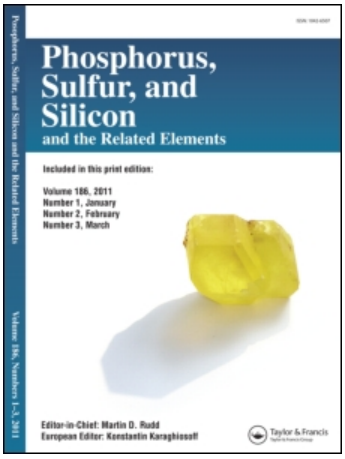

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PHOSPHONIC SYSTEMS. 6. DIETHYL 2-METHYLPENTENYLPHOSPHONATES AS A MODEL FOR STUDIES OF THE STABILITY OF UNSATURATED PHOSPHONIC ESTERS

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PHOSPHONIC SYSTEMS. 6. DIETHYL 2-METHYLPENTENYLPHOSPHONATES AS A MODEL FOR STUDIES OF THE STABILITY OF UNSATURATED PHOSPHONIC ESTERS

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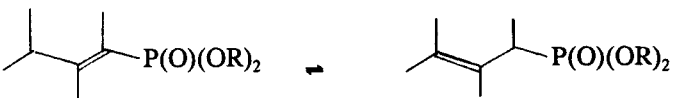
The composition of a thermodynamically controlled mixture of diethyl esters of α,β and β,γ-unsaturated phosphonates was determined by NMR spectroscopy and gas chromatography. The location of the double bond is determined by alkyl substitution and by hyperconjugation, but not by the position of the phosphorus-containing group.

Key words: Alkenylphosphonates; prototropic equilibria.

The effect of the dialkoxyphosphoryl group, $P(O)(OR)_2$, on the relative stability of the isomeric alkenylphosphonates **1** and **2** (Equation 1) is related to the general problem of structural effects on the prototropic equilibria in allylic systems.[1] It is also relevant to the synthetic applications of phosphonic esters,[2] since the regioselectivity in the reactions of the ambident carbanions derived from alkenylphosphonates could be determined by the relative stability of the isomeric products. It has been recently reported that the carbanion derived from diethyl allylphosphonate, in reactions with such carbon electrophiles as alkyl halides,[3] aromatic aldehydes,[4] or α,β-unsaturated carbonyl compounds,[5] gives rise to both, α-, or γ-substitution products. We currently investigate[6] base-catalysed isomerisation of a number of diethyl alkenylphosphonates (Equation 1, R = Et) in an attempt to identify structural factors that determine the prototropic equilibrium.

In this work we report on results on the dehydrohalogenation of diethyl 2-chloro-2-methylpentylphosphonate (**3**) (Equation 2) and on the mutual interconversion of the alkenylphosphonates formed.



(1)

1 **2**

RESULTS AND DISCUSSION

Elimination of HCl from diethyl 2-chloro-2-methylpentylphosphonate (**3**) can lead to the formation of three isomeric alkenylphosphonates, two of which can exist as a pair of stereoisomers.

$$\underset{\mathbf{3}}{PrCCl(Me)CH_2P} \xrightarrow[-HCl]{Base} \underset{\mathbf{1a}\ (E/Z)}{Pr(Me)C{=}CHP} + \underset{\mathbf{2a}\ (E/Z)}{EtCH{=}C(Me){-}CH_2P} + \underset{\mathbf{2b}}{CH_2{=}C(Et)CH_2P} \quad (2)$$

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

Since the isomeric products **1a**, **2a**, **2b** differ in a number of carbon and phosphorus atoms attached to the double bond, as well as in the number of hydrogen atoms available for hyperconjugation, they should serve as suitable system for evaluating the relative importance of these factors in stabilising an alkene function. The preparation of the starting ester **3** was based on the addition of PCl_5[7] to 2-methyl-1-pentene, followed by the esterification of the intermediate 2-chlorophosphonyldichloridate. This approach was used successfully for the preparation of diethyl 2-chloropentylphosphonate from 1-pentene[8]; the intermediate phosphonyl dichloride could be then treated with ethanol in the presence of pyridine without any elimination to an unsaturated phosphonate. In the case of 2-methyl-1-pentene, however, significant elimination took place during the preparation of the phosphonyl dichloride (**4**), yielding invariably a mixture of **4** and its dehydrohalogenation products, **5a** and **5b** (Equation 3).

$$\underset{}{Pr(Me)C{=}CH_2} \xrightarrow{(i)} \underset{\mathbf{4}}{PrCCl(Me)CH_2POCl_2} + \underset{\mathbf{5a}\ (E/Z)}{Pr(Me)C{=}CHPOCl_2} + \underset{\mathbf{5b}\ (E/Z)}{EtCH{=}C(Me)CH_2POCl_2} \quad (3)$$

(i) PCl_5, C_6H_6, followed by P_4O_{10}

According to the ^{31}P n.m.r. spectroscopy, the proportion of products **4**, **5a**, and **5b** was 44%, 46%, and 10%, respectively. Since this composition remained virtually unchanged upon heating the mixture in benzene or CCl_4 under reflux for 95 h, the elimination of HCl occurs probably before the treatment of the initial adduct of PCl_5 with P_4O_{10}, and results from the known susceptibility of tertiary halides to the El reaction.[9] It was decided therefore to convert the mixture of phosphonyl dichlorides prepared according to Equation 3 into the mixture of the corresponding diethyl esters. Thus, the treatment of the mixture of dichlorides with two mole-equivalents of ethanol and two mole-equivalents of pyridine, afforded a mixture of esters **3**, **1a**, and **2a** in a proportion of 40%, 52% and 8%, respectively. It is clear that little, if any, of the isomerisation of the alkenylphosphonates occurs during the esterification. When the ethanol-pyridine system was however replaced by 3.3 mole-equivalents of sodium ethanolate in ethanol, the dehydrohalogenation

was complete, and a new mixture, containing all five isomeric diethyl alkenylphosphonates (Equation 4) was formed.

$$\textbf{4/5a/5b}\ (44\%,\ 46\%,\ 10\%) \xrightarrow[EtOH]{3.3\,EtONa} \textbf{1a}\ (70\%) + \textbf{2a/2b}\ (30\%) \qquad (4)$$

A new feature of this reaction product was the presence of an additional β,γ-unsaturated phosphonate (δ_p 25.0 ppm), which was tentatively identified as **2b**, formed in the base-catalysed prototropic isomerisation. The composition of the mixture of esters obtained according to Equation 4 reflex the kinetic factors operating during the preparation of **4** (Equation 3) and during the elimination by EtONa (Equation 4), as well as some isomerisation occurring in the EtONa/EtOH system. When the partially eliminated mixture of esters **3**, **1a**, **2a** (40%, 52%, 8%) was treated with sodium ethanolate (2.2 mole-equivalent) in ethanol and the composition of the mixture was monitored (^{31}P n.m.r. spectroscopy) as a function of time, the concentration-time plot was obtained (Figure 1), from which the following conclusions can be drawn.

Since the concentration of **1a** shows the initial increase, the rate of its formation *via* the elimination, $k_E(\alpha,\beta)$ is greater than the rate of the elimination leading to the isomers **2**, $k_E(\beta,\gamma)$, and greater than the rate of the prototropic isomerisation:

$$k_E(\alpha,\beta) > k_E(\beta,\gamma); \quad k_E(\alpha,\beta) > k_{isom}$$

The fact that the plots for the α,β- and β,γ-unsaturated esters cross each other at a certain point means that they are mutually interconvertible, with the α,β-isomers representing the kinetically, and the β,γ-isomers the thermodynamically

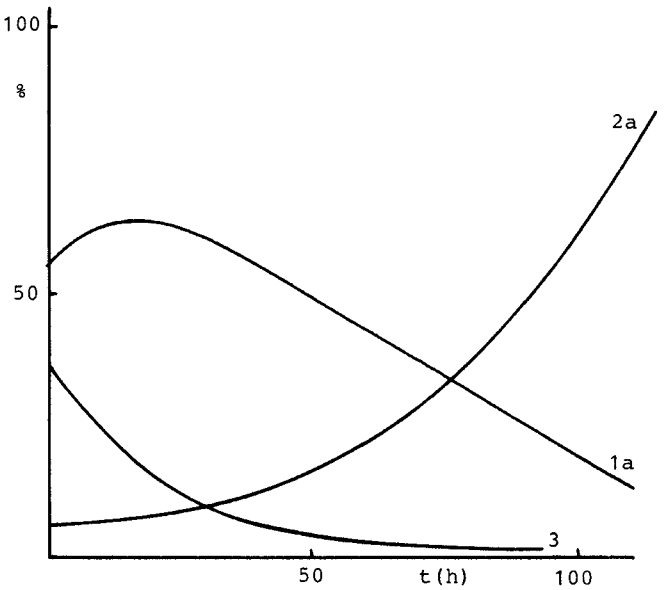


FIGURE 1 Concentration-time plot for the reaction of the mixture of esters **3**, **1a**, **2a**, with sodium ethanolate in ethanol (25°C).

controlled products. Since we were interested in structural factors determining the relative stability of isomeric alkenylphosphonates, we carried out the base-catalysed isomerisation of the mixture of esters until the constant composition was obtained, indicating that full prototropic equilibration has been achieved. This was accomplished by incubating the mixture at 30°C with *ca.* one mole-equivalent of t-BuOK in t-butanol for at least 30 h. The approximate composition of the equilibrium mixture was determined by ^{31}P n.m.r. spectroscopy, while the accurate proportion of the products was obtained after the quantitative separation of the mixture into individual components (including stereoisomers) by gas chromatography. The identity of the phosphonates **1a** and **2a** was confirmed by the independent synthesis of these compounds and by the comparison of the spectroscopic and chromatographic (gc) properties of the authentic samples with those of the components of the mixture. The phosphonate **2b** has not been independently prepared, and it was identified and determined from the n.m.r. (^{31}P, ^{1}H) spectra of the reaction mixture, and from the chromatographic separation. Table I gives the composition of the "thermodynamically controlled" alkenylphosphonate system **1/2**, obtained after the base-catalysed isomerisation. The Table also includes for each of the isomers the structural factors which we believe to be the most important in stabilising a given isomer: (i) number of carbon atoms attached to the double bond; (ii) number of phosphorus-containing groups (one or nil) attached to the double bond; (iii) number of hydrogen atoms available for hyperconjugation.

It is obvious that the thermodynamically most favored product (**2a**) is that which contains the maximum number of alkyl groups substituted at the olefinic bond, and of the allylic hydrogen atoms; the direct bonding of the vinylic carbon to the phosphorus group being only of secondary importance. Reported[10] enthalpies of hydrogenation of alkenes show that the $\Delta\Delta H$ values for two isomeric alkenes differing only by one allylic hydrogen atom are *ca.* 0.4 Kcal mol^{-1}. Taking this value as a starting point, consideration of the equilibrium between **2a** and **2b** ($K = 21$, difference in structural factors: 1C, 3H) leads to the value of *ca.* 3.8 Kcal mol^{-1} as a measure of the stabilising effect of one carbon substituent on the olefinic

TABLE I

Equilibrium composition (30°C) and structural factors for diethyl alkenylphosphonates

Compound	Abundance (%)	#C	#P	#H
Pr(Me)C=CHP **1a** (E/Z)	12	2	1	5
EtCH=C(Me)CH_2P **2a** (E/Z)	84	3	0	7
CH_2=C(Pr)CH_2P **2b**	4	2	0	4

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

bond. The equilibrium between **1a** and **2b**, on the other hand (K = 3, difference: 1H, 1P) gives for the stabilising effect of the $P(O)(OEt)_2$ group the value of *ca.* 1,4 Kcal mol^{-1}. We conclude therefore, the crudity of this analysis notwithstanding, that the dialkoxyphosphoryl group has only a mild stabilising effect on an olefinic function and should not be expected to control significantly the selectivity of any product-determining step in which the newly formed double bond can occupy an α,β- or β,γ-position with respect to the phosphorus atom.

Diethyl 2-methyl-1-pentenylphosphonate (**1a**), required for the identification of the reaction products, was prepared by the Horner, Wadsworth-Emmons reaction between sodium derivative of tetraethyl methylenediphosphonate and 2-pentanone in DMF[11] (Equation 5).

$$CH_2(PO_3Et_2)_2 \xrightarrow[(ii)\ MeCOPr]{(i)\ NaH} \mathbf{1a} \qquad (5)$$

In agreement with the general observations on the stereochemistry of the PO-activated olefinations,[12] E-isomer of **1a** was formed as a major product (60%), together with 25% of Z-isomer. Under the basic reaction conditions and because of long reaction time, some isomerisation to the β,γ-unsaturated product could not be avoided, and, consequently, 15% of **2a** was also obtained.

Diethyl (E)-2-methyl-2-pentenylphosphonate (E-**2a**) was prepared in the Arbuzov reaction between triethyl phosphite and (E)-1-bromo-2-methyl-2-pentene (Equation 6).

$$\text{(E) } EtCH{=}C(Me)CH_2Br \xrightarrow{(EtO)_3P} \text{(E)-}\mathbf{2a} \qquad (6)$$

Since the allyl bromide used in the Arbuzov reaction was prepared from (E)-2-methyl-2-pentenoic acid in a series of reactions not involving the olefinic function, the final product, **2a**, was also of E-configuration and thus could be used directly to identify that stereoisomer of **2a** formed in the dehydrohalogenation of **3** and in the prototropic reactions. The product of the reaction described by Equation (6) contained small quantity of another component with the n.m.r. (^1H, ^{31}P) spectroscopic characteristics identical to those observed for one of the products of the original reaction mixtures. This component was identified as (Z)-**2a** (probably resulting from a small quantity of (Z)-isomer present in 2-methyl-2-pentenoic acid), and therefore allowed full identification of the **2a** fraction of the mixtures studied.

Isomer **2b**, although not synthesised independently, was easily identified by its value of δ_p (25.0 ppm), typical for the β,γ-unsaturated phosphonate esters (for E-**2a** and Z-**2a**, the values of δ_p are 25.8 and 25.4 ppm, respectively). We have also succeeded in separating this compound from its isomers in the equilibrium mixtures by means of gas chromatography (retention time 29.5 min).

EXPERIMENTAL

Solvents and commercially available reagents were purified and dried by standard methods. All reactions involving metal alkoxides and organometallic reagents were carried out in an atmosphere of dry nitrogen. Bulb to bulb distillations were carried out on a Buchi GKR-50 Glass Tube Oven. Merck Silica Gel 60 (0.063–0.200 mm) and Merck Silica Gel 60F 254 sheets were used for the column and thin layer chromatography, respectively. N.m.r. spectra were recorded in $CDCl_3$ on a FT Bruker AC 300 MHz spectrometer and the chemical shift values are given relative to TMS (^1H) and trimethyl phosphate

(^{31}P, external standard). Gas chromatography analysis was performed on a HP 5890 Gas Chromatograph coupled to a HP 5988 Quadrupole Mass Spectrometer. CW 20M (carbowax/polyethylene glycol) and SE 30 (polydimethylsiloxane) glass capillary columns were prepared and used after deactivation and statically coating. Both columns were of 0.4 mm film thickness in 0.35 mm i.d. glass tubing with attached flexible fused silica-end pieces.[14] Both columns (50 m and 12.5 m, respectively) were connected with press-fit couplings[15] to get a complete separation. One μL of sample solution in acetone (AnalaR) was injected at the injector temperature 230°C. He was used as a carrier gas at flow speed 25 cm s^{-1}. The following temperature program was used: 30°C (1 min)–10°C min^{-1}–160°C–1°C min^{-1}–170°C; the following temperatures were applied: GC-MS interface, 280°C; analyser, 180°C. A full scan was made from 20–500 a.m.u. (2 scans per second); a flame ionisation detector was used for quantitative determinations. Gas chromatographic separation of the reaction and independently prepared mixtures is given in Table II.

Preparation of Substrates.

Diethyl 2-Methyl-1-pentenylphosphonate (**1a**). A solution of tetraethyl methylene-diphosphonate (5.36 g, 0.018 mol; prepared from triethyl phosphite and diiodomethane[16]; 31%; b_p 120–125°C/0.35 Torr; δ_p 17.1) in dimethoxyethane (DME, 10 mL) was added dropwise at room temperature to a slurry of NaH (0.48 g, 0.020 mol) in DME (40 mL). After the evolution of H_2 had ceased, the solution was stirred for 15 min and the solvent was removed under reduced pressure. The residue was dissolved in DMF (20 mL) and 2-pentanone (3.1 g, 0.036 mol) was added. The solution was heated under reflux for 4 h, poured into water (150 mL) and extracted with benzene (3 × 60 mL). After drying and evaporation of the solvent, the crude product was purified by bulb to bulb distillation (oven temp. 90–100°C/0.4 Torr). Colorless oil, 2.50 g (63%). δ_H: 0.87 (3H, t, *J* 7.3 Hz, C(5)H_3), 1.28 (6H, t, *J* 7.0 Hz, 2 × Me of OEt), 1.45 (2H, q of t, *J* 7.4 Hz, δ-CH_2), 1.86 (3H, s, C(2)Me), 2.09 (2H, t, *J* 7.5 Hz, γ-CH_2), 4.03 (4H, quint, *J* 7.5 Hz, 2 × CH_2 of OEt), 5.32 (1H, d, *J* 18.9 Hz, α-CH). δ_p: 15.5 (Z-**1a**), 16.3 (E-**1a**), 25.6 (**2a**).

(E)-Diethyl 2-Methyl-2-pentenylphosphonate (E-**2a**). A mixture of triethyl phosphite (3.26 g, 0.020 mol) and (E)-2-methyl-1-bromo-2-pentene (3.20 g, 0.020 mol; prepared from (E)-2-methyl-2-penten-1-ol and PBr_3[17]; 65%) was heated at 150°C until no more EtBr distilled off. The crude product was purified by bulb to bulb distillation (oven temp. 90–110°C/0.28 Torr). Colorless oil, 4.22 g (98%). δ_H: 0.90 (3H, t, *J* 7.5 Hz, C(5)H_3), 1.25 (6H, t, *J* 7.0 Hz, 2 × Me of EtO), 1.70 (3H, s, C(2)Me), 2.00

TABLE II

Composition of the "thermodynamic" mixture of phosphonates **1**, **2**, and of the independently prepared components of the mixture, as determined by gas chromatography

Sample	Retention time (min)	Abundance (%)	Compound
Synthetic **2a**	29.11	7.4	Z-**2a**
	30.62	92.6	E-**2a**
Synthetic **1a**	29.11	1.1	Z-**2a**
	29.42	15.2	**2b**
	30.20	21.4	Z-**1a**
	30.55	2.0	E-**2a**
	33.68	60.3	E-**1a**
Thermodynamic mixture[a]	29.15	39.1	Z-**2a**
	29.45	3.9	**2b**
	30.22	3.9	Z-**1a**
	30.60	44.9	E-**2a**
	33.70	8.2	E-**1a**

[a] t-BuOK/t-BuOH; 30°C; 30 h

(2H, d of q, J 7.3 Hz, δ-CH_2), 2.47 (2H, d, J 21.9 Hz, α-CH_2), 4.04 (4H, quint, J 7.1 Hz, 2 × CH_2 of EtO), 5.24 (1H, t, J 7.0 Hz, γ-CH). δ_p: 25.8, 25.4 (trace, Z-**2a**).

Addition of PCl_5 to 2-methyl-1-pentene. 2-Methyl-1-pentene (9.0 g, 0.107 mol) diluted with 5 mL of benzene was added dropwise to a cooled and vigorously stirred suspension of PCl_5 (20.8 g, 0.10 mol) in benzene (35 mL) and the temperature of the slightly exothermic reaction was maintained at 15°C. When the addition was completed, P_4O_{10} (5.0 g, 0.035 mol) was added to the reaction flask and the mixture was stirred and heated at 60°C for 3.5 h. The stirring was then continued at room temperature overnight, the mixture was filtered and the precipitate was washed with benzene (20 mL). The filtrate was evaporated under reduced pressure and the crude product was purified by bulb to bulb distillation (oven temp. 75–95°C/0.25 Torr). Colorless oil, 16.8 g (78%). ^{31}P n.m.r. spectrum demonstrated that the product contained five components; δ_p: 28.0, 28.9 (46%); 38.0 (44%); 42.5, 44.6 (10%). Selected δ_H values: 3.26 (d, J 14.8 Hz), 3.29 (d, J 17.2 Hz), 3.40 (d, J 18.4 Hz) (α-CH_2 groups of **4**, E & Z **5b**); 5.51 (t, J 7.5 Hz, γ-CH of E & Z **5b**), 5.86 (d, J 38.6 Hz, α-CH of E & Z **5a**).

Conversion of the mixture of phosphonyl dichlorides into the mixture of diethyl esters.

(i) The mixture of dichlorides described above (2.0 g, 0.010 mol) was dissolved in benzene (3 mL) and added dropwise with stirring at room temperature to a solution of ethanol (1.5 mL, 0.020 mol) and pyridine (2.0 mL, 0.020 mol) in benzene (8 mL). The mixture was then heated at 50°C for 2h, cooled, filtered, and the precipitate was washed with benzene (3 × 5 mL). The benzene solution was washed with dil. aq. Na_2CO_3 (3 × 15 mL), dried and evaporated under reduced pressure. The crude product was purified by bulb to bulb distillation (oven temp. 90–120°C/0.3 Torr). Colorless oil, 1.17 g (80%). ^{31}P n.m.r. spectrum revealed that the product contained five components; δ_p: 15.5 (Z-**1a**), 16.3 (E-**1a**) (52%); 22.2 (**3**, 40%); 25.4 (Z-**2a**), 25.8 (E-**2a**) (8%). Assignment of signals was based on the comparison with the independently prepared compounds **1a** and **2a**.

(ii) The mixture of phosphonyl dichlorides (11.02 g, 0.048 mol) dissolved in ethanol (10 mL) was added dropwise with stirring and cooling (5–10°C) to a solution of EtONa (0.16 mol) in ethanol (50 mL). After addition the mixture was stirred at room temperature for 24 h, neutralised with trifluoroacetic acid, and filtered. Water (60 mL) was added and the solution was extracted with CCl_4 (3 × 20 mL). After drying and evaporating the solvent under reduced pressure, the crude product was purified by bulb to bulb distillation (oven temp. 100–125°C/0.5 mm), 8.10 g (76%). The product consisted of five components; δ_p: 15.7 (Z-**1a**), 16.5 (E-**1a**) (70%); 25.0 (**2b**), 25.5 (Z-**2a**), 26.0 (E-**2a**) (30%).

Reaction of the mixture of esters **3**, **1a**, **2a** *(40%, 52%, 8%) with 2.2 mol-equiv. EtONa.* The mixture of esters was added to a solution of 2.2 mol-equiv. of EtONa in ethanol, and the solution was incubated at 25°C. Samples were periodically withdrawn, neutralised, and worked-up as above. The relative amounts of the individual phosphonates were determined by ^{31}P NMR spectroscopy.

Preparation of the thermodynamically controlled mixture of phosphonates **1** *and* **2**. The mixture of esters obtained according to Equation (4) (*ca.* 2 × 10^{-3} mol) was dissolved in t-butanol (1.6 mL) containing *ca.* one mole-equivalent of t-BuOK (1.3 M) and the solution was incubated at 30°C until the ^{31}P NMR spectrum of a sample of the mixture showed no further change in the composition (*ca.* 30 h). After the usual work-up, the accurate composition was determined by gas chromatography (see Table II).

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