mmol) of **36** in 125 mL of triethylene glycol under nitrogen was heated at 140 °C for 1 h. The temperature was increased to 250 °C (bath) and a two-phase distillate allowed to distill from the flask. The collected material was diluted with 50 mL of water and 50 mL of pentane. The separated aqueous layer was extracted with two 20-mL portions of pentane, and the combined organic phases were washed repeatedly with water, dried ($MgSO_4$), and concentrated at aspirator pressure. The residual oil was distilled at reduced pressure to yield 8.4 g (68%) of a clear, colorless oil, which by VPC analysis (column G, 110 °C) was ≥95% the trans isomer: bp 84–85 °C (25 torr); IR 2995, 1655, 756, 675 cm^{-1}; ^1H NMR (CCl_4) δ 0.7–2.25 (m, 13), 0.94 (d, J = 7.5 Hz, 3), 5.42 (m, 2); mass spectrum (70 eV), m/e 150, 135, 121, 109, 67. Anal. ($C_{11}H_{18}$) C, H.

***trans*-3,4-Dibromo-2-methyl-*trans*-bicyclo[4.4.0]decane (38).** To a stirred solution of 7.50 g (50 mmol) of **37** in 25 mL of chloroform at 0 °C was added dropwise a solution of 8.10 g (51 mmol) of bromine in 5 mL of chloroform over a 30-min period. The solution was stirred at 0 °C for 1 h, the cooling bath was removed, and 2 mL of water and sufficient sodium hydrogen sulfite to quench the excess bromine were added. The organic phase was washed with two 10-mL portions of water, dried over anhydrous $MgSO_4$, and concentrated at reduced pressure. The solid residue was recrystallized in a minimum amount of hot 95% ethanol to yield 12.8 g (83%) of **38** as white plate crystals: mp 39–40 °C; IR (KBr) 2890, 1358, 709 cm^{-1}; ^1H NMR δ 0.8–2.4 (m, 13), 1.01 (d, J = 7.0 Hz, 3), 4,56 (m, 1), 4.82 (q, J = 1.5 Hz, 1); mass spectrum (70 eV), m/e 312, 310, 308, 150, 135. Anal. ($C_{11}H_{18}Br_2$) C, H, Br.

2-Methyl-*trans*-bicyclo[4.4.0]deca-2,4-diene (30). To a stirred suspension of 2.03 g (18 mmol) of potassium *tert*-butoxide in 50 mL of anhydrous tetrahydrofuran at room temperature was added 0.93 g (3 mmol) of **38** in one portion. The resulting mixture was heated at reflux for 2 h, cooled to room temperature, and diluted with 100 mL of water. The separated aqueous phase was extracted with three 50-mL portions of pentane, and the combined organic layers were washed with five 50-mL portions of water and dried over anhydrous $MgSO_4$. The solvent was removed at reduced pressure and the residue distilled by using a Büchi-Kugelrohr apparatus to yield 0.37 g (83%) of a clear colorless oil which by VPC analysis (column A) was shown to be a mixture of 2-methyl-*trans*-bicyclo[4.4.0]deca-2,4-diene (**30**) and 2-methylene-*trans*-bicyclo[4.4.0]dec-3-ene (**39**) in a 55:45 ratio, respectively, by the following isolation procedure. The mixture was chromatographed on 15 g of silver nitrate impregnated silica gel by using benzene as the eluting solvent and collecting 3-mL fractions. Fraction 5 contained 100 mg of a clear colorless oil identified as **39** on the basis of the following spectral data: IR 3067, 3016, 1638, 1600, 892, 881, 778, 683 cm^{-1}; UV max (hexane) 230 nm (ε 14950); ^1H NMR δ 0.7–2.4 (m, 12), 4.83 (brs, $W_{1/2}$ = 5.0 Hz, 2), 5.70 (m, 1), 6.13 (d, J = 10.0 Hz, 1); ^{13}C NMR δ 26.12 (t), 26.41 (t), 28.98 (t), 33.98 (t), 34.27 (t), 38.88 (d), 42.43 (d), 108.60 (t), 128.51 (d), 130.50 (d), 147.68 (s); mass spectrum (70 eV), m/e 148.91. Anal. ($C_{11}H_{16}$) C, H.

Fractions 6 and 7 (150 mg) proved to be a mixture of dienes **39** and **30** in roughly equal amounts. Fractions 8 and 9 contained 110 mg of a clear colorless oil which was spectrally identical in every respect with diene **30** isolated from the thermal rearrangement of **19**.

***trans,cis,cis*-Cycloundeca-1,3,5-triene.** The compound was prepared by following published procedures:[12] ^{13}C NMR δ 25.54, 26.70, 27.28, 28.20, 30.25, 124.96, 126.56, 128.94, 131.08, 132.39, 135.21.

Phospho-Cope Rearrangement of Sodium Allylvinylphosphinate

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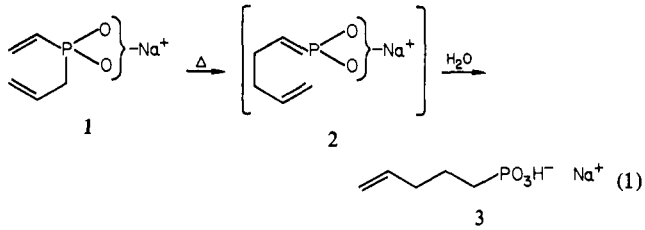
Abstract: Sodium allylvinylphosphinate (**1**) rearranges thermally to sodium hydrogen pent-4-enephosphonate (**3**) in virtually quantitative yield. The reaction probably constitutes a phospho-Cope rearrangement and presumably proceeds by way of the monomeric metaphosphonate **2** as a reactive intermediate. The half-time for the reaction is 4.67 h in water at 193.6 ± 1.0 °C and 6.03 h in ethanol. By contrast, ethyl allylvinylphosphinate reacts in ethanol to give a mixture of compounds; although some of the product expected for a phospho-Cope is present in the mixture, the rearrangement is slower than that of the anion by a factor of at least 16. The mechanistic implications of these facts are discussed.

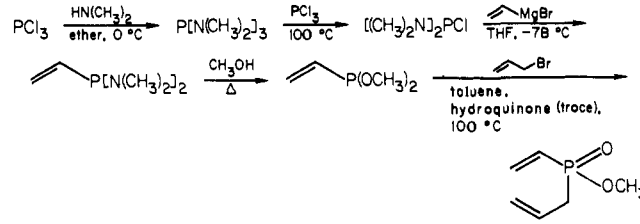
The Cope rearrangement has proved to be of great preparative and theoretical importance. The present research was designed to test whether an analogous reaction, where a PO_2^- unit is incorporated into the chain of carbon atoms, can be carried out. The simplest structure that comes into consideration for such a phospho-Cope rearrangement is the anion of allylvinylphosphinic acid.

When sodium allylvinylphosphinate is heated in water at temperatures near 200 °C, it undergoes a virtually quantitative rearrangement to sodium hydrogen pent-4-enephosphonate. This reaction probably consititutes a phospho-Cope rearrangement, and presumably proceeds as shown in eq 1 by way of a monomeric metaphosphonate as intermediate. (See, however, the Discussion for an alternative explanation.)



1 2 3

Scheme I



When **1** is heated in alcohol, the major product is ethyl hydrogen pent-4-enephosphonate, $CH_2{=}CH(CH_2)_3P{=}O(OH)(OC_2H_5)$ (**4**), the compound expected from addition of ethanol to the metaphosphonate **2**. When the ethyl ester of **1** is heated in alcohol, it undergoes rearrangement to yield diethyl pent-4-enephosphonate, but in poor yield and at a rate smaller than that for the anion by a factor of at least 16. This paper presents the data to support these statements and a discussion of the mechanism of the reaction.

Sodium allylvinylphosphinate was prepared from its methyl ester; the synthesis of the latter is outlined in Scheme I. The corresponding ethyl ester was prepared by an analogous series of reactions, substituting ethanol for methanol. Allylvinylphosphinic acid was prepared from its methyl ester by reaction with tri-

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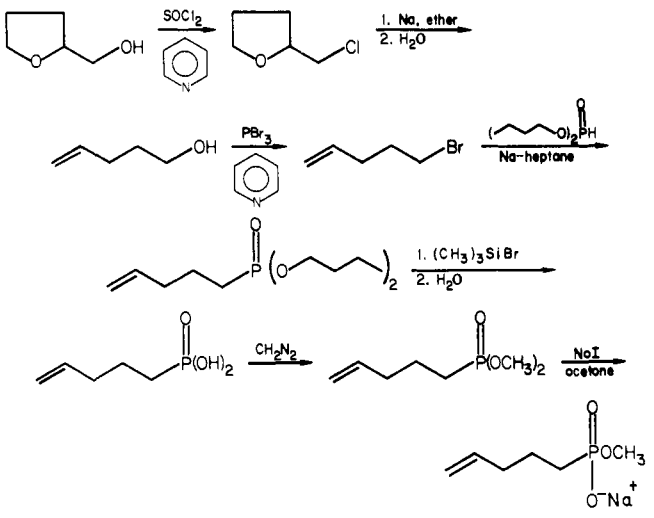
Scheme II



methylsilyl bromide followed by hydrolysis of the trimethylsilyl ester. Sodium allylvinylphosphinate was prepared from the methyl ester by reaction with sodium iodide in acetone.

The product of the rearrangement of **1** in methanol was independently synthesized as shown in Scheme II. The barium salt of the acid salt, **3**, was prepared from the corresponding methyl ester with trimethylsilyl bromide by a procedure similar to that cited above for the preparation of allylvinylphosphinic acid, followed by metathesis to form the barium salt.

Experimental Section

Materials and Methods. ^{1}H NMR spectra were recorded on either a Varian T-60 or a Varian CFT-20/HFT-80 spectrometer, with tetramethylsilane as an internal reference unless otherwise noted. Proton-decoupled ^{31}P NMR spectra were recorded at 40.5 MHz on a Varian XL-100 spectrometer equipped for Fourier transform. Chemical shifts are given relative to 85% phosphoric acid.[1] Infrared spectra were obtained with a Perkin-Elmer 137 spectrometer. Melting points are uncorrected unless otherwise noted. Elemental analyses were performed by Galbraith Laboratories, Inc.

Mallinckrodt anhydrous ether and Fisher dichloromethane were used as supplied; all other solvents were dried by conventional methods, distilled, and then stored over molecular sieves.

Bis(dimethylamino)vinylphosphine[2] was synthesized from **tris(dimethylamino)phosphine**[3] (^{1}H NMR ($CDCl_3$) δ 2.49 (d, J_{H-P} = 9 Hz)) and vinylmagnesium bromide:[4] bp 64–66 °C (24 mm); ^{1}H NMR ($CDCl_3$) δ 2.73 (d, J_{H-P} = 9 Hz, 12 H), 5.25–6.51 (m, 3 H).

Dimethoxyvinylphosphine[2] boiled at 72–75 °C (157 mm). The product was better than 90% pure by NMR analysis: ^{1}H NMR ($CDCl_3$) δ 3.58 (d, J_{H-P} = 11 Hz, 6 H), 5.55–6.65 (m, 3 H); IR (thin film) 2900, 1448, 1380, 1175, 1030 (br) cm^{-1}.

Methyl allylvinylphosphinate was synthesized from 65 g of allyl bromide and 6.5 g of dimethoxyvinylphosphine by a procedure analogous to that previously used by Kabachnik et al.[5] for the corresponding butyl ester. Fractional distillation at 0.04 mm through a 1 × 11 cm column packed with coiled 24-gauge nickel–chrome wire gave 1.6 g of a forerun (a mixture of the desired product and methyl methylvinylphosphinate) and 4.50 g of product boiling at 43 °C: ^{31}P NMR ($CDCl_3$) δ −40.00 (s); ^{1}H NMR ($CDCl_3$) δ 2.61 (dd, J_{H-P} = 18 Hz, J_{H-H} = 9 Hz, 2 H), 3.67 (d, J_{H-P} = 11 Hz, 3 H), 4.95–6.60 (m, 6 H); IR (thin film) 3480, 2950, 1650, 1395, 1230, 1035 cm^{-1}. Anal. Calcd for $C_6H_{11}O_2P$: C, 49.35; H, 7.53; P, 21.20. Found: C, 49.18; H, 7.66; P, 20.89.

Sodium Allylvinylphosphinate. A solution of methyl allylvinylphosphinate (1.1 g) and sodium iodide (1.2 g) in 25 mL of dry acetone was refluxed for 6 days and then filtered; the filtrate was refluxed for 10 days more and again filtered. The combined precipitates were washed with acetone and ether and dried over phosphorus pentoxide. The white semicrystalline solid (0.85 g; mp 195.0–196.5 °C) required hard burning with vanadium pentaoxide to give correct analytical data: ^{31}P NMR (D_2O) δ −29.74 (s); ^{1}H NMR (CD_3OD) δ 2.36 (dd, J_{H-P} = 18 Hz, J_{H-H} 8 Hz, 2 H), 4.75–6.55 (m, 6 H); IR (KBr) 3000 (br, w) 1635, 1390, 1210, 1165, 1068, 988, 955, 898, 837, 783 cm^{-1}. Anal. Calcd for $C_5H_8NaO_2P$: C, 38.99; H, 5.19; P, 20.11; Na, 14.93. Found: C, 38.82; H, 5.12; P, 20.04; Na, 14.79.

Diethoxyvinylphosphine was synthesized analogously to dimethoxyphosphine. Bis(dimethylamino)vinylphosphine (10.0 g) and dry ethanol (6.30 g) were stirred at reflux under nitrogen for 5 h; bp 76–78 °C (65 mm). The product was better than 95% pure by NMR analysis: ^{1}H NMR ($CDCl_3$) δ 1.27 (t, J_{H-H} = 7 Hz, 6 H), 3.77 (pseudo q, J_{H-H} = 7 Hz, 4 H), 5.50–6.70 (m, 3 H).

Ethyl allylvinylphosphinate was prepared analogously to the corresponding methyl ester. Allyl bromide (17 g) and a trace of hydroquinone in 50 mL of dry toluene were heated under nitrogen at 100 °C while diethoxyvinylphosphine (2.1 g) in 100 mL of dry toluene was added over 4.5 h. The reaction mixture was further heated at 100 °C overnight, the toluene removed in vacuo, and the ester distilled through a 1 × 11 cm column packed with a coil of 24-gauge nichrome wire: Yield 1.26 g (56%); bp 44 °C (0.05 mm); ^{31}P NMR ($CDCl_3$) δ −38.27 (s); ^{1}H NMR ($CDCl_3$) δ 1.32 (t, J_{H-H} = 7 Hz, 3 H), 2.63 (dd, J_{H-P} = 18 Hz , J_{H-H} = 8 Hz, 2 H), 4.03 (m, 2 H), 4.95–6.65 (m, 6 H); IR (thin film) 2950, 1640, 1610 (w), 1390, 1230, 1035, 955, 848 cm^{-1}. Anal. Calcd for $C_7H_{13}O_2P$: C, 52.53; H, 8.12; P, 19.35. Found: C, 52.39; H, 8.10, P, 19.46.

Allylvinylphosphinic acid was prepared by two routes. (a) Methyl allylvinylphosphinate (2 g) and trimethylsilyl bromide (3.3 g)[6,7] were stirred overnight under argon at room temperature, and the product was hydrolyzed with 1 mL of water. Volatiles were removed under vacuum, and residual water was removed by azeotroping with alcohol and then with ether. Molecular distillation in a Hickman still at 50 °C (10^{-5} mm) yielded 1.20 (66%) of a clear oil. (b) Sodium allylvinylphosphinate, dissolved in a small amount of deionized water, was passed through a Dowex 50W-X8 ion-exchange column in the protonated form. The water was removed in vacuo and the product dried over phosphorus pentoxide. The products from the two methods had identical spectra: ^{31}P NMR (D_2O) δ −37.70 (s); ^{1}H NMR ($CDCl_3$) δ 2.56 (dd, J_{H-P} = 18 Hz, J_{H-H} = 8 Hz, 2 H), 4.90–6.40 (m, 6 H), 9.35 (br s, 1 H); IR (thin film) 2600, 2300, 1650, 1170, 980 cm^{-1}.

Phenyl Allylvinylphosphinate. Allylvinylphosphinic acid (1 g) was refluxed under nitrogen for 1 h in 25 mL of dry benzene with phosphorus pentachloride (1.6 g) and then allowed to stand at room temperature overnight. The benzene and phosphorus oxychloride were removed in vacuo, and the residue was redissolved in 20 mL of dry benzene. Phenol (0.71 g) and triethylamine (0.77 g) were added slowly under nitrogen with stirring, and the reaction mixture was relfuxed overnight. The white precipitate (triethylammonium chloride) was removed by filtration and the benzene by rotoevaporation. Distillation [bp 108–111 °C (2 mm)] yielded 1.03 g of a clear oil. The phenyl ester was further purified by high-pressure LC with a Waters Associates ALC Model 202 apparatus equipped with a 24 × 1/8 in. Corasil II column, and the progress of the chromatography was monitored at 254 nm. The ester eluted at 35–50 min with isooctane–ethanol (67:1) at 1000 psi and a flow rate of 1.5 mL/min. After the solvents were evaporated, the product was dried in vacuo over phosphorus pentoxide: ^{31}P NMR ($CDCl_3$) δ −37.76 (s); ^{1}H NMR ($CDCl_3$) δ 2.82 (dd, J_{H-P} = 18 Hz, J_{H-H} = 8 Hz, 2 H), 5.00–6.60 (m, 6 H), 7.20 (m, 5 H); IR (thin film) 3200, 3030, 1580, 1480, 1385, 1200, 1165, 1070, 1028, 990, 918 cm^{-1}. On the basis of the ^{31}P spectrum, the compound appeared to be about 95% pure.

Pent-4-en-1-ol, prepared from tetrahydrofurfuryl chloride, by the method of Brooks and Snyder,[8] was converted to the corresponding bromide.[9] **Dibutyl pent-4-enephosphonate** was prepared by the general procedure of Kosolapoff.[10] Sodium metal (0.62 g) was suspended in 80 mL of dry heptane, and the solvent was heated to reflux under nitrogen with vigorous stirring. Freshly distilled dibutyl phosphonate (5.21 g, Aldrich) was added over 30 min and the mixture refluxed until almost all of the sodium had reacted (4 h); the excess sodium was then removed. 1-Bromopent-4-ene (4.02 g) was added over 10 min, and the reaction mixture was refluxed for 6 h and then allowed to stand overnight. The

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(8) Brooks, L. A.; Snyder, H. R. "Organic Syntheses"; Wiley: New York, 1955; Collect. Vol. III, p 698.
(9) La Forge, F. B.; Green, N.; Gersdorff, W. A. *J. Am. Chem. Soc.* **1948**, *70*, 3707.
(10) Kosolapoff, G. N. *J. Am. Chem. Soc.* **1945**, *67*, 1180.

heptane was extracted three times with 30 mL of water, the water back-extracted with 30 mL of heptane, and the combined heptane solution evaporated. Distillation of the residue [bp 99–101 °C (0.15 mm)] gave 4.38 g of a clear oil: ^{31}P NMR ($CDCl_3$) δ −32.29 (s); ^{1}H NMR ($CDCl_3$) δ 0.90 (t, J_{H-H} = 6 Hz, 6 H), 1.10–2.25 (m, 14 H), 3.96 (pseudo q, 4 H), 4.80–5.95 (m, 3 H); IR (thin film) 3500 (w), 2930, 1650, 1465, 1385, 1250, 1025 (br), 910 cm^{-1}. Anal. Calcd for $C_{13}H_{27}O_3P$: C, 59.57; H, 10.30; P, 11.82. Found: C, 59.14; H, 10.11, P, 11.63.

Dimethyl Pent-4-enephosphonate. Dibutyl pent-4-enephosphonate (2 g) and trimethylsilyl bromide (3.5 g) were stirred overnight under dry argon. The mixture was stirred briefly with water (3 mL), and the volatiles were removed in vacuo. Excess diazomethane (prepared from Aldrich Diazald) in ether was added to the residue; the ether was then removed; distillation of the residue [bp 69–70 °C (3.5 mm)] yielded 0.97 g of clear oil: ^{31}P NMR ($CDCl_3$) δ −34.93 (s); ^{1}H NMR ($CDCl_3$) δ 1.20–2.40 (m, 6 H), 3.76 (d, J_{H-P} = 11 Hz, 6 H), 4.85–6.10 (m, 3 H); IR (thin film) 3420, 2925, 1650, 1460, 1242, 1060, 1032, 918 cm^{-1}. Anal. Calcd for $C_7H_{15}O_3P$: C, 47.22; H, 8.43; P, 17.39. Found: C, 47.35; H, 8.46; P, 17.20.

Sodium Methyl Pent-4-enephosphonate. Dimethyl pent-4-enephosphonate (1.0 g) and sodium iodide (1.0 g) were refluxed for 5 days under argon in 40 mL of dry acetone. The white precipitate (0.80 g) that formed was filtered, washed with cold acetone, and dried over phosphorus pentoxide in vacuo at 80 °C: mp 190–190.5 °C; ^{31}P NMR (D_2O) δ −30.37; ^{1}H NMR (CD_3OD) δ 1.20–2.30 (m, 6 H), 3.52 (d, J_{H-P} = 11 Hz, 3 H), 4.70–6.05 (m, 3 H); IR (KBr) 3340, 2870, 1630, 1445, 1208, 1175, 1095, 1048, 998, 917 cm^{-1}. Anal. Calcd for $C_6H_{12}NaO_3P$: C, 38.74; H, 6.45; P, 16.65; Na, 12.36. Found: C, 38.55; H, 6.58; P, 16.45; Na, 12.10.

Diethyl pent-4-enephosphonate was prepared from diethyl phosphonate (0.88 g, Victor Chemicals), sodium metal (0.15 g), and 1-bromopent-4-ene (0.95 g) by the general method used for the corresponding dibutyl ester, except that tetrahydrofuran rather than heptane was used as solvent. Distillation of the product yielded 0.76 g (58%) of clear oil: bp 53 °C (0.05 mm); ^{31}P NMR ($CDCl_3$) δ −31.58; ^{1}H NMR ($CDCl_3$) δ 1.42 (t, J_{H-H} = 7 Hz, 6 H), 1.50–2.30 (m, 6 H), 4.07 (pseudo q, 4 H), 4.85–6.05 (m, 3 H); mass spectrum (70 eV), m/e 206; IR (thin film) 3490, 2950, 1650, 1400, 1235, 1030, 953 cm^{-1}. Anal. Calcd for $C_9H_{19}O_3P$: C, 52.46; H, 9.22; P, 15.03. Found: C, 52.25; H, 8.75; P, 14.78.

Barium Pent-4-enephosphonate. Diethyl pent-4-enephosphonate (0.052 g) and trimethylsilyl bromide (0.11 g) were stirred overnight in methylene chloride solution (10 mL) under nitrogen at room temperature. Triethylamine (0.075 g) in 1 mL of water was added under nitrogen at 0 °C to the reaction mixture. The volatiles were removed under vacuum, and the residue was dissolved in 2 mL of water that contained barium bromide (0.073 g). The solution was titrated to pH 10 with triethylamine and filtered; the filtrate was diluted with 3 mL of ethanol. The precipitate that formed after several minutes was filtered, washed with ethanol, and dried over phosphorus pentoxide at 120 °C (0.01 mm): mp >300 °C; ^{31}P NMR (D_2O) δ −23.40 (s); ^{1}H NMR (D_2O, $(CH_3)_3SiCD_2CD_2CO_2Na$ as internal reference) δ 1.0–1.85 (m, 4 H), 1.85–2.30 (m, 2 H), 4.80–6.20 (m, 3 H). Anal. Calcd for $C_5H_9O_3PBa$: C, 21.04; H, 3.15; P, 10.85. Calcd for $C_5H_9O_3PBa \cdot {}^1/_2 H_2O$: C, 20.40; H, 3.40; P, 10.52. Found: C, 20.45; H, 3.49; P, 10.51. Analysis for barium was not satisfactory.

Crude *vinylphosphonic acid* was prepared by treating diethyl vinylphosphonate (Aldrich) with trimethylsilyl bromide, with subsequent hydrolysis of the presumed trimethylsilyl ester.

Methods. Thermolyses of sodium allylvinylphosphinate were carried out on a preparative scale in 5-mL, Teflon-lined, brass bombs in an oven at 190 ± 5 °C. For kinetic experiments, solutions of sodium allylvinylphosphinate or of allylvinylphosphinic acid or its esters were sealed in 5-mL glass vials (2-mm walls) fully immersed in a silicone oil thermostat at 193.6 ± 1.0 °C. Some of the thermolyses were carried out in sealed glass tubes rather than in Teflon-lined brass bombs. This allowed inspection of the reaction mixture during the rearrangement; most of the solvent remains in the liquid phase, and no reactant was observed to come out of solution. Methanol and ethanol used in these reactions were dried by the magnesium method; deionized water was used throughout. Except as otherwise noted, reaction products were identified by ^{31}P NMR spectroscopy in the absence and again in the presence of authentic material. Since the ^{31}P chemical shifts of organophosphorus compounds are solvent dependent, this method was needed to ensure proper identification of reaction products.

In kinetic studies, standard solutions of the salt or ester of allylvinylphosphinic acid were pipetted into the glass tubes, which were degassed twice by freeze–thawing techniques before they were sealed. After the solutions had been heated for appropriate times, the tubes were cooled and opened and the contents diluted to 3 mL with deuterium oxide that contained methyltriphenylphosphonium bromide as a standard for integration. The proton-decoupled ^{31}P NMR spectra were then recorded and integrated. In studies of salt effects with sodium perchlorate, triethyl phosphate was used as standard, since methyltriphenylphosphonium perchlorate precipitates from water. When the reaction of sodium allylvinylphosphinate was carried out in ethanol, triethyl phosphate was again used as the NMR standard. When the reaction of ethyl allylvinylphosphinate was carried out in ethanol, the reaction mixture was diluted with 1 g of acetone-d_6 with triethyl phosphate as standard.

Table I. Rate of Rearrangement of Sodium Allylvinylphosphinate (1) at 193.6 ± 1.0 °C

[1], M	[$NaClO_4$], M	solvent	$t_{1/2}$,[a] h	r
0.69		H_2O	4.50 ± 0.30	0.985
0.162		H_2O	4.12 ± 0.33	0.971
0.162	0.484	H_2O	4.99 ± 0.30	0.984
0.042		alcohol	6.03 ± 0.12	0.99

[a] Average of two determinations.

Results

Products. Sodium allylvinylphosphinate (0.050 g) in 1 mL of water (0.325 M) reacted (eq 1) after 48 h at 190 ± 5 °C to yield the expected product of a phospho-Cope rearrangement, i.e., sodium pent-4-enephosphonate; the yield was at least 98%. The product was characterized by converting it (by the method outlined in the Experimental Section) to the corresponding barium salt, which was identical by IR and ^{31}P and ^{1}H NMR spectroscopy with synthetic material. No evidence of polymeric pent-4-enephosphonate was observed in either phosphorus or proton NMR spectra. Similarly, sodium allylvinylphosphinate (0.050 g) in 1 mL of dry methanol reacted after 72 h at 190 ± 5 °C to give a reaction mixture, analyzed by ^{31}P NMR spectroscopy, that contained 88 ± 2% of sodium methyl pent-4-enephosphonate, the product expected for a phospho-Cope rearrangement in methanol. This product was isolated by recrystallizing the mixture of products from ethanol–THF; the recrystallized product gave a mixture melting point with synthetic sodium methyl pent-4-enephosphonate of 187.5–190 °C and was analytically and spectroscopically identical with authentic synthetic material. In addition to the major product, a small quantity of starting material and four minor products (not yet identified) were observed.

When ethyl allylvinylphosphinate (0.025 g) in 1 mL of dry ethanol (0.156 M solution) was heated at 193.6 ± 1 °C, diethyl pent-4-enephosphonate, the expected product of a phospho-Cope rearrangement, was indeed formed. The reaction was complicated by the appearance of allylvinylphosphinic acid and, at long reaction times, by the appearance of hydrogen ethyl pent-4-enephosphonate. In addition, hydrogen ethyl vinylphosphonate and vinylphosphonic acid were slowly formed. When allylvinylphosphinic acid (0.016 g) was heated at 193.6 ± 1 °C in 1 mL of water (0.12 M solution), only the cleavage product, vinylphosphonic acid, was found.

When in preliminary experiments phenyl allylvinylphosphinate was heated neat in sealed tubes at 200 °C for 24 h, the ^{1}H NMR spectrum of the product suggested that isomerization of the double bond, rather than a phospho-Cope rearrangement, had occurred. When phenyl allylvinylphosphinate (0.25 g) was heated in 1.6 g of phenol in a sealed tube at 193.6 ± 1.0 °C for 12 h, the ^{31}P NMR spectrum showed slow decomposition to several products. The reaction was not further investigated.

Kinetics. The rates of rearrangement of sodium allylvinylphosphinate are presented in Table I. The ^{31}P spectra for a typical determination are shown in Figure 1. First-order half-lives were calculated by the least squares method; the data yield rate constants of high quality (r > 0.97; see Table I). The ^{31}P NMR spectra for the rearrangement of ethyl allylvinylphosphinate in ethanol are shown in Figure 2. These data are not adequate for the determination of a half-life. Nevertheless, the small peak for the rearrangement product, diethyl pent-4-enephosphonate, can be seen while substantial quantities of starting materials are still present, so the initial rate of rearrangement is not diminished to any large extent by the side reactions. Furthermore, the rearrangement product appears immediately; there is no lag to suggest

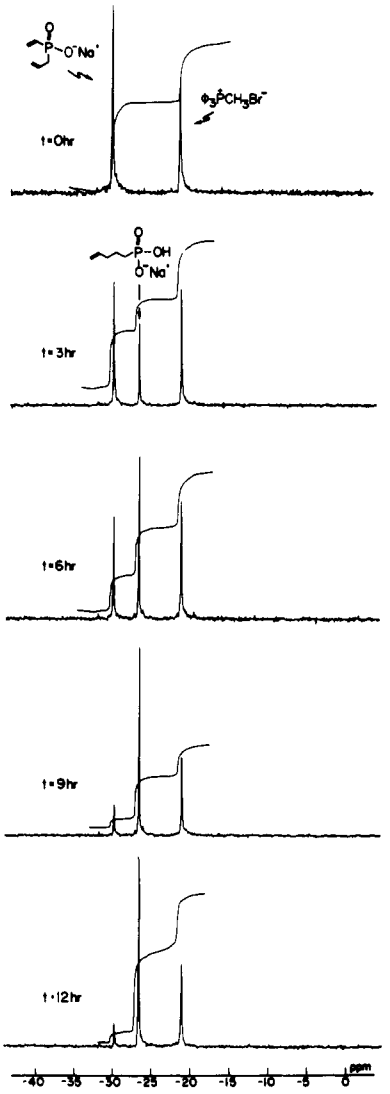


Figure 1. ^{31}P NMR spectra (D_2O) of the thermolysis of sodium allylvinylphosphinate (0.649 M) in water at 193.6 ± 1.0 °C.

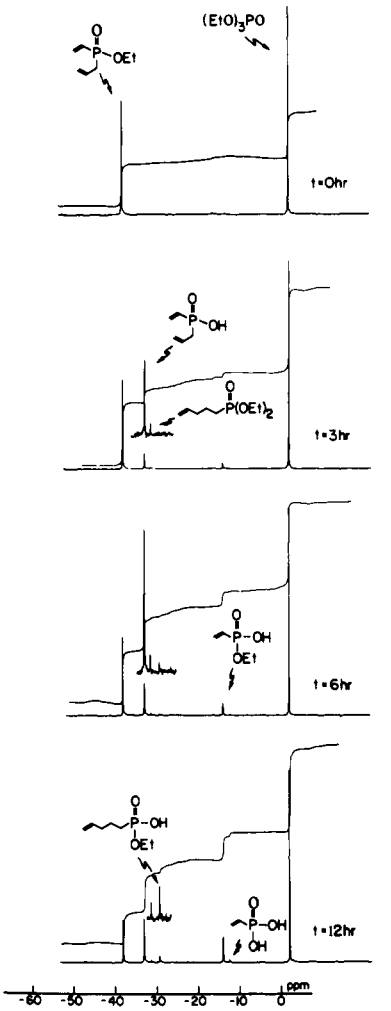


Figure 2. ^{31}P NMR spectra (acetone-d_6/ethanol) of the reaction products from the thermolysis of ethyl allylvinylphosphinate (0.156 M) in ethanol (triethyl phosphate added).

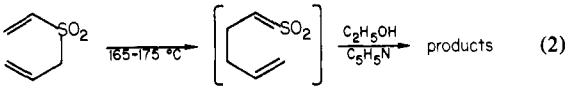
that it is formed in a secondary reaction. Under these circumstances, a crude estimate of the rate of rearrangement of the ester in ethanol is possible; it is about 6% of the rate for the rearrangement of the salt under the same experimental conditions.

Since the half-time for the rearrangement is essentially independent of the concentration of starting material over a fourfold change in concentration, the reaction is clearly first order. In fact, the small change in rate with change in initial concentration appears to be at least in part the result of the modest salt effect that was independently observed.

Discussion

The simplest mechanism for the rearrangement of sodium allylvinylphosphinate to sodium hydrogen pent-4-enephosphonate is that shown in eq 1: a concerted Cope rearrangement, to yield the monomeric metaphosphonate **2** followed by nucleophilic trapping of **2** by water. The data here presented are consistent with this pathway. The rearranement is clean and first order in the substrate, with only a small positive salt effect. The anion reacts more rapidly than does the corresponding ester, ethyl allylvinylphosphinate. This parallels the results with other pericyclic rearrangements where oxyanions undergo rearrangement much more rapidly than do their electrically neutral conjugate acids.[11,12] In the present study, however, the anion undergoes rearrangement only about 16 times as rapidly as does the corresponding ester; this factor is much smaller than those observed by Evans and Golob[11] for the oxy-Cope rearrangement. The possibility of a 1,3 instead of a 3,3 shift is not ruled out by these studies, although the 3,3-rearangement has much greater precedent both in Cope and Claisen rearrangements and in their oxygen and sulfur analogues. The distinction between a 1,3 and 3,3-rearrangement could be made with appropriately substituted deuterium analogues; however, these experiments have not yet been carried out.

A number of pericyclic rearrangements similar to that here postulated have been achieved[13] with oxygen, nitrogen, and sulfur atoms, in addition to carbon atoms, in the chain. In particular, King and Harding[14] observed the sulfo-Cope rearrangement of allyl vinyl sulfone in pyridine–ethanol as solvent and suggested that the reaction takes place by way of the sulfene **5** (eq 2).



(2)

5

The postulate of a monomeric metaphosphonate as an intermediate in eq 1 is reasonable and has ample precedent. Mo-

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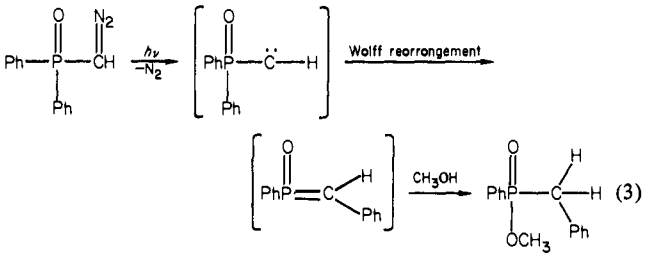
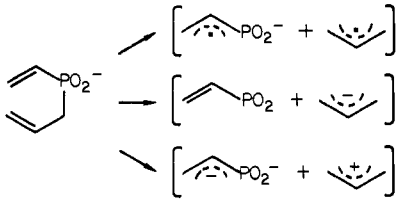
nomeric metaphosphinates have been postulated by Regitz and his co-workers[15] to explain the products they have obtained on photolysis of α-diazophosphine oxides, e.g., eq 3.



(3)

The chemistry of monomeric metaphosphates,[16-23] monomeric metaphosphoramidates, monomeric metaphosphonates, and monomeric metathiophosphoramidates has been extensively investigated. In some cases the metaphosphate analogues have been isolated; for example, Niecke and his collaborators[23] prepared $[[(CH_3)_3Si]_2N]_2P{=}NSi(CH_3)_3$ and established its structure by X-ray crystallography. The postulate of a monomeric metaphosphonate as an intermediate in the rearrangement shown in eq 1 is then a reasonable one. Although Cope rearrangements involving heteroatoms are well documented and although the proposed metaphosphonate intermediate is a reasonable one in the light of the known chemistry of monomeric metaphosphate and its analogues, other possible pathways for the rearrangement here observed must nevertheless be considered. In particular, the process might proceed by dissociation of an allylic anion, cation, or radical from the starting material (eq 4), followed by recombination. The formation of an allylic cation is essentially ruled



(4)

out since this would require the concurrent formation of a dianionic metaphosphonate; such a species would be prohibitively high in energy. The formation of an allylic anion is unlikely, since this would require the concurrent formation of vinylmetaphosphonate; if this species were ever free, it would react with solvent to yield vinylphosphonic acid. Cleavage was observed on heating allylvinylphosphinic acid but not on heating the anion; a mechanism that requires the formation of the allyl anion should be more prominent from an anionic than from an electrically neutral starting material. The question of transitory, caged radicals as contrasted with a concerted reaction for pericyclic processes has long been a perplexing one;[24] we have no firm evidence for one as compared to the other but prefer the simpler picture shown as eq 1, lacking evidence to the contrary.

In summary, then, the work here presented offers an example of a phospho-Cope rearrangement; the reaction probably proceeds by way of a monomeric metaphosphonate as intermediate.

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