

Retrodienic Reactions. Part 2. Vinyl- and Propenyl-phosphines: Synthesis by Flash Vacuum Thermolysis and Characterization

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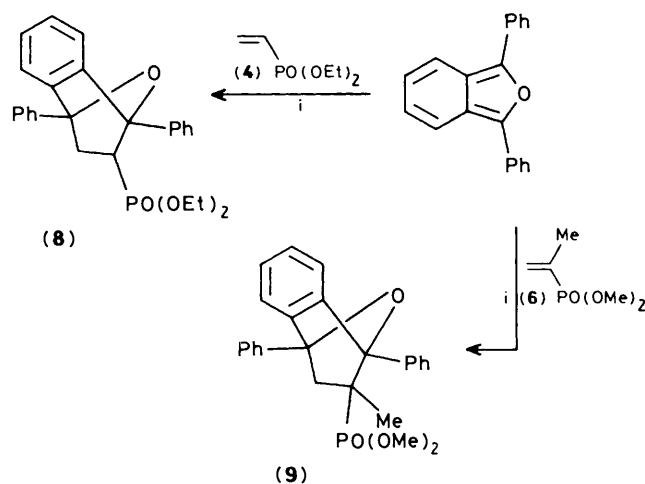
The primary unsaturated phosphines, vinylphosphine (**1**), isopropenylphosphine (**2**) and (*E*)-prop-1-enylphosphine (**3**) have been synthesized by flash vacuum thermolysis of their formal Diels–Alder adducts with anthracene, cyclopentadiene, or 1,3-diphenylisobenzofuran, obtained by cycloaddition of these dienes with the corresponding dialkyl alkenylphosphonates, followed by reduction with lithium aluminium hydride–chlorotrimethylsilane. Compounds (**1**)–(**3**) were characterized from their spectral data and also as tungsten complex derivatives. The phosphines (**1**)–(**3**) exhibit a remarkable and unexpected stability [$t_{1/2}$ ca. 8 days for (**1**) and 5 days for (**2**) and (**3**)] under neutral conditions, in the dark, at room temperature, and were also observed by direct reduction of the corresponding phosphonates in tetrahydrofuran solution.

Low-co-ordination phosphorus compounds, including alkenylphosphines, have been shown to be valuable intermediates in the field of co-ordination chemistry.¹ Because of the high reactivity of the P–H bonds towards multiple bonds in acidic, basic, and even neutral conditions, the synthesis of primary alkenylphosphines, with the exception of β -styrylphosphine,² has remained an unsolved problem. The addition of phosphine, PH_3 , to propadiene³ led mainly to polymers and divinyl- and phenylvinyl-phosphines were characterized only as their tungsten complexes.^{4,5} To date, only few theoretical data have been published on vinylphosphine.^{6–8}

We have previously reported that $(4\pi + 2\pi)$ cycloreversion under flash vacuum thermolysis conditions constitutes an efficient synthesis of unsaturated, reactive compounds⁹ including, *inter alia*, primary enamines.¹⁰ We now report the synthesis, by the same method, of vinylphosphine (**1**), its spectral identification (see ref. 11 for a preliminary communication), and the corresponding tungsten complex. Also described is the preparation and characterization of isopropenylphosphine (**2**) and prop-1-enylphosphine (**3**). The unexpected stability of these primary alkenylphosphines led us to attempt the direct reduction of the corresponding phosphonates.

Synthesis of Diels–Alder Precursors.—In spite of its low dienophilicity, it has been reported that diethyl vinylphosphonate (**4**) undergoes cycloaddition either thermally with acyclic dienes and cyclopentadiene¹² or with gallium trichloride catalysis with 1,3-diphenylisobenzofuran.¹³ From the whole of the results presented in Schemes 1, 2, and 3 it appears that the optimum conditions are quite dependent on the dienophile [diethyl and dimethyl vinylphosphonates (**4**) and (**5**), dimethyl isopropenylphosphonate (**6**), (*E*)-diethyl prop-1-enylphosphonate (**7**) (containing <5% of *Z*-isomer)] and the diene.

In the case of 1,3-diphenylisobenzofuran, owing to its low thermal stability, catalytic conditions were used and the yield of the adduct (**8**) with phosphonate (**4**) was improved to 75% with boron trifluoride–diethyl ether. Under the same conditions, the phosphonate (**6**) led to the cycloaddition product (**9**) in 45% yield, and no reaction was observed when (**7**) was used as the dienophile. When anthracene was used as the diene, the above catalytic conditions gave only low yields [$< 25\%$ with (**4**)], and therefore thermal cycloadditions were always preferred, the best results being obtained with dimethyl phosphonates. On the other hand, when anthracene and the thermally less stable diethyl phosphonates (**4**), or (**7**), were heated at 200 °C for 3 days in

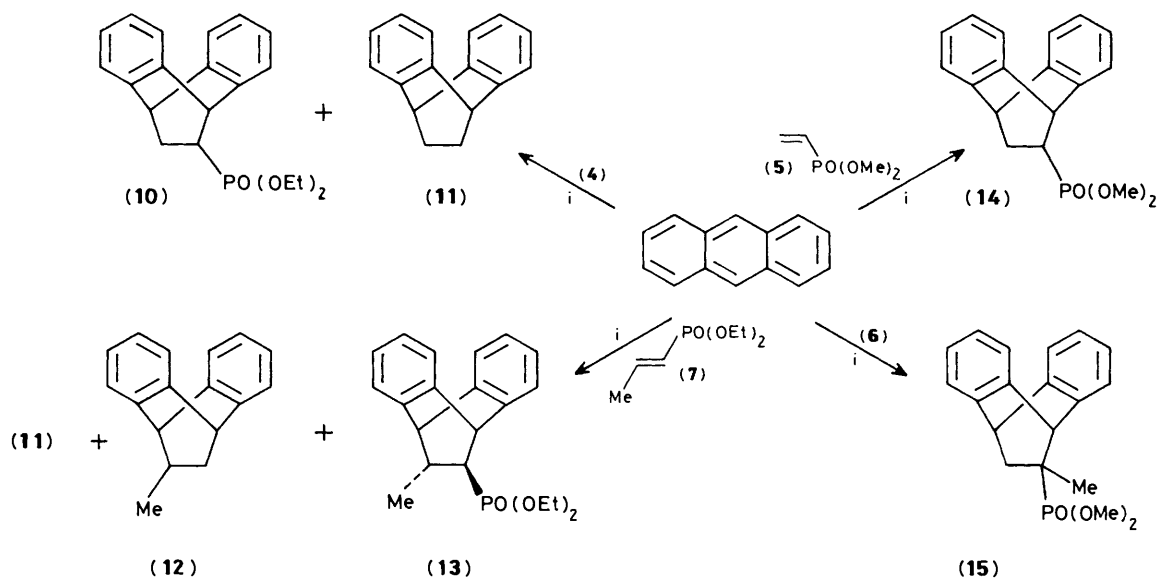


Scheme 1. Reagents and conditions: i, $\text{BF}_3\text{--Et}_2\text{O}$, CH_2Cl_2 , room temperature, 12 h

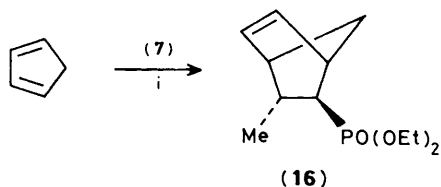
a sealed tube, the hydrocarbon (**11**), or the mixture (**11**) and its methyl analogue (**12**) (ratio 1:1), were obtained with the expected adducts (**10**) or (**13**) respectively. Formation of these could result from the thermal decomposition of the phosphonates (**10**) and (**13**) [or (**4**) and (**7**)] yielding ethylene which also cycloadds with anthracene.¹⁴ Phosphonate (**14**) [or (**15**)] was the sole product of reaction of anthracene with (**5**) [or (**6**)]. At 175 °C, cyclopentadiene and (**7**) gave the norbornene derivative (**16**) in 35% yield.

On reduction with lithium aluminium hydride–chlorotrimethylsilane,¹⁵ the phosphonates (**8**)–(**10**) and (**13**)–(**16**) were converted into the corresponding primary phosphines (**17**)–(**22**) (yield 60–80%) (Schemes 4, 5, and 6). However, owing to their low thermal stability and high air sensitivity, these phosphines were characterized and used without complete purification (see the Experimental section).

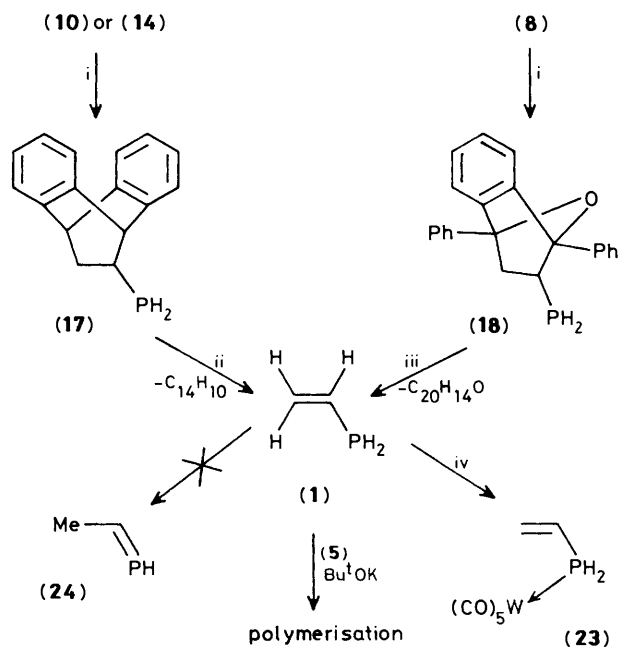
Flash Vacuum Thermolysis of the Primary Phosphines (17**)–(**22**).**—When the phosphine (**17**) was thermolysed (Scheme 4) at 650 °C under 10^{-6} Torr, vinylphosphine (**1**) (70%, as determined by n.m.r. spectroscopy) was the sole volatile product trapped at -196 °C. In the case of the benzofuran adduct (**18**) (thermolysis at 450 °C), small amounts of PH_3 and P_2H_4 ¹⁶ (<10%) were also present. The structure of (**1**) was assigned on the basis of its mass



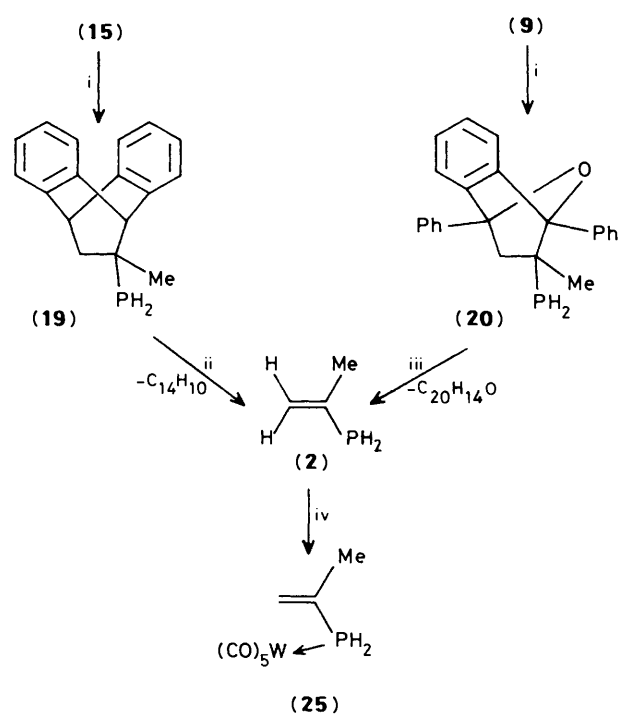
Scheme 2. Reagents and conditions: i, 200 °C, sealed tube, 3 days



Scheme 3. Reagents and conditions: i, 175 °C, sealed tube, 18 h

Scheme 4. Reagents and conditions: i, $\text{LiAlH}_4\text{-Me}_3\text{SiCl}$, room temperature, 12 h; ii, 650 °C, 10^{-6} Torr; iii, 450 °C, 10^{-6} Torr; iv, $\text{W}(\text{CO})_5\text{-THF-THF}$, room temperature, 1 h

spectrum (Found: M^+ , 60.0114. Calc. for $\text{C}_2\text{H}_5\text{P}$: M , 60.0128), the characteristic absorption of a PH_2 group at 2295 cm^{-1} in the i.r. spectrum and the ^{31}P , ^1H , and ^{13}C n.m.r. spectra recorded at -20°C (see the Table). A solution of the phosphine



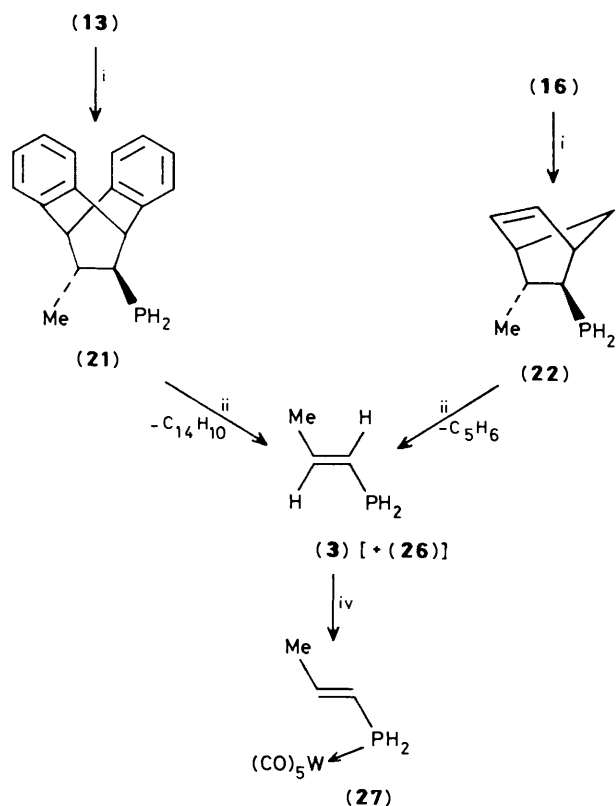
Scheme 5. Reagents and conditions: As Scheme 4

(1) in CCl_4 at room temperature, in the dark, and under nitrogen is fairly stable ($t_{1/2}$ ca. 8 days) and slowly gave a white insoluble polymer. Treatment of (1) in THF with pentacarbonyl(tetrahydrofuran)tungsten⁴ led to the complex (23) (see the Experimental section) which was characterized spectroscopically. Polymerisation is the sole reaction observed when (1) is allowed to react with vinylphosphonate (5) using potassium *t*-butoxide as a catalyst,¹⁷ or when kept at room temperature with cyclopentadiene or 1,3-diphenylisobenzofuran. This lack of cycloaddition shows that no tautomerisation into the strongly dienophilic¹⁸ phospho-alkene (24) occurred.

In the same way (Scheme 5), isopropenylphosphine (2) [$t_{1/2}$ ca.

Table. δ (p.p.m.) and J (Hz) For the phosphines (1)–(3)

	$\begin{matrix} \text{H}^{\text{A}} > \text{C}^2 = \text{C}^1 < \text{H}^{\text{C}} \\ \text{H}^{\text{B}} < \text{PH}_2^{\text{X}} \end{matrix}$ (1)	$\begin{matrix} \text{H}^{\text{A}} > \text{C}^2 = \text{C}^1 < \text{CH}_3 \\ \text{H}^{\text{B}} < \text{PH}_2^{\text{X}} \end{matrix}$ (2)	$\begin{matrix} \text{H}_3\text{C} > \text{C}^2 = \text{C}^1 < \text{H}^{\text{C}} \\ \text{H}^{\text{B}} < \text{PH}_2^{\text{X}} \end{matrix}$ (3)
$\delta\text{H}^{\text{A}}$	5.99	5.58	
$\delta\text{H}^{\text{B}}$	6.01	5.60	6.35
$\delta\text{H}^{\text{C}}$	6.52		6.13
$\delta\text{H}^{\text{X}}$	3.64	3.53	3.47
δCH_3		2.22	2.03
^{31}P	-132.9	-116.2	-136.3
$^{13}\text{C}^1$	126.0	136.7	116.8
$^{13}\text{C}^2$	130.8	126.0	142.3
$^{13}\text{C}\text{H}_3$		28.3	21.2
$J^{\text{H}^{\text{A}}\text{H}^{\text{B}}}$	1.9	2.9	
$J^{\text{H}^{\text{A}}\text{H}^{\text{C}}}$	9.4		
$J^{\text{H}^{\text{B}}\text{H}^{\text{C}}}$	17.3		16.5
$J^{\text{H}^{\text{A}}\text{CH}_3}$		0.5	
$J^{\text{H}^{\text{B}}\text{CH}_3}$		0.5	6.7
$J^{\text{H}^{\text{C}}\text{CH}_3}$			1.2
$J^{\text{H}^{\text{A}}\text{H}^{\text{X}}}$	2–3	<i>a</i>	
$J^{\text{H}^{\text{B}}\text{H}^{\text{X}}}$	2–3	<i>a</i>	4
$J^{\text{H}^{\text{C}}\text{H}^{\text{X}}}$	5		<i>a</i>
$J^{\text{PH}^{\text{X}}}$	199	191	200
$J^{\text{PH}^{\text{C}}}$	5.5		8
$J^{\text{PH}^{\text{A}}}$	13.5	31.4	
$J^{\text{PH}^{\text{B}}}$	6.5	15.8	14
J^{PCH_3}		<i>ca.</i> 0	<i>ca.</i> 0
$J^{\text{C}^1\text{H}^{\text{C}}}$	151		143
$J^{\text{C}^1\text{H}^{\text{A}}}$	<i>a</i>	<i>a</i>	
$J^{\text{C}^1\text{H}^{\text{B}}}$	<i>a</i>	7	6.8
$J^{\text{C}^2\text{H}^{\text{A}}}$	158	160	
$J^{\text{C}^2\text{H}^{\text{B}}}$	158	160	157
$J^{\text{C}^2\text{H}^{\text{C}}}$	7.8		10.5
$J^{\text{C}^1\text{P}}$	12	12	5
$J^{\text{C}^2\text{P}}$	20	30	31

^a Not determined.**Scheme 6.** Reagents and conditions: as above

5 days (Found: M^+ 74.0292. Calc. for $\text{C}_3\text{H}_7\text{P}$: M , 74.0286; $\nu_{\text{max}}(\text{CCl}_4)$ 2295 cm^{-1} (PH_2)] was obtained, with the corresponding diene, in nearly a pure state from the thermolysis of (19) (55% yield) or (20) (30%). It was characterized spectroscopically (see the Table for the n.m.r. data) and trapped as the tungsten complex (25). Flash thermolysis (Scheme 6) of the adducts (21) or (22) (>95% *E*-isomer) led to the expected (*E*)-prop-1-enylphosphine (3) [t_3 *ca.* 5 days (Found: M^+ , 74.0286. Calc. for $\text{C}_3\text{H}_7\text{P}$: M , 74.0286); $\nu_{\text{max}}(\text{CCl}_4)$ 2295 cm^{-1} (PH_2); n.m.r. data, see the Table] in *ca.* 25% yield. The presence of a small amount of (*Z*)-prop-1-enylphosphine, corresponding to the ratio of the isomers in phosphonate (7), was also detected by ^{31}P n.m.r. spectroscopy at -161.3 p.p.m. ($^1J_{\text{PH}}$ 200, $^2J_{\text{PH}}$ 9, $^3J_{\text{PH}}$ 18 Hz); a non-identified compound (26) [$\delta_{\text{p}}(\text{THF})$ -128.1 p.p.m. ($^1J_{\text{PH}}$ 191 Hz); $\delta_{\text{H}}(\text{CCl}_4)$ among other masked signals, multiplet at 5.0–5.1 p.p.m.] was also formed besides (3) [ratio (3):(26) 1:1]. The phosphine (3) was also trapped as the complex (27).

The n.m.r. data given in the Table allow an unambiguous structural assignment of the phosphines (1)–(3). The chemical shifts and coupling constants J_{HH} are typical of vinylic compounds (5.5 < δ < 6.5 p.p.m. J_{gem} 2–3, J_{trans} 16–17, J_{cis} 9–10 Hz). In the ^{31}P n.m.r. spectra, the presence of a PH_2 group is indicated by a triplet (of multiplets) with $^1J_{\text{PH}}$ 190–200 Hz at a chemical shift in accordance with that deduced from empirical rules.¹⁹ The $^2J_{\text{PH}}$ value, smaller [5.5, 8, and 9 Hz for compounds (1), (*E*)-(3) and (*Z*)-(3) respectively] than the one described for trivinylphosphine (13.6 Hz),²⁰ can be attributed to an increase in the dihedral angle between the vinyl group and phosphorus electronic doublet when the phosphorus atom is not substituted.²¹ The observed values of the ^{13}C chemical shifts in compounds (1)–(3) fit very well with those predicted

from the empirical increments reported for alkenes.²² The couplings J_{PC} are also in good agreement with those previously described.^{20,23}

The relative stabilities of the alkenylphosphines (1)–(3) led us to investigate the direct reduction of the phosphonates (4)–(7) with chlorotrimethylsilane–lithium aluminium hydride in THF. After hydrolysis of the reaction mixture, the organic layer, as revealed by ³¹P n.m.r. spectroscopy contained the corresponding phosphines (1)–(3) (also identified as their tungsten complexes) mixed with phosphorus-containing impurities in an approximate ratio of 30:10:5 for the phosphine (1), (2), and (3), respectively. Owing to the as yet unsolved difficulties of isolation of the free phosphines (1)–(3) from the reaction media, the retrodienic cleavage of the easily available Diels–Alder precursors still remains the best way of obtaining [in pure state for (1) and (2)] these primary alkenylphosphines as well as their tungsten complexes.

Experimental

General Procedures.—All reactions, manipulations, and purifications involving phosphines were performed under a dry nitrogen atmosphere. High resolution mass spectra were recorded on a JEOL JMS D 300, and infrared spectra, given in cm^{-1} , on Perkin-Elmer 684 or 1420 spectrometers. ¹H n.m.r. spectra were determined either at 60 (Varian A 60) or 300 MHz (Bruker AM-300). ¹³C and ³¹P n.m.r. spectra were obtained on Bruker WP 80 at 20.1 and 32.4 MHz or AM-300 instruments at 75.5 and 121.5 MHz. Chemical shifts are given in p.p.m. relative to internal SiMe₄ for ¹H and ¹³C and to external 85%–H₃PO₄ for ³¹P n.m.r. spectra. Chemical shifts upfield of the standard are defined as negative. Coupling constants were determined by selective phosphorus and proton decoupling experiments at 300 MHz.

Dimethyl vinylphosphonate (5),^{12b} dimethyl prop-1-en-2-ylphosphonate (6)²⁴ and (*E*)-diethyl prop-1-enylphosphonate (7)²⁵ (containing <5% of the *Z*-isomer) were prepared by described methods. Commercial diethyl vinylphosphonate (4) was used. Owing to the difficulties encountered during attempted purification of the phosphonates (8)–(10) and (13)–(16) (attempts at crystallization led to formation of clathrates and sublimation resulted in partial retro Diels–Alder decomposition), precise mass determinations are given for these compounds instead of elemental analyses. The thermally unstable primary phosphines (17)–(22) were immediately thermolysed without purification.

Diethyl 1,4-Epoxy-1,4-diphenyl-1,2,3,4-tetrahydronaphthalen-2-ylphosphonate (8).—To a solution of diethyl vinylphosphonate (4) (0.537 ml, 3.5 mmol) in dichloromethane (4 ml) was added boron trifluoride–diethyl ether (0.432 ml, 3.5 mmol), followed by 1,3-diphenylisobenzofuran (1 g, 3.5 mmol) in dichloromethane after 1 h at room temperature. After 12 h, the mixture was poured onto cold water and the organic layer was dried and column chromatographed on alumina. After the impurities had been eliminated with ether, elution with ether–ethanol (7:3) gave the phosphonate (8) (mixture of two isomers) (1.134 g, 75%) [Found: ($M^+ - \text{H}_2\text{O}$), 416.1548. Calc. for C₂₆H₂₅O₃P: ($M - \text{H}_2\text{O}$), 416.1542]; ν_{max} (film) 2 980, 1 460, 1 450, 1 355, 1 310, 1 235, 1 060, and 1 030 cm^{-1} ; δ_{H} (CDCl₃) 0.95 and 1.10 (6 H, 2 × t, *J* 7 Hz), 1.9–4.1 (7 H, m), and 6.7–8.1 (14 H); δ_{P} (CDCl₃) 26.2 and 27.9 p.p.m.

Dimethyl 1,4-Epoxy-2-methyl-1,4-diphenyl-1,2,3,4-tetrahydronaphthalen-2-ylphosphonate (9).—The reaction was carried out as described above, with 1,3-diphenylisobenzofuran and dimethyl prop-1-en-2-ylphosphonate (6) to give the phosphonate (9) (as a mixture of isomers) (45%) (Found: M^+ ,

420.1556. Calc. for C₂₅H₂₅O₄P: M , 420.1490); ν_{max} (film) 2 950, 1 460, 1 450, 1 350, 1 300, 1 225, 1 055, and 1 030 cm^{-1} ; δ_{H} (CDCl₃) 1.25 and 1.32 (3 H, 2 × d, *J* 15.5 and 16 Hz), 1.7–2.5 (2 H, m), 3.21, 3.36, 3.41, and 3.61 (6 H, 4 × d, *J* 10.5 Hz), and 6.8–8.0 (m, 14 H); δ_{P} (CDCl₃) 32.7 and 33.8 p.p.m.

Diethyl 9,10-Dihydro-9,10-ethanoanthracen-11-ylphosphonate (10).—(a) A mixture of anthracene (1.78 g, 10 mmol), diethyl vinylphosphonate (4) (1.64 g, 10 mmol), and hydroquinone (0.1 g) was heated in an autoclave for 3 days at 200 °C in a sealed tube. The resulting oil was chromatographed on alumina to afford 9,10-dihydro-9,10-ethanoanthracene (11) (0.35 g, 17%); m.p. 145 °C, ¹H n.m.r. data in accordance with that given in ref. 26; δ_{C} (CDCl₃) 25.64, 43.06, 122.15, 124.45, and 142.74 p.p.m., after elution with pentane–ether (3:1) and then phosphonate (10) eluting with ether (0.365 g, 11%) (Found: M^+ , 342.1391. Calc. for C₂₀H₂₃O₃P: M , 342.1385); ν_{max} (CCl₄) 2 990, 1 290, 1 245, 1 065, and 1 035 cm^{-1} ; δ_{H} (CDCl₃) 0.92 and 1.02 (6 H, 2 × t, *J* 6 Hz), 1.7–2.5 (3 H, m), 3.68 (4 H, m), 4.23 (1 H, m), 4.53 (1 H, m), and 6.9–7.4 (8 H, m); δ_{C} (CDCl₃) 16.0–61.5 (8 × C *sp*³) and 122.9–143.9 (12 × Ar C); δ_{P} (CDCl₃) 30.3 p.p.m.

(b) To a solution of boron trifluoride–diethyl ether (0.125 ml, 1 mmol) in chlorobenzene (2 ml), diethyl vinylphosphonate (4) (0.164 g, 1 mmol) was added, followed after a few minutes of stirring by anthracene (0.178 g, 1 mmol) in chlorobenzene (0.25 ml). The mixture was refluxed for 15 h, quenched with ice, and extracted with dichloromethane. The organic layer was washed (water and brine), dried, and concentrated. Column chromatography of the residue on alumina gave anthracene (0.072 g, 40% recovered) on elution with pentane–ether (7:3) and the phosphonate (10) (0.073 g, 25%) on elution with ether.

trans-Diethyl 12-Methyl-9,10-dihydro-9,10-ethanoanthracen-11-ylphosphonate (13).—Compound (13) was prepared and purified according to the procedure described for the phosphonate (10). Elution with pentane–ether (3:1) gave a mixture of hydrocarbons (11) (see above) and (12), identified by comparison of their n.m.r. spectra with those of authentic samples [(12), ¹H n.m.r. data as in ref. 27; δ_{C} (CDCl₃) 21.4 (q), 32.8 (d), 36.1 (t), 44.6 (d), 51.2 (d), and 122.8–145.0 (12 ArC)]. The phosphonate (13) was then eluted with ether (5–10%) (Found: M^+ , 356.1548. Calc. for C₂₁H₂₅O₃P: M , 356.1541); ν_{max} (CCl₄) 2 960, 1 475, 1 465, 1 395, 1 260, and 1 050 cm^{-1} ; δ_{H} (CDCl₃) 0.6–1.3 (9 H, m), 1.3–2.1 (2 H, m), 3.4–4.4 (6 H, m), and 6.6–7.2 (8 H, m); δ_{P} (CDCl₃) 23.0 p.p.m.

Dimethyl 9,10-Dihydro-9,10-ethanoanthracen-11-ylphosphonate (14).—Using the procedure described for the phosphonate (10), heating dimethyl vinylphosphonate (5) (5.44 g, 0.04 mol), anthracene (7.12 g, 0.04 mol), and hydroquinone (0.1 g) at 200 °C afforded after column chromatography of the crude product the phosphonate (14) (7 g, 56%). An analytical sample was obtained by distillation of the eluate in a Kugelrohr apparatus (Found: M^+ , 314.1076. Calc. for C₁₈H₁₉O₃P: M , 314.1072); ν_{max} (CCl₄) 2 950, 1 460, 1 285, 1 242, 1 062, and 1 040 cm^{-1} ; δ_{H} (CDCl₃) 1.6–2.4 (3 H, m), 3.18 (3 H, d, *J* 10 Hz), 3.35 (3 H, d, *J* 10 Hz), 4.23 (1 H, m), 4.54 (1 H, m), and 6.8–7.3 (8 H, m); δ_{C} (CDCl₃) 29.4–52.5 (6 × C *sp*³) and 123.3–144.4 (12 × ArC); δ_{P} (CDCl₃) 32.9 p.p.m.

Dimethyl 11-Methyl-9,10-dihydro-9,10-ethanoanthracen-11-ylphosphonate (15).—Compound (15) was obtained from anthracene and dimethyl prop-1-en-2-ylphosphonate (6) in the conditions described for the phosphonate (10) (24%) [Found: 178.0783 and 150.0459. Calc. for C₁₄H₁₀ and C₅H₁₁O₃P (retro Diels–Alder fragments) 178.0783 and 150.0446]; ν_{max} (CCl₄) 2 960, 1 465, 1 245, 1 065, and 1 040 cm^{-1} ; δ_{H} (CCl₄) 0.91 (3 H, d,

J 16.5 Hz), 1.28 (1 H, m), 2.28 (1 H, m), 3.13 and 3.43 (6 H, 2 \times d, J 10 Hz), 4.22 (2 H, m), and 7.2—7.4 (8 H, m); δ_C (CDCl₃) 24.4—52.8 (7 \times C sp³) and 123.2—143.2 (12 \times ArC); δ_P (CDCl₃) 36.1 p.p.m.

Diethyl 3-Methylbicyclo[2.2.1]hept-5-en-2-ylphosphonate (16).—Cyclopentadiene (0.6 g, 9.1 mmol), diethyl prop-1-enylphosphonate (7) (1.20 g, 6.74 mmol) and hydroquinone (0.1 g) were heated at 175 °C for 18 h in a sealed tube and the reaction product was purified by column chromatography on alumina. After the impurities had been eliminated with pentane-ether (7:3), elution with ether gave the phosphonate (16) (mainly *trans:endo-exo* and *exo-endo* 50:50); Kugelrohr distillation of the eluate gave an analytical sample (Found: M^+ , 244.1233. Calc. for C₁₂H₂₁O₃P: M , 244.1228; ν_{\max} (CCl₄) 2 965, 1 265, 1 245, 1 100, 1 060, and 1 035 cm⁻¹; δ_H (CDCl₃) 0.78 and 0.98 (3 H, d, J 6 Hz), 1.31 (6 H, ~t, J 7 Hz), 1.6—3.0 (6 H), 4.03 (4 H, m), and 5.8—6.3 (2 H, m); δ_P (CDCl₃) 33.9 and 33.1 p.p.m.

Reaction of the Phosphonates (8)—(10) and (13)—(16): Preparation of the Phosphines (17)—(22).—Chlorotrimethylsilane (0.127 ml, 1 mmol) was added to a stirred solution of lithium aluminium hydride in THF (0.5M; 2 ml, 1 mmol) at -78 °C. The reducing mixture was allowed to warm to room temperature and was stirred for 2 h. A solution of the phosphonate (0.165 mmol) in THF (0.5 ml) was then added at -78 °C. After the reaction mixture had been warmed to room temperature and stirred for a further 12 h, water (0.25 ml) and aqueous potassium hydroxide (1M; 0.3 ml) were added. The aqueous layer was extracted with pentane and the combined organic extracts were dried and evaporated under reduced pressure. The thermally-labile, air-sensitive phosphines (17)—(22) were thus obtained as pale yellow oils in 60—80% yield and were characterized and used without further purification (CAUTION: all reactions and handling of phosphines should be carried out under an inert atmosphere in a well-ventilated hood).

9,10-Dihydro-9,10-ethanoanthracen-11-ylphosphine (17): ν_{\max} (CCl₄) 2 925, 2 295, 1 465, 1 170, 1 140, 1 080, and 1 025 cm⁻¹; δ_H (CCl₄) 1.4—2.3 (3 H, m), 2.41 (2 H, d, J 190 Hz, PH₂), 3.9—4.3 (2 H, m), and 6.8—7.4 (8 H, m); δ_C (CCl₄; -20 °C) 6.0—50.2 (4 C, sp³) and 128.5—147.6 (12 \times ArC); δ_P (CCl₄; -20 °C) -115.6 p.p.m. ($^1J_{PH}$ 192 Hz).

1,4-Epoxy-1,4-diphenyl-1,2,3,4-tetrahydronaphthalen-2-ylphosphine (18): 2 isomers; ν_{\max} (CCl₄) 2 930, 2 300, 1 500, 1 450, 1 390, 1 360, and 1 320 cm⁻¹; δ_H (CCl₄) 1.7—3.2 (3 H), *ca.* 2.5 (PH₂), and 7.0—8.1 (14 H); δ_P (CDCl₃) -123.9 ($^1J_{PH}$ 205 Hz) and -126.4 p.p.m. ($^1J_{PH}$ 198 Hz).

11-Methyl-9,10-dihydro-9,10-ethanoanthracen-11-ylphosphine (19): ν_{\max} (CCl₄) 2 950, 2 300, 1 475, 1 465, 1 380, 1 175, 1 110, and 1 075 cm⁻¹; δ_H (CCl₄) 1.08 (3 H, d, J 9 Hz), 1.5—1.9 (2 H, m), *ca.* 2.2 (PH₂), 4.05 (2 H, m), and 6.8—7.3 (8 H, m); δ_H (CCl₄) 13.3—66.1 (5 \times C sp³) and 122.0—141.4 (12 \times ArC); δ_P (CCl₄) -81.7 p.p.m. ($^1J_{PH}$ 193 Hz).

1,4-Epoxy-2-methyl-1,4-diphenyl-1,2,3,4-tetrahydronaphthalen-2-ylphosphine (20): 2 isomers; ν_{\max} (CCl₄) 2 950, 2 290, 1 495, 1 455, 1 375, 1 350, and 1 300 cm⁻¹; δ_H (CCl₄) 1.1—2.8 (5 H), *ca.* 2.2 (PH₂), and 6.8—8.0 (14 H); δ_P (CCl₄; -20 °C) -90.0 ($^1J_{PH}$ 197 Hz) and -95.9 ($^1J_{PH}$ 190 Hz).

trans-12-Methyl-9,10-dihydro-9,10-ethanoanthracen-11-ylphosphine (21): ν_{\max} (CCl₄) 2 975, 2 300, 1 470, and 1 385 cm⁻¹; δ_H (CCl₄) 0.78 (3 H, d, J 6 Hz), 1.5—2.2 (2 H), 2.45 (2 H, *ca.* d, J 194 Hz, PH₂), 3.7—4.0 (2 H, m), and 6.8—7.3 (8 H, m); δ_P (CCl₄; -20 °C) -114.9 p.p.m. ($^1J_{PH}$ 198 Hz) [also -139.2 p.p.m. ($^1J_{PH}$ 192 Hz) due to the *cis*-isomer of (21)].

3-Methylbicyclo[2.2.1]hept-5-en-2-ylphosphine (22): 2 isomers; ν_{\max} (CCl₄) 2 970, 2 940, 2 340, 1 550, 1 470, and 1 385 cm⁻¹; δ_H (CCl₄) 0.6—2.9 (8 H, m), 3.9—4.4 (3 H, m), 5.8—6.2

(2 H, m); δ_P (CCl₄; -20 °C) -115.4 ($^1J_{PH}$ 192 Hz) and -117.3 p.p.m. ($^1J_{PH}$ 190 Hz).

General Procedure for Thermolysis Experiments.²⁸—The phosphine precursors (17)—(21) (100—500 mg) each in a quartz test tube was introduced into the thermolysis oven (l 60 cm, i.d. 2.5 cm) at *ca.* 10⁻⁶ Torr by means of a sliding steel spatula. The alkenylphosphines (1)—(3) (and in some cases other volatile products formed) were trapped at -196 °C (as a film or over a solvent) for spectroscopic or chemical analysis, and the heavy dienes (anthracene or 1,3-diphenylisobenzofuran), and eventually, the recovered starting material and hydrocarbons (11) and (12), were condensed at the oven exit. In the thermolysis of compound (22), the phosphine (3) was trapped with cyclopentadiene.

Vinylphosphine (1): ν_{\max} (film; -196 °C) 3 065m, 3 020w, 2 995m, 2 290s, 1 595m, 1 435w, 1 400s, 1 2^t_{J.H.I.}, 1 080m, 1 065m, 990s, 955s, 925s, 875s, 850m, 830m, 680m, and 655w, cm⁻¹; m/z (relative intensity, composition) 60.0114 (M^+ , 100%, C₂H₅P), 57.9956 (96, C₂H₃P), 56.9879 (96, C₂H₂P), 55.9804 (32, C₂HP), 44.9947 (22, CH₂P), and 43.9898 (12, CHP); see the Table for the n.m.r. spectroscopic data.

Prop-1-en-2-ylphosphine (2): ν_{\max} (CCl₄) 3 100m, 3 080m, 3 050m, 2 970s, 2 295s, 1 625w, 1 490m, 1 460w, 1 445w, 1 270s, 1 255m, 1 100s, 1 040m, 1 020s, 930m, 905m, and 865s cm⁻¹; m/z (relative intensity, composition) 74.0292 (M^+ , 15%, C₃H₇P), 72.0119 (4, C₃H₅P), 56.9882 (8, C₂H₂P), and 43.9898 (100, CHP); see the Table for the n.m.r. spectroscopic data.

(E)-Prop-1-enylphosphine (3): ν_{\max} (CCl₄) 3 100w, 3 080w, 3 050m, 2 970s, 2 300s, 1 635w, 1 485m, 1 450m, 1 265s, 1 080s, 1 025s, 920m, and 870m cm⁻¹; m/z (relative intensity, composition) 74.0286 (M^+ , 100%, C₃H₇P), 72.0136 (14, C₃H₅P), 71.0057 (28, C₃H₄P), 57.9978 (10, C₂H₃P), 56.9904 (30, C₂H₂P), 45.9968 (16, CH₃P), 44.9900 (16, CH₂P), and 43.9898 (30, CHP); see the Table for the n.m.r. spectroscopic data.

Preparation of Tungsten Complexes.—A THF solution of W(CO)₅·THF⁴ was added, in stoichiometric amount, to the alkenylphosphine (1), (2), or (3) trapped in THF. The mixture was stirred for 1 h at room temperature and the solvent then evaporated. Column chromatography of the residue on silica gel eluting with pentane gave the corresponding complex (23), (25), or (27) as an oil which was analyzed by i.r. and n.m.r. spectroscopy.

Vinylphosphine-pentacarbonyltungsten complex (23): ν_{\max} (CCl₄) 2 080, 1 990, and 1 970—1 935 cm⁻¹; δ_H (CDCl₃) 5.45 (2 H, dm, $^1J_{PH}$ 356 Hz), and 5.7—6.4 (3 H, m); δ_P (THF) -99.2 p.p.m. ($^1J_{PH}$ 356 Hz, $J_{31P^{183}W}$ 216 Hz).

Prop-1-en-2-ylphosphine-pentacarbonyltungsten complex (25): ν_{\max} (CCl₄) 2 080, 1 990, and 1 970—1 940 cm⁻¹; δ_H (CDCl₃) 2.10 (3 H, dt, J 12.5 and 1 Hz), 5.22 (2 H, d, $^1J_{PH}$ 336 Hz), 5.63 (1 H, d, J_{PH} 21 Hz), and 5.66 (1 H, d, J_{PH} 41.5 Hz); δ_P (THF) -85.4 p.p.m. ($^1J_{PH}$ 336 Hz, $J_{31P^{183}W}$ 216 Hz).

(E)-Prop-1-enylphosphine-pentacarbonyltungsten complex (27): ν_{\max} (CCl₄) 2 080, 1 990, and 1 980—1 940 cm⁻¹; δ_H (CDCl₃) 1.90 (3 H, dm, J 7 Hz), 5.16 (2 H, ddd, $^1J_{PH}$ 349 Hz, J_{HH} 6.5 and 1 Hz), and 5.4—6.7 (2 H, m); δ_P (THF) -103.7 p.p.m. ($^1J_{PH}$ 349 Hz, $J_{31P^{183}W}$ 217 Hz [and -126.0 p.p.m. ($^1J_{PH}$ 351 Hz, $J_{31P^{183}W}$ 214 Hz) due to the *Z*-isomer]).

Direct Reduction of the Phosphonates (4)—(7).—This was carried out according to the method described above. After hydrolysis of the crude reaction product, the organic layer was decanted, dried and either analyzed by ³¹P n.m.r. spectroscopy or allowed to react with W(CO)₅·THF at room temperature, thus showing, besides impurities, the presence of either phosphines (1)—(3) or the corresponding tungsten complexes (23), (25), and (27).

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