosphonic esters prepared by unambiguous routes. Our objective was to compare the effect of the PO_3Et_2 group with two other factors that influence the equilibrium: (i) the number of carbon atoms attached to the olefinic function; (ii) the number of hydrogen atoms available for hyperconjugative interactions with that function. Although the stabilizing effect of alkyl substitution on a carbon–carbon double bond is a well-established fact [6], the C–H hyperconjugation effects are also indicated as important factors in determining the relative stability of isomeric alkenes [7].

RESULTS AND DISCUSSION

Five 2-alkenyl (allylic) phosphonats, **1b**, **c**, **d**, **j**, **k**, and five 1-alkenyl (vinylic) phosphonates, **2e**, **f**, **g**, **h**, **j**, were synthesized and their base-catalyzed prototropic equilibria in *t*-BuOK/*t*-BuOH (or EtONa/EtOH) systems determined. The results, to-

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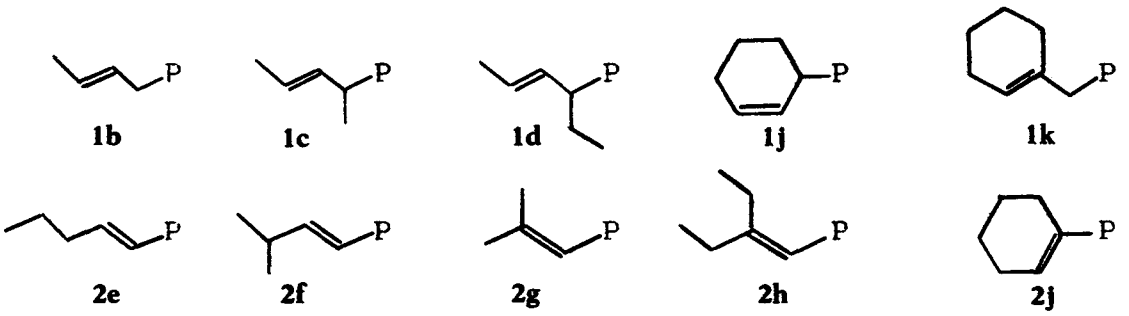


P = $P(O)(OEt)_2$

gether with other equilibrium data obtained in our laboratory or reported in the literature, allowed us to identify the effect of the $P(O)(OEt)_2$ substituent on the adjacent olefinic bond.

Synthesis

Diethyl 2-butenylphosphonate (**1b**) was prepared via the Arbuzov reaction between crotyl bromide and triethyl phosphite [8] (Equation 2). Although the yield of pure **1b** was

$$\longrightarrow \mathbf{1b} + EtBr \qquad (2)$$

low, there was no evidence for the formation of the isomeric products, from either the allylic rearrangement or the double bond migration. Substrate **1j** was synthesized in the same manner from 3-bromocyclohexene. The 2-alkyl derivatives of **1b** (**1c** and **1d**) were obtained in good yield from **1b** via deprotonation, followed by alkylation (Equation 3).

$$\mathbf{1b} \xrightarrow[2.\ RI]{1.\ BuLi} \mathbf{1c,\ 1d} \qquad (3)$$

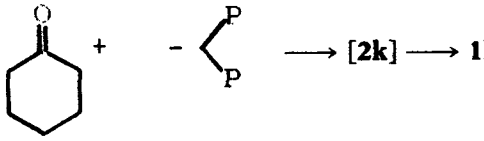
As previously observed for 2-pentenylphosphonate [9], alkylation of the lithium derivative of **1b** occurred regiospecifically at position 1, and the products were formed as ca. 8:1 and 4:1 mixtures of stereoisomers.

1-Alkenylphosphonates (**2e–h**) were prepared according to the Wadsworth and Emmons procedure [10] involving the reaction between the sodium derivative of tetraethyl methylenebisphosphonate and the required aldehyde or ketone (Equation 4).

$$CH_2(PO_3Et_2)_2 \xrightarrow[2.\ RR'CO]{1.\ NaH} \mathbf{2e–2h} \qquad (4)$$

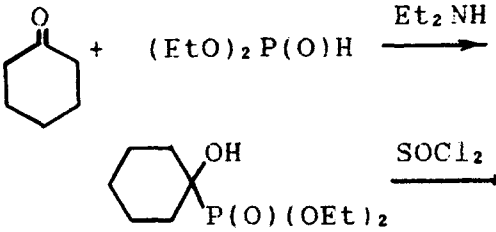
Products **2e, f** were obtained as single stereoisomers (E), and no isomerization to the corresponding 2-alkenyl derivatives was observed under the reaction conditions.

1k was prepared from cyclohexanone and sodium tetraethyl methylenebisphosphonate [10]. In this case, however, the initially formed 1-alkenylphosphonate undergoes in situ complete isomerization to the thermodynamically more stable 2-alkenyl form (Equation 5).



(5)

Finally, the isomer of **1j**, compound **2j**, was prepared by the addition of diethyl phosphite to cyclohexanone [11], followed by the dehydration of the 2-hydroxyphosphonate by means of thionyl chloride (Equation 6) [12].



(6)

The structure of the prepared phosphonic diesters was confirmed by NMR (^1H and ^{31}P) spectroscopy and mass spectrometry. In three cases (**2f**, **2g**, and **1f** obtained by isomerization of **2f**) the structure of the products was additionally confirmed by converting them to the corresponding phosphonic acids [13], identified as their monoanilinium salts **3** (Equation 7).

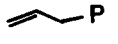
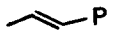
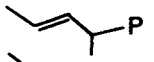
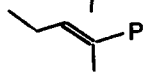
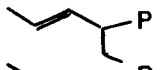
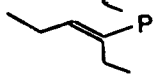
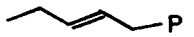
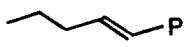
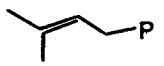
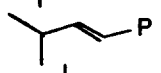
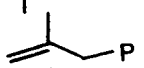
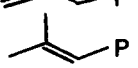
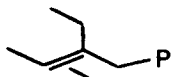
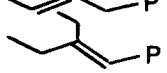
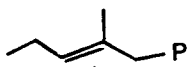
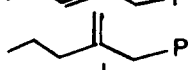
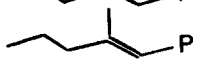
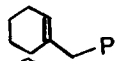
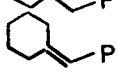
$$\mathbf{1f, 2f, 2g} \xrightarrow{Me_3SiCl,\ NaI} R{-}PO_3H_2 \xrightarrow{PhNH_2} R{-}PO_3H^-PhNH_3^+ \qquad (7)$$

3 R = $Me_2C{=}CHCH_2$, $Me_2CHCH{=}CH$, $Me_2C{=}CH$

Prototropic Equilibria

Base-catalyzed isomerization of compounds **1b–d** and **2e–h** was studied by incubating the substrates at 25°C in *tert*-butyl alcohol containing ca. 0.3 mol-equivalents of *t*-BuOK or in ethanol containing the corresponding amount of EtONa. The progress of

TABLE 1 Prototropic Equilibria of Diethyl Alkenylphosphonates; *t*-BuOK/*t*-BuOH (or EtONa/EtOH), 25°C[a]

	Compound	% (equil)	(i)	(ii)	(iii)	α,β–β,γ (i)	α,β–β,γ (ii)	α,β–β,γ (iii)
1a[b]		0	1	0	2	0	1	1
2a		100	1	1	3			
1b		81	2	0	5	−1	1	−3
2b		7[c]	1	1	2			
1c		29	2	0	4	0	1	1
2c		71	2	1	5			
1d		49	2	0	4	0	1	0
2d		51	2	1	4			
1e		79	2	0	4	−1	1	−2
2e		10[c]	1	1	2			
1f		99	3	0	8	−2	1	−7
2f		1	1	1	1			
1g		20	2	0	5	0	1	1
2g		80	2	1	6			
1h		96	3	0	7	−1	1	−3
2h		4	2	1	4			
1i[d]		84	3	0	7			
1i′		4	2	0	4	−1 0	1 1	−2 1
2i		12	2	1	5			
1j		5	2	0	3	0	1	1
2j		95	2	1	4			
1k		100	3	0	6	−1	1	−2
2k		0	2	1	4			

[a] P = P(O)(OEt)$_2$.
[b] Ref. 3.
[c] Total <100%. ^{31}P NMR spectrum revealed the presence of third phosphorus-containing product; see Discussion.
[d] M. P. Belciug, M.Sc. Thesis, University of Pretoria, 1991.

the reaction was monitored by ^1H and ^{31}P NMR spectroscopy, and when the equilibrium was reached, the relative amounts of each isomer were determined from the integrated areas of the corresponding signals. For one system, where both isomers were independently prepared (**1j** and **2j**), the reaction carried out with each isomer yielded the identical equilibrium mixture. Table 1 lists the results of the prototropic equilibria determined for the prepared substrates and some other closely related systems. For each substrate, the proportion of the 1,2- (**2**) and 2,3-unsaturated (**1**) isomers is given as a percentage of the total mixture. In addition, for each **1** and **2** we indicated the number of (i) carbon atoms attached to the olefinic bond, (ii) PO_3Et_2 groups attached to the olefinic bond (nil or one), and (iii) hydrogen atoms available for hyperconjugation with the carbon–carbon double bond. The last column of Table 1 shows the difference in the structural factors (i), (ii), (iii) between the α,β- and β,γ-alkenylphosphonates.

For two systems (**1b/2b** and **1e/2e**) the equilibrium mixture contained additional organophosphorus product that gave rise to a lowest-field signal in the ^{31}P NMR spectrum ($\delta_P > 28$). These products were tentatively identified as the corresponding saturated 2-*tert*-butoxyalkylphosphonates formed by the addition of *t*-BuOH to the 1,2-alkenylphosphonate isomer 2. The proportion of those products increased when the sterically less hindered base (EtO^-/EtOH) was used as a catalyst for the prototropic isomerization. We have previously observed [9] the complete addition of ethanol to diethyl 1-propenylphosphonate, with the same sequence of the δ_P values for the 1-alkenyl, 2-alkenyl, and 2-ethoxyalkylphosphonates (ca. 18, ca. 26, and ca. 28, respectively).

The composition of the equilibrium mixtures shown in Table 1 indicates clearly that the thermodynamic stability of an alkenylphosphonate ester is determined by the alkyl substitution of the olefinic bond and by the C–H hyperconjugation, but *not* by the position of the phosphorus-containing function. For 12 pairs of isomeric diethyl 1- and 2-alkenylphosphonates studied, we have observed variations in the equilibrium mixtures from the exclusive α,β- to the exclusive β,γ-isomer present. All systems **2/1** can be divided according to five individual patterns in terms of the difference in factors (i), (ii), (iii) between the α,β- and β,γ-unsaturated compounds. Those patterns, and the ratio of the isomers in the equilibrium mixture are shown in Table 2. The first entry in the table (substrates **a**, **c**, **g**, **i'**, **j**) demonstrates that the presence of the $P(O)(OEt)_2$ group at the double bond, together with one extra hydrogen atom in the allylic position, are enough to shift the equilibrium strongly in favor of the α,β-unsaturated isomer; the average **2/1** ratio for the structurally similar systems **c**, **g**, **i'** being 3.1 ± 0.8. A somewhat high value (19.0) obtained for the pair **j** probably results from steric effects operating in the cyclohexenyl system. We believe that the exceptionally high value of the **2/1** ratio (100% of **2**) reported [3] for the propenyl system **a**, does not represent a true ratio of the thermodynamic stability of both isomers. It is more likely, in view of our recent observation [9], that in this case the competing addition of *tert*-butyl alcohol to 1-propenylphosphonate shifts the prototropic equilibrium even more in favor of the α,β-isomer.

The typical value of 2:1 = ca. 3, characteristic for the "0,1,1" structural pattern, is to a great extent the result of the stabilizing hyperconjugative effect of one additional hydrogen atom. An analysis of the enthalpies of hydrogenation of several hexenes, *n*-heptenes, and methylheptenes revealed that the ΔH values for two isomeric alkenes differing by one allylic hydrogen atom vary in the range of 0.34–0.43 kcal mol^{-1} [14], which corresponds at 25°C to the equilibrium constant of approximately two. The slightly higher value observed for systems **c**, **g**, **i'** reflects the additional effect of the diethoxyphosphoryl group as an alkene substitutent. This effect is *weakly stabilizing*, and it is best demonstrated in the second entry of Table 2 (system **d**, pattern "0,1,0"), where the only major difference in the substitution pattern of the carbon–carbon double bond is the direct presence (or absence) of the $P(O)(OEt)_2$ group. Although we did observe some excess of the 1-alkenylphosphonate, the equilibrium constant is not far from one. In fact, the diethoxyphosphoryl group probably represents, as far as its effect on

TABLE 2 Isomers Ratio (**2/1**) of Diethyl Alkenylphosphonates as a Function of "Structural Factors" (i), (ii), (iii)

Pairs of Isomers **1,2**	*Differences in "Structural Factors"* (*i*)	(*ii*)	(*iii*)	*Ratio* **2:1**
a, c, g, i', j	0	1	1	∞, 2.4, 4.0, 3.0, 19.0
d	0	1	0	1.04
e, i, k	−1	1	−2	0.13, 0.14, 0.00
b, h	−1	1	−3	0.09, 0.04
f	−2	1	−7	0.01

the olefinic bond is concerned, a substituent *resembling the hydrogen atom* more closely than any of the substituents studied so far.

Gradual increase of the number of carbon atoms and allylic hydrogens around the double bond in the 2,3-alkenylphosphonates **1** (3rd, 4th, and 5th entries in Table 2) shifts the prototropic equilibrium increasingly toward that isomer. Although it is difficult to evaluate the effect of those two factors independently, they seem to contribute to the net result in a comparable degree. The only anomalous result in this group is that for system **k**, where no α,β-unsaturated phosphonate was observed at the equilibrium. The cyclic structure of the carbon skeleton is again responsible for the deviation; methylidenecyclohexane is known to isomerize to the more stable 1-methylcyclohexene [15]—the factor that is superimposed on the effect of alkyl substitution and hyperconjugation.

In conclusion, we have demonstrated that the stabilizing effect of the $P(O)(OEt)_2$ group on an adjacent carbon–carbon double bond is very weak, not far from that of hydrogen, for which the double-bond stabilization parameter is arbitrarily set equal to zero [2a]. It may be expected, therefore, that in condensations involving carbanions derived from alkenylphosphonates [5], thermodynamically controlled products will be determined by structural factors other than the mutual relation between the olefinic bond and the phosphorus-containing substituent.

EXPERIMENTAL

Solvents and commercially available reagents were purified by standard methods. All reactions involving organometallic reagents were carried out in an atmosphere of dry nitrogen. Solvents were dried over anh. $MgSO_4$ and evaporated on a Buchi rotary evaporator. Bulb-to-bulb distillations were carried out on a Buchi GKR-50 Glass Tube Oven. Melting points are uncorrected. NMR spectra were recorded on a FT Bruker AC 300 MHz spectrometer and the chemical shift values are given relative to TMS (^1H) and 85% H_3PO_4 (^{31}P). Mass spectra were recorded on a Varian MAT-212 double focusing direct inlet spectrometer at an ionization potential of 70 eV. Only the values of M^+ and selected ions are reported.

Substrates

Diethyl 2-Butenylphosphonate (**1b**). A mixture of crotyl bromide (8.8 g, 0.065 mol) and triethyl phosphite (10.8 g, 0.065 mol) was placed in a flask equipped with a Vigreux column and a condensor, and was heated on an oil bath at 160°C for 80 min, until no more bromoethane collected in a receiver. The crude product was purified by bulb-to-bulb distillation (oven temp. 95–120°C/0.2 torr); 4.2 g (34%). n_D^{25} 1.4356; ^1H NMR ($CDCl_3$); δ: 1.3 (6H, t, J 7.1 Hz, 2 × Me of EtO), 1.6 (3H, t, $J(1, 2) = J(1, 3)$ 5.7 Hz, δ-Me), 2.4 (2H, ddd, J 21.8, 7.2, 0.9 Hz, α-CH_2), 4.0 (4H, quint, $J_{HH} = J_{HP}$ 7.1 Hz, 2 × CH_2 of EtO), 5.3 5.3 (1H, m, β-CH), 5.5 (1H, m, γ-CH). ^{31}P NMR δ 25.2. MS: m/z 192 (M^+, 100%), 177(3), 164(29), 138(79).

Diethyl 1-Methyl-2-butenylphosphonate (**1c**). *n*-Butyllithium (15% sol. in hexane, 7.8 mL, 12 mmol) was added slowly to a stirred solution of **1b** (2.0 g, 10 mmol) in THF (20 mL) at −70 to −80°C and the mixture was stirred at this temperature for 90 min. Iodomethane (0.86 mL, 10 mmol) was added dropwise to the solution, stirring was continued for an additional 30 min, and the mixture was allowed to warm up to room temperature. An excess of 10% aq. ammonium chloride was added, and the product was extracted with ether (2 × 20 mL). After drying and evaporating the solvent, the crude product was purified by bulb-to-bulb distillation (oven temp. 85–90°C/0.07 Torr); 1.7 g (83%). n_D^{25} 1.4360; ^1H NMR ($CDCl_3$, major compound) δ: 1.1 (3H, d,d, J 7.2, 0.6 Hz, α-Me), 1.2 (6H, t, J 7.1 Hz, 2 × Me of EtO), 1.6 (3H, t, J 5.7 Hz, δ-Me), 2.54 1H, ddq, J 22.5, 7.2, 1.6 Hz, α-CH), 4.1 (4H, quint, J 7.1 Hz, 2 × CH_2 of EtO), 5.4 (1H, m, β-CH), 5.5 (1H, m, γ-CH). ^{31}P NMR δ: 28.0, 28.3 (8:1), E and Z isomers. MS: m/z 206 (M^+, 81%), 191(22), 178(15), 138(100), 69(51).

Diethyl 1-Ethyl-2-butenylphosphonate (**1d**). Prepared as (**1c**), using iodoethane and purified by bulb-to-bulb distillation (oven temp. 130°C/0.45 Torr); yield 67%. n_D^{25} 1.4354. ^1H NMR ($CDCl_3$, major component) δ: 0.8 (3H, t, J 7.9 Hz, Me of α-Et), 1.2 (6H, two t, J 7.0 Hz, 2 × Me of EtO), 1.5 (1H, m, one H of CH_2 of α-Et), 1.7 (3H, t, J 5.8 Hz, δ-Me), 1.8 (1H, m, one H of CH_2 of α-Et), 2.2 (1H, dtd, J 20.9, 10.0, 3.7 Hz, α-CH), 4.0 (4H, quint, $J_{HH} = J_{HP}$ 7.6 Hz, 2 × CH_2 of EtO), 5.1–5.3 (1H, β-CH), 5.5–5.6 (1H, m, γ-CH). ^{31}P NMR δ: 27.2, 27.3 (1:4), E and Z isomers. MS: m/z 220 (M^+, 100%), 205(25), 192(28), 191(99), 138(93).

Diethyl 3-Cyclohexenylphosphonate (**1j**). Prepared from triethyl phosphite and 3-bromohexene in a manner analogous to that for **1b**. Purified by bulb-to-bulb distillation (oven temp. 100°C/0.4 Torr); yield 65%. ^1H NMR ($CDCl_3$) δ: 1.2 (3H, t, J 7.0 Hz, Me of EtO), 1.3 (3H, t, J 7.0 Hz, Me of EtO), 1.5 (2H, m, ring CH_2), 1.8 (2H, m, ring CH_2), 2.0 (2H, m, ring CH_2), 2.5 (1H, unresolved dd, J_{HP} 27.1 Hz, α-CH), 4.1 (4H, quint, $J_{HH} = J_{HP}$ 7.3 Hz, 2 × CH_2 of EtO), 5.7 (1H, m, β-CH), 5.9 (1H, m, γ-CH). ^{31}P NMR δ: 30.9. $\nu_{(C=C)}$ 1650 cm^{-1}. MS: m/z 218 (M^+, 36%), 190(7), 162(7), 139(52), 111(91), 80(100).

Diethyl 1-Cyclohexenylmethylphosphonate (**1k**) *and Diethyl 1-Alkenylphosphonates* **2e–h**; *General*

dure. Sodium hydride (washed with pet. ether and dried under reduced pressure; 0.49 g, 0.020 mol) was added to dry dimethoxyethane. To this suspension tetraethyl methylenebisphosphonate [16] (5.3 g, 0.018 mol) in dimethoxyethane (30 mL) was added dropwise with stirring at room temperature. After the evolution of hydrogen had subsided, the mixture was stirred for 1 h, and the corresponding aldehyde or ketone was added dropwise with cooling (if necessary) at 25°C. After the addition the reaction mixture was either left for 1 h at room temperature (for aldehydes) or heated under reflux (6 h for acetone, 12 h for cyclohexanone and 22 h for 3-pentanone). Water (300 mL) was added, and the aqueous solution was extracted with ether (3 × 100 mL). After drying and removal of ether, the crude products were obtained as colorless oils.

Diethyl 1-Cyclohexenylmethylphosphonate (**1k**). Purified by bulb-to-bulb distillation (oven temp 110°C/0.2 Torr); yield 53%. ^{1}H NMR ($CDCl_3$) δ: 1.3 (6H, t, J 7.1 Hz, 2 × Me of EtO), 1.5 (4H, m, ring C(4)H_2, C(5)H_2), 2.0 (2H, m, ring CH_2), 2.0 (2H, m, ring CH_2), 2.4 (2H, d, J 21.7 Hz, α-CH_2), 4.0 (4H, quint, J 7.2 Hz, 2 × CH_2 of EtO), 5.6 (1H, m, β-CH). ^{31}P NMR δ: 28.8. $V_{(C=C)}$ 1636 cm^{-1}. MS: m/z 232 (M^+, 25%), 218(36), 204(11), 189(17), 175(15), 139(54), 111(91), 80(100).

Diethyl 1-Pentenylphosphonate (**2e**). Purified by bulb-to-bulb distillation (oven temp. 145–155°C/0.5 Torr); 54%. ^{1}H and ^{31}P NMR spectra of this product were identical to those reported before [4] for **2e** prepared via a different route.

Diethyl 3-Methyl-1-Butenylphosphonate (**2f**). Purified by bulb-to-bulb distillation (oven temp. 115–118°C/0.1 Torr); 67%. n_D^{25} 1.4385. ^{1}H NMR ($CDCl_3$) δ: 1.0 (6H, d, J 6.7 Hz, 2 × γ-Me), 1.3 (6H, t, J 7.1 Hz, 2 × Me of EtO), 2.3–2.4 (1H, m, γ-CH), 4.0 (4H, quint, J 7.1 Hz, 2 × CH_2 of EtO), 5.5 (1H, ddd, J 20.6, 17.2, 1.6 Hz, α-CH), 6.7 (1H, ddd, J 22.3, 17.0, 6.2 Hz, β-CH). ^{31}P NMR δ: 19.4. MS: m/z 206 (M^+, 69%), 191(16), 178(39), 150(100), 138(49), 69(52).

Diethyl 2-Methyl-1-Propenylphosphonate (**2g**). Purified by bulb-to-bulb distillation (oven temp. 80°C/0.03 Torr); 37%. n_D^{25} 1.4386. ^{1}H NMR ($CDCl_3$) δ: 1.3 (6H, t, J 7.1 Hz, 2 × Me of EtO), 1.9 (3H, s, γ-Me *trans* to P), 2.1 (3H, d, J 3.1 Hz, γ-Me *cis* to P), 4.0 (4H, quint, J 7.2 Hz, 2 × CH_2 of EtO), 5.4 (qd, J 20.0, 1.1 Hz, α-CH). ^{31}P NMR δ: 17.8. MS: m/z 192 (M^+, 36%), 177(11), 164(64).

Diethyl 2-ethyl-1-butenylphosphonate (**2h**). Bulb-to-bulb distillation led to isomerization to **1h**, and the compound was used without further purification; 46%. ^{1}H NMR ($CDCl_3$) δ: 1.0 (6H, two overlapping t, 2 × δ-Me), 1.3 (6H, t, J 7.0 Hz, 2 × Me of EtO), 2.2 (2H, q, J 7.5 Hz, γ-CH_2 *trans* to P), 2.5 (2H, dq, J 7.6, 2.2 Hz, γ-CH_2 *cis* to P), 4.0 (4H, quint, J 7.2 Hz, 2 × CH_2 of EtO), 5.3 (1H, d, J 17.8 Hz, α-CH). ^{31}P NMR δ: 18.8.

Diethyl 1-Hydroxycyclohexylphosphonate. A mixture of diethyl phosphite (10.0 g, 0.072 mol), cyclohexanone (7.1 g, 0.072 mol), and diethylamine (5.8 g, 0.079 mol) in ether (50 mL) was stirred at room temperature for 24 h. After evaporation of volatile material under reduced pressure, the residue was dissolved in dichloromethane and the solution was washed with diluted aq. HCl. After drying and evaporation of CH_2Cl_2 the crude product was purified by crystallization from chloroform/hexane; yield 15.3 g (90%). Mp 71–72°C (lit. [17] mp 72–73°C). ^{1}H NMR ($CDCl_3$) δ: 1.1 (6H, t, J 7.1 Hz, 2 × Me of EtO), 1.3 (2H, m, ring CH_2), 1.5 (4H, m, 2 × ring CH_2), 1.6 (2H, m, ring CH_2), 1.8 (2H, m, ring CH_2), 4.0 (4H, quint, J 7.1 Hz, 4 × CH_2 of EtO), 4.3 (1H, br s, OH). ^{31}P NMR δ: 26.6. $V_{(OH)}$ 3100 cm^{-1}. Anal. calcd for $C_{10}H_{21}O_4P$: C, 50.87; H, 9.00. Found: C, 50.85; H, 8.70.

Diethyl 1-Cyclohexenylphosphonate (**2j**). 1-Hydroxyphosphonate (1 mol-equiv) was dissolved in benzene, and thionyl chloride (1.2 mol-equiv) was added. The solution was heated at 60°C for 4 h, washed with dilute aq. $NaHCO_3$, dried, and evaporated under reduced pressure. Crude **2j** was purified by bulb-to-bulb distillation (oven temp. 100°C/0.5 Torr); yield 70%. ^{1}H NMR ($CDCl_3$) δ: 1.3 (6H, t, J 7.1 Hz, 2 × Me of EtO), 1.6 (4H, m, 2 × ring CH_2), 2.1 (4H, m, 2 × ring CH_2), 4.0 (4H, quint, $J_{HH} = J_{HP}$ 7.4 Hz, 2 × CH_2 of EtO), 6.8 (1H, m, J_{HP} 22.2 Hz, β-CH). ^{31}P NMR δ: 20.2. $V_{(C=C)}$ 1634; $V_{(PO)}$ 1234 cm^{-1}. MS: m/z 218 (M^+, 68%), 190(29), 162(76), 147(22), 138(15), 111(39), 108(46), 80(100).

Preparation of the Anilinium Salts **3**. Chlorotrimethylsilane (1.05 g, 9.7 mmol) was added dropwise to a mixture of the phosphonate (4.8 mmol), anh. NaI (11.45 g, 9.7 mmol) and dry acetonitrile (5 mL). The reaction mixture was stirred at 40°C for 30 min, filtered, and the precipitate was washed with ether (2 × 5 mL). The solution was evaporated under reduced pressure at <50°C, and a solution of aniline (0.9 mL, 9.7 mmol) in methanol (5 mL) was added with stirring. Crude salt was obtained by evaporation of the solvent under reduced pressure.

Anilinium 3-Methyl-1-Butenylphosphonate (from **2f**). Yield 54%. Mp 149–151°C (from acetone/methanol, 10:1, followed by acetone). ^{1}H NMR (D_2O) δ: 0.9 (6H, d, J 7.0 Hz, 2 × δ-Me), 2.3 (1H, m, γ-CH), 5.6–5.7 (1H, m, α-CH), 6.4 (1H, ddd, J 21.2, 16.4, 6.1 Hz, β-CH), 7.3–7.5 (5H, m, Ph). ^{31}P NMR δ: 17.4. Anal. calcd for $C_{11}H_{18}NO_3P$: C, 54.3; H, 7.5; N, 5.8. Found: C, 54.3; H, 8.2; N, 5.6%.

Anilinium 2-Methyl-1-Propenylphosphonate (from **2g**). Yield 50%. Mp 158–160°C (from acetone). ^{1}H NMR (D_2O) δ: 1.8 (3H, s, β-Me *cis* to α-CH), 1.9 (3H, s, β-Me *trans* to α-CH), 5.5 (1H, d, J 19.4 Hz, α-CH), 7.3–7.5 (5H, m, Ph). ^{31}P NMR δ: 16.0. Anal. calcd for $C_{10}H_{16}NO_3P$: C, 52.4; H, 7.0; N, 6.1. Found: C, 49.5; H, 6.2; N, 5.2%.

Isomerization of Diethyl Alkenylphosphonates. Substrates **1b–d** and **2e–h** were isomerized using the *t*-BuOK/*t*-BuOH system. The phosphonate (0.5–2.0 g) was added to a solution of *t*-BuOK (ca. 0.3 mol-equiv, 1.5 M) in *t*-BuOH and the solution was kept in a thermostated bath at 25°C. At selected intervals samples of the solution were withdrawn, solvent was removed under reduced pressure, water was added, and the pH of the mixture was adjusted to 7–8 by the addition of trifluoroacetic acid. The mixture was extracted with chloroform (2 × 5 mL per 0.5 g of substrate), and the extract was dried and evaporated under reduced pressure. The ^{1}H and ^{31}P NMR spectra of the residue were recorded, and the proportion of the isomers was determined from the ratio of the integrated signals in both spectra. The procedure was repeated until a constant ratio of isomers was obtained. For all substrates the equilibrium was reached after a period not longer than 72 h.

Substrates **1j**, **2j**, **1k** were isomerized in a similar manner, but in ethanol containing 1.1 mol-equiv of sodium ethanolate (2.2 M). For **1j/2j** the equilibrium was reached after ca. 48 h, whereas **1k** did not undergo any noticeable change over the period of 4 days.

The isomerization product of **2f** (compound **1f**), representing 99% of the equilibrated mixture, was isolated and characterized.

Diethyl 3-Methyl-2-Butenylphosphonate (**1f**). Purified by bulb-to-bulb distillation (oven temp. 165°C/0.5 Torr); yield 50%. n_D^{25} 1.4402. ^{1}H NMR ($CDCl_3$) δ: 1.3 (6H, t, J 7.1 Hz, 2 × Me of EtO), 1.6 (3H, d, J 4.0 Hz, γ-Me *cis* to β-CH), 1.7 (3H, d, J 5.4 Hz, γ-Me *trans* to β-CH), 2.5 (2H, dd, J 21.7, 7.7 Hz, α-CH_2), 4.0 (4H, quint, J 7.1 Hz, 2 × CH_2 of EtO), 5.1 (1H, m, β-CH). ^{31}P NMR δ: 28.6. MS: m/z 206 (M^+, 100%), 191(9), 178(33), 150(71), 138(60).

Anilinium 3-Methyl-2-Butenylphosphonate (from **1f**). Yield 86%. Mp 161–162°C (from acetone). ^{1}H NMR (D_2O) δ: 1.6 (3H, d, J 3.3 Hz, γ-Me *cis* to β-CH), 1.7 (3H, d, J 4.8 Hz, γ-Me *trans* to β-CH), 2.4 (2H, dd, J 20.9, 7.7 Hz, α-CH_2), 5.2 (1H, m, β-CH), 7.3–7.5 (5H, m, Ph). ^{31}P NMR δ: 26.6. Anal. found: C, 53.2; H, 7.5; N, 5.0%.

Isomerization products obtained from other substrates were identified and determined in the equilibrium mixtures without isolation. There was always a characteristic difference in the δ_P values for the 1-alkenyl- and 2-alkenylphosphonates **1** and **2**, thus the proportion of both products could be determined easily from the ^{31}P NMR spectra. The following δ_P values were obtained: **2b**, 18.4; **2c**, 19.1; **2d**, 19.6; **1e**, 27.9 (major), 27.8 (minor), E/Z isomers; **1g**, 27.0; **1h**, 27.8 (70%), 28.2 (30%), E/Z isomers.

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REFERENCES

[1] J. Hine, *Structural Effects on Equilibria in Organic Chemistry*, Wiley, New York, 1975, chap. 8.
[2] (a) J. Hine, M. J. Skoglund, *J. Org. Chem.*, *47*, 1982, 4766; (b) J. Hine, S-M. Linden, *J. Org. Chem.*, *48*, 1983, 584.
[3] G. Sturtz, A. Pondaven-Raphalen, *J. Chem. Res.* (*S*), 1980, 175.
[4] A. M. Modro, T. A. Modro, *Can. J. Chem.*, *66*, 1988, 1541.
[5] A. M. M. Phillips, T. A. Modro, *J. Chem. Soc., Perkin Trans. 1*, in press.
[6] See, for example, M. H. Whangbo, K. R. Stewart, *J. Org. Chem.*, *47*, 1982, 736.
[7] K. L. Rinehart, L. J. Dolby, *J. Org. Chem.*, *22*, 1957, 13.
[8] W. G. Young, J. F. Lane, *J. Am. Chem. Soc.*, *57*, 1937, 2051.
[9] A. M. M. Phillips, T. A. Modro, *Phosphorus, Sulfur and Silicon*, *55*, 1991, 41.
[10] W. S. Wadsworth, W. D. Emmons, *J. Am. Chem. Soc.*, 1961, *83*, 1733.
[11] G. A. Tudrii, A. V. Fuzhenkova, *J. Gen. Chem. USSR*, Engl. Transl., *48*, 1978, 492.
[12] U. Hasserodt, F. W. Korte, Ger. Pat. 1,159,443 (1963); *Chem. Abstr.*, *60*, 1964, 10718.
[13] T. Morita, Y. Okamoto, H. Sakurai, *Bull. Chem. Soc. Jpn.*, *54*, 1981, 267.
[14] (a) D. W. Rogers, E. Crooks, K. Dejroongruang, *J. Chem. Thermodyn.*, *19*, 1987, 1209; (b) D. W. Rogers, K. Dejroongruang, *J. Chem. Thermodyn.* *20*, 1988, 675.
[15] J. Wolinsky, R. V. Novak, K. L. Erickson, *J. Org. Chem.*, *34*, 1969, 490.
[16] G. M. Kosolapoff, *J. Am. Chem. Soc.*, *75*, 1953, 1500.
[17] V. S. Abramov, *J. Gen. Chem. USSR*, Engl. Transl., *22*, 1952, 647.