J. Chem. Sci., Vol. 121, No. 1, January 2009, pp. 23–36.

Allenylphosphonates with a 1,3,2-dioxaphosphorinane ring: Synthesis, structures, stability and utility

N N BHUVAN KUMAR, MANAB CHAKRAVARTY, N SATISH KUMAR, K V SAJNA and K C KUMARA SWAMY*

School of Chemistry, University of Hyderabad, Hyderabad 500 046
e-mail: kckssc@uohyd.ernet.in; kckssc@yahoo.com

MS received 17 July 2008; revised 15 October 2008

Abstract. Synthesis, structures and stability (thermal and air) of allenylphosphonates of the type $(OCH_2CMe_2CH_2O)P(O)C(R)=C=CR'R''$ and $[R''R'C=C=C(R)P(O)(OCH_2)_2]_2C$ are discussed. Thermally activated dimerization (cycloaddition) of $(OCH_2CMe_2CH_2O)P(O)C(H)=C=CMe_2$ leads to the phosphonocyclobutane $[(OCH_2CMe_2CH_2O)P(O)C(H)=]_2[C–CMe_2]_2$ (**18**). Many of these allenes undergo addition of diethylamine to lead to enaminophosphonates that are readily hydrolysed by water to lead to β-ketophosphonates. The latter compounds are useful as Horner–Wadsworth–Emmons (HWE) reagents. Molecular structures of $(OCH_2CMe_2CH_2O)P(O)C(CH_2OH)=C=CH_2$ (**6**), $[H_2C=C=C(H)P(O)(OCH_2)_2]_2C$ (**9**), $(OCH_2CMe_2CH_2O)P(O)CH=C=CH_2$ (**12**), $[(OCH_2CMe_2CH_2O)P(O)C(H)=]_2[C–CMe_2]_2$ (**18**), and the β-ketophosphonate $(OCH_2CMe_2CH_2O)P(O)CH_2)–C(O)CHMe_2$ (**24**) have been determined. In compound **6**, intermolecular hydrogen bonding between the phosphoryl oxygen and the hydroxyl group leading to an infinite chain is observed. In **6**, there is a significant deviation (ca 7°) from the orthogonality expected between the planes containing 4 atoms of (a) $H_2C=C$ and (b) $C=C(H)P$ in the allene part. In **9**, weak C–H…O interaction between the phosphoryl oxygen atom and a CH_2 proton of the six-membered ring is present.

Keywords. Allenylphosphonate; phosphonyl–cyclobutane; cycloaddition; X-ray crystal structure; Horner–Wadsworth–Emmons reaction.

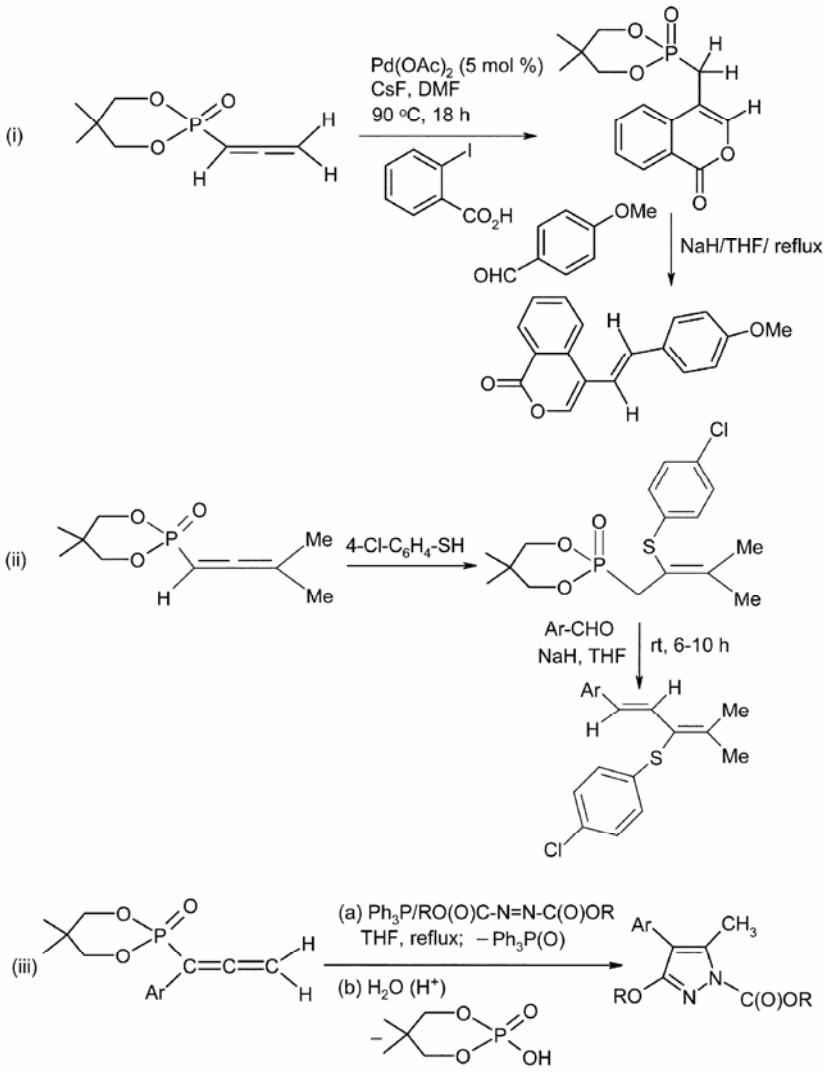
1. Introduction

Allenes have two cumulative but orthogonal C=C bonds that can undergo a variety of reactions and hence can be transformed into a variety of other useful organic compounds.[1] Phosphorylated allenes (allenylphosphonates) that constitute a subclass of allenes are also synthetically useful.[2] In our work on organophosphonates,[3] we needed to synthesize different allenylphosphonates as substrates for a variety of reactions.[4–7] Three synthetically useful reactions using allenylphosphonates developed from our laboratory are shown in scheme 1.[4a,6,7] However, the number of readily accessible allenylphosphonates that are convenient to handle as solids is rather limited. Solid state structural studies on such phosphonates are also rather limited.[8] In addition, very little information is available on the thermal stability as well as allenic group reactivity (in allenylphosphonates) towards water. These are some of the points we address in this paper.

2. Experimental

Chemicals were procured from Aldrich or from local manufacturers; they were purified when required according to standard procedures.[9] All reactions, unless stated otherwise, were performed in a dry nitrogen atmosphere. ^1H, ^{13}C and $^{31}P\{H\}$ NMR spectra were recorded using a 200 or a 400 MHz spectrometer in $CDCl_3$ (unless stated otherwise) with shifts referenced to $SiMe_4$ ($\delta = 0$) or 85% H_3PO_4 ($\delta = 0$). Infrared spectra were recorded on a JASCO FT/IR 5300 FT–IR spectrometer. Mass spectra were recorded using a LCMS 2010A. LC-MS data were obtained using electrospray ionization (positive mode) on a C-18 column at a flow rate 0·2 mL/min using MeOH/water (90 : 10) as eluent. Melting points were determined by using a local hot-stage melting point apparatus and are uncorrected. Microanalyses were performed using a Thermo Finnigan EA1112 analyser. Com-

*For correspondence



Scheme 1.

pounds **1**[10]and **2**[11] were prepared by methods reported in the literature.

2.1 *Synthesis of allenylphosphonates* $(OCH_2CMe_2CH_2O)P(CR^3{=}C{=}CR^1R^2)$ ***(3–5)***

To a solution of substituted propargyl alcohol $R^3C{\equiv}CCR^1R^2OH$ (23·5 mmol) in dry THF (50 mL) was added triethylamine (2·47 g, 3·40 mL, 23·5 mmol), the mixture stirred for 5 min, and then ($OCH_2CMe_2CH_2O$)PCl (**1**) (4·11 g, 3·37 mL, 23·5 mmol) in THF (20 mL) was added drop-wise (~ 0·5 h) at 0°C. The contents were brought to room temperature, stirred further for 1 h, and then refluxed for 16 h. Triethylamine hydrochloride formed was filtered off and solvent removed *in vacuo* from the filtrate. Allenes **3**–**5** were purified by column chromatography (silica gel; ethyl acetate-hexane 2 : 3).

2·1a *$(OCH_2CMe_2CH_2O)PC[(CH_2)_4CH_3]{=}C{=}CH_2$ (3)*: Yield: 4·87 g (80%; using 23·5 mmol of **1**). M.p.: 57–60°C. IR (KBr): 3071, 2928, 2855, 1944, 1769, 1470, 1372, 1258, 1047, 993, 824 cm^{-1}. ^1H NMR: δ 0·90 (*t*, ^3J(H-H) = 6·8 Hz, 3 H, CH_2CH_3), 0·99 and 1·20 (2*s*, 6 H, $C(CH_3)_2$), 1·33–1·35 (*m*, 4 H, $CH_2CH_2CH_3$), 1·52–1·56 (*m*, 2H, $PCCCH_2$), 2·16–2·23 (*m*, 2H, $PCCH_2$), 3·93–4·09 (*m*, 4H, OCH_2), 5·04 (*td*, ^4J(P–H) = 13·6 Hz, ^5J(H–H) ~ 3·1 Hz, 2H, $=CH_2$). ^{13}C NMR: δ 14·0 (*s*, CH_2CH_3), 21·0 and 21·7 (2*s*, $C(CH_3)_2$), 22·3 (*s*, CH_2CH_3), 27·6 (*d*, ^4J(P–C) = 6·1 Hz, $CH_2CH_2CH_3$), 27·8 (*d*, ^3J(P–C) = 6·1 Hz, $PCCH_2CH_2$), 31·2 [*s* (^2J(P–C) < 2·0 Hz), $PCCH_2$], 32·6 (*d*, ^3J(P–C) = 7·3 Hz, $C(CH_3)_2$), 76·7 (*s*, $2OCH_2$), 77·3 (*s*, $=CH_2$), 92·0 (*d*, ^1J(P–C) = 180·7 Hz, PC), 211·5 (*d*, ^2J(P–C) = 6·1 Hz, PCC) [the assignment of the alkyl carbons is tentative]. ^{31}P NMR: δ 11·3· LC/MS *m/z* 259 $[M + 1]^+$·

2.1b *($OCH_2CMe_2CH_2O$)PC[$(CH_2)_5CH_3$]=C=CH_2 (**4**)*: Yield: 4·99g (78% using 23·5 mmol of **1**). M.p.: 58–61°C; IR (KBr): 3075, 2926, 2857, 1943, 1773, 1470, 1372, 1258, 1047, 997, 826 cm^{-1}. ^1H NMR: δ 0·89 (*t*, ^3J(H–H) ~ 6·8 Hz, 3H, CH_2CH_3), 0·99 and 1·19 (2*s*, 6H, $C(CH_3)_2$), 1·30–1·37 (*m*, 6H, $CH_2CH_2CH_2CH_2CH_3$), 1·50–1·55 (*m*, 2H, PCCCH_2), 2·16–2·21 (*m*, 2H, PCCH_2), 3·92–4·09 (*m*, 4H, OCH_2), 5·04 (*d*, ^4J(P–H) = 13·6 Hz, 2H, =CH_2). ^{13}C NMR: δ 14·0 (*s*, CH_2CH_3), 21·0 and 21·7 (2*s*, $C(CH_3)_2$), 22·5 (*s*, CH_2CH_3), 27·7$_7$, 27·8$_3$, 28·7 and 31·5 (4*s*, PC$CH_2CH_2CH_2CH_2CH_3$), 32·5 (*d*, ^3J(P–C) = 6·6 Hz, $C(CH_3)_2$), 76·6 and 76·7 (2*s*, OCH_2), 77·2 (*d*, ^3J(P–C) = 15·8 Hz, =CH_2), 92·0 (*d*, ^1J(P–C) = 181·3 Hz, P*C*), 211·5 (*d*, ^2J(P–C) = 5·9 Hz, PC*C*). ^{31}P NMR: δ 12·2. Anal. Calc. for $C_{14}H_{25}O_3P$: C, 61·75; H, 9·25. Found: C, 61·76; H, 9·23.

2.1c *($OCH_2CMe_2CH_2O$)PC(Ph)=C=CH(CH=CHMe) (**5**)*: Yield: 5·01 g (70% using 23·5 mmol of **1**). M.p.: 122–124°C; IR (KBr): 2961, 2926, 1927, 1815, 1597, 1491, 1476, 1456, 1267, 1055, 1003 cm^{-1}. ^1H NMR: δ 0·91 and 1·33 (2*s*, 6H, $C(CH_3)_2$), 1·85 (*dd*, ^3J(H–H) = 5·3 Hz, ^4J(H–H) = 3·5 Hz, 3H, CH_3), 3·96–4·02 (*m*, 4H, OCH_2), 5·92–5·97 (*m*, 2H, C*H*=C*H*–CH_3), 6·44 (*dd*, 1H, ^4J(P–H) ~ 12·0 Hz, ^3J(H–H) ~6·0 Hz, C=C=C*H*), 7·28–7·63 (*m*, 5H, Ar*C*). ^{13}C NMR (100 MHz, $CDCl_3$): δ 18·5 (*s*, =C(H)CH_3), 20·9 and 22·0 (2*s*, $C(CH_3)_2$), 32·6 (*d*, ^3J(P–C) = 7·0 Hz, $C(CH_3)_2$), 77·2 and 77·6 (2*d*, ^2J(P–C) = 7·0 Hz, OCH_2), 97·7 (*d*, ^3J(P–C) = 16·0 Hz, C=C=*C*H), 97·3 (*d*, ^1J(P–C) = 181·0 Hz, P*C*), 122·8 (*d*, ^4J(P–C) = 10·0 Hz, C=C=CH–*C*H), 127·8, 127·9, 128·1, 128·8, 131·2$_6$, 131·3$_4$ (Ar*C*), 132·0 (*d*, ^5J(P–C) = 5·0 Hz, CH=*C*H(Me)), 212·8 (*d*, ^2J(P–C) = 3·0 Hz, PC*C*). ^{31}P NMR (160 MHz, $CDCl_3$): δ 6·7. Anal. Calc. for $C_{17}H_{21}O_3P$: C, 67·09; H, 6·96. Found: C, 67·05; H, 6·96.

2.2 *Synthesis of the phosphonate allenol $C(CH_2O)_2${P(O)C[CH_2(OH)]=C=CH_2} (**6**) and the phosphono-butadiene [($OCH_2CMe_2CH_2O$)(O)P-C(=CH_2)]$_2$ (**7**)*

To a solution of diol (4·60 g, 53·4 mmol) and triethylamine (5·41 g, 7·45 mL, 53·4 mmol) in THF (135 mL), compound **1** (9·00 g, 7·40 mL, 53·4 mmol) in THF (25 mL) was added drop-wise at –78°C, the mixture stirred for 2 h, brought to room temperature and was then heated under reflux for 15–18 h. Triethylamine hydrochloride formed was filtered off and the solvent removed *in vacuo*. Yield was 80% on the basis of ^{31}P NMR; the remaining material was the 1,3-butadiene [($OCH_2CMe_2CH_2O$)(O)P–C(=CH_2)]$_2$ (**7**). Pure compound **6** [isolated yield 2·0 g (17%); low yield because of the other product] was obtained by crystallization from THF. M.p.: 134–138°C. IR (KBr): 3304, 3069, 2975, 2938, 1968, 1939, 1827, 1719, 1472, 1238, 1061, 1009, 839 cm^{-1}. ^1H NMR: 0·99 and 1·19 (2*s*, 6H, $C(CH_3)_2$), 2·50 (*br*, 1H, OH), 4·00–4·12 (*m*, 4H, OCH_2), 4·33 (*td*, ^3J(P–H) = 14·0 Hz, ^5J(H–H) = 2·0 Hz, 2H, CH_2OH), 5·15 (*td*, ^4J(P–H) = 12·8 Hz, ^5J(H–H) = 2·0 Hz, 2H, C=CH_2). ^{13}C NMR: 20·9 and 21·7 (2s, $C(CH_3)_2$), 32·5 (*d*, ^3J(P–C) = 7·0 Hz, $C(CH_3)_2$), 60·3 (*d*, ^2J(P–C) = 8·0 Hz, CH_2OH), 77·1 (*d*, ^2J(P–C) = 6·0 Hz, POCH_2), 78·0 (*d*, ^3J(P–C) = 14·0 Hz, C=CH_2), 92·9 (*d*, ^1J(P–C) = 183·0 Hz, P*C*), 211·3 (*d*, ^2J(P–C) = 6·0 Hz, PC=*C*). ^{31}P NMR: 10·1. Anal. Calcd for $C_9H_{15}O_4$: C: 49·54, H 6·93. Found: C, 49·47; H, 7·02.

Compound 7: This was isolated from the same reaction in low yield (0·93 g, 5%), but a *quantitative* yield could be obtained by using 1 : 2 molar reaction of propargylic alcohol to **1**. M.p.: 182–186°C; IR (KBr): 2973, 2888, 1931, 1578, 1478, 1265, 1055, 1005, 957 cm^{-1}. ^1H NMR: δ 0·96 and 1·24 (2*s*, 12 H, $C(CH_3)_2$), 3·98–4·11 (*m*, 8H, OCH_2), 6·27 (*d*, ^3J(P–H) = 20·1 Hz, 1H, =CH_AH_B, *cis* to P), 6·56 (*d*, ^3J(P–H) = 44·9 Hz, 1H, =CH_AH_B, *trans* to P). ^{13}C NMR: δ 21·1, 21·9 (2*s*, $C(CH_3)_2$), 32·5 (*d* with virtual coupling (?), ^3J(P–C) ~ 6·0 Hz, CMe_2), 76·9 (*d* with virtual coupling (?), ^2J(PC) ~ 6·0 Hz, OCH_2), 132·1 (*d*, ^1J(P–C) = 182·0 Hz, P*C*), 134·2 (*d* with virtual coupling (?), ^2J(P–C) ~ 12·0 Hz, PC=*C*)· ^{31}P NMR: δ 9·0. Anal. Calcd for $C_{14}H_{24}O_6P_2$: C: 49·54, H 6·93. Found: C, 47·97; H, 6·93.

2.3 *Synthesis of bis(allenyl)phosphonates [R^1R^2C=C=C(H)P(O)$(OCH_2)_2$]$_2$C (R^1 = R^2 = H (**9**), R^1 = Me, R^2 = Et (**10**), R^1 = R^2 = Me (**11**)): Typical procedure for **9** and identification of the intermediate **8***

To a solution of **2** (2·04 g, 7·4 mmol) and triethylamine (1·49 g, 14·8 mmol) in dry THF (30 mL) at 0°C, the propargyl alcohol (14·8 mmol) was added at 0°C with continuous stirring. The reaction mixture was brought to room temperature, stirred for 3 h and filtered. The tricoordinate compound **8** [>90% by ^{31}P NMR] was characterized by ^1H and ^{31}P NMR spectra [^1H NMR: 2·43 (*s*, 2H, C≡C*H*), 3·30–3·35 and 3·92–

3·96 (m each, 2 + 2 H, OCH_2–C≡CH; the two groups are in slightly different environments), 4·20–4·46 (*m*, 8H, CH_2OP). ^{31}P NMR: 125·7]. In the ^{1}H NMR spectrum taken at this stage, solvent peaks (THF: δ 1·80 and 3·70) were also observed. The filtrate was heated under reflux for 15–18 h and the solvent removed in vacuo. Compound **9** (1·72 g, 79%) was purified by crystallization from methanol. M.p.: 199–201°C. IR (KBr): 3069, 2984, 2915, 1944, 1474, 1279, 1237, 1194, 1156, 1024, 843 cm^{-1}. ^{1}H NMR: 4·17–4·27 and 4·42–4·52 (2 m, 8H, OCH_2), 5·16–5·21 (*m*, 4H, C=CH_2), 5·40–5·42 (*m*, 2H, PC*H*). The compound had a poor solubility and hence ^{13}C NMR spectrum was not recorded. ^{31}P NMR: 11·36. Anal. Calcd. $C_{11}H_{14}O_6P_2$: C, 43·44; H, 4·64. Found: C, 43·42; H, 4·69.

Compounds **10** and **11** were purified using column chromatography (ethyl acetate). Compound **12** was purified by column chromatography using hexane-ethyl acetate (1 : 1) mixture. Yields were above 95% for all these compounds on the basis of crude ^{31}P NMR using the *same* molar quantities; isolated yields are given below.

2.3a *C(CH_2O)$_4${P(O)C(H)=C=CMeEt}$_2$ (**10**):* Yield: 2·11 g, 74%. M.p.: 106–110°C. IR (KBr): 2972, 2915, 1962, 1698, 1458, 1370, 1269, 1200, 1150, 1020, 828 cm^{-1}. ^{1}H NMR: δ 1·07 (*t*, ^3J(H–H) = 7·2 Hz, 6H, CH$_2$CH_3), 1·80–1·83 (*m*, 6H, C=CCH_3), 2·04–2·13 (*m*, 4H, CH_2CH$_3$), 4·16–4·48 (*m*, 8H, OCH_2), 5·30–5·35 (*m*, 2H, PC*H*). ^{13}C NMR: δ 11·9 (*s*, CH$_2$CH_3), 17·5 and 17·6 (2*s*, *C*H$_2$CH$_3$), 26·0 and 26·1 (2*s*, C=C*C*H$_3$), 37·3 (*t*, ^3J(P–C) = 6·0 Hz, OCH$_2$*C*), 67·5, 67·6, 67·7 and 67·9 (4*d*, ^2J(P–C) ~ 6·0 Hz, O*C*H$_2$), 77·3 (*d*, ^1J(P–C) = 199·1 Hz, P*C*), 104·5 (*d*, ^3J(P–C) = 17·4 Hz, P-C=C=*C*(Me)(Et)), 211·8 (*s*, PC=*C*). ^{31}P NMR: δ 13·0. LC/MS *m/z* 389 [M + 1]$^+$. Diastereomers may be expected in this case, but we did not get evidence for the presence of these in our studies.

2.3b *C(CH_2O)$_4${P(O)C(H)=C=CMe$_2$}$_2$ (**11**):* Yield: 1·98 g, 76%. M.p.: 140–144°C. IR (KBr): 2986, 2907, 1964, 1682, 1364, 1269, 1200, 1152, 1020, 820 cm^{-1}. ^{1}H NMR: δ 1·80–1·88 (*m*, 12H, C=C(CH_3)$_2$), 4·09–4·50 (*m*, 8H, OCH_2), 5·22–5·25m, 2H, PC*H*). ^{13}C NMR: δ 19·0 and 19·1 (2*s*, C=C(*C*H$_3$)$_2$), 37·2 (*s*, OCH$_2$*C*), 67·7 and 67·9 (2*d*, ^2J(P–C) = 6·5 Hz, O*C*H$_2$), 75·4 (*d*, ^1J(P–C) = 199·1 Hz, P*C*), 98·6 (*d*, ^3J(P–C) = 17·2 Hz, C=*C*Me$_2$), 212·3 (*s*, PC=*C*). ^{31}P NMR: δ 12·6. LC/MS *m/z* 361 [M + 1]$^+$.

Allenylphosphonates **12–16** Compounds **12** and **14** were prepared by using literature procedures.[10] Allenes **13** and **15–16** were synthesized similarly using 10·0 mmol of **1**.

2.3c *(OCH$_2$CMe$_2$CH$_2$O)P(O)CH=C=CMe(H) (**13**):* Yield: 1·74 g (86%). M.p.: 50–52°C. IR (KBr): 1956, 1476, 1373, 1281, 1061, 1011 cm^{-1}. ^{1}H NMR: δ 0·94 and 1·16 (2*s*, 6H, C(CH_3)$_2$), 1·68–1·82 (*m*, 3H, C=C(H)CH_3), 3·96–4·12 (*m*, 4H, OCH_2), 5·24–5·32 (*m*, 1H, C*H*Me), 5·33–5·59 (*m*, 1H, PC*H*). ^{13}C NMR: δ 12·3 (*d*, ^4J(PC) = 7·0 Hz, CH*C*H$_3$), 20·4 and 21·3 (2*s*, C(*C*H$_3$)$_2$), 32·1 (*d*, ^3J(PC) = 6·0 Hz, *C*Me$_2$), 76·4 and 76·5 (2*d*, ^2J(PC) = 6·0 Hz each, OCH$_2$), 77·5 (*d*, ^1J(PC) = 192·0 Hz, P*C*), 86·9 (*d*, ^3J(PC) = 16·0 Hz, C=*C*H$_2$), 212·3 (*br s*, C=*C*=CHMe). ^{31}P NMR: δ 7·9.

2.3d *(OCH$_2$CMe$_2$CH$_2$O)P(O)CH=C=CMeEt (**15**):* Yield: 1·79 g (78%). M.p.: 93–94°C. IR (KBr): 1958, 1474, 1372, 1277, 1061, 1009 cm^{-1}. ^{1}H NMR: δ 0·83 and 1·04 (2*s*, 6H, C(CH_3)$_2$), 0·92 (*t*, ^3J(HH) = 7·8 Hz, 3H, C=CMeCH$_2$CH_3), 1·65 (*dd*, ^5J(PH) = 6·8 Hz, ^5J(HH) = 2·9 Hz, 3H, C=CCH_3Et), 1·88–1·97 (*m*, 2H, C=CMeCH_2CH$_3$), 3·79–3·96 (*m*, 4H, OCH_2), 5·14–5·19 (*m*, 1H, PC*H*). ^{13}C NMR: δ 11·7 (*d*, ^5J(PC) = 2·4 Hz, C=CMeCH$_2$*C*H$_3$), 17·5 (*d*, ^4J(PC) = 7·3 Hz, =CMe*C*H$_2$CH$_3$), 20·8 and 21·5 (2*s*, C(*C*H$_3$)$_2$), 26·0 (*d*, ^4J(PC) = 7·3 Hz, C*C*H$_3$Et), 32·3 (*d*, ^3J(PC) = 6·1 Hz, *C*Me$_2$), 77·9 (2*d*, ^1J(PC) = 195·3 Hz, P*C*), 76·2 and 76·3 (2*s*, OCH_2), 103·3 (*d*, ^3J(PC) = 17·0 Hz, C=*C*MeEt), 210·3 (*br s*, C=*C*=CMeEt). ^{31}P NMR: δ 9·3. Anal. Calcd for $C_{11}H_{19}O_3P$: C, 57·39; H, 8·26. Found: C, 57·64; H, 8·13.

2.3e *(OCH$_2$CMe$_2$CH$_2$O)P(O)C(Ph)=C=C(H)Et (**16**)*: Yield: 2·45 g (84%). M.p.: 108–109°C. IR (KBr): 3057, 3022, 1948, 1597, 1493, 1372, 1262, 1059, 1009 cm^{-1}. ^{1}H NMR: δ 0·83 and 1·23 (2*s*, 6H, C(CH_3)$_2$), 1·09 (*t*, ^3J(HH) = 7·6 Hz, 3H, CH$_2$CH_3), 2·18 (*qrt*, ^3J(HH) = 7·6 Hz, 2H, CH_2CH$_3$), 3·77–4·01 (*m*, 4H, OCH_2), 5·70–5·89 (*m*, 1H, PC*H*), 7·17–7·28 (*m*, 3H, Ar-*H* (meta and para)), 7·55 (*d*, ^3J(HH) ~ 7·0 Hz, Ar-*H* (ortho)). ^{13}C NMR: δ 13·4 (*s*, CH$_2$CH_3), 20·8 (*s*, *C*H$_3$), 21·4 (*d*, ^4J(PC) = 6·1 Hz, *C*H$_2$CH$_3$), 21·9 (*s*, *C*H$_3$), 32·5 (*d*, ^3J(PC) = 6·6 Hz, *C*Me$_2$), 76·8 and 76·9 (2*s*, OCH_2), 96·4 (*d*, ^1J(PC) ~ 185·0 Hz, P*C*), 96·8 (*d*, ^3J(PC) = 14·9 Hz, C=*C*HEt), 127·5, 127·6, 127·7, 128·6, 132·3, 132·4, 209·5 (*br s*, C=*C*=CHEt). ^{31}P NMR: δ 7·3.

2.3f *[H$_2$C=C=C(Ph)P(O)(OCH$_2$)$_2$]$_2$C (**17**):* This compound was prepared in a manner similar to that for **9** using the same molar quantities. Yield: 2·59 g

(74%). M.p. >300°C. IR (KBr): 3059, 2982, 1939, 1595, 1493, 1269, 1155, 1076, 1020, 938 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 3·99–4·04, 4·22–4·33 and 4·58–4·65 (three groups of *m*, 8H, OCH_2), 5·42 (*d*, 4H, ^4J(P–H) = 13·2 Hz, $=CH_2$), 7·26–7·55 (*m*, 10 H, Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 37·5 (*t*, ^3J(P–C) = 5·7 Hz, OCH_2C), 68·5 and 68·9 (2*d*, ^2J (P–C) = 7·0 Hz each, OCH_2), 79·5 (*d*, ^3J(P–C) = 15·1 Hz, C=CH_2), 94·8 (*d*, ^1J(P–C) = 185·2 Hz, P*C*), 127·7, 127·8, 128·5, 129·0, 129·9, 130·0 (Ar*C*), 213·5 (*d*, ^2J(P–C) ~4·6 Hz, C=*C*=C). ^{31}P NMR (160 MHz, $CDCl_3$): δ 10·6. LC/MS *m/z* 457 $[M + 1]^+$.

2.4 *Synthesis of the allene dimer [(OCH$_2$C Me$_2$CH$_2$O)PCH=]$_2$[C-CMe$_2$]$_2$ (**18**):* Allene **14** (0·2 g, 0·92 mmol) was heated at 185°C for 6 h. TLC (EtOAc/hexane) showed two spots (approximate ratio 4 : 1) under the UV lamp. The major component (**18**) was separated by column chromatography (silica gel, ethyl acetate-hexane, 3 : 2). Yield (isolated): 0·14 g (68%). M.p.: 226–228°C. IR (KBr): 1622, 1476, 1372, 1265, 1061, 1013 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 1·07 and 1·10 (2*s*, 12H, C(CH_3)$_2$), 1·33 (*s*, 12H, =C(CH_3)$_2$), 3·87 (*dd* $\rightarrow$ *t*, ^3J(P–H) ~ 11·3 Hz each, 2 H, OCH_2), 4·15 (*dd* $\rightarrow$ *t*, ^3J(P–H) ~ 11·3 Hz each, 2H, OCH_2), 5·62 (*d*, ^2J(P–H) = 16·3 Hz, 1H, P*CH*). ^{13}C NMR (50 MHz, $CDCl_3$): δ 21·5 and 22·1 (2*s*, CH(CH_3)$_2$ + =C(CH_3)$_2$, two methyl signals have merged), 32·6 (*br*, CMe_2), 49·7 (*br*, CMe_2 of four membered ring), 75·6 (OCH_2), 105·2 (*d*, ^1J(P–C) = 186·8 Hz, P*C*H), 170·8 (*d*, ^2J(*P–C*) = 43·5 Hz, PC=*C*). ^{31}P NMR (160 MHz, $CDCl_3$): δ 11·0. LC-MS: *m/z* 434 $[M + 2]^+$. Anal. Calcd. for $C_{20}H_{34}O_6P_2$: C, 55·54; H, 7·92. Found: C, 55·47; H, 7·97.

This reaction was also performed in the presence of hydroquinone (radical quencher), but the ^{31}P NMR spectrum of the reaction mixture showed several products [δ (*P*): –12·3, 10·1, 10·2, 11·0, 11·3, 13·3, 21·8, 23·9] and hence was not analysed further.

2.4a *Attempted synthesis of the anthracene adduct (OCH$_2$CMe$_2$CH$_2$O)PCH(C$_{14}$H$_{10}$) C=CMe$_2$ (**19**):* A mixture of allene **14** (0·9 g, 4·16 mmol) and anthracene (1·13 g, 6·30 mmol) was heated at 185°C for 5–6 h. TLC (EtOAc/hexane) showed a new UV active spot under the UV lamp and some unreacted starting material **14**. The compound corresponding to the UV active spot (**18**) was separated by column chromatography [silica gel, ethyl acetate-hexane, 3 : 2; yield 0·36 g (20%)]. X-ray structure was determined for this sample. The expected compound **19** could not be identified.

2.5 *Synthesis of the enaminophosphonates (OCH$_2$CMe$_2$CH$_2$O)P(O)CH=C(NEt$_2$)CH$_2$R [R = H (**20**), Me (**21**)]*

To a solution of allenylphosphonates (**12**–**13**) (1·0 mmol) in acetonitrile (15 mL), diethylamine (1·0 mmol) was added slowly via syringe. The reaction mixture was heated under reflux for 4 h with continuous stirring. Solvent was removed *in vacuo* to obtain the required compound. The reaction was very clean without any side products. These were characterized spectroscopically, because of their hydrolytic instability leading to the β-ketophosphonates.

2.5a *Compound **20**:* Yield: Quantitative. M.p.: 58–60°C. IR (KBr): 1570, 1439, 1219, 1061, 1001 cm^{-1}. ^1H NMR: δ 0·92 and 1·10 (2*s*, 6H, C(CH_3)$_2$), 1·09 (*t*, ^3J(H-H) = 7·1 Hz, 3H, N(CH_2CH_3)$_2$), 2·26 (*d*, ^4J(P–H) = 1·5 Hz, 3H, C(NEt$_2$)CH_3), 3·20 (*q*, ^3J(H–H) = 7·1 Hz, 2H, N(CH_2CH_3)$_2$), 3·65–3·74 (*m*, 3H, OCH_2 + P*CH*), 4·16–4·20 (*dd* $\rightarrow$ *t*, ^2J(H–H) = 2·3 Hz, ^3J(P–H) ~ 9·4 Hz, 2H, OCH_2). ^{13}C NMR: δ 12·4 (*s*, C(NCH_2CH_3)$_2$Me), 17·2 (*d*, ^3J(P–C) = 4·4 Hz, C(NEt$_2$)CH_3), 21·2 and 21·6 (2*s*, C(CH_3)$_2$), 32·1 (*d*, ^3J(P–C) = 4·8 Hz, CMe_2), 43·6 (*s*, C(NCH_2 CH_3)$_2$Me), 70·1 (*d*, ^1J(P–C) = 218·9 Hz, P*C*), 74·3, 74·4 (2*s*, OCH_2), 160·0 (*d*, ^2J(P–C) = 21·6 Hz, PCH=*C*). ^{31}P NMR: δ 24·7.

2.5b *Compound **21**:* Yield: Quantitative. M.p.: 55–56°C. IR (KBr): 1573, 1474, 1360, 1217, 1059, 1005 cm^{-1}. ^1H NMR: δ 0·84 (*s*, 3H, C(CH_3)), 0·99–1·06 (many lines, 12H, C(CH_3) + N(CH_2CH_3)$_2$) + =C(CH_2CH_3)), 1·89 (*d*, ^4J(P–H) = 1·5 Hz, 3H, C(CH_2CH_3), 2·56 (*q* ^3J(H–H) = 6·6 Hz, 2H, CH_2CH$_3$), 3·10 (*q*, ^3J(H–H) = 6·9 Hz, 2H, N(CH_2CH_3)$_2$), 3·55–3·63 (*m*, 3H, OCH_2 + P*CH*), 4·06 (*t*, ^3J(P–H) = 10·5 Hz, 2H, OCH_2). ^{13}C NMR: δ 12·3 (*s*, C(NCH_2CH_3)$_2$Et), 13·6 (*s*, (CH_2CH_3), 19·6, 21·0 (2*s*, C(CH_3)$_2$), 23·2 (*d*, ^3J(P–C) = 4·4 Hz, C(CH_2CH_3), 31·9 (*d*, ^3J(P–C) = 5·2 Hz, CMe_2), 43·0 (*s*, C(NCH_2CH_3)$_2$ Et), 69·5 (*d*, ^1J(P–C) = 217·9 Hz, P*C*), 74·2 and 74·3 (2*s*, OCH_2), 165·3 (*d*, ^2J(P-C) = 22·1 Hz, PCH=*C*). ^{31}P NMR: δ 23·8.

2.6 *Synthesis of β-ketophosphonates (OCH$_2$CMe$_2$CH$_2$O)P(O)CR^{3}C(O)CHR^{1}R^2 (**22–26**)*

To a solution of allenyl phosphonates **12–16** (10·0 mmol) in dry acetonitrile (20 mL) was added

diethylamine (0·73 g, 1·03 mL, 10·0 mmol) and the mixture stirred for 4 h. The reaction mixture was then treated with 2N HCl, stirred for 8 h and extracted with dichloromethane (CH_2Cl_2) (3 × 30 mL). The CH_2Cl_2 layer was dried (Na_2SO_4), solvent was removed and the residue purified by column chromatography (silica gel; hexane-ethyl acetate) to obtain **22–26**.

2.6a *$(OCH_2CMe_2CH_2O)P(O)CH_2C(O)Me$ (22)*: Yield: 1·94 g (94%). M.p.: 85–86°C. IR (KBr): 1714, 1273, 1061, 1009 cm^{-1}. ^1H NMR: δ 0·90 and 0·99 (2*s*, 6H, $C(CH_3)_2$), 2·30 (*s*, 3H, $C(O)CH_3$), 3·09 (*d*, ^2J(P–H) = 21·5 Hz, 2H, PCH_2), 3·80–4·05 (*m*, 4H, OCH_2). ^{13}C NMR: δ 21·0 and 21·5 (2*s*, $C(CH_3)_2$), 31·5 (*d*, ^3J(P–C) = 4·1 Hz, $C(O)CH_3$), 32·5 (*d*, ^3J(P–C) = 5·3 Hz, CMe_2), 41·7 (*d*, ^1J(P–C) = 123·9 Hz, P*C*), 76·1, 76·2 (2*s*, OCH_2), 199·3 (*d*, ^2J(P–C) = 6·0 Hz, $PCH_2C(O)$). ^{31}P NMR: δ 13·8. Anal. Calcd for $C_8H_{15}O_4P$: C, 46·60; H, 7·33. Found: C, 46·84; H, 7·32.

2.6b *$(OCH_2CMe_2CH_2O)P(O)CH_2C(O)Et$ (23)*: Yield: 1·87 g (85%). M.p.: 98–100°C. IR (KBr): 1715, 1267, 1063, 1007 cm^{-1}. ^1H NMR: δ 0·93–1·09 (3 lines, 9H, $C(CH_3)_2 + CH_2CH_3$), 2·58 (*qrt*, ^3J(H–H) ~ 6·0 Hz, 2H, CH_2CH_3), 3·12 (*d*, ^2J(P–H) = 21·0 Hz, 2H, PCH_2), 3·83–4·12 (*m*, 4H, OCH_2). ^{13}C NMR: δ 7·4 (*s*, CH_2CH_3), 21·1 and 21·5 (2*s*, $C(CH_3)_2$), 32·5 (*d*, ^3J(P–C) = 6·6 Hz, CMe_2), 37·5 (*s*, CH_2CH_3), 40·2 (*d*, ^1J(P–C) = 122·6 Hz, P*C*), 76·0 and 76·1 (2*s*, OCH_2), 201·9 (*d*, ^2J(P–C) = 6·1 Hz, $PCH_2C(O)$). ^{31}P NMR: δ 14·0. Anal. Calcd for $C_9H_{17}O_4P$: C, 49·09; H, 7·78. Found: C, 48·88; H, 7·75.

2.6c *$(OCH_2CMe_2CH_2O)P(O)CH_2C(O)CHMe_2$ (24)*: Yield: 1·42 g (61%). M.p.: 102–104°C. IR (KBr): 1713, 1474, 1267, 1059, 1009 cm^{-1}. ^1H NMR: δ 1·00, 1·10 (2*s*, 6H, $C(CH_3)_2$), 1·06 (*d*, ^3J(H–H) = 6·8 Hz, 6H, $CH(CH_3)_2$), 2·77–2·87 (*qnt*, ^3J(H–H) = 6·8 Hz, 1H, $CH(CH_3)_2$), 3·12 (*dd*, ^2J(P–H) = 19·6 Hz, ^2J(H–H) = 2·0 Hz, 2H, PCH_2), 3·88–4·14 (*m*, 4H, OCH_2). ^{13}C NMR: δ 17·9 (*s*, $CH(CH_3)_2$), 21·2 and 21·6 (2*s*, $C(CH_3)_2$, 32·5 (*d*, ^3J(P–C) = 6·6 Hz, CMe_2), 37·3 (*s*, $CH(CH_3)_2$), 40·9 (*d*, ^1J(P–C) = 104·3 Hz, P*C*), 76·0 and 76·1 (2*s*, OCH_2), 205·5 (*d*, ^2J(P–C) = 6·0 Hz, $PCH_2C(O)$). ^{31}P NMR: δ 14·2.

2.6d *$(OCH_2CMe_2CH_2O)P(O)CH_2C(O)CH(Me)Et$ (25)*: Yield: 1·30 g (56%). M.p.: 92–94°C. IR (KBr): 1711, 1634, 1273, 1063, 1009 cm^{-1}. ^1H NMR: δ 0·81 (*t*, ^3J(H–H) = 7·4 Hz, 3H, CH_2CH_3), 1·00 and 1·06 (2*s*, 6H, $C(CH_3)_2$), 1·07 (*d*, ^3J(H–H) = 6·7 Hz, 3H, $CHCH_3$), 1·27–1·42, 1·54–1·73 (2*m*, 2H, CH(Me) CH_2CH_3), 2·69 (*m*, 1H, $CH(CH_3)CH_2CH_3$), 3·20 (*d*, ^2J(P–H) = 22·3 Hz, 2H, PCH_2), 3·89–4·14 (*m*, 2H, OCH_2). ^{13}C NMR: δ 11·3 (*s*, $CHCH_2CH_3$), 15·2 (*s*, $CH(CH_3)CH_2CH_3$), 21·1 and 21·6 (2*s*, CMe_2), 25·4 (*s*, $CH(CH_3)CH_2CH_3$), 32·5 (*d*, ^3J(PC) = 7·3 Hz, $C(CH_3)_2$), 38·1 (*d*, ^1J(P–C) = 126·1 Hz, P*C*), 48·8 (*s*, $CH(CH_3)CH_2CH_3$), 76·0 and 76·1 (2*s*, OCH_2), 205·4 (*d*, ^2J(P–C) = 6·0 Hz, $PCH_2C(O)$). ^{31}P NMR: δ 14·6.

2.6e *$(OCH_2CMe_2CH_2O)P(O)CHPhC(O)CH_2CH_2CH_3$ (26)*: Yield: 1·33 g (43%). M.p.: 138–140°C. IR (KBr): 1717, 1263, 1059, 1005 cm^{-1}. ^1H NMR: δ 0·82 and 1·01 (2*s*, 6 H, $C(CH_3)_2$), 0·84 (*t*, ^3J(H–H) = 6·3 Hz, 3H, $CH_2CH_2CH_3$), 1·58 (*m*, 2H, $CH_2CH_2CH_3$), 2·51–2·64 (*m*, 2H, $CH_2CH_2CH_3$), 3·67–3·88 (*m*, 2H, OCH_2), 4·03 (*t*, ^3J(P-H) ~ 6·0 Hz, 2H, OCH_2), 4·53 (*d*, ^2J(P–H) = 21·2 Hz, 2H, PCH_2), 7·23–7·49 (*m*, 5H, Ar-*H*). ^{13}C NMR: δ 13·3 (*s*, $CH_2CH_2CH_3$), 16·9 (*s*, $CH_2CH_2CH_3$), 21·1 and 21·7 (2*s*, $C(CH_3)_2$), 32·6 (*d*, ^3J(P–C) = 7·4 Hz, CMe_2), 45·2 (*s*, $CH_2CH_2CH_3$), 58·5 (*d*, ^1J(P–C) = 129·0 Hz, P*C*), 76·0 and 76·1 (2*d*, ^3J(PC) = 6·7 Hz each, $2OCH_2$), 128·1, 128·8, 129·6, 129·9, 130·5, 202·9 (*d*, ^2J(PC) = 4·9 Hz, $PCH_2C(O)$). ^{31}P NMR: δ 12·3.

2.7 *HWE reaction using the β-ketophosphonates **22–23**: Synthesis of α,β-unsaturated ketones **27a–e** and **28a–f***

To the *β*-ketophosphonate **22** or **23** (10·0 mmol) in dry THF (20 mL), K_2CO_3 (1·66 g, 12·0 mmol) was added and the reaction mixture stirred for 30 min at room temperature. Then aldehyde (10·0 mmol) was added in one lot and the reaction mixture was refluxed for 24 h. After cooling to room temperature, the reaction mixture was quenched with cold water (20 mL) and extracted with ether (2 × 30 mL). The ether layer was dried (Na_2SO_4), the solvent removed and the residue was purified by column chromatography (silica gel; hexane-ethyl acetate) to obtain **27a–e** or **28a–f**.

2.7a *C_6H_4-4-Me(H)C=C(H)C(O)Me (27a)*: Yield: 1·26 g (79%). M.p.: liquid. IR (KBr): 1667, 1611, 1258, 1208, 1179, 980 cm^{-1}. ^1H NMR: δ 2·36 (*s*, 6H, Ar-CH_3 + $C(O)CH_3$), 6·67 (*d*, ^3J(H–H) = 16·6 Hz, 1H, HC=C*H*C(O)Me), 7·19 (*d*, ^3J(H–H) = 8·8 Hz, 2H, Ar-*H*), 7·41–7·53 (3 lines, 3H, Ar-*H* + C_6H_4-4-Me-

*H*C=CH). ^{13}C NMR: δ 21·4 (*s*, Ar*C*H$_3$), 27·4 (*s*, C(O)*C*H$_3$), 126·3, 128·3, 129·7, 131·7, 141·0, 143·4, 198·3 (*s*, *C*(O)Me). Anal. Calcd for $C_{11}H_{12}O$: C, 82·50; H, 7·50. Found: C, 82·68; H, 7·38.

2.7b *C_6H_4-3-Me(H)C=C(H)C(O)Me* ***(27b)****:* Yield: 1·3 g (81%). M.p.: liquid. IR (KBr): 1669, 1611, 1258, 1229, 978 cm^{-1}. ^{1}H NMR: δ 2·37 (*s*, 6H, Ar-C*H*$_3$ + C(O)C*H*$_3$), 6·69 (*d*, ^3J(H-H) = 15·6 Hz, 1H, C$_6$H$_4$-3-Me(H)C=C*H*), 7·22–7·35 (*m*, 4H, C$_6$H$_4$-3-Me(*H*)C=CH), 7·48 (*d*, ^3J(H–H) = 15·6 Hz, 1H, C$_6$H$_4$-3-Me(*H*)C=CH). ^{13}C NMR: δ 21·3 (*s*, Ar-*C*H$_3$), 27·5 (*s*, C(O)*C*H$_3$), 125·5, 127·0, 128·9, 131·3, 134·4, 138·6, 143·6, 198·3 (*s*, *C*(O)Me).

2.7c *C_6H_4-4-OMe(H)C=C(H)C(O)Me* ***(27c)****:* Yield: 1·53 g (87%). M.p.: 62–64°C. IR (KBr): 1771, 1744, 1229, 1103, 959 cm^{-1}. ^{1}H NMR: δ 2·35 (*s*, 3H, C(O)C*H*$_3$), 3·83 (*s*, 3H, OC*H*$_3$), 6·59 (*d*, ^3J(H–H) = 16·3 Hz, 1H, C$_6$H$_4$-4-OMe(H)C=C*H*), 6·90 (*d*, ^3J(H–H) = 8·7 Hz, 2H, Ar-ortho-*H*), 7·46 (*d*, ^3J(H–H) = 16·3 Hz, 1H, C$_6$H$_4$-4-OMe*H*C=CH), 7·48 (*d*, ^3J(H–H) = 8·7 Hz, 2H, Ar-*H*). ^{13}C NMR: δ 27·4 (*s*, C(O)*C*H$_3$), 55·4 (*s*, Ar-O*C*H$_3$), 114·5, 125·1, 127·1, 130·0, 143·2, 161·6, 198·3 (*s*, *C*(O)Me)); Anal. Calcd for $C_{11}H_{12}O_2$: C, 75·00; H, 6·82. Found: C, 75·22; H, 6·95.

2.7d *3,4-Cl_2-C_6H_3-(H)C=C(H)C(O)Me* ***(27d)****:* Yield: 1·68 g (78%). M.p.: 52–54°C. IR (KBr): 1672, 1615, 1470, 1258, 1134, 1030, 978 cm^{-1}. ^{1}H NMR: δ 2·32 (*s*, 3H, C(O)C*H*$_3$), 6·62 (*d*, ^3J(H-H) = 16·6 Hz, 1H, C$_6$H$_3$-3,4-Cl$_2$(H)C=C*H*), 7·29–7·54 (*m*, 4H, 3Ar-*H* + C$_6$H$_3$-3,4-Cl$_2$*H*C=CH). ^{13}C NMR: δ 27·8 (*s*, C(O)*C*H$_3$), 127·1, 128·4, 129·7, 130·9, 133·2, 134·2, 134·6, 140·2, 197·4 (*s*, *C*(O)Me).

2.7e *$C_{14}H_9$(H)C=C(H)C(O)Me* ***(27e)****:* Yield: 1·92 g (78%). M.p.: 100–102°C. IR (KBr): 1660, 1653, 1541, 1520, 1362, 1250, 988 cm^{-1}. ^{1}H NMR: δ 2·54 (*s*, 3H, C(O)C*H*$_3$), 6·68 (*d*, ^3J(H–H) = 16·6 Hz, 1H, C$_{14}$H$_9$(H)C=C*H*), 7·46–7·50 (*m*, 4H, Ar-*H*), 7·94–7·80 (*m*, 2H, Ar-*H*), 8·15–8·20 (*m*, 2H, Ar-*H*), 8·38 (*s*, 1H, Ar-*H*), 8·42 (*d*, ^3J(H–H) = 16·6 Hz, 1H, C$_{14}$H$_9$(*H*)C=CH). ^{13}C NMR: δ 27·9 (*s*, C(O)*C*H$_3$), 125·1, 125·4, 126·4, 128·5, 128·9, 129·2, 129·4, 131·3, 135·8, 140·3, 197·7 (*s*, *C*(O)Me).

2.7f *(4-Me-C_6H_4)(H)C=C(H)C(O)Et* ***(28a)****:* Yield: 1·27 g (73%). M.p.: Liquid. IR (KBr): 1661, 1611, 1362, 1192, 1119, 988 cm^{-1}. ^{1}H NMR: δ 1·16 (*t*, ^3J(H–H) = 7·4 Hz, 3H, CH$_2$C*H*$_3$), 2·36 (*s*, 3H, Ar-C*H*$_3$), 2·67 (*q*, ^3J(H–H) = 7·4 Hz, 2H, C*H*$_2$CH$_3$), 6·69 (*d*, ^3J(H–H) = 16·0 Hz, 1 H, HC=C*H*C(O)Et), 7·18 (*d*, ^3J(H–H) = 7·8 Hz, 2H, Ar-ortho-*H*), 7·42 (*d*, ^3J(H–H) = 7·8 Hz, 2H, Ar-meta-*H*), 7·53 (*d*, 3H, ^3J(H–H) = 16·0 Hz, 1H, C$_6$H$_4$-4-Me(*H*)C=CH). ^{13}C NMR: δ 8·2 (*s*, CH$_2$*C*H$_3$), 21·4 (*s*, Ar-*C*H$_3$), 33·9 (*s*, *C*H$_2$CH$_3$), 125·2, 128·3, 129·7, 131·9, 140·8, 142·2, 200·9 (*s*, *C*(O)Et).

2.7g *(C_6H_4-4-OMe)(H)C=C(H)C(O)Et* ***(28b)****:* Yield: 1·68 g (89%). M.p.: 48–50°C. IR (KBr): 1684, 1657, 1601, 1572, 1512, 1254, 1177, 1119, 1026, 988, 831 cm^{-1}. ^{1}H NMR: δ 1·13 (*t*, ^3J(H-H) = 6·8 Hz, 3H, CH$_2$C*H*$_3$), 2·64 (*q*, ^3J(H–H) = 6·8 Hz, 2H, C*H*$_2$CH$_3$), 3·80 (*s*, 3 H, Ar-OC*H*$_3$), 6·59 (*d*, ^3J(H–H) = 16·6 Hz, 1H, HC=C(*H*)C(O)Et), 6·87 (*d*, ^3J(H–H) = 8·8 Hz, 2H, Ar-Ortho-*H*), 7·43–7·53 (*m*, 3H, 2Ar-*H* + C$_6$H$_4$-4-OMe(*H*)C=CH). ^{13}C NMR: δ 8·3 (*s*, CH$_2$*C*H$_3$), 33·9 (*s*, *C*H$_2$CH$_3$), 55·3 (*s*, Ar-O*C*H$_3$), 114·4, 123·9, 127·3, 129·9, 141·9, 161·5, 200·8 (*s*, *C*(O)Et).

2.7h *C_6H_5CH=CH-(H)C=C(H)C(O)Et* ***(28c)****:* Yield: 1·21 g (65%). M.p.: Liquid. IR (KBr): 1678, 1622, 1589, 1451, 1358, 1287, 1192, 1123, 999, 748 cm^{-1}. ^{1}H NMR: δ 1·14 (*t*, ^3J(H-H) = 6·7 Hz, 3H, CH$_2$C*H*$_3$), 2·61 (*q*, ^3J(H–H) = 6·7 Hz, 2H, C*H*$_2$CH$_3$), 6·27 (*d*, ^3J(H–H) = 16·0 Hz, 1H, (H)C=C*H*C(O)Et), 6·85–6·90 (*m*, 2H, C$_6$H$_5$(H)C=C(H)-(*H*)C=CH + 1 Ar-*H*), 7·31–7·48 (*m*, 6H, C$_6$H$_5$(*H*)C=C(*H*)-(H)C=CH + 4Ar-*H*). ^{13}C NMR: δ 8·3 (*s*, CH$_2$*C*H$_3$), 33·9 (*s*, *C*H$_2$CH$_3$), 126·8, 127·2, 128·8, 129·0, 129·4, 131·2, 136·2, 141·0, 142·1, 152·4, 193·3 (*s*, *C*(O)Et).

2.7i *$C_{14}H_9$(H)C=C(H)C(O)Et* ***(28d)****:* Yield: 1·77 g (68%). M.p.: 94–98°C. IR (KBr): 1661, 1616, 1194, 1019, 982 cm^{-1}. ^{1}H NMR: δ 1·27 (*t*, ^3J(H–H) = 7·6 Hz, 3H, CH$_2$C*H*$_3$), 2·83 (*q*, ^3J(H–H) = 7·6 Hz, 2H, C*H*$_2$CH$_3$), 6·71 (*d*, ^3J(H–H) = 16·4 Hz, 1H, HC=C*H*C(O)Et), 7·44–7·50 (*m*, 4H, Ar-*H*), 7·97–8·02 (*m*, 2H, Ar-*H*), 8·17–8·21 (*m*, 2H, Ar-*H*), 8·43 (*s*, 1H, Ar-*H*), 8·48 (*d*, ^3J(H–H) = 16·4 Hz, 1H, C$_{14}$H$_9$(*H*)C=CH). ^{13}C NMR: δ 8·2 (*s*, CH$_2$*C*H$_3$), 34·6 (*s*, *C*H$_2$CH$_3$), 125·2, 125·4, 126·3, 128·2, 128·9, 129·5, 131·4, 134·9, 139·2, 200·8 (*s*, *C*(O)Et).

2.7j *$C_5H_5FeC_5H_4$(H)C=C(H)C(O)CH$_2$CH$_3$* ***(28e)****:* Yield: 1·82 g (68%). M.p.: 98–100°C. IR (KBr): 1686, 1657, 1605, 1360, 1125, 1034, 980 cm^{-1}. ^{1}H NMR: δ 1·14 (*t*, ^3J(H–H) = 6·8 Hz, 3H, CH$_2$C*H*$_3$), 2·58 (*q*, ^3J(H–H) = 6·8 Hz, 2H, C*H*$_2$CH$_3$), 4·13 (*s*,

5H, ferrocenyl-*H*), 4·41–4·42 (*m*, 2H, ferrocenyl-*H*), 4·48–4·49 (*m*, 2H, ferrocenyl-*H*), 6·34 (*d*, ^3J(H–H) = 15·6 Hz, 1H, HC=C*H*(CO)Et), 7·44 (*d*, ^3J(H–H) = 15·6 Hz, 1H, $C_5H_5FeC_5H_4$(*H*)C=CH). ^{13}C NMR: δ 8·5 (*s*, CH_2CH_3), 33·6 (*s*, CH_2CH_3), 68·7, 69·7, 70·9, 78·9 (ferrocenyl-*C*), 123·6 (*s*, HC=*C*H (CO)Et), 143·6 (*s*, $C_5H_5FeC_5H_4H$ *C*=CH), 200·2 (*s*, *C*(O)Et). Anal. Calcd. for $C_{15}H_{16}FeO$: C, 67·16; H, 5·97. Found: C, 67·34; H, 6·08.

2.7k *EtC(O)C(H)=C(H)–C$_6$H$_4$–(H)C=C(H)C(O)Et (**28f**):* Yield: 1·91 g (79%). M.p.: 112–116°C. IR (KBr): 1657, 1366, 1192, 1065, 990 cm^{-1}. ^{1}H NMR: δ 1·16 (*t*, ^3J(H–H) = 7·8 Hz, 3H, CH_2CH_3), 2·68 (*q*, ^3J(H–H) = 7·8 Hz, 2H, CH_2CH_3), 6·75 (*d*, ^3J(H–H) = 16·6 Hz, 1H, HC=C(*H*)C(O)Et), 7·48–7·56 (3 lines, 3H, 2Ar-*H* + (H)C=C(*H*)–C_6H_4–(*H*)C=C(H)). ^{13}C NMR: δ 8·1 (*s*, CH_2CH_3), 34·2 (*s*, CH_2CH_3), 126·5, 128·7, 136·5, 140·9, 200·5 (*s*, *C*(O)Et). Anal. Calcd. for $C_{16}H_{18}O_2$: C, 79·34; H, 7·44. Found: C, 79·48, H, 7·32.

2.8 *Allylation of β-ketophosphonates **22–23**: Isolation of allylated products ($OCH_2CMe_2CH_2O$)P(O)CH_2C(OH)(CH_2CH=CH)CH_2R [R = H (**29**), Me (**30**)]*

To a solution of *β*-ketophosphonate **22** or **23** (1·0 mmol) in dichloromethane (20 mL) kept over molecular sieves (4 Å, ~0·5 g), diallyltin dibromide (0·33 g, 1·0 mmol)[13] was added *via* syringe at room temperature and the mixture stirred for 20 h. The reaction mixture was quenched with 8% aq. NaOH (20 mL) and extracted with dichloromethane (2 × 30 mL). The organic layer was dried (Na_2SO_4) and the solvent was removed to obtain the crude *β*-hydroxyphosphonate **29** or **30**. These were purified by column chromatography (silica gel; hexane-ethyl acetate).

2.8a *Compound **29**:* Yield: 0·12 g (49%). M.p.: 82–84°C. IR (KBr): 3349, 1642, 1260, 1067 cm^{-1}. ^{1}H NMR: δ 1·00, 1·11 (2*s*, 6H, C(CH_3)$_2$), 1·36 (*s*, 3H, C(OH)CH_3), 2·08 (*dd*, ^2J(H–H) = 10·9 Hz, ^2J(P–H) = 17·3 Hz, 2H, PCH_2), 2·37 (*d*, ^3J(H–H) = 7·3 Hz, 2H, CH_2CH=CH$_2$), 3·79 (*dd*, ^2J(H–H) = 12·6 Hz, ^3J(P–H) = 11·3 Hz, 2H, OCH_AH$_B$), 4·20 (*t*, ^3J(P–H) = 11·3 Hz, 2H, OCH$_A$$H_B$), 5·04 (*d*, ^3J(H–H) = 13·0 Hz, 2H, CH$_2$CH=CH_2), 6·82 (*m*, 1H, CH$_2$C*H*=CH$_2$). ^{13}C NMR: δ 21·3, 21·7 (2*s*, C(CH_3)$_2$), 28·2 (*d*, ^3J(PC) = 9·4 Hz, CH(OH)CH_3), 32·7 (*s*, CMe_2), 35·5 (*d*, ^1J(PC) = 131·3 Hz, P*C*), 47·8 (*d*, ^3J(P–C) = 12·3 Hz, *C*H$_2$CH=CH$_2$), 70·2 (*d*, ^2J(P-C) = 4·8 Hz, *C*H(OH)), 74·8, 75·0 (2*s*, O*C*H$_2$), 118·6 (*s*, CH$_2$CH=*C*H$_2$), 133·8 (*s*, CH$_2$*C*H=CH$_2$). ^{31}P NMR: δ 25·9.

2.8b *Compound **30**:* Yield: 0·16 g (62%). M.p.: 74–76°C. IR (KBr): 3434, 1647, 1240, 1060, 1015 cm^{-1}. ^{1}H NMR: δ 0·88 (*t*, ^3J(H–H) = 7·2 Hz, 3H, CH$_2$CH_3), 0·97, 1·08 (2*s*, 6H, C(CH_3)$_2$), 1·62 (*q*, ^3J(H–H) = 7·2 Hz, 3H, CH_2CH$_3$), 2·05 (*d*, ^2J(P–H) = 17·7 Hz, 2H, PCH_2), 2·34 (*d*, ^3J(H–H) = 7·3 Hz, 2H, CH_2CH=CH$_2$), 3·76 (*t*, ^3J(P–H) = ^2J(H–H) = 13·7 Hz, 2H, OCH_AH$_B$), 4·16 (*t*, ^3J(P–H) = 10·2 Hz, 2H, OCH$_A$$H_B$), 5·07 (*d*, ^3J(H–H) = 13·3 Hz, 2H, CH$_2$CH=CH_2), 6·78 (*m*, 1H, CH$_2$C*H*=CH$_2$). ^{13}C NMR: δ 7·8 (*s*, CH$_2$$CH_3$), 21·3, 21·7 (2*s*, C($CH_3$)$_2$), 32·4 (*d*, ^3J(P–C) = 5·8 Hz, CMe_2), 32·9 (*d*, ^3J(P–C) = 9·1 Hz, CH(OH)CH_2CH_3), 33·7 (*d*, ^2J(P–C) = 131·0 Hz, PCH_2), 44·2 (*d*, ^3J(P–C) = 9·9 Hz, CH_2CH=CH$_2$), 72·3 (*d*, ^2J(P–C) = 4·8 Hz, *C*H(OH)), 74·8, 74·9 (2*s*, O*C*H$_2$), 118·4 (*s*, CH$_2$CH=*C*H$_2$), 133·7 (*s*, CH$_2$*C*H=CH$_2$). ^{31}P NMR: δ 26·4.

2.9 *X-ray structural analysis of **6**, **9**, **12**, **18** and **24***

X-ray data were collected on a Bruker AXS SMART diffractometer using Mo-K$_\alpha$ (λ = 0·71073 Å) radiation. The structures were solved by direct methods;[14] all non-hydrogen atoms were refined anisotropically. The allenic C–H hydrogen atoms were located by difference Fourier maps in both the cases, and refined isotropically. In the case of **6**, the O–H hydrogen was also located by difference Fourier map, and refined isotropically. All the other hydrogen atoms were placed geometrically and refined using a riding model with CH_2 (methylene) constrained to 0·97 Å with U_{iso}(H) = 1·2U_{eq}(C), and CH_3 constrained to 0·96 Å with U_{iso}(H) = 1·5U_{eq}(C). In compound **12** pseudosymmetry is indicated, but we could not refine the structure in any other space group; the Flack parameter using 'twin' command was reduced to zero. The quality of data for **18** was not good, but the structure could be unambiguously characterized.

2.10 *Crystal data*

Compound **6**: $C_9H_{15}O_4P$, M = 218·18, Monoclinic, space group $P2_1/n$, a = 8·7632(8), b = 9·3504(9), c = 13·8022(13) Å, β = 105·62(10), V = 1089·18 (18) Å^3, Z = 4, ρ = 1·331 g cm^{-3}, F(000) = 464,

$\mu = 0{\cdot}240$ mm^{-1}, data/restraints/parameters: 2634/0/138. *S* (all data) = 1·024, *R* indices ($I > 2\sigma(I)$): *R*1 = 0·0448, *wR2* (all data) = 0·1314. Max./min. residual electron density (eÅ^{-3}) 0·381/–0.251.

2.10a *Compound* ***9****:* $C_{11}H_{14}O_6P_2$, $M = 304{\cdot}16$, Tetragonal, space group $I4_1/a$, $a = 12{\cdot}9203(4)$, $b = 12{\cdot}9203(4)$, $c = 16{\cdot}8163(11)$ Å, $V = 2807{\cdot}2(2)$ Å^3, $Z = 8$, $\rho = 1{\cdot}439$ g cm^{-3}, $F_{000} = 1264$, $\mu = 0{\cdot}328$ mm^{-1}, data/restraints/parameters: 1369/0/115. *S* (all data) = 1·095. *R* indices ($I > 2\sigma(I)$): *R*1 = 0·0334, *wR*2 (all data) = 0·0943. Max./min. residual electron density (eÅ^{-3}) 0·239/–0·240.

2.10b *Compound* ***12****:* $C_8H_{13}O_3P$, $M = 188{\cdot}15$, orthorhombic, space group $P2_12_12_1$, $a = 8{\cdot}8325(5)$, $b = 8{\cdot}9436(5)$, $c = 12{\cdot}0211(7)$ Å, $V = 949{\cdot}60(9)$ Å^3, $Z = 4$, $\rho = 1{\cdot}316$ g cm^{-3}, $F_{000} = 400$, $\mu = 0{\cdot}256$ mm^{-1}, data/restraints/parameters: 1678/0/118. *S* (all data) = 1·012. *R* indices ($I > 2\sigma(I)$): *R*1 = 0·0334, *wR*2 (all data) = 0·0980. Flack parameter (using 'twin' command in SHELXL) 0·00. Max./min. residual electron density (eÅ^{-3}) 0·189/–0·258.

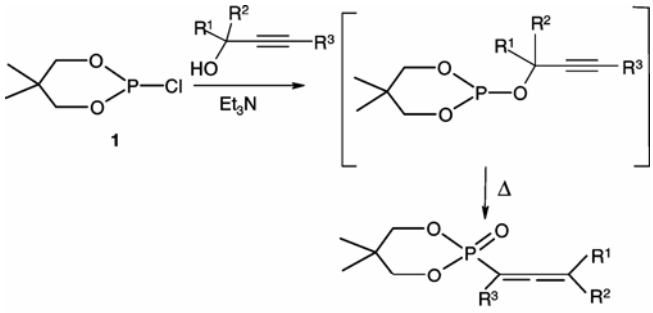
2.10c *Compound* ***18****:* $C_{20}H_{34}O_6P_2$, $M = 432{\cdot}41$, orthorhombic, space group *Pbca*, $a = 19{\cdot}684(4)$, $b = 11{\cdot}340(2)$, $c = 41{\cdot}629(8)$ Å, $V = 9292(3)$ Å^3, $Z = 16$, $\rho = 1{\cdot}236$ g cm^{-3}, $F_{000} = 3712$, $\mu = 0{\cdot}218$ mm^{-1}, data/restraints/parameters: 8181/0/521. *S* (all data) = 0·977. *R* indices ($I > 2\sigma(I)$): *R*1 = 0·0961, *wR*2 (all data) = 0·2331. Max./min. residual electron density (eÅ^{-3}) 0·786/–0·286.

2.10d *Compound* ***24****:* $C_{20}H_{38}O_8P_2$, $M = 468{\cdot}44$, monoclinic, space group $P2_1$, $a = 6{\cdot}9687(9)$, $b = 19{\cdot}661(3)$, $c = 9{\cdot}0871(12)$ Å, $\beta = 96{\cdot}102(2)°$, $V = 1238{\cdot}0(3)$ Å^3, $Z = 2$, $\rho = 1{\cdot}257$ g cm^{-3}, $F_{000} = 504$, $\mu = 0{\cdot}215$ mm^{-1}, data/restraints/parameters: 4345/1/279. *S* (all data) = 1·225. Flack parameter (using 'twin' command in SHELXL) 0·13(15). *R* indices ($I > 2\sigma(I)$): *R*1 = 0.0811, *wR*2 (all data) = 0·1646. Max./min. residual electron density (eÅ^{-3}) 0·525/–0·257.

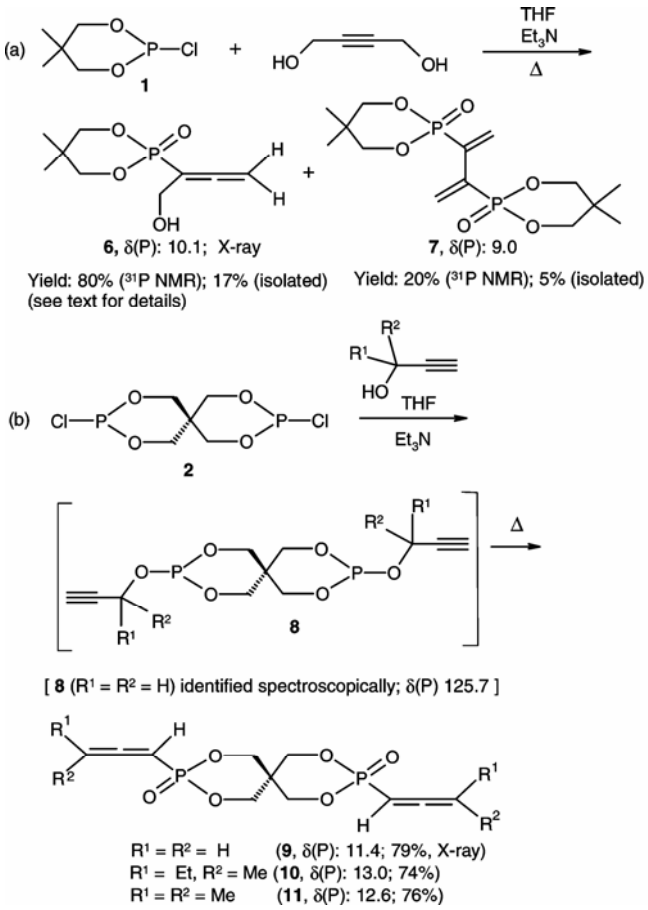
Further details as CIF files are available from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK on request, quoting the deposition numbers CCDC 695272–695276.

3. Results and discussion

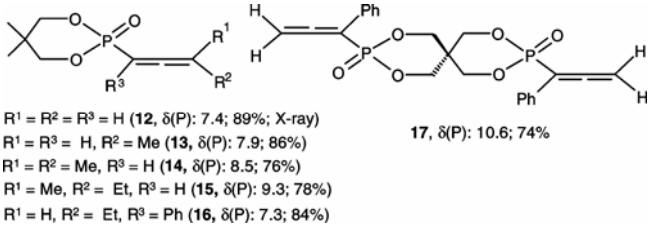
The reaction of $(OCH_2CMe_2CH_2O)PCl$ (**1**) or $[ClP(OCH_2)_2]_2C$ (**2**) with the appropriate propargyl alcohol in the presence of a base leads to the allenylphosphonates **3–6** and **9–17** (schemes 2 and 3a–b) after rearrangement of the initially formed P^{III} intermediate; the butadiene **7** was a by-product during the synthesis of **6** and species **8** is the P^{III} intermediate prior to the formation of **9**. The yields reported in these and subsequent schemes are those



Scheme 2.



Scheme 3.



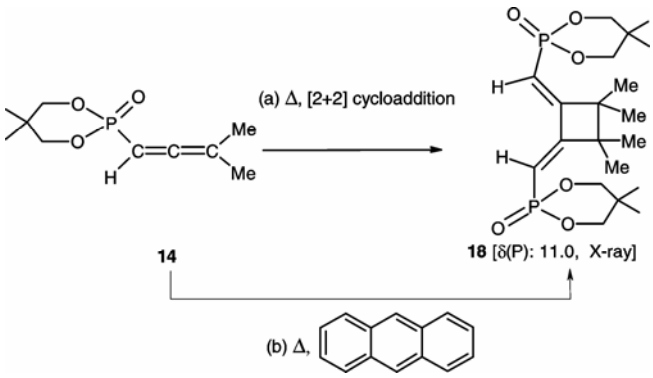
for isolated compounds unless stated otherwise**.** This type of reaction is known for the synthesis of allenylphosphonates.[10] A slightly modified procedure was utilized to prepare compounds **9–11** (scheme 3b) and **17** that contain the 1,3,2-dioxaphosphorinane ring with two reactive allene residues.

Although in the reaction using **1** we could not detect the P^{III} intermediate alkoxide, we could do so in the synthesis of **9**; the species **8** [$R^1 = R^2 = H$] was clearly identified by the ^{31}P NMR [δ(P) 125·7] spectrum as essentially a single component prior to refluxing. Compound **9** was obtained as a crystalline material from methanol; it had low solubility in normal organic solvents like toluene, dichloromethane, etc. Since the P^{III} precursor **1** can be prepared by simply stirring phosphorus trichloride with the 1,3-diol for 24 h followed by distillation in low vacuum, we think that our allenylphosphonates are more convenient to synthesize when compared to several non-phosphorylated allenes. All these allenylphosphonates could be handled in air in general, but over a period of ca 15 d, **9–11** and **17** turned into liquids. Our attempts to analyse/separate the components of these liquids (column chromatography/ NMR), were not successful.

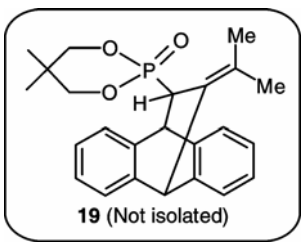
In the synthesis of **6**, the product has to be crystallized carefully because the 1,3-butadiene [$(OCH_2CMe_2CH_2O)(O)P\text{-}C(=CH_2)]_2$ (**7**) was also formed in the same reaction (cf. scheme 3a). A chromatographic separation was rendered difficult because of similar polarities of **6** and the butadiene by-product **7**. We isolated **7** also quantitatively by using 1 : 2 stoichiometry of the propargylic alcohol and **1**. Since there are a couple of compounds analogous to **7**,[12] and since this compound did not react with dimethyl acetylenedicarboxylate (DMAD) or diisopropyl azodicarboxylate (DIAD), we did not explore its chemistry further.

Allenes may be expected to behave as dienophiles in Diels–Alder reaction. Our intention was to incorporate anthracene moiety but when we treated **14** with anthracene (which is expected to behave as a diene to lead to a [4 + 2] cycloaddition product) at 185°C for 5 h, we obtained only the dimerized allene **18** in a fair yield (scheme 4). Although the reaction mixture showed other products also [^{31}P NMR evidence], we isolated only **18** and not the expected compound **19**. We then tried this reaction in the absence of anthracene and found that **18** could be obtained in better yields.[15] The presence of the PCH=C moiety in this compound was shown by a doublet at δ 5·62 [^2J(P–H) = 16·3 Hz] in the ^1H NMR spectrum and a doublet at δ 105·2 (^1J(P–C) = 186·8 Hz) in the ^{13}C NMR spectrum. Only one report on such a reaction is available in the literature, but without an X-ray structural proof.[16] In our case, we characterized **18** by single crystal X-ray diffraction (figure 4). Although the crystal quality was only moderate, the molecular structure was unambiguously determined. The alkenic protons (rather than the phosphonate phosphorus atoms) of the two C=C*H*[P(O)($OCH_2CMe_2CH_2O$)] moieties are in close proximity to each other most likely to avoid steric effects. Since the reaction takes place thermally at elevated temperatures, a diradical mechanism is likely to be involved in the formation of **18**; this is similar to the dimerization of many non-phosphorylated allenes.[17]

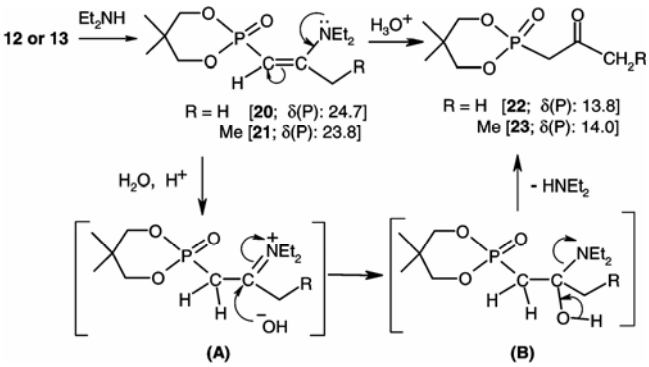
In our previous paper, we have reported the addition reactions of secondary amines with allenylphosphonates.[4] In a similar manner, enaminophosphonates **20–21** were prepared by starting with **12**–**13**.



Scheme 4.



Hydrolysis of **20–21** by 2N HCl afforded the *β*-ketophosphonates **22–23** (scheme 5). In reactions using **14–16**, we were able to isolate the *β*-ketophosphonates **24**–**26** although the corresponding enaminophosphonates could not be isolated. Addition of 2N HCl to **20** in an NMR tube experiment showed only **22** along with the starting phosphonate [^{31}P NMR] suggesting that the intermediates [**A** or **B**] are very reactive and rapidly lead to **22** or **23**. Some reports on this type of hydrolysis are known in the literature,[18] but the present series of compounds are well-defined solids that can be stored indefinitely in air. In the IR spectra, they show a band at ~ 1715 cm^{-1} corresponding to the carbonyl stretch. In the ^{1}H NMR, a characteristic doublet at δ 3·3–3·5 [^2J(P–H) ~ 22·0 Hz] for the PCH_2 protons clearly shows that a rearrangement of the carbon skeleton has taken place. The ^{31}P NMR spectra show a single peak in the range δ 12–15 that are distinctly downfield to those of the parent allenes [δ 7–10]. For ease of comparison, the ^{31}P NMR data of compounds **3**–**18** and **20–26** are given in table 1. The carbon α to phosphorus appears as a doublet around δ 40.0 in the ^{13}C NMR spectrum; the magnitude of ^1J(P–C) [122·5 Hz] clearly shows that this carbon has less *s* character than the corresponding one in **12–16** [^1J(P–C) 190–200 Hz].



Scheme 5.

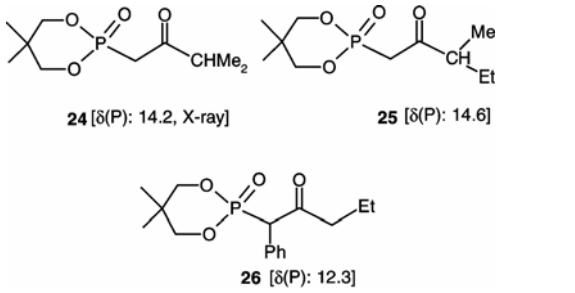
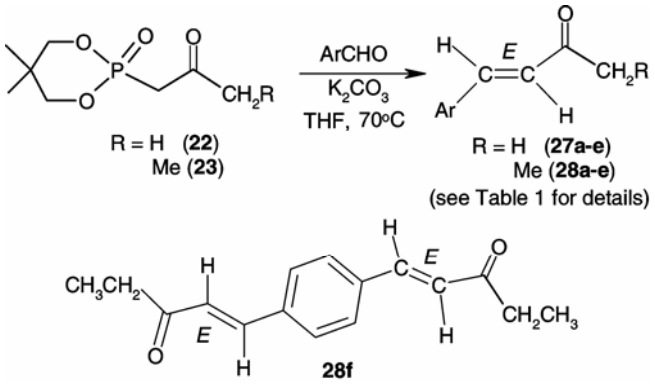


Table 1. ^{31}P NMR chemical shifts for compounds **3**–**18** and **20–26**.

Compound no.	$\delta(P)$ (ppm)	Compound no.	$\delta(P)$ (ppm)
3	11·3	**15**	9·3
4	12·2	**16**	7·3
5	6·7	**17**	10·6
6	10·1	**18**	11·0
7	9·0	**20**	24·7
8	125·7	**21**	23·8
9	11·4	**22**	13·8
10	13·0	**23**	14·0
11	12·6	**24**	14·2
12	7·4	**25**	14·6
13	7·9	**26**	12·3
14	8·5		

Compounds **22**–**26** are interesting reagents for Horner-Wadsworth-Emmons (HWE) reaction.[19] They can also be used as ketonic substrates.[20] Our initial attempts of the HWE reaction using NaH/THF gave either none or only very low yields of olefinic products. However, when K_2CO_3 was used in place of NaH in refluxing THF, the reaction using **22–23** proceeded smoothly to afford the *α,β*-



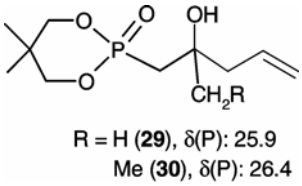
Scheme 6.

Table 2. Details on the HWE reaction of the *β*-ketophosphonates **22–23** with aromatic aldehydes.

Entry	R	Ar	Product (*E*)	Isolated yield (%)
1	H	4-Me-C_6H_4	**27a**	79
2	H	3-Me-C_6H_4	**27b**	81
3	H	4-MeO-C_6H_4	**27c**	87
4	H	3,4-Cl_2-C_6H_3	**27d**	78
5	H	9-anthryl	**27e**	78
6	Me	4-Me-C_6H_4	**28a**	73
7	Me	4-MeO-C_6H_4	**28b**	89
8	Me	PhCH=CH	**28c**	65
9	Me	9-anthryl	**28d**	68
10	Me	ferrocenyl	**28e**	68
11	Me	4-CHO-C_6H_4	**28f**	79

unsaturated ketones **27a–e** and **28a–f** in moderate to high yields (scheme 6, table 2). It is true that aldol condensation is the more straightforward route to α,β-unsaturated ketones than this, but in specific cases where a particular stereo-/region-chemistry of the products is required, our procedure offers as an alternative.

The β-ketophosphonates **22–23** also undergo allylation readily with diallyltin dibromide at room temperature in dichloromethane in the presence of molecular sieves (4 Å) to give β-hydroxyphosphonates ($OCH_2CMe_2CH_2O$)P(O)CH_2C(OH)(CH_2CH=CH)CH_2R [R = H (**29**), Me (**30**)]. Although similar indium mediated allylation reactions have been reported before,[19] our precursors may offer an advantage because they are relatively easier to synthesize.



3.1 *A brief discussion of the structures of **6**, **9**, **12**, **18** and **24***

The structures of **6**, **9** and **12** are shown in figures 1–3; only half of the molecule is present in the asym-

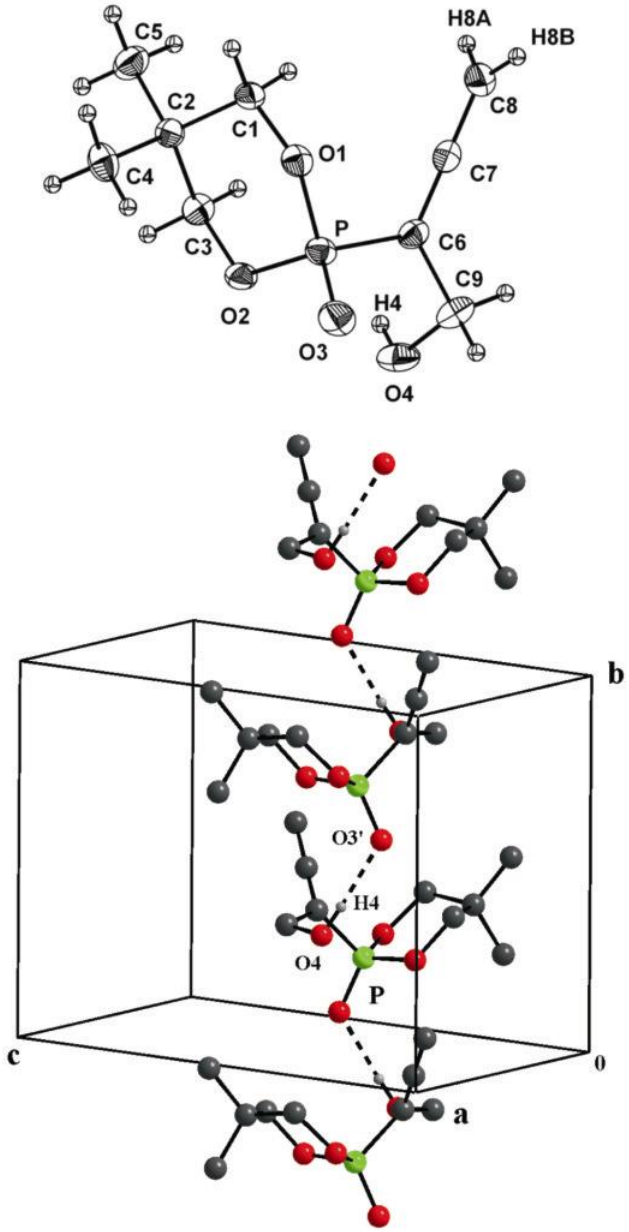


Figure 1. Top: The molecular structure of **6** showing the atom numbering scheme at 30% probability level of the thermal ellipsoids. Bottom: hydrogen bonding in **6** [O(4)–H(4)...O(3′) 0·82, 1·95, 2·764(2) Å, 174·7°. Symmetry code: 1·5 – *x*, 0·5 + *y*, 0·5 – z].

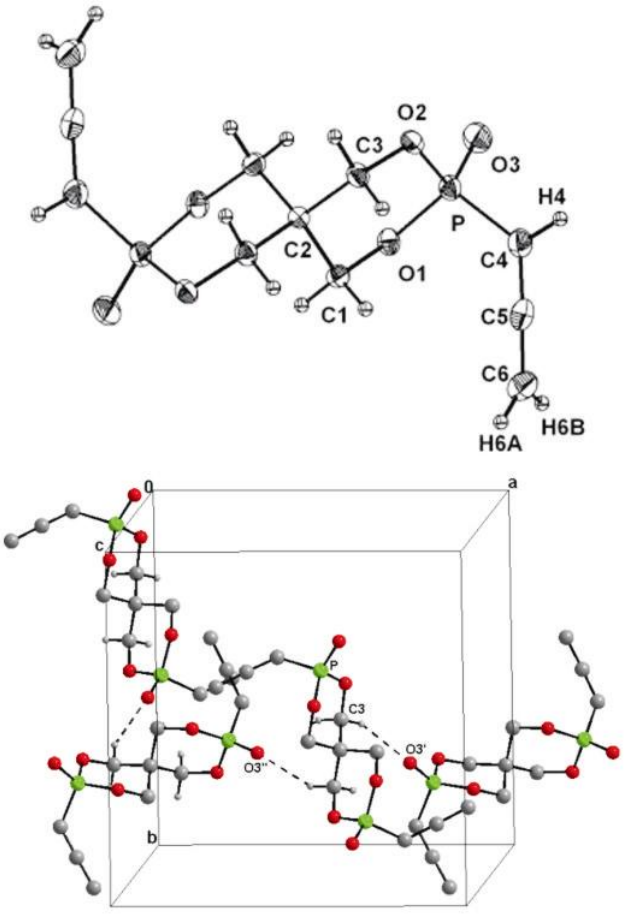


Figure 2. Top: The molecular structure of **9** showing the atom numbering scheme at 30% probability level of the thermal ellipsoids. Bottom: hydrogen bonding in **9** [C(3)–H(3A)...O(3′) 0·97, 2·41, 3·286(4) Å, 150·3°. Symmetry code: (i) 3/4 + *y*, 3/4 – *x*, –1/4 + *z*)].

Table 3. Selected bond parameters for **6**, **9** and **12** (Å).

Parameter	**6**	**9**	**12**
P–O (ring)	1·565(2)	1·569(1)	1·583(2)
P–O (ring)	1·573(2)	1·568(1)	1·588(3)
P=O	1·456(2)	1·466(1)	1·475(3)
P–C	1·771(2)	1·779(2)	1·777(4)
C(P)=C	1·288(3)	1·302(2)	1·306(6)
C=CH_2	1·280(4)	1·290(3)	1·307(6)
C=C=C	179·1(2)	178·8(2)	178·7(5)

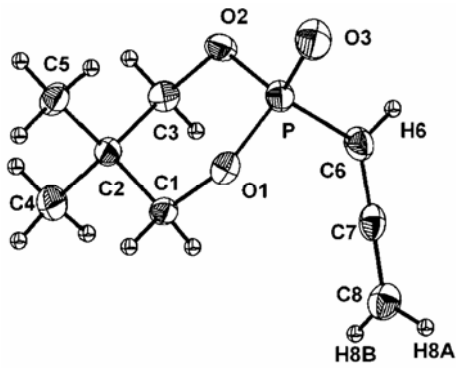


Figure 3. An ORTEP drawing of **12** (see table 3 for bond parameters).

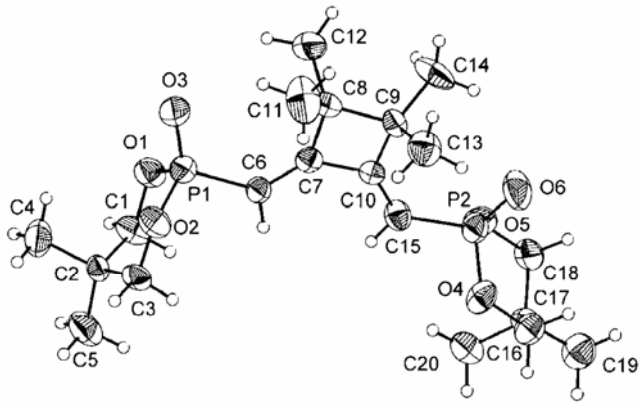


Figure 4. An ORTEP picture of compound **18**. Selected bond lengths (Å) and angles (°) with esd's in parentheses: P(1)–C(6) 1·763(7), P(2)–C(15) 1·761(7), C(6)–C(7) 1·331(8), C(7)–C(8) 1·518(9), C(8)–C(9) 1·577(9), C(9)–C(10) 1·514(8), C(10)–C(7) 1·458(9); C(7)–C(8)–C(9) 88·1(5), C(8)–C(9)–C(10) 87·0(5), C(7)–C(10)–C(9) 92·7(5), C(10)–C(7)–C(8) 91·3(5).

metric unit of **9**. Selected bond parameters are given in table 3. The P–O (ring), P=O and P–C distances are in the normal range expected for these compounds.[8a–b] In contrast to many previously reported

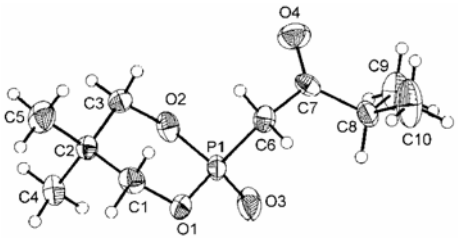


Figure 5. An ORTEP drawing of **24**. Only one of the two molecules in asymmetric unit is shown. Selected bond lengths (Å) with esd's in parentheses: P(1)–C(6) 1·802(5), C(6)–C(7) 1·509(8), C(7)–O(4) 1·193(6), C(7)–C(8) 1·507(8).

structures,[8b–e] the two adjacent C=C bonds of the allenyl group are much closer in length, a feature similar to that reported by Angelov *et al* [1·296(4) and 1·299(4) Å].[8a] The C=C=C unit is essentially linear in all the compounds reported here with a deviation of ~ 1·3° from 180°. The dihedral angle between the planes containing (i) H(8A), H(8B), C(8) and C(7), and (ii) P, C(6), C(7) and C(9) in compound **6** is 83(1)° which is significantly different from the expected orthogonality. In **9** and **12**, the analogous dihedral angles are, respectively, 87(1) and 89(1)°. The six-membered 1,3,2-dioxaphosphorinane ring has a chair conformation in these structures. Compound **9** has a spirocyclic carbon center; the angles at this center are within 2° of the ones required for tetrahedral geometry.

As expected, hydrogen-bonding between the phosphoryl oxygen and the –OH group is present in **6**. This leads to chain type of structure (figure 1, bottom). In **9**, there are weak C–H...O interactions between the OCH_2 protons of the six-membered phosphorinane ring and the phosphoryl oxygen as shown in figure 2 (bottom). Thus each oxygen atom has close contacts with the protons of different methylene groups in the extended structure.

There are two molecules in the asymmetric unit of **18** and only one of these is shown in figure 4. The cyclobutane ring in **18** can be considered to be planar. The distances C(6)–C(7) and C(10)–C(15) are clearly in the double bond region but the corresponding P–C single bond distances are quite short. In fact, these bonds are shorter than even that seen in the allenes **6**, **9** and **12**. It may be noted that two orientations are possible for the phosphonate moiety with respect to the C=C, but in the structure, the one that places the two phosphorus atoms with less steric interactions is observed. Compound **24**, interestingly, crystallizes in the chiral space group $P2_1$ with two molecules in the asymmetric unit. In this β-

ketophosphonate (cf. figure 5), the phosphorus is connected to an sp^3 carbon, and hence the P–C bond distance is longer than those in the structures discussed above. Other structural parameters are normal.

4. Summary

In summary, we have described the synthesis of several readily accessible and fairly stable solid allenylphosphonates that can be used as potential candidates for exploring allene chemistry; two of these bear additional functionalities like –OH or CH=CHMe. Bis-allenylphosphonates of type **9**–**11** and **17** may be useful precursors for polymerization. An allene dimer (**18**) that contains a substituted cyclobutane ring has been structurally characterized. Horner–Wadsworth–Emmons reaction using the β-ketophosphonates derived from allenylphosphonates serves as an alternative (compared to aldol condensation) source for α,β-unsaturated ketones.

Acknowledgements

We thank the Department of Science and Technology (DST, New Delhi) for funding and for setting up a Single Crystal X-ray Diffractometer Facility at the University of Hyderabad and for financial support. Authors also thank University Grants Commission UGC (New Delhi) for equipment under the UPE program. NNBK, MC, NSK, KVS thank Council of Scientific and Industrial Research (CSIR) for fellowships.

References

1. Selected reviews: (a) Yamamoto Y and Radhakrishnan U 1999 *Chem. Soc. Rev.* **28** 199; (b) Zimmer R, Dinesh C U, Nandanan E and Khan F A 2000 *Chem. Rev.* **100** 3067; (c) Lu X, Zhang C and Xu Z 2001 *Acc. Chem. Res.* **34** 535; (d) Ma S 2005 *Chem. Rev.* **105** 2829; (e) Hassan H H A M 2007 *Current Organic Synthesis* **4** 413; (f) Brummond K M and DeForrest J E 2006 *Synthesis* 795
2. Some key references: (a) Alabugin I V and Brel V K 1997 *Russ. Chem. Rev.* **66** 205; (b) Nishimura T, Hirabayashi S and Hayashi T 2006 *J. Am. Chem. Soc.* **126** 2556; (c) Ma S, Guo H and Yu F 2006 *J. Org. Chem.* **71** 6634
3. (a) Kumara Swamy K C, Kumaraswamy S, Senthil Kumar K, Muthiah C 2005 *Tetrahedron Lett.* **46** 3347; (b) Kommana P, Satish Kumar N, Vittal J J, Jayasree E G, Jemmis E D, Kumara Swamy K C 2004 *Org. Lett.* **6** 145
4. (a) Chakravarty M and Kumara Swamy K C 2006 *J. Org. Chem.* **71** 9128; (b) Kumara Swamy K C, Balaraman E and Satish Kumar N 2006 *Tetrahedron* **62** 10152
5. Bhuvan Kumar N N and Kumara Swamy K C 2007 *Polyhedron* **26** 883
6. Chakravarty M and Kumara Swamy K C 2007 *Synthesis* 3171
7. Chakravarty M, Bhuvan Kumar N N, Sajna K V and Kumara Swamy K C 2008 *Eur. J. Org. Chem.* 4500
8. (a) Angelov C M, Mazzuca D A, van den Heever J P, McDonald R, McEwen A J B and Mercer J R 2002 *Acta Cryst.* **E58** o399; (b) Xu W-M, Hu X-R and Gu J-M 2004 *Acta Cryst.* **E60** o2214; (c) Ansorge M, Polborn K and Muller T J J 1999 *Eur. J. Inorg. Chem.* 225; (d) Muller T J J and Ansorge M 1997 *Chem. Ber.* **130** 1135; (e) Santelli-Rouvier C, Toupet L and Santelli M 1997 *J. Org. Chem.* **62** 9039
9. Perrin D D, Armarego W L F and Perrin D R 1986 *Purification of Laboratory Chemicals* (Oxford, UK: Pergamon)
10. (a) Guillemin J C, Savignac P and Denis J M 1991 *Inorg. Chem.* **30** 2170; (b) Iorga B, Eymery F, Carmichael D and Savignac P 2000 *Eur. J. Org. Chem.* 3103; (c) Satish Kumar N 2004 *Studies on the synthesis, reactivity and utility of cyclic phosphorus(III) compounds and organophosphonates* Ph D thesis, University of Hyderabad, India
11. Fang X-M, Wang Y, Liu Z-G, Xu Y-Q and Ding T 2004 *Huaxue Yanjiu* **15** 43; *Chemical Abstr.* **141** 296087
12. (a) Pollok T and Schmidbaur H 1987 *Tetrahedron Lett.* **28** 1085; (b) Pudovik A N and Aladzheva I M 1963 *Zh. Obshch. Khim.* **33** 708; *Chemical Abstr.* **59**, 15743
13. Sisido K and Takeda Y 1961 *J. Org. Chem.* **26** 2301
14. (a) Sheldrick G M *SADABS*, *Siemens Area Detector Absorption Correction*, University of Göttingen, Germany, 1996; (b) Sheldrick G M *SHELXTL NT Crystal Structure Analysis Package*, Bruker AXS, Analytical X-ray System, WI, USA, 1999, version 5.10
15. We sincerely thank a referee for constructive suggestions in this regard.
16. Trifonov L S, Simove S D and Orahovats A S 1987 *Tetrahedron Lett.* **28** 3391
17. Murakami M and Matsuda T 2004 in *Modern allene chemistry* (eds) N Krause and A S K Hashmi (Weinheim: Wiley-VCH) Vol 2, Chapter 12, pp 727–816
18. Altenbach H and Korff R 1981 *Tetrahedron Lett.* **22** 5175
19. See, for example: (a) Abiko A and Masamune S 1996 *Tetrahedron Lett.* **37** 1077; (b) Muthiah C, Kumar K P, Kumaraswamy S and Kumara Swamy K C 1998 *Tetrahedron* **54** 14315; (b) Chakravarty M, Srinivas B, Muthiah C and Kumara Swamy K C 2003 *Synthesis* 2368
20. Ranu B C, Samanta S and Hajra A 2001 *J. Org. Chem.* **66** 7519