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Thermal Fragmentation of 2-Chloropentylphosphonic Salts in the Solid State. Counter-Ion Effects on Reactivity and Selectivity

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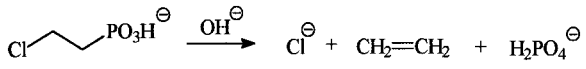
ABSTRACT

The monoanion of 2-chloropentylphosphonic acid was thermally decomposed in the solid state, and the products of the fragmentation were identified and quantitatively determined. The reaction can involve either the elimination of HCl or the Cl ion and the metaphosphate (HPO_3), and it was found that the nature of the counter ion affects strongly the selectivity of the fragmentation. © *1997 John Wiley & Sons, Inc. Heteroatom Chem* **8***: 421–428, 1997*

INTRODUCTION

1,2-Elimination of a halide ion and the phosphorus group (P–C bond cleavage) of 2-haloalkylphosphonic acids was discovered more than 70 years ago [1] and still attracts considerable attention for the following reasons. First, the ability of 2-chloroethylphosphonic acid (*ethephon*) to release ethylene via a slow fragmentation process (Scheme 1) led to the application of the acid as a regulator of plant growth and fruit maturation [2] and still illustrates the agricultural use of organophosphorus compounds [3]. Second, the reaction, "rediscovered" in the early 1960s by Maynard and Swan [4], and believed to involve monomeric metaphosphate as the primary product, can be used for the phosphorylation of alcohols. Finally, mechanistic studies of the reaction contribute to the knowledge of the reactivity of the phosphorus—carbon bond — and of the role of metaphosphate species as reactive intermediates in organophosphorus chemistry [5]. Although the stereochemistry (*trans*) of the elimination has been demonstrated by Keynon and Westheimer [6], several mechanistic problems, such as nucleophilic assistance of the P–C bond cleavage [4] or the degree of the bond breaking of the leaving group in the transition state [7], remain unresolved. It is obvious that the fragmentation of a 2-haloalkylphosphonc acid **1** can involve the phosphorus atom, as well as the α-hydrogen as the electrophilic fragment (Scheme 2). Competitive formation of the vinylphosphonic product **2** was reported by several researchers [2,4,8], and



SCHEME 1

Dedicated to Prof. William McEwen on the occasion of his seventy-fifth birthday.

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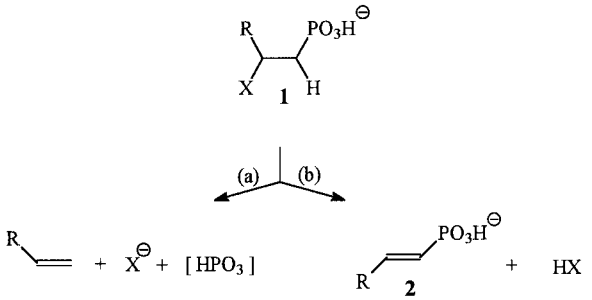


SCHEME 2

it seems that the relative contributions of pathways (a) and (b) (Scheme 2) to the fragmentation of the 2-haloalkylphosphonic system is a complex function of the medium, the base, the temperature, and the substituents in the phosphonate group (e.g., phosphonic acids vs. phosphonic monoesters). It has been demonstrated that samples of technical *ethephone* (Union Carbide Agricultural Products) contain up to 1.8% of vinylphosphonic acid, the product of a spontaneous dehydrochlorination of the plant growth regulator [9]. Since it is well established that the ionized (mono- or dianionic) form of a 2-haloalkylphosphonic acid represents the reactive species, it is likely that the nature of the counter ion has an effect on the fragmentation. The effect may be negligible in a dilute aqueous solution, but in more concentrated solutions, and certainly in the solid state, the ionic interactions involving the phosphonate function cannot be ignored.

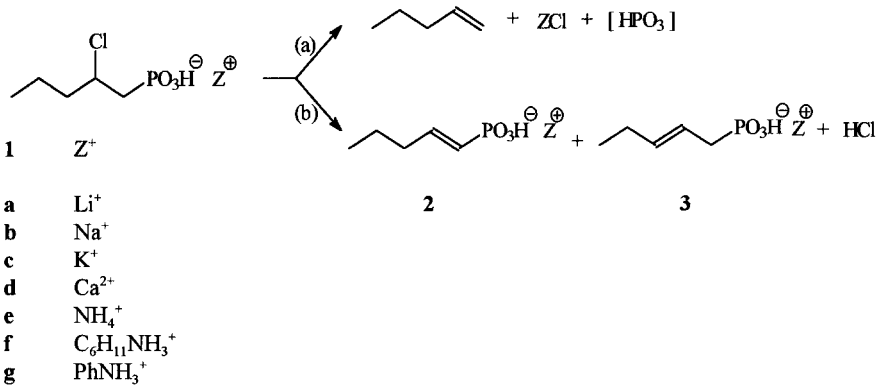
In this, the first article of this series, we report on the solid-state fragmentation of a selected phosphonic substrate studied from a point of view of the effect of the counter ion on the reactivity and the selectivity of the reaction.

RESULTS AND DISCUSSION

2-Chloropentylphosphonic acid (**1**, X = Cl; R = Pr) was chosen as a model substrate because we have established before [10] that the decomposition of the salts of its monoanion is rather slow, and because the major organic product of the fragmentation is 1-pentene, an alkene suitable for quantitative determination. A series of salts of the monoanion of **1a** was prepared, and thermal decomposition of the salts was studied under various conditions. Scheme 3 shows the expected products of the fragmentation. 1-Pentene, one of the volatile products, was trapped in a solution of an excess of bromine in CCl_4, and the 1,2-dibromopentane formed was identified by ^{1}H NMR spectroscopy and quantitatively determined by gas chromatography (GC), using the authentic material as a standard. The unsaturated phosphonic acids **2** and **3** were identified by ^{31}P and ^{1}H NMR spectroscopy after the authentic samples of both regional isomers were synthesized as standards. The ratio of the products **2** and **3** was determined from the integrated signals in the ^{31}P NMR spectra of the product. The identification and quantitative determination of the phosphorus-containing products of the P–C bond cleavage ("metaphosphate" species) were based on the analysis of the ^{31}P NMR spectra of the water-soluble products of the fragmentation. In order to evaluate the importance of the 2-halosubstituent in **1**, the unsubstituted substrate, pentylphosphonic acid **4** was also synthesized, and its monoanionic salts were studied under the conditions of thermal degradation.

The Li^+, Na^+, and K^+ salts of **4** are thermally stable up to ca. 170°C, 240°C, and 190°C, respectively. At higher temperatures, thermal analysis demonstrated that all three salts undergo slow mass loss, corresponding well to the loss of half of a mole of water per mole of the salt. The obvious conclusion is that the monoanionic salts undergo thermal dehydration, yielding the corresponding salts of the phosphonic anhydride, **5** (Scheme 4). The dehydration of salts **4** was accompanied by an up-field shift of the signal in the ^{31}P NMR spectrum: for **4**, δ_P (D_2O) $\approx$ 27; for **5**, δ_P (D_2O) $\approx$ 20. Anhydride **5** was prepared independently as a bis-cyclohexylammonium salt from **4** and DCC [11], and its ^{31}P NMR signal corresponded closely to that of the product of the thermal degradation; δ_P (D_2O) = 20.5. The thermogravimetric analysis graph for **4** ($Z^+ = Li^+$) is shown in Figure 1. After the loss of 0.5 H_2O (6.2%, calculated 5.6%) at 170–200°C, the product (**5a**, $Z^+ = Li^+$) is thermally stable up to ca. 350°C, at which temperature further decomposition commences. The second reaction is completed at ca. 520°C and involves further loss of 46.5% of the mass, which corresponds to the loss of both organic (pentyl) groups (calculated 47.6%), leaving a nonvolatile, inorganic phosphate residue. The Na^+ and K^+ salts of **4** behaved in an analogous way with the total degradation of the phosphonate skeleton occurring at 340–510°C and 320–500°C, respectively.

Introduction of the 2-chloro substituent to the molecule of **4** had a dramatic effect on the thermal stability of the system. Figure 2 illustrates the thermal behavior of **1a** that can be directly compared with that of **4**($Z^+ = Li^+$). The first reaction commences, as before, at a relatively low temperature (ca. 140°C) and again consists mainly of the dehydration to the phosphonic anhydride **6a** (Scheme 5,



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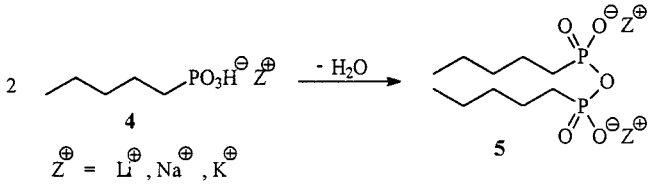

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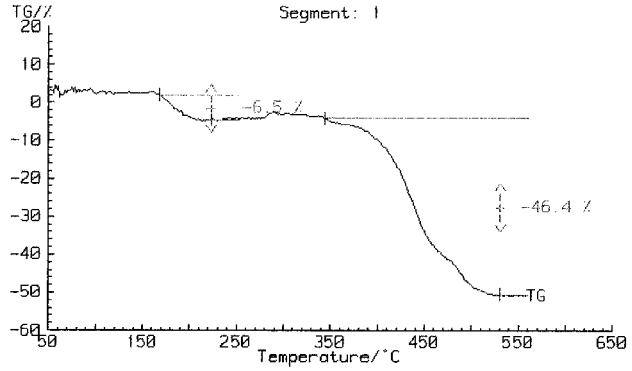


FIGURE 1 Thermal decomposition of lithium pentylphosphonate **4.**

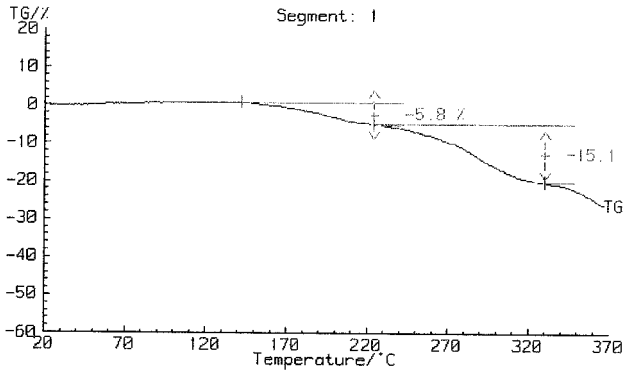
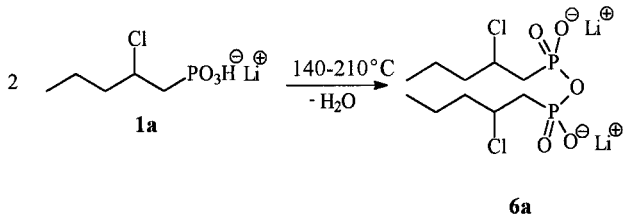


FIGURE 2 Thermal decomposition of lithium 2-chloropentylphosphonate **1a.**



SCHEME 5

calculated loss of mass 4.7%). Contrary to the previous system, **6a** is thermally unstable, and its further fragmentation partially overlaps with the dehydration step, yielding a continuous mass loss over the whole range of the applied temperature. The behavior of other metallic salts (**1b, 1c,** and **1d**) is very similar: The initial step of dehydration (loss of 7.9%, 6.8%, and 4.2%, vs. calculated loss of 4.3%, 4.0%, and 4.2%, respectively, for the loss of 0.5 H_2O) overlaps with further fragmentation steps. The mass loss determined for the individual sections of the graph results from the parallel pathways (a) and (b) of the fragmentation (Scheme 3), most likely commencing before the dehydration step is completed (e.g., for **1b,** in the first step, 7.9% loss vs. calculated 4.3%). The relative contributions of pathways (a) and (b) to the fragmentation of **1a** were determined from a products study (*vide infra*) as 56% and 44%, respectively. Considering a loss of 0.5 mol equivalent of H_2O, 56% of C_5H_{10}, and 44% of HCl, the total mass loss for **1a** should amount to 31%, which corresponds well to the value of 34.1% obtained in the thermal analysis experiment. Similarly, approximate agreement between the determined total mass loss and the product determination was obtained for the

solid-state decomposition of **1b, 1c,** and **1d.** The ammonium salts **1e, 1f,** and **1g** were not subjected to thermal analysis because their melting points are lower than a minimum temperature at which the fragmentation could be observed.

^{31}P NMR chemical shifts of all salts **1a–1g** as ca. 0.5 M solutions in D_2O are approximately identical ($\delta_P = 20.6 \pm 0.4$), indicating negligible phosphonate anion–cation interactions. Heating those solutions at 100°C for 3 hours led to complete degradation of **1,** and the product analysis demonstrated the formation of 69% of inorganic phosphate (Scheme 3, pathway a), 3% of **2a,** 25% of **2b** (Scheme 3, pathway b), and 3% of unidentified phosphorus-containing products. Thus the (a)/(b) ratio of 69/(3 + 25) = 2.5 was taken as a "standard" value for the selectivity of the fragmentation of the "free" anion of **1** in aqueous solution. Individual anhydrous salts **1a–1g** were then decomposed in the solid state in order to determine the effect of the counter ion Z^+ on the selectivity of the fragmentation. 1-Pentene, the volatile product of the "metaphosphate" mechanism of the fragmentation, was identified as its 1,2-dibromo adduct. We found that the most reliable measure of the proportions of the products of the fragmentation can be obtained from the ^{31}P NMR spectra of the aqueous solutions of the nonvolatile residue of the reaction product. The results of the thermal fragmentation are summarized in Table 1. The phosphorus-containing products yielded two groups of the ^{31}P NMR signals: the "high field" signals ($\delta_P \approx 0$ and $\delta_P \approx -10$) and the "low field" signals ($\delta_P \approx 14$ and $\delta_P \approx 23$). The former group results from the P–C bond cleavage (Scheme 3, pathway a), which gives, after aqueous treatment, the orthophosphate ion, $H_2PO_4^-$ ($\delta_P \approx 0$) and linear-branched polymetaphosphate $(PO_3^-)_n$ ($\delta \approx -10$ [12]). The polymetaphosphate product results from self-condensation of the monomeric HPO_3 (Scheme 3) and gives support for the "metaphosphate" mechanism of the fragmentation, operating under conditions of thermolysis in the solid state. The $H_2PO_4^-$ ion is produced in the hydrolytic cleavage of the polymetaphosphate, and the proportions of those two inorganic phosphorus products varied from experiment to experiment depending on the advancement of the hydrolysis.

TABLE 1 Selectivity in the Solid-State Fragmentation of Salts **1a–1g**

		Products (%)[b]				
		Pathway (a)[c]		Pathway (b)[c]		
Salt	Temp. (°C) /Time (h)[a]	$H_2PO_4^-$	$(PO_3^-)_n$	**2**[d]	**3**[d]	Selectivity (a)/(b)
1a	150/16	47	30	23	[e]	3.3
1b	150/16	6	51	21	22	1.3
1c	150/16	65	[e]	20	15	1.9
1d	150/16	3	29	40	28	0.47
1e	100/16	9	[e]	22	69	0.10
1f	110/4	13	30	31	26	0.75
1g	120/4	9	28	23	40[f]	0.59

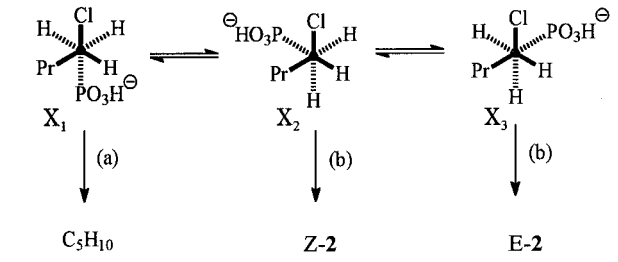
[a]Necessary for complete conversion of **1.**
[b]Determined from the integrated signals in the ^{31}P NMR spectra of the aqueous (D_2O) solution of the solid residue after the degradation. The total yields of the products listed in the table amounted to ≥90% of all phosphorus-containing products; up to 10% of some unidentified compounds was occasionally observed.
[c]Scheme 3.
[d]Usually two signals of both stereoisomers were observed.
[e]No signal detected in the ^{31}P NMR spectrum.
[f]Single stereoisomer.

The "low field" signals are derived from pentenylphosphonic acids **2** and **3,** formed via the elimination of HCl from **1**. As can be seen from the table, with the exception of **1a,** all salts show little selectivity in the dehydrochlorination pathway, yielding both the vinylic (**2**) and the allylic (**3**) phosphonates in comparable quantities. Thermal decomposition of **1** in aqueous solution yields, on the other hand, the allylic product as the major product of pathway (b). The variable proportions of the unsaturated phosphonates can, however, be explained by their mutual interconversion via prototrophic equilibria [10], occurring after the dehydrochlorination step, and favoring in this case the pent-2-enyl isomer [13]. In all cases, both unsaturated phosphonates were formed predominantly or exclusively as E-stereoisomers. Since in pathway (b), the deprotonation involves hydrogens of two methylene groups (α-CH_2 and γ-CH_2), conformational preferences of the system always favor the formation of E-**2** and E-**3,** irrespective of whether the elimination follows the "classical" antistereochemistry, or the syngeometry, observed for thermal eliminations [14].

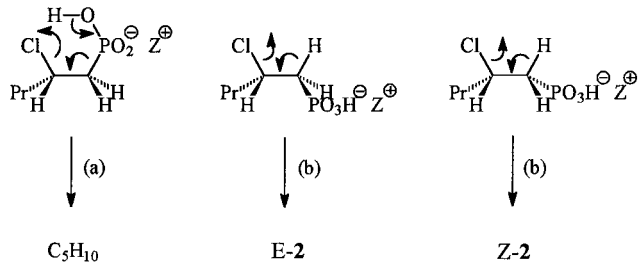
The most important result contained in Table 1 is, however, the effect of cations (Z^+) on the thermal stability of the salts and the selectivity of the fragmentation in the sense of the cleavage of the P–C bond vs. the cleavage of one of the C_α–H or C_γ–H bonds. While thermal stability of the metallic salts (**1a–1d**) is very similar, the ammonium salts (**1e–1g**) require significantly lower temperatures and shorter times to achieve full conversion. The selectivity, as measured by the product ratio (a)/(b) (the last column of the table), varies within the range of salts studied by a factor of ca. 30. Salts **1** can be divided into two broad groups. The group of the alkali metal salts (**1a, 1b,** and **1c**) gives the value of (a)/(b) > 1, similar to the value (2.5) observed for decomposition of **1** in aqueous solution. For those substrates, although the dehydrochlorination competes successfully with pathway (a), the salts can be considered

primarily as substrates for the "metaphosphate" fragmentation. The calcium salt **1d** and the ammonium salts **1e, 1f,** and **1g** display a reversed selectivity [(a)/(b) < 1] and thus are not good precursors for the alkene (and the metaphosphate) product. Assuming that the dehydrochlorination initially yields the kinetic product **2** [10] (which can subsequently isomerize to **3**), selectivity (a)/(b) is determined primarily by the relative rates of the cleavage of the C_α–P and the C_α–H bonds, that is, by the relative involvement of the metaphosphate (HPO_3) and the proton as the electrophilic fragments of the elimination. In solution, both reactions follow an antiperiplanar stereochemical mechanism with three conformers of **1** as reactive species (Scheme 6). While electronic factors (electrostatic repulsion between two electronegative substituents) favor the X_1 conformer (precursor of pentene), steric effects ($Pr–PO_3H^-$ interactions) should favor the conformer leading to the E-**2** product (X_3). In solution, fast exchange between the conformers should exist, and the product distribution should be, according to the Curtin–Hammett principle [15], determined by the conformational equilibria and by the rate ratio of the dehydrochlorination and of metaphosphate expulsion.

In the solid state, the situation is essentially different. Although the exact mechanisms and stereochemistry of both 1,2-elimination reactions (Scheme 3, pathways a and b) may not be the same, to simplify the discussion, it may be assumed that both reactions occur with synperiplanar geometry [14] (Scheme 7). Since no equilibration between the conformers would be expected in the solid state, product distribution should directly reflect the crystal lattice preferences for the specific molecular conformations resembling as much as possible the geometry required for a specific elimination route. Those preferences will be necessarily dependent on the nature of the counter ion Z^+, due to its variable size, association with the PO_2^- group, or its hydrogen-bonding properties. Alkali metal salts probably exist as close cation–anion associates and seem to favor the conformation that can lead to P–C bond cleavage; as expected [16], the effect being most pronounced in the case of the Li^+ salt [highest (a)/(b) ratio]. The calcium, and the ammonium salts, on the other hand, seems to give preference to the solid-state conformations acting as precursors for the elimination of HCl. In the case of the ammonium salts, strong hydrogen-bonding effects operating between the ions [17] can considerably change the conformation of the salt in the crystal lattice. Unfortunately, until now, we have failed to prepare any of the salts **1** in a form of single crystals, suitable for X-ray diffraction. The salts are virtually insoluble in nonhydroxylic solvents; all attempts to grow crystals from aqueous or aqueous–alcohol solutions led to gradual deposition of the Z^+Cl^- salt as the expected product from slow fragmentation of the parent salt according to the "metaphosphate" mechanism. The results presented in this work demonstrate, however, that the selection of the counter ion for the fragmentation of a 2-haloalkylphosphonic acid can strongly influence the chemoselectivity of the reaction. This observation may be directly relevant to the efficiency of *ethephon* as a plant growth regulator. Further attempts to correlate the solid-state fragmentation behavior of the ions of the type **1** with the structure of the salts are continuing in our laboratory.



SCHEME 6



SCHEME 7

EXPERIMENTAL

Solvents and commercially available substrates were purified by conventional methods. NMR spectra were recorded on a Bruker AC 300 spectrometer and the ^1H chemical-shift values are given relative to $CDCi_3$ (7.24 ppm). ^{31}P NMR chemical-shift values are given relative to 85% H_3PO_4 as an external standard. Elemental analyses (C/H/N) were carried out at the Chemistry Department, University of Cape Town. GC analysis was carried out using a Varian 3700 gas chromatograph linked to a Varian 4270 recorder/integrator. A 25 m long glass capillary column of 0.3 mm i.d. with a 0.3μm thick stationary phase film of polymethylsiloxane (SE30) was used throughout. Hydrogen was used as a carrier gas at a linear flow rate of 50 cm s^{-1} at an oven temperature of 170°C. A

flame ionization detector was employed at a temperature of 275°C. Samples were introduced as solutions in CCl_4, containing a known concentration of *n*-octane as the standard for quantitative determination. Thermogravimetric data were collected using a Netzsch STA 409 simultaneous TG/DSC instrument. Nitrogen was employed as a dynamic atmosphere with a flow rate of approximately 20 cm^3 min^{-1}. Platinum sample pans were used. Temperature calibration was achieved using the ICTAC recommended DTA standards. Best results were obtained using a heating rate of 2°C min^{-1}.

Preparation of 2-Chloropentylphosphonic Acid **1** *and Salts* **1a–1g**

2-Chloropentylphosphonodichloridate was prepared from 1-pentene and PCi_5 [7]; δ_P ($CDCI_3$) 42.7. The phosphonodichloridate (5.00 g, 23.0 mmol) was dissolved in an ethanol–water mixture (2:1, v/v, 15 mL), conc. HCI solution (15 mL) was added, and the solution was heated under reflux for 10 hours. Water and ethanol were removed under reduced pressure, benzene (10 mL) was added twice to the residue and evaporated under reduced pressure. The crude product was dissolved in a small volume of $CHCi_3$ and precipitated by the addition of a large volume of pet. ether (40–60°C). After filtration, acid **1** was finally purified by crystallization from benzene. Yield 2.28 g (55%) mp 92–93°C. ^{1}H NMR ($CDC1_3$) δ 0.94 (t, J = 6.7 Hz, 3H), 1.35–1.73 (m, 2H), 1.60–1.83 (m, 2H), 2.35 (dd, J = 20.0, 8.0 Hz, 2H), 4.19–4.39 (m, 1H), 11.1 (br, s, 2H); ^{31}P NMR δ ($CDCi_3$) 31.8; δ (D_2O) 24.3.

Acid **1** (1.0 mmol) was dissolved in absolute ethanol (12 mL), and the solution was carefully neutralized with one mole equivalent of Z^+OH^- dissolved in ethanol. The pH of the solution was monitored by means of a METROHM 691 pH meter until the value of pH stabilized at the level of the first neutralization ($4 < pH < 5$). Ethanol was removed under reduced pressure, and the salts were dried at room temperature under high vacuum.

1a, 77%, ^{31}P NMR δ (D_2O) 20.4 (accompanied by a growing signal of the decomposition product at δ 0.7). Anal. calcd for $C_5H_{11}ClLiO_3P$: C, 31.25; H, 5.73. Found: C, 31.00; H, 5.39.

1b, 79%, ^{31}P NMR δ (D_2O) 20.8. Anal. calcd for $C_5H_{11}ClNaO_3P$: C, 28.85; H, 5.28. Found: C, 27.09; H, 5.12.

1c, 68%, ^{31}P NMR δ (D_2O) 21.4. Anal. calcd for $C_5H_{11}ClKO_3P$: C, 26.79; H, 4.90. Found: C, 26.01; H, 5.24.

1d, 58%, mp 165–168°C (dec); ^{31}P NMR δ (D_2O) 20.5.

1e, 52% (hygroscopic), ^{31}P NMR δ (D_2O) 20.2. Anal. calcd for $C_5H_{15}ClNO_3P$: C, 29.50; H, 7.43; N, 6.88. Found: C, 29.34; H, 7.70; N, 6.76.

1f, 93%, mp 123–125°C; ^{31}P NMR δ (D_2O) 20.5. Anal. calcd for $C_{11}H_{25}ClNO_3P$: C, 46.24; H, 8.82; N, 4.90. Found: C, 46.64; H, 9.15; N, 5.64.

1g, 91%, mp 126–128°C; ^{31}P NMR δ (D_2O) 20.6. Anal. calcd for $C_{11}H_{19}ClNO_3P$: C, 47.24; H, 6.85; N, 5.01. Found: C, 47.50; H, 6.97; N, 5.09.

Pentylphosphonic Acid **4**

Diethyl pentylphosphonate (prepared from triethyl phosphite and 1-bromopentane) was hydrolyzed to the free acid according to the literature procedure [18]. Yield 73%, mp 121.1–121.7°C (Ref. [18] mp 120.5–121°C); ^{31}P NMR δ (D_2O) 32.9. The salts of the monoanion of **4** were prepared as described above for acid **1.** Li^+ salt of **4**: 62%. Anal. calcd for $C_5H_{12}LiO_3P$: C, 37.99; H, 7.65. Found: C, 36.72; H, 7.56. Na^+ salt of **4**: 91%. Anal. calcd for $C_5H_{12}NaO_3P$: C, 34.48; H, 6.95. Found: C, 33.95; H, 6.80. K^+ salt of **4**: 62%. Anal. calcd for $C_5H_{12}KO_3P$: C, 31.56; H, 6.36. Found: C, 31.12; H, 6.60.

Pent-l-enylphosphonic Acid **2**

Dimethyl pent-1-enylphosphonate (prepared according to the literature procedure [10]) was converted to the free acid by treatment with Me_3SiCl/NaI [19] and isolated and purified in the form of the monosalts with primary amines.

Anilinium Pent-1-enylphosphonate. Crystallized from acetone–methanol, (9:1, v/v), washed with cold ether, and dried in vacuo; mp 140–142°C. ^{1}H NMR δ (D_2O) 0.83 (t, J = 7.4 Hz, 3H), 1.38 (tq, J = 7.3, 7.4 Hz, 2H), 2.08 (dtdd, J = 7.0, 7.0, 1.8, 1.8 Hz, 2H), 5.69 (ddt, J = 20.4, 17.1, 1.6 Hz, 1H), 6.39 (ddt, J = 20.9, 17.1, 6.5 Hz, 1H), 7.33–7.52 (m, 5H); ^{31}P NMR δ (D_2O) 14.6.

Cyclohexylammonium pent-1-enylphosphonate. Crystallized from acetone–ethanol (4:1, v/v), washed with cold acetone, and dried in vacuo; mp 194–196°C. ^{31}P NMR δ (D_2O) 13.1. Anal. calcd for $C_{11}H_{24}NO_3P$: C, 53.00; H, 9.70; N, 5.62. Found: C, 53.40; H, 10.08; N, 5.81.

Pent-1-enylphosphonic Acid. Anilinium (or cyclohexylammonium) pent-1-enylphosphonate was dissolved in a minimum volume of 15% aqueous H_2SO_4, and the solution was extracted several times with chloroform. After drying ($MgSO_4$) and evaporating the solvent, acid **2** was obtained as a viscous oil; ^{1}H NMR δ ($CDCl_3$) 0.90 (t, J = 7.4 Hz, 3H), 1.45

(tq, J = 7.4, 7.4 Hz, 2H), 2.16 (dtdd, J = 7.2, 7.0, 1.9, 1.9 Hz, 2H), 5.71 (ddt, J = 23.1, 17.1, 1.6 Hz, 1H), 6.73 (ddt, J = 23.4, 17.1, 6.6 Hz, 1H), 7.88 (s, 2H); ^{31}P NMR δ ($CDCl_3$) 22.2 (major, E-isomer), 20.6 (minor, Z-isomer).

Pent-2-enylphosphonic Acid **3**

1-Bromopent-2-ene (containing ca. 20% of 3-bromopent-1-ene) was prepared according to the literature procedure [20] and purified by bulb-to-bulb distillation (oven temp. 60°/130 mmHg). The mixture of bromopentenes (4.0 g, 46.4 mmol) was added to trimethyl phosphite (5.52 mL, 46.4 mmol), and the solution was heated under reflux, with stirring, in a stream of nitrogen, for 3 hours. The resulting product containined as (shown by ^{31}P NMR spectroscopy) 45% of dimethyl methylphosphonate and 55% of dimethyl pent-2-enylphosphonate. The required product was separated by bulb-to-bulb distillation (oven temp. 45°C/0.05 mmHg; the volatile methylphosphonate escaping to the liquid-nitrogen-cooled trap); 4.2 g (51%); ^{31}P NMR δ ($CDCl_3$) 31.1 (major, E-isomer), 30.7 (minor, Z-isomer).

Free pent-2-enylphosphonic acid was prepared from the dimethyl ester as described for the pent-1-enyl isomer and was identified as two ammonium salts.

Anilinium Pent-2-enylphosphonate. Crystallized from acetone–ethanol (4:1, v/v), washed with cold acetone and dried in vacuo; mp 128–130°C. ^{1}H NMR δ (D_2O) 0.87 (t, J = 7.5 Hz, 3H), 1.93 (m, 2H), 2.30 (dd, J = 20.5, 7.3 Hz, 2H), 5.38 (dt, J = 15.0, 7.2 Hz, 1H), 5.55 (m, 1H), 7.30–7.50 (m, 5H); ^{31}P NMR δ (D_2O) 23.4 (major, E-isomer), 23.0 (minor, Z-isomer). Anal. calcd for $C_{11}H_{18}NO_3P$: C, 54.32; H, 7.46; N, 5.76. Found: C, 53.77; H, 7.45; N, 5.55.

Cyclohexylammonium Pent-2-enylphosphonate. Purified as above, mp 192–195°C. ^{31}P NMR δ (D_2O) 22.6. Anal. calcd for $C_{11}H_{24}NO_3P$: C, 53.00; H, 9.70; N, 5.62. Found: C, 54.03; H, 10.13; N, 6.00.

Pent-2-enylphosphonic acid was prepared from an ammonium salt as described for the pent-1-enyl isomer, but, because of higher solubility of the acid in water, the aqueous solution was saturated with NaCl before the extraction. Viscous oil; ^{1}H NMR δ ($CDCl_3$), 0.96 (t, J = 7.4 Hz, 3H), 2.03 (dq, J = 6.6, 6.7 Hz, 2H), 2.56 (dd, J = 22.1, 7.2 Hz, 2H), 5.33 (dt, J = 15.2, 6.7 Hz, 1H), 5.67 (m, 1H), 6.89 (s, 2H); ^{31}P NMR δ ($CDCl_3$) 32.5.

Pentylphosphonic anhydride **5** was prepared from the phosphonic acid **4** and dicyclohexylcarbodiimide according to the literature procedure [11]. Hygroscopic solid; converted into bis-cyclohexylammonium salt, mp 75–78°C (dec); ^{31}P NMR δ ($CDCl_3$) 18.4, δ (D_2O) 20.5. Anal. calcd for $C_{22}H_{47}N_2O_5P_2$: C, 54.87; H, 9.84; N, 5.82. Found: C, 54.25; H, 10.02; N, 5.63.

2-Chloropentylphosphonic anhydride **6** was prepared from **1** and DCC [11]; viscous oil, which was dissolved in $CDCl_3$ and examined by ^{31}P NMR spectroscopy, δ ($CDCl_3$) 28.9. The acidic anhydride was converted to the bis-cyclohexylammonium salt; white crystals decomposing upon heating. The ^{31}P NMR spectrum of the salt could not be recorded, since as soon as it was dissolved in D_2O, the spectrum showed exclusively the signals corresponding to complete fragmentation of the salt to inorganic phosphoric products (δ 2.7, −4.5).

1,2-Dibromopentane was prepared from pent-1-ene, according to the procedure given for the addition of bromine to 3-bromopropene [21]. Yield: 85%; bp 35–38°C/0.1 mmHg. ^{1}H NMR δ ($CDCl_3$), 0.93 (t, J = 7.4 Hz, 3H), 1.45 (m, 1H), 1.59 (m, 1H), 1.75 (m, 1H), 2.08 (m, 1H), 3.59 (dd, J = 9.8, 9.8 Hz, 1H), 3.82 (dd, J = 10.1, 9.5 Hz, 1H), 4.14 (m, 1H).

Fragmentation of Salts **1**

A rigorously dried and accurately weighed sample of a salt **1** was placed in a small two-necked flask with one neck converted into a capillary tube. The short neck of the flask was sealed, the tip of the capillary tube was immersed in a flask containing a solution of Br_2 in CCl_4 cooled in an ice bath, and the reaction flask was placed in a thermostated oil bath and heated at the temperature and for the period of time found previously to be necessary for the complete decomposition of the substrate. When the reaction was completed, the CCi_4 solution was washed with aqueous $Na_2S_2O_3$, dried, and made up to a known volume in a volumetric flask. The known amount of *n*-octane was added to the solution, and the solution was then analyzed by GC; the concentration of 1,2-dibromopentane was determined relative to *n*-octane with the retention times of CCi_4, octane, and 1,2-dibromopentane being ca. 2.4, 3.1, and 6.8 minutes, respectively.

The residue after thermal decomposition was quantitatively dissolved in D_2O and analyzed by ^{31}P NMR spectroscopy. The phosphorus-containing products were identified by the addition of samples of the authentic compounds, and their relative yields were determined from the integrated ^{31}P NMR signals. Good agreement was found between the amount of 1,2-dibromopentane determined in CCl_4 solution and the proportion of the "high field" (in-

organic) phosphorus products observed in the ^{31}P NMR spectra.

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