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Synthesis, structure and pyrolysis of stabilised phosphonium ylides containing saturated oxygen heterocycles†

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A range of twelve stabilised phosphonium ylides containing tetrahydrofuran, tetrahydropyran or 2,2-dimethyl-1,3-dioxolane rings have been prepared and fully characterised, including one X-ray structure determination of each type. The X-ray structures confirm the P=C and C=O functions to be *syn* and all the compounds undergo thermal extrusion of Ph_3PO to give the corresponding alkynes. In some cases there is also competing loss of Ph_3P to give different carbene-derived products and evidence has been obtained for the generation of 2-phenyloxete in this way. Raising the pyrolysis temperature leads in several cases to new secondary reactions of the alkyne products involving a sequence of alkyne to vinylidene isomerisation, intramolecular CH insertion, and retro Diels Alder reaction.
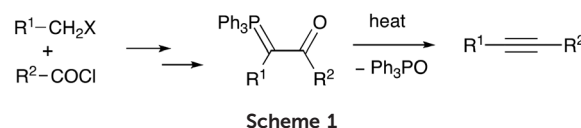
Introduction

Thermal extrusion of Ph_3PO from suitably substituted β-oxophosphonium ylides in the so-called "intramolecular Wittig reaction" is a versatile method of alkyne synthesis.[1] The ylides are readily prepared in a few simple steps from alkyl halides and acid chlorides as stable crystalline solids, and overall this represents an unusual way to construct the alkyne triple bond (Scheme 1). The process was first described in 1959 for $R^1 = R^2$ = Ph where simply heating the ylide at 300 °C resulted in the desired elimination of Ph_3PO to give diphenylacetylene in 59% yield.[2] Shortly thereafter a convenient synthesis of acetylenic esters by pyrolysis of the ylides with $R^1 = CO_2Me$ was reported.[3] Over the next 25 years many further examples appeared, but using conventional pyrolysis the scope was limited to examples where R^1 was an electron withdrawing group.[4] This restriction was overcome by the use of flash vacuum pyrolysis (FVP) which allowed synthesis of purely aliphatic and terminal alkynes from ylides with $R^1 = $ alkyl or H.[5] Using this method, a wide range of functionalised alkynes have been prepared and typical examples include the synthesis of fused ring heterocycles *via* cascade cyclisation[6,7] and chiral amino acid-derived

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†Electronic supplementary information (ESI) available: Copies of ^{1}H and ^{13}C NMR spectra of all compounds. CCDC 1435297–1435299. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c5ob02467f
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Scheme 1

alkynes.[8] FVP is a technique of increasing importance in the synthesis of heterocyclic compounds,[9] but has not so far seen any significant application in carbohydrate chemistry. In fact the use of FVP in carbohydrate chemistry is effectively limited to a single example: the pyrolytic elimination of acetic acid to form a derivative of zanamivir (Relenza).[10] In this paper we describe the preparation and pyrolysis behaviour of a series of ylides containing tetrahydrofuran, tetrahydropyran and 2,2-dimethyl-1,3-dioxolane rings to check the compatibility of these ring systems common in carbohydrates with the conditions required for alkyne formation. There has been considerable interest in acetylenic carbohydrate derivatives, both in their own right,[11] and as intermediates in synthesis of modified nucleosides.[12,13] Alkyne-containing 2,2-dimethyl-1,3-dioxolanes have also found use in total synthesis.[14,15] There is a single previous example of this approach in which a tetrahydropyran-containing ylide **1** was prepared and subjected to conventional pyrolysis at 200–250 °C (heating the solid above its mp) to afford alkyne **2** in 75% yield (Scheme 2).[16]
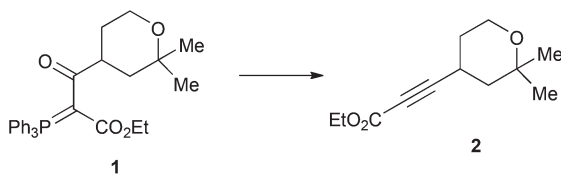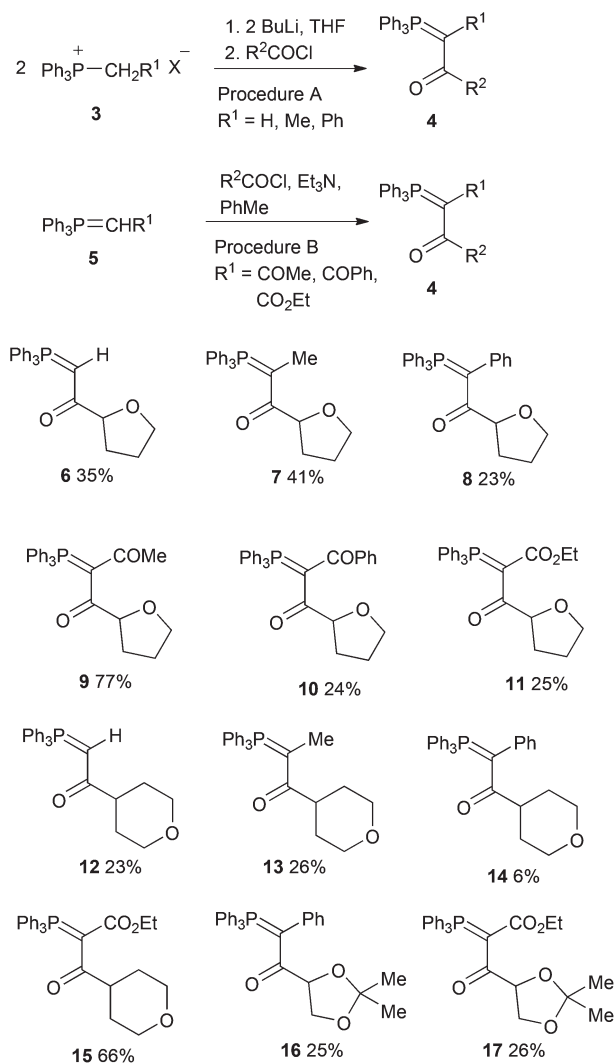
Results and discussion

The ylides **4** were prepared by two different methods depending on the nature of R^1 (Scheme 3). For monostabilised ylides

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Scheme 2

Scheme 3 Synthetic routes used and new ylides prepared.

(R^1 = H, Me, Ph) reaction of the appropriate phosphonium salt **3** with butyllithium in THF followed by the acid chloride proceeded with "transylidation"[17] requiring a 2 : 1 reacting ratio, while for distabilised ylides (R^1 = COMe, COPh, CO_2Et) reaction of **5** with the acid chloride and triethylamine in toluene was used.[18] Tetrahydrofuran-2-carbonyl chloride was prepared by reaction of the commercially available acid with oxalyl chloride, tetrahydropyran-4-carbonyl chloride was prepared by hydrolysis of methyl tetrahydropyran-4-carboxylate using

sodium hydroxide followed by reaction with thionyl chloride, while 2,2-dimethyl-1,3-dioxolane-4-carbonyl chloride was prepared from mannitol diacetonide by sodium periodate cleavage[19] followed by potassium permanganate oxidation of the resulting aldehyde and treatment of the potassium carboxylate with oxalyl chloride.[20] The 12 ylides **6–17** were obtained in low to moderate yield as colourless or pale yellow crystals (Scheme 3). They all gave ^{31}P NMR chemical shifts in the range δ_P +14.9–17.9 and the ^{13}C NMR spectra showed a highly consistent and informative pattern of phosphorus coupling. X-Ray diffraction has previously been used to obtain valuable information on the structure of stabilised ylides, particularly in respect of the P=C–C=O torsion angle which is important for successful pyrolytic alkyne formation.[21] Since no X-ray structures of ylides containing saturated oxygen heterocycles are known, we have determined the structure of one representative example from each of the three ring systems.

The structure of compound **10** (Fig. 1) shows an almost planar tetrahydrofuran ring and both carbonyl groups *syn* to the P=C bond. However the degree of delocalisation in the sense P^+–C=C–O^- as indicated by the CC and CO bond lengths is much greater for the CO–THF function with a torsion angle of 0.7° than for the COPh with a torsion angle of 34°.

In the tetrahydropyran series, the structure of the monostabilised ylide **13** was determined (Fig. 2) and this shows the tetrahydropyran in an almost perfect chair conformation with the oxo ylide function equatorial. The bond lengths again show the oxo ylide function to be substantially delocalised in the sense P^+–C=C–O^- and P=C and C=O are *syn*.

The structure of **17** proved to be more complex with two separate and slightly different molecules in the unit cell (Fig. 3). In each case the ester carbonyl is *anti* to the P=C bond while the dioxolanyl ketone is *syn* to it but, while the molecule containing P(41) has these functions almost coplanar (torsion angles 178.7 and 1.0°), the geometry for the other molecule containing P(1) is less ideal (torsion angles 156.8 and 10.6°).
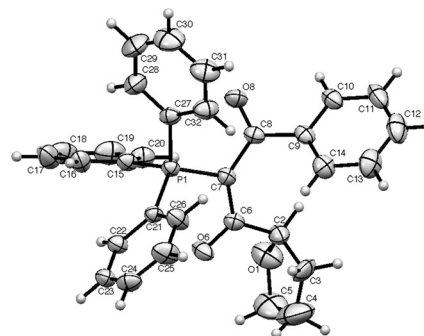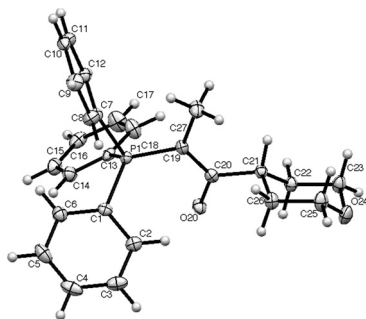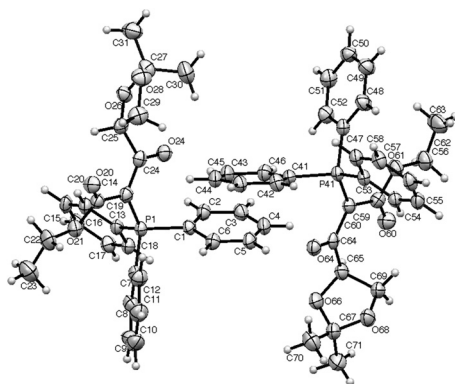

Fig. 1 X-ray structure of **10** showing numbering scheme. Selected bond lengths and torsion angles: P(1)−C(7) 1.752(2), C(7)−C(8) 1.459(3), C(8)−O(8) 1.232(2), C(7)−C(6) 1.423(3), C(6)−O(6) 1.240(2) Å; P(1)−C(7)−C(8)−O(8) 34.2(2), P(1)−C(7)−C(6)−O(6) 0.7(2)°.

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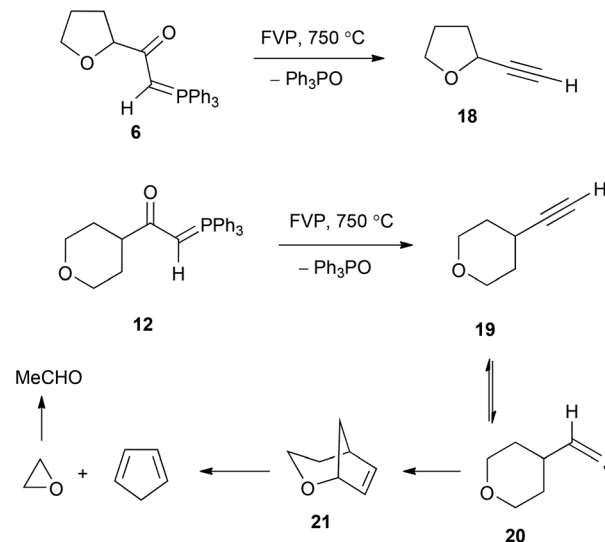
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Fig. 2 X-ray structure of 13 showing numbering scheme. Selected bond lengths and torsion angle: P(1)−C(19) 1.729(2), C(19)−C(20) 1.396(2), C(20)−O(20) 1.267(2) Å; P(1)−C(19)−C(20)−O(20) 2.4(2)°.
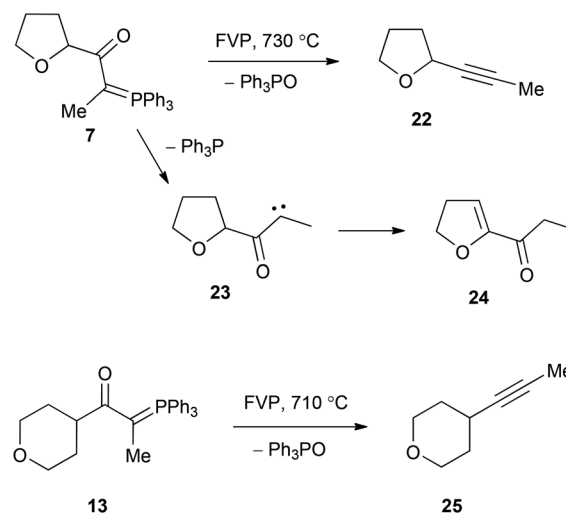

Fig. 3 X-ray structure of 17 showing numbering scheme. Selected bond lengths and torsion angles: P(1)−C(19) 1.751(5), C(19)−C(24) 1.434(6), C(24)−O(24) 1.227(7), C(19)−C(20) 1.445(9), C(20)−O(20) 1.208(7), P(41)−C(59) 1.760(6), C(59)−C(60) 1.445(9), C(60)−O(60) 1.215(7), C(59)−C(64) 1.444(6), C(64)−O(64) 1.224(7) Å; P(1)−C(19)−C(24)−O(24) 10.6(7), P(1)−C(19)−C(20)−O(20) 156.8(4), P(41)−C(59)−C(60)−O(60) 178.7(4), P(41)−C(59)−C(64)−O(64) 1.0(7)°.

The behaviour of the compounds was now studied under flash vacuum pyrolysis conditions. The apparatus used has been described previously,[22] and based on our extensive experience with oxo stabilised ylides, temperatures in the range 500–750 °C were used with a pressure of $1–5 \times 10^{-2}$ Torr. The two compounds with a hydrogen atom on the ylidic bond, 6 and 12, reacted completely at 750 °C with clean extrusion of Ph_3PO being observed in each case (Scheme 4). For 6 the other product was the expected terminal alkyne 18 (36%) together with a little furan and benzene from thermal degradation. In the case of the tetrahydropyran compound 12, the expected alkyne 19 (42%) was again formed but this was now accompanied by low yields of cyclopentadiene and acetaldehyde. We believe these to result from the mechanism shown in Scheme 4 in which the alkyne isomerises to the vinylidene 20 and this undergoes intramolecular CH insertion at the 2-position of the tetrahydropyran to form the bicyclic product 21. This is then set up to undergo a retro Diels–Alder reaction with formation of cyclopentadiene and oxirane, which
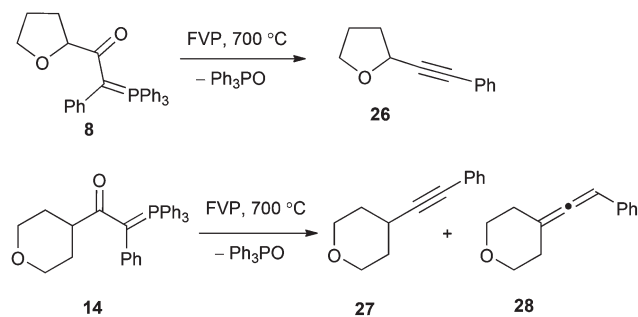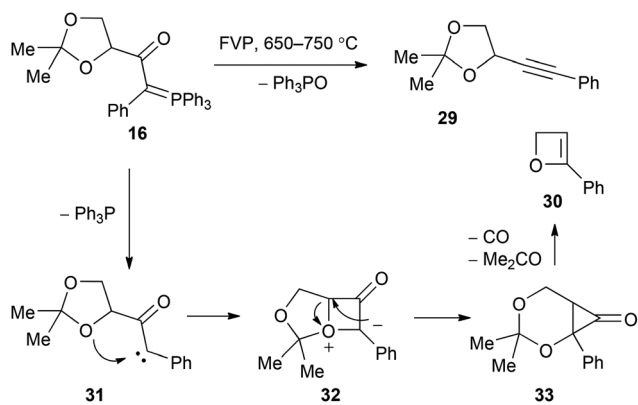

Scheme 4

Scheme 5

isomerises to acetaldehyde. The formation of vinylidenes such as 20 by rearrangement of alkynes under FVP conditions is well known,[23] and will be encountered again in the FVP of 9 and 10.

The ylide 7 with a methyl group on the ylidic position reacted completely at 730 °C to give a 2 : 1 mixture of Ph_3P and Ph_3PO at the furnace exit. In the cold trap the expected alkyne 22 (20%) from loss of Ph_3PO was accompanied by 2-propionyl-4,5-dihydrofuran 24 (30%) (Scheme 5). We propose that this product is formed by loss of Ph_3P to give the (triplet) carbene 23, which then undergoes twofold intramolecular hydrogen atom abstraction to afford the product. In contrast the corresponding tetrahydropyran ylide 13 underwent exclusive elimination of Ph_3PO at 710 °C to give the expected alkyne 25 in

Scheme 6

Scheme 7
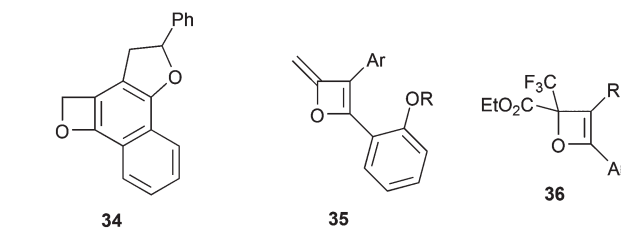
Scheme 8 Previously reported oxetes.

good yield as the only product. The extrusion of a phosphine as opposed to phosphine oxide from β-oxophosphonium ylides is very unusual, but has been observed in the FVP of a benzotriazolyl ylide,[24,25] and also upon photolysis of Ph₃P=CHCOPh.[26]

The two compounds **8** and **14** with a phenyl substituent on the ylidic carbon both reacted completely at 700 °C with exclusive elimination of Ph₃PO. With the tetrahydrofuran compound **8** the product was the known alkyne **26** (56%) (Scheme 6), which showed good agreement with literature spectroscopic data,[27,28] while for the tetrahydropyran compound **14**, the expected alkyne product **27** (46%) was accompanied by the isomeric allene **28** (20%). The ylide **16** containing phenyl and 2,2-dimethyl-1,3-dioxolane groups was found to undergo loss of both Ph₃PO and Ph₃P to give separate products with the relative importance of the two competing pathways varying with temperature (Scheme 7). Thus at 650 °C, there was predominant loss of Ph₃PO (Ph₃PO/Ph₃P 8 : 1) to afford the expected alkyne **29** in 48% yield readily identified by comparison with reported spectroscopic data.[29] By increasing the pyrolysis temperature to 750 °C the importance of the Ph₃P elimination route was increased (Ph₃PO/Ph₃P 3 : 1) and this allowed tentative identification of the resulting product as 2-phenyloxete **30**. A correct HRMS measurement corresponding to **30** was obtained and, although peak overlap prevented full spectroscopic characterisation, the key signals in ¹H and ¹³C NMR spectra were consistent with a highly shielded (enol ether) =CH– [δ_H 6.16 (1 H, t, J 6.9); δ_C 93.9] adjacent to a –CH₂O– [δ_H 5.14 (2 H, d, J 6.9); δ_C 78.7] function. The latter compares well with the value of δ_H 5.44 observed for the oxete CH₂ in compound **34** (Scheme 8).[30]

Simple oxetes such as this are almost unknown but there has been recent interest in more highly substituted examples such as the 4-methylene compounds **35** obtained by gold-catalysed cyclisation of α-hydroxybenzylallenes,[31] and stable fully substituted compounds **36** prepared in high enantiomeric purity from ethyl trifluoropyruvate and alkynes.[32] The parent compound has also been generated[33] and was stable enough for a ¹H NMR spectrum to be recorded at −25 °C [δ_H 6.70 (1 H, br s), 5.73 (1 H, br s) and 5.27 (2 H, br s)], but it isomerised to acrolein on warming to room temperature.
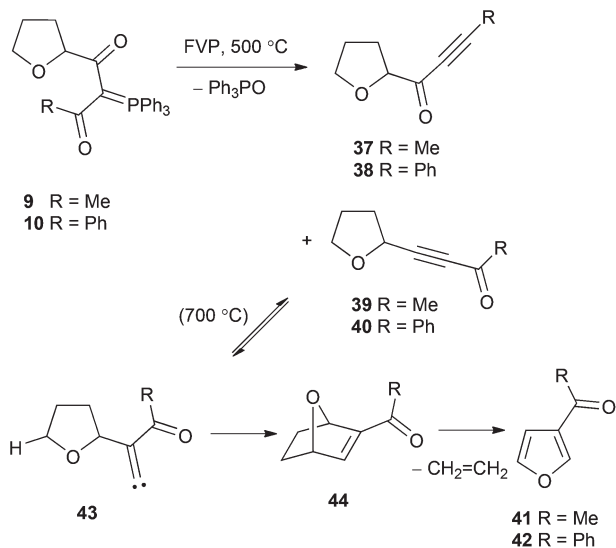
We rationalise the formation of **30**, as shown in Scheme 7, by initial loss of Ph₃P from ylide **16** to give the carbene **31** which undergoes intramolecular oxonium ylide formation to form **32**. This can then rearrange as shown to give **33**, which loses CO and acetone to afford the oxete. Further support for this route was provided by the observation of acetone among the pyrolysis products.

We next examined the two ylides **9** and **10** where there is potentially a choice between elimination of Ph₃PO in two directions to give isomeric alkynyl ketones. In previous such cases there has been little selectivity with almost equal proportions of the two possible products being formed.[34,35] This also proved to be the case here, with compound **9** undergoing complete extrusion of Ph₃PO at 500 °C to afford a mixture of **37** (26%) and **39** (58%), while the benzoyl compound **10** gave a mixture of **38** (29%) and **40** (30%) under the same conditions (Scheme 9). All these alkynyl ketone products are previously unknown.

When ylides **9** and **10** were pyrolysed at the higher temperature of 700 °C an interesting new process was observed. In each case the previously observed alkynyl ketones were still formed but these were accompanied by the 3-acylfurans **41** and **42**, readily identified by comparison with literature spectroscopic data.[36,37] Thus FVP of **9** at 700 °C gave **37** (18%), **39** (33%) and **41** (17%) while under the same conditions **10** gave **38** (12%), **40** (14%) and **42** (37%). As shown we propose that this involves isomerisation[23] of the alkynyl ketones **39** and **40** to the vinylidene **43** which undergoes intramolecular
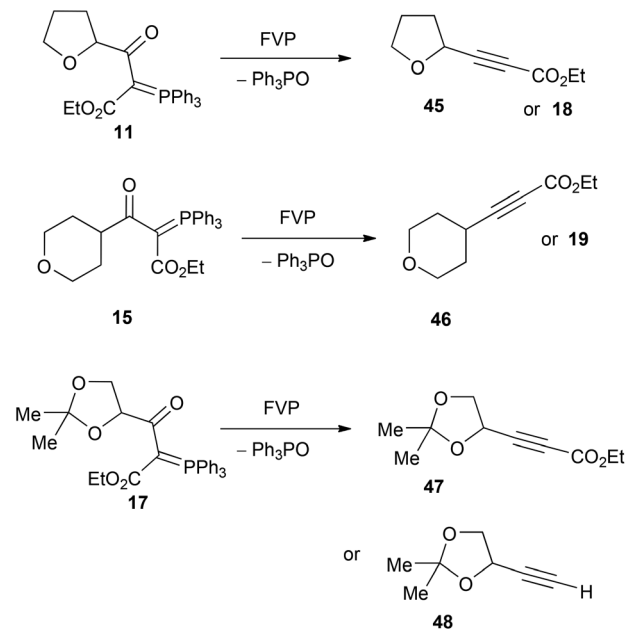
Scheme 9

Scheme 10

insertion into the marked CH bond to give the oxabicyclic compounds **44** which are ideally set up to undergo retro-Diels Alder elimination of ethene to afford the observed acylfuran products.

Pyrolysis of ylides containing both adjacent ester and ketone carbonyl functions is well known to result in elimination of Ph₃PO only from the latter to give acetylenic esters. The method was first developed by Märkl using conventional pyrolysis of methyl esters,[3] but was later shown to also be amenable to FVP conditions using ethyl esters.[38] An added advantage of using the latter technique is that, while efficient Ph₃PO elimination to give the acetylenic esters occurs at 500 °C, simply increasing the temperature to 750 °C additionally leads to loss of the whole ester group to afford the alk-1-ynes. Mechanistic studies of this unusual process have been described.[39] In agreement with this pattern, when the three ester-containing ylides **11**, **15**, and **17** were subjected to FVP, mixtures of the acetylenic esters and the alk-1-ynes were obtained with the ratio depending on the temperature (Scheme 10). Thus at 500 °C, FVP of **11** gave ester **45** (42%) together with the alkyne **18** (16%). At 750 °C, there was extensive decomposition with only products such as furan and cyclopentadiene isolated in low yield. FVP of the tetrahydropyran ylide **15** at 500 °C gave the ester **46** in 60% yield, while increasing the furnace temperature to 750 °C led to alkyne **19** (30%) together with the decomposition products cyclopentadiene (20%) and acetaldehyde (25%) formed from **19** as shown in Scheme 4.

FVP of **17** at 600 °C gave mainly the ester **47** (68%) with a little of the alkyne **48** (9%) while at 650 °C the ratio of products had changed to **47** (39%) and **48** (30%). It therefore appears that lower temperature FVP of these three ylides provides an effective route to the acetylenic esters but for the alk-1-ynes FVP of ylides such as **6** and **12** is preferable.

Experimental

Instrumentation, general techniques and starting materials

Melting points were recorded on a Kofler hot-stage microscope and are uncorrected. Infra red spectra were recorded as Nujol mulls for solids and as thin films for liquids on a Perkin Elmer 1420 instrument. NMR spectra were obtained for ¹H at 300, 400 or 500 MHz, for ¹³C at 75, 100 or 125 MHz and for ³¹P at 121 MHz all using Bruker instruments. All spectra were run on solutions in CDCl₃ with internal Me₄Si as reference for ¹H and ¹³C and external H₃PO₄ for ³¹P. Chemical shifts are reported in ppm to high frequency of the reference and coupling constants J are in Hz. Mass spectra were obtained on a Micromass LCT spectrometer using electrospray ionisation.

Tetrahydrofuran-2-carbonyl chloride was prepared (87%) by reaction of the commercially available acid with oxalyl chloride, tetrahydropyran-4-carbonyl chloride was prepared by hydrolysis of methyl tetrahydropyran-4-carboxylate using sodium hydroxide (quant.) followed by reaction with thionyl chloride (84%), while 2,2-dimethyl-1,3-dioxolane-4-carbonyl chloride was prepared from mannitol diacetonide by sodium periodate cleavage[19] followed by potassium permanganate oxidation of the resulting aldehyde and treatment of the potassium carboxylate with oxalyl chloride.[20]

General procedure A for synthesis of monostabilised ylides

A suspension of the appropriate phosphonium salt (1 equiv.) in dry THF was stirred at rt under nitrogen while a solution of n-BuLi in hexanes (2.5 M, 1 equiv.) was added dropwise by syringe. After the addition the mixture was stirred for 30 min and then a solution of the acid chloride (0.5 equiv.) in dry THF was added dropwise. The mixture was stirred for 12 h and then

partitioned between water and diethyl ether. The organic extract was dried (MgSO$_4$) and evaporated to give the product. If necessary a little EtOAc was added to induce crystallisation and the products were recrystallised from EtOAc.

General procedure B for synthesis of distabilised ylides

A solution of the appropriate stabilised ylide (1 equiv.) and triethylamine (1 equiv.) in dry toluene (15 cm^3) was stirred at rt while a solution of the acid chloride (1 equiv.) in dry toluene (5 cm^3) was added dropwise. After stirring for 12 h, the mixture was filtered to remove triethylamine hydrochloride and the filtrate was evaporated to give the product. If necessary a little EtOAc was added to induce crystallisation and the products were recrystallised from EtOAc.

Tetrahydrofuran-containing ylides

1-(Tetrahydrofuran-2-yl)-2-(triphenylphosphoranylidene)ethan-1-one 6. Reaction using procedure A with methyltriphenylphosphonium bromide (10.62 g, 29.7 mmol) in THF (50 cm^3), 2.5 M n-BuLi (12.34 cm^3, 29.7 mmol) and tetrahydrofuran-2-carbonyl chloride (2.00 g, 14.86 mmol) in THF (20 cm^3) gave the product (1.97 g, 35%) as pale yellow crystals, mp 187–189 °C (from EtOAc) (Found 375.1504. C$_{24}$H$_{24}$O$_2$P (M + H) requires 375.1514); ν_{max}/cm^{-1} 1531 (CO), 1102, 1072, 872, 758, 716 and 696; δ_H (300 MHz) 7.70–7.60 (6 H, m), 7.60–7.50 (3 H, m), 7.50–7.40 (6 H, m), 4.40–4.30 (1 H, m, 2-H), 4.16 (1 H, d, J 26.3, CH=P), 4.10–4.00 (1 H, m, 5-H), 3.90–3.80 (1 H, m, 5-H), 2.30–2.15 (1 H, m) and 2.10–1.80 (3 H, m); δ_C (100 MHz) 193.6 (d, J 3, CO), 133.0 (d, J 10, C-2 of Ph), 132.0 (d, J 1, C-4 of Ph), 128.8 (d, J 12, C-3 of Ph), 127.0 (d, J 90, C-1 of Ph), 83.0 (d, J 13, 2-CH), 68.9 (5-CH$_2$), 48.5 (d, J 109, P=CH), 30.9 (3-CH$_2$) and 25.7 (4-CH$_2$); δ_P (121 MHz) +16.2; m/z (ESI) 771.28 (2M + Na, 7%), 397.13 (M + Na, 12) and 375.15 (M + H, 100).

1-(Tetrahydrofuran-2-yl)-2-(triphenylphosphoranylidene)propan-1-one 7. Reaction using procedure A with ethyltriphenylphosphonium bromide (5.6 g, 15 mmol) in THF (40 cm^3), 2.5 M n-BuLi (6.0 cm^3, 15 mmol) and tetrahydrofuran-2-carbonyl chloride (1.0 g, 7.43 mmol) in THF (10 cm^3) gave the product (1.20 g, 41%) as colourless crystals, mp 115–117 °C (from EtOAc) (Found 389.1620. C$_{25}$H$_{26}$O$_2$P (M + H) requires 389.1670); ν_{max}/cm^{-1} 1520 (CO), 1105, 923, 750, 711 and 693; δ_H (300 MHz) 7.60–7.39 (15 H, m), 4.87 (1 H, td, J 7.2, 1.2, 2-H), 4.04–3.97 (1 H, m, 5-H), 3.90–3.83 (1 H, m, 5-H), 2.15–2.07 (1 H, m), 2.00–1.60 (3 H, m) and 1.68 (3 H, d, J 16.5, Me); δ_C (75 MHz) 188.4 (d, J 4, CO), 133.4 (d, J 10, C-2 of Ph), 131.3 (d, J 3, C-4 of Ph), 128.5 (d, J 12, C-3 of Ph), 127.3 (d, J 90, C-1 of Ph), 78.8 (d, J 14, 2-CH), 68.8 (5-CH$_2$), 55.7 (d, J 107, P=C), 29.3 (3-CH$_2$), 25.9 (4-CH$_2$) and 12.3 (d, J 12, Me); δ_P (121 MHz) +17.9; m/z (ESI) 389.16 (M + H, 100).

2-Phenyl-1-(tetrahydrofuran-2-yl)-2-(triphenylphosphanylidene)ethan-1-one 8. Reaction using procedure A with benzyltriphenylphosphonium chloride (5.78 g, 14.86 mmol) in THF (20 cm^3), 2.5 M n-BuLi (6.0 cm^3, 15.0 mmol) and tetrahydrofuran-2-carbonyl chloride (1.0 g, 7.43 mmol) in THF (10 cm^3) gave the product (0.78 g, 23%) as pale yellow crystals, mp 179–182 °C (from EtOAc) (Found 451.1809. C$_{30}$H$_{28}$O$_2$P (M + H) requires 451.1827); ν_{max}/cm^{-1} 1530 (CO), 1223, 1106, 1068, 746, 701 and 693; δ_H (300 MHz) 7.57–7.42 (9 H, m), 7.38–7.32 (6 H, m), 7.05–6.95 (5 H, m), 4.58 (1 H, t, J 6.4, 2-H), 4.00–3.92 (1 H, m, 5-H), 3.80–3.73 (1 H, m, 5-H), 1.99–1.82 (3 H, m) and 1.73–1.65 (1 H, m); δ_C (125 MHz) 189.0 (d, J 5, CO), 137.2 (d, J 11, C-1 of Ph), 135.0 (d, J 5, C-2 of Ph), 133.6 (d, J 10, C-2 of PPh), 131.4 (d, J 3, C-4 of PPh), 128.4 (d, J 12, C-3 of PPh), 127.5 (d, J 1, C-3 of Ph), 126.8 (d, J 90, C-1 of PPh), 125.2 (d, J 3, C-4 of Ph), 78.2 (d, J 12, 2-CH), 70.2 (d, J 106, P=C), 69.2 (5-CH$_2$), 30.4 (3-CH$_2$) and 26.2 (4-CH$_2$); δ_P (121 MHz) +15.5; m/z (ESI) 923.34 (2M + Na, 42%), 473.16 (M + Na, 6) and 451.18 (M + H, 100).

1-(Tetrahydrofuran-2-yl)-2-(triphenylphosphoranylidene)butane-1,3-dione 9. Reaction using procedure B with triphenylphosphoranylideneacetone (2.37 g, 7.43 mmol), triethylamine (1.03 cm^3, 0.75 g, 7.43 mmol) and tetrahydrofuran-2-carbonyl chloride (1.00 g, 7.43 mmol) in toluene (20 cm^3) gave the product (2.4 g, 77%) as colourless crystals, mp 127.5–129.5 °C (from EtOAc) (Found 439.1421. C$_{26}$H$_{25}$NaO$_3$P (M + Na) requires 439.1439); ν_{max}/cm^{-1} 1553 (CO), 1108, 1066, 757 and 698; δ_H (300 MHz) 7.70–7.60 (6 H, m), 7.50–7.35 (9 H, m), 4.86 (1 H, dd, J 7.5, 5.4, 2-H), 3.89–3.82 (1 H, m, 5-H), 3.76–3.69 (1 H, m, 5-H), 2.15–2.00 (2 H, m), 2.09 (3 H, d, J 0.6, Me) and 1.82–1.72 (2 H, m); δ_C (75 MHz) 196.2 (d, J 7, 1-CO), 192.7 (d, J 10, 3-CO), 133.0 (d, J 10, C-2 of Ph), 131.6 (d, J 3, C-4 of Ph), 128.5 (d, J 12, C-3 of Ph), 126.3 (d, J 91, C-1 of Ph), 86.0 (d, J 100, P=C), 80.9 (d, J 6, 2-CH), 68.8 (5-CH$_2$), 30.1 (d, J 4, Me), 29.6 (3-CH$_2$) and 25.3 (4-CH$_2$); δ_P (121 MHz) +15.6; m/z (ESI) 855.30 (2M + Na, 12%), 439.14 (M + Na, 100) and 417.16 (M + H, 18).

1-Phenyl-3-(tetrahydrofuran-2-yl)-2-(triphenylphosphoranylidene)propane-1,3-dione 10. Reaction using procedure B with triphenylphosphoranylideneacetophenone (2.83 g, 7.43 mmol), triethylamine (1.03 cm^3, 0.75 g, 7.43 mmol) and tetrahydrofuran-2-carbonyl chloride (1.00 g, 7.43 mmol) in toluene (20 cm^3) gave the product (0.84 g, 24%) as pale yellow crystals, mp 179–181 °C (from EtOAc) (Found 479.1762. C$_{31}$H$_{28}$O$_3$P (M + H) requires 479.1776); ν_{max}/cm^{-1} 1546 (CO), 1317, 1105, 1061, 713 and 694; δ_H (300 MHz) 7.70–7.60 (8 H, m), 7.50–7.25 (12 H, m), 4.54 (1 H, t, J 6.7, 2-H), 3.85–3.70 (1 H, m, 5-H), 3.65–3.55 (1 H, m, 5-H), 1.85–1.75 (2H, m) and 1.70–1.57 (2 H, m); δ_C (75 MHz) 195.0 (d, J 3, CO), 192.8 (d, J 10, CO), 143.4 (d, J 8, C-1 of COPh), 133.2 (d, J 10, C-2 of PPh), 131.7 (d, J 3, C-4 of PPh), 130.8 (C-4 of COPh), 128.8 (2CH of COPh), 128.5 (d, J 12, C-3 of PPh), 128.1 (2CH of COPh), 125.7 (d, J 92, C-1 of PPh), 83.3 (d, J 100, P=C), 79.7 (d, J 9, 2-CH), 69.1 (5-CH$_2$), 30.1 (3-CH$_2$) and 25.4 (4-CH$_2$); δ_P (121 MHz) +17.5; m/z (ESI) 979.33 (2M + Na, 62%), 501.16 (M + Na, 55) and 479.18 (M + H, 100).

Ethyl 3-oxo-3-(tetrahydrofuran-2-yl)-2-(triphenylphosphoranylidene)propanoate 11. Reaction using procedure B with ethyl triphenylphosphoranylideneacetate (2.58 g, 7.43 mmol), triethylamine (1.03 cm^3, 0.75 g, 7.43 mmol) and tetrahydrofuran-2-carbonyl chloride (1.00 g, 7.43 mmol) in toluene (20 cm^3) gave the product (0.82 g, 25%) as colourless crystals, mp 175–177 °C (from EtOAc) (Found 447.1712. C$_{27}$H$_{28}$O$_4$P

(M + H) requires 447.1725); ν_{max}/cm^{-1} 1654 (CO), 1575 (CO), 1299, 1105, 1082, 750 and 692; δ_H (300 MHz) 7.70–7.60 (6 H, m), 7.58–7.38 (9 H, m), 5.51 (1 H, ddd, J 8.2, 5.2, 1.0, 2-H), 3.95–3.80 (2 H, m, 5-H), 3.80–3.65 (2 H, m, CH$_2$ of Et), 2.50–2.38 (1 H, m), 2.10–1.90 (1H, m), 1.90–1.75 (2 H, m) and 0.67 (3 H, t, J 7.1, CH$_3$ of Et); δ_C (100 MHz) 196.6 (d, J 3, 3-CO), 167.4 (d, J 15, 1-CO), 133.0 (d, J 10, C-2 of Ph), 131.5 (d, J 2, C-4 of Ph), 128.4 (d, J 12, C-3 of Ph), 126.5 (d, J 93, C-1 of Ph), 80.7 (d, J 9, 2-CH), 69.1 (5-CH$_2$), 68.8 (d, J 109, P=C), 58.4 (OEt), 30.9 (3-CH$_2$), 25.2 (4-CH$_2$) and 13.7 (OEt); δ_P (121 MHz) +17.1; m/z (ESI) 915.32 (2M + Na, 20%) and 447.17 (M + H, 100).

Tetrahydropyran-containing ylides

1-(Tetrahydropyran-4-yl)-2-(triphenylphosphoranylidene) ethanone 12. Reaction using procedure A with methyl-triphenylphosphonium bromide (9.61 g, 26.9 mmol) in THF (50 cm^3), 2.5 M n-BuLi (11.17 cm^3, 26.9 mmol) and tetrahydro-pyran-4-carbonyl chloride (2.00 g, 13.45 mmol) in THF (20 cm^3) gave the product (1.21 g, 23%) as pale orange crystals, mp 162–164 °C (from EtOAc) (Found 389.1659. C$_{25}$H$_{26}$O$_2$P (M + H) requires 389.1670); ν_{max}/cm^{-1} 1540 (CO), 1400, 1110, 1082, 860, 752, and 697; δ_H (300 MHz) 7.70–7.60 (6 H, m), 7.60–7.50 (3 H, m), 7.50–7.40 (6 H, m), 4.10–3.95 (2 H, m), 3.70 (1 H, d, J 25.8, CH=P), 3.50–3.35 (2 H, m), 2.45–2.30 (1 H, m, 4-H) and 1.90–1.75 (4 H, m); δ_C (100 MHz) 195.1 (d, J 1, CO), 132.9 (d, J 10, C-2 of Ph), 131.9 (d, J 1, C-4 of Ph), 128.8 (d, J 12, C-3 of Ph), 127.2 (d, J 90, C-1 of Ph), 68.1 (2,6-CH$_2$), 49.2 (d, J 107, P=CH), 46.2 (d, J 14, 4-CH) and 30.8 (3,5-CH$_2$); δ_P (121 MHz) +15.9; m/z (ESI) 389.17 (M + H, 100).

1-(Tetrahydropyran-4-yl)-2-(triphenylphosphoranylidene) propan-1-one 13. Reaction using procedure A with ethyltriphe-nylphosphonium bromide (5.00 g, 13.4 mmol) in THF (40 cm^3), 2.5 M n-BuLi (5.40 cm^3, 13.4 mmol) and tetrahydro-pyran-4-carbonyl chloride (1.00 g, 6.73 mmol) in THF (10 cm^3) gave the product (0.71 g, 26%) as yellow crystals, mp 183–185 °C (from EtOAc) (Found 403.1810. C$_{26}$H$_{28}$O$_2$P (M + H) requires 403.1827); ν_{max}/cm^{-1} 1520 (CO), 1099, 856, 754, 716 and 697; δ_H (300 MHz) 7.60–7.35 (15 H, m), 4.10–3.95 (2 H, m), 3.50 (2 H, td, J 12, 3), 2.93 (1 H, tt, J 7.8, 3.9, 4-H), 1.95–1.80 (2 H, m), 1.66 (3 H, d, J 16.2, Me) and 1.66–1.55 (2 H, m); δ_C (75 MHz) 191.2 (d, J 4, CO), 133.3 (d, J 10, C-2 of Ph), 131.2 (d, J 3, C-4 of Ph), 128.4 (d, J 12, C-3 of Ph), 128.0 (d, J 90, C-1 of Ph), 68.1 (2,6-CH$_2$), 55.4 (d, J 106, P=C), 40.7 (d, J 10, 4-CH), 29.2 (3,5-CH$_2$) and 12.7 (d, J 14, Me); δ_P (121 MHz) +16.8; m/z (ESI) 425.16 (M + Na, 12%) and 403.18 (M + H, 100).

2-Phenyl-1-(tetrahydropyran-4-yl)-2-(triphenylphosphoranyl-idene)ethan-1-one 14. Reaction using procedure A with benzyl-triphenylphosphonium chloride (5.23 g, 13.4 mmol) in THF (20 cm^3), 2.5 M n-BuLi (5.4 cm^3, 13.46 mmol) and tetrahydro-pyran-4-carbonyl chloride (1.00 g, 6.73 mmol) in THF (10 cm^3) gave the product (0.20 g, 6%) as pale yellow crystals, mp 178–182 °C (from EtOAc) (Found 465.1962. C$_{31}$H$_{30}$O$_2$P (M + H) requires 465.1983); ν_{max}/cm^{-1} 1520 (CO), 1124, 1105, 861, 756, 709 and 691; δ_H (300 MHz) 7.60–7.40 (9 H, m), 7.40–7.30 (6 H, m), 7.05–6.95 (5 H, m), 3.95–3.85 (2 H, m), 3.24 (2 H, td, J 12, 2), 2.74 (1 H, tt, J 11.4, 3.9, 4-H), 1.95–1.75 (2 H, m) and

1.55–1.48 (2 H, m); δ_C (125 MHz) 191.4 (d, J 5, CO), 137.9 (d, J 13, C-1 of Ph), 134.8 (d, J 5, C-2 of Ph), 133.5 (d, J 10, C-2 of PPh), 131.2 (d, J 3, C-4 of PPh), 128.3 (d, J 12, C-3 of PPh), 127.6 (d, J 2, C-3 of Ph), 127.4 (d, J 90, C-1 of PPh), 125.1 (d, J 2, C-4 of Ph), 70.1 (d, J 108, P=C), 67.8 (2,6-CH$_2$), 41.1 (d, J 9, 4-CH) and 29.6 (3,5-CH$_2$); δ_P (121 MHz) +14.9; m/z (ESI) 951.37 (2M + Na, 18%), 487.18 (M + Na, 27%) and 465.20 (M + H, 100).

Ethyl 3-oxo-3-(tetrahydropyran-4-yl)-2-(triphenylphosphora-nylidene)propanoate 15. Reaction using procedure B with ethyl triphenylphosphoranylideneacetate (2.34 g, 6.73 mmol), triethylamine (0.94 cm^3, 0.68 g, 6.73 mmol) and tetrahydro-pyran-4-carbonyl chloride (0.89 g, 6.73 mmol) in toluene (20 cm^3) gave the product (2.05 g, 66%) as pale yellow crystals, mp 170–171 °C (from EtOAc) (Found 461.1867. C$_{28}$H$_{30}$O$_4$P (M + H) requires 461.1882); ν_{max}/cm^{-1} 1657 (CO), 1556 (CO), 1291, 1107, 1080, 1063, 746 and 693; δ_H (300 MHz) 7.65–7.55 (6 H, m), 7.55–7.35 (9 H, m), 4.01–3.93 (2 H, m), 3.81 (1 H, tt, J 11.4, 3.9, 4-H), 3.70 (2 H, q, J 7.1, OEt), 3.54 (2 H, td, J 11.3, 3.0), 1.85–1.60 (4 H, m, 3,5-H) and 0.63 (3 H, t, J 7.1, OEt); δ_C (100 MHz) 198.9 (d, J 5, 3-CO), 167.5 (d, J 15, 1-CO), 132.9 (d, J 10, C-2 of Ph), 131.5 (d, J 3, C-4 of Ph), 128.4 (d, J 12, C-3 of Ph), 126.9 (d, J 93, C-1 of Ph), 69.8 (d, J 109, P=C), 68.0 (2,6-CH$_2$), 58.3 (OEt), 43.3 (d, J 7, 4-CH), 29.4 (3,5-CH$_2$) and 13.7 (OEt); δ_P (121 MHz) +17.5; m/z (ESI) 943.35 (2M + Na, 32%), 483.17 (M + Na, 7%) and 461.19 (M + H, 100).

1,3-Dioxolane-containing ylides

1-(2,2-Dimethyl-1,3-dioxolan4-yl)-2-phenyl-2-(triphenylphos-phoranylidene)ethan-1-one 16. Reaction using procedure A with benzyltriphenylphosphonium chloride (3.31 g, 8.5 mmol) in THF (40 cm^3), 2.5 M n-BuLi (3.4 cm^3, 8.5 mmol) and 2,2-dimethyl-1,3-dioxolane-4-carbonyl chloride (0.70 g, 4.25 mmol) in THF (10 cm^3) gave the product (0.51 g, 25%) as colourless crystals, mp 169–171 °C (from EtOAc) (Found 481.1914. C$_{31}$H$_{30}$O$_3$P (M + H) requires 481.1933); ν_{max}/cm^{-1} 1717, 1549 (CO), 1523, 1103, 870, 761 and 694; δ_H (300 MHz) 7.60–7.40 (9 H, m), 7.40–7.30 (6 H, m), 7.00–6.95 (5 H, m), 4.75 (1 H, ddd, J 8.4, 6.9, 1.2), 3.895 (1 H, half AB pattern of d, J 7.5, 6.9), 3.86 (1 H, half AB pattern of d, J 8.4, 7.5), 1.41 (3 H, s, Me) and 1.31 (3 H, s, Me); δ_C (75 MHz) 184.3 (d, J 6, CO), 136.5 (d, J 11, C-1 of Ph), 135.0 (d, J 5, C-2 of Ph), 133.6 (d, J 10, C-2 of PPh), 131.5 (d, J 3, C-4 of PPh), 128.4 (d, J 12, C-3 of PPh), 127.7 (d, J 2, C-3 of Ph), 126.3 (d, J 91, C-1 of PPh), 125.6 (d, J 3, C-4 of Ph), 109.7 (dioxolane C-2), 76.4 (d, J 13, dioxolane C-4), 71.0 (d, J 107, P=C), 68.0 (dioxolane C-5), 26.2 (Me) and 26.0 (Me); δ_P (121 MHz) +16.1; m/z (ESI) 481.19 (M + H, 100).

Ethyl 3-(2,2-dimethyl-1,3-dioxolan-4-yl)-3-oxo-2-(triphenyl-phosphoranylidene)propanoate 17. Reaction using procedure B with ethyl triphenylphosphoranylideneacetate (1.47 g, 4.25 mmol), triethylamine (0.60 cm^3, 0.43 g, 4.25 mmol) and 2,2-dimethyl-1,3-dioxolan-4-carbonyl chloride (0.70 g, 4.25 mmol) in toluene (10 cm^3) gave the product (0.52 g, 26%) as colourless crystals, mp 154–156 °C (Found 477.1819. C$_{28}$H$_{30}$O$_5$P (M + H) requires 477.1831); ν_{max}/cm^{-1} 1655, 1597 (CO), 1300, 1288, 1104, 1088, 842, 756 and 689; δ_H (500 MHz)

7.70–7.60 (6 H, m), 7.60–7.50 (3 H, m), 7.50–7.40 (6 H, m), 5.51 (1 H, ddd, J 7.5, 5.4, 1.2), 4.57 (1 H, dd, J 8.2, 7.5), 4.16 (1 H, dd, J 8.2, 5.4), 3.74 and 3.66 (2 H, AB pattern of q, J 10.5, 7.2), 1.39 (3 H, s, Me), 1.36 (3 H, s, Me) and 0.64 (3 H, t, J 7.2, OEt); δ_C (125 MHz) 193.2 (d, J 3, 3-CO), 167.5 (d, J 14, 1-CO), 133.1 (d, J 10, C-2 of Ph), 131.6 (d, J 3, C-4 of Ph), 128.5 (d, J 12, C-3 of Ph), 126.1 (d, J 94, C-1 of Ph), 109.9 (dioxolane C-2), 79.1 (d, J 9, dioxolane C-4), 68.94 (d, J 110, P=C), 68.89 (dioxolane C-5), 58.4 (OEt), 26.1 (Me), 25.7 (Me) and 13.6 (OEt); δ_P (121 MHz) +16.9; m/z (ESI) 975.34 (2M + Na, 35%), 499.16 (M + Na, 60) and 477.18 (M + H, 100).

X-ray structure determination

Compound **10**, $C_{31}H_{27}O_3P$, M 478.53, yellow prism. Monoclinic, space group $P2_1/c$, a 9.9232(13), b 21.836(2), c 11.4086(13) Å, β 96.272(4)°, V 2457.3(5) Å^3, Z 4, D_c 1.293 Mg m^{-3}, T 173 K, 26 295 reflections, 4506 unique (R_{int} 0.048). R_1 0.0484, wR_2 0.1407, R indices based on 3994 data with $I > 2\sigma(I)$, 316 parameters. Data were recorded using a Rigaku XtaLB P200, Mo Kα radiation (confocal optic, λ 0.71073 Å) and Saturn detector. The structure was solved by direct methods and refined using full-matrix least-squares methods.

Compound **13**, $C_{26}H_{27}O_2P$, M 402.47, colourless prism. Monoclinic, space group $P2_1/c$, a 11.829(3), b 11.011(3), c 16.248(4) Å, β 93.341(7)°, V 2112.7(9) Å^3, Z 4, D_c 1.265 Mg m^{-3}, T 93 K, 23 466 reflections, 3850 unique (R_{int} 0.0592). R_1 0.0369, wR_2 0.1090, R indices based on 3336 data with $I > 2\sigma(I)$, 263 parameters. Data were recorded using a Rigaku XtaLB P200, Mo Kα radiation (confocal optic, λ 0.71073 Å) and Saturn detector. The structure was solved by direct methods and refined using full-matrix least-squares methods.

Compound **17**, $C_{28}H_{29}O_5P$, M 476.51, colourless prism. Triclinic, space group P1, a 9.345(4), b 10.512(3), c 14.341(4) Å, α 98.497(2), β 106.816(11), γ 110.513(8)°, V 1213.3(7) Å^3, Z 2, D_c 1.304 Mg m^{-3}, T 125 K, 13 591 reflections, 6259 unique (R_{int} 0.0836). R_1 0.0570, wR_2 0.1352, R indices based on 5802 data with $I > 2\sigma(I)$, 619 parameters. Data were recorded using a Rigaku XtaLB P200, Cu Kα radiation (confocal optic, λ 1.54187 Å) and Saturn detector. The structure was solved by direct methods and refined using full-matrix least-squares methods.

Crystallographic data (excluding structure factors) for the structures included in this paper have been deposited at the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC 1435297 (**10**), 1435298 (**13**) and 1435299 (**17**).

Flash vacuum pyrolysis (FVP)

This was carried out using the apparatus previously described.[22] The contact time in the hot zone was estimated to be ∼10 ms. In each case a solid collected at the furnace exit which was found to be either Ph$_3$PO or a mixture of Ph$_3$PO and Ph$_3$P. In the cold trap the other product(s) collected as a liquid or oil and this was dissolved out using either CDCl$_3$ (small scale) for direct NMR analysis, or CH$_2$Cl$_2$ (large scale) for purification and characterisation by the usual methods.

FVP of ylide 6 (150 mg) at 750 °C gave at the furnace exit Ph$_3$PO; δ_P +29.2, and in the cold trap:

2-Ethynyltetrahydrofuran 18 (14 mg, 36%) as a colourless liquid (Found 95.0493. C_6H_7O (M − H) requires 95.0497); δ_H (300 MHz) 4.62–4.58 (1 H, m, 2-H), 4.00–3.92 (1 H, m, 5-H), 3.86–3.75 (1 H, m, 5-H), 2.43 (1 H, d, J 2.0, ≡CH) and 2.24–1.85 (m, 4H, 3,4-H); δ_C (75 MHz) 83.8 (C, –C≡), 72.5 (CH, –C≡), 67.9 (CH$_2$, C-5), 67.8 (CH, C-2), 33.2 (CH$_2$) and 25.3 (CH$_2$).

FVP of ylide 12 (110 mg) at 750 °C gave at the furnace exit Ph$_3$PO; δ_P +29.2, and in the cold trap:

A mixture containing **4-ethynyltetrahydropyran 19** (13 mg, 42%) as a colourless liquid (Found: 111.0812. $C_7H_{11}O$ (M + H) requires 111.0810); ν_{max}/cm^{-1} 3293 (≡C–H), 2240 (C≡C), 1262, 1090, 1058 and 813; δ_H (400 MHz) 3.905 (2 H, ddd, J 11.6, 5.6, 3.6, 2,6-H), 3.505 (2 H, ddd, J 11.6, 8.4, 3.2, 2,6-H), 2.68–2.61 (1 H, m, 4-H), 2.11 (1 H, d, J 2.4, ≡CH), 1.88–1.80 (2 H, m, 3,5-H) and 1.74–1.64 (2 H, m, 3,5-H); δ_C (100 MHz) 86.6 (C, –C≡), 69.1 (CH, –C≡), 66.2 (CH$_2$), 32.0 (CH$_2$) and 25.9 (CH), together with cyclopentadiene (4%); δ_H 6.57 (2 H, m), 6.47 (2 H, m) and 2.99 (2 H, m); δ_C 133.1 (CH), 132.2 (CH) and 41.6 (CH$_2$) and acetaldehyde (3%); δ_H 9.79 (1 H, q, J 3) and 2.21 (3 H, d, J 3).

FVP of ylide 7 (200 mg) at 730 °C gave at the furnace exit a 2 : 1 mixture of Ph$_3$P; δ_P −5.5 and Ph$_3$PO; δ_P +29.2, and in the cold trap:

A colourless liquid consisting of a mixture of **2-(prop-1-ynyl)tetrahydrofuran 22** (20%); δ_H (400 MHz) 4.58–4.50 (1 H, m, 2-H), 3.98–3.85 (2 H, m, 5-H), 1.90–1.80 (2 H, m), 1.75–1.70 (2 H, m) and 1.84 (3 H, d, J 1.8); δ_C (100 MHz) 79.0 (C, –C≡), 70.7 (C, –C≡), 68.3 (CH), 67.8 (CH$_2$), 33.3 (CH$_2$), 25.3 (CH$_2$) and 3.5 (Me) [good agreement of δ_H with lit.[40]] and **2-(propionyl)-4,5-dihydrofuran 24** (30%) (Found 127.0754. $C_7H_{11}O_2$ (M + H) requires 127.0759); δ_H (300 MHz) 5.94 (1 H, t, J 3.0), 4.47 (2 H, t, J 9.8), 2.82 (2 H, td, 9.8, 3.0), 2.65 (2 H, q, J 7.2) and 1.12 (3 H, t, J 7.2); δ_C (100 MHz) 193.0 (CO), 156.0 (=C–), 110.7 (=CH–), 70.1 (OCH$_2$), 32.0 (COCH$_2$), 30.5 (4-CH$_2$) and 8.0 (CH$_3$). Preparative TLC allowed separation of the latter in pure form.

FVP of ylide 13 (70 mg) at 710 °C gave at the furnace exit Ph$_3$PO; δ_P +29.2, and in the cold trap:

4-(Prop-1-ynyl)tetrahydropyran 25 (65%) (Found: 125.0969. $C_8H_{13}O$ (M + H) requires 125.0966); ν_{max}/cm^{-1} 2233 (C≡C); δ_H (300 MHz) 3.89 (2 H, ddd, J 11.7, 5.1, 3.9, 2,6-H), 3.47 (2 H, ddd, J 11.7, 8.7, 2.8, 2,6-H), 2.60–2.50 (1 H, m, 4-H), 1.81 (3 H, d, J 2.0) 1.82–1.74 (2 H, m, 3,5-H) and 1.68–1.55 (2 H, m, 3,5-H); δ_C (75 MHz) 81.7 (C, –C≡), 76.4 (C, –C≡), 66.5 (CH$_2$), 32.6 (CH$_2$), 26.3 (CH) and 3.5 (Me).

FVP of ylide 8 (80 mg) at 700 °C gave at the furnace exit Ph$_3$PO; δ_P +29.2, and in the cold trap:

2-(Phenylethynyl)tetrahydrofuran 26 (56%) as a colourless liquid (Found 195.0776. $C_{12}H_{12}ONa$ (M + Na) requires 195.0786); ν_{max}/cm^{-1} 2231 (C≡C), 1727, 1599, 1490, 1054, 757 and 692; δ_H (300 MHz) 7.6–7.2 (5 H, m), 4.81 (1 H, dd, J 7.2, 5.0, 2-H), 4.05–3.98 (1 H, m, 5-H), 3.89–3.82 (1 H, m, 5-H), 2.25–2.15 (1 H, m), 2.15–2.00 (2 H, m) and 2.00–1.85 (1 H, m);

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δ_C (75 MHz) 131.7 (2 CH), 128.22 (CH), 128.17 (2 CH), 122.8 (C), 89.0 (C, –C≡), 84.4 (C, –C≡), 68.6 (CH$_2$), 67.9 (CH), 33.4 (CH$_2$) and 25.5 (CH$_2$) [good agreement of δ_H[27] and δ_C[28] with lit.].

FVP of ylide 14 (70 mg) at 700 °C gave at the furnace exit Ph$_3$PO; δ_P +29.2, and in the cold trap:

A mixture of **4-(phenylethynyl)tetrahydropyran 27** (46%) (Found 186.1042. C$_{13}$H$_{14}$O (M) requires 186.1045); δ_H (300 MHz) 7.45–7.25 (5 H, m), 4.00–3.89 (2 H, m, 2,6-H), 3.60–3.50 (2 H, m, 2,6-H), 2.90–2.80 (1 H, m, 4-H), 1.95–1.85 (2 H, m, 3,5-H) and 1.82–1.70 (2 H, m, 3,5-H); δ_C (75 MHz) 131.6 (2 CH), 128.2 (2 CH), 126.6 (CH), 123.6 (C), 92.2 (C, –C≡), 81.5 (C, –C≡), 66.4 (CH$_2$), 32.3 (CH$_2$) and 26.8 (CH), and **4-(phenylvinylidene)tetrahydropyran 28** (20%); δ_H (300 MHz) 7.45–7.25 (5 H, m), 6.10 (1 H, quintet, J 2.1), 3.89–3.75 (2 H, m, 2,6-H), 2.38–2.33 (2 H, m, 3,5-H); δ_C (75 MHz) 200.7 (=C=), 135.2 (C), 128.6 (2 CH), 127.7 (2 CH), 126.7 (CH), 101.9 (=C<), 93.7 (=CH), 68.8 (CH$_2$) and 31.3 (CH$_2$).

FVP of ylide 16 (65 mg) at 650 °C gave at the furnace exit an 8 : 1 mixture of Ph$_3$PO; δ_P +29.2 and Ph$_3$P; δ_P −5.5, and in the cold trap:

4-Phenylethynyl-2,2-dimethyl-1,3-dioxolane 29 (48%) (Found 225.0883. C$_{13}$H$_{14}$O$_2$Na (M + Na) requires 225.0891); ν_{max}/cm^{-1} 2234, 2212 (C≡C), 1709, 1680, 1599, 1491, 1065, 758 and 692; δ_H (300 MHz) 7.48–7.40 (2 H, m), 7.35–7.25 (3 H, m), 4.95 (1 H, t, J 6.3, 4-H), 4.24 (1 H, dd, J 8.0, 6.3, 5-H), 4.01 (1 H, dd, J 8.0, 6.3, 5-H), 1.54 (3 H, q, J 0.6) and 1.43 (3 H, q, J 0.6); δ_C (75 MHz) 131.7 (2 C), 128.6 (C-4 of Ph), 128.2 (2 C), 122.2 (C-1 of Ph), 110.3 (dioxolane C-2), 86.2 (–C≡), 85.8 (–C≡), 70.0 (dioxolane C-5), 66.0 (dioxolane C-4), 26.2 and 26.0 (CMe$_2$) [good agreement of δ_H and δ_C with lit.[27]]. Acetone (20%); δ_H 2.17; δ_C 207.0 and 30.9, was also present.

FVP of ylide 16 (107 mg) at 750 °C gave at the furnace exit a 3 : 1 mixture of Ph$_3$PO; δ_P +29.2 and Ph$_3$P; δ_P −5.5, and in the cold trap a mixture of **29** (data as above), acetone, and:

2-Phenyloxete 30 (Found 133.0649. C$_9$H$_9$O (M + H) requires 133.0653); δ_H (300 MHz) 6.16 (1 H, t, J 6.9) and 5.14 (2 H, d, J 6.9); δ_C (75 MHz) 93.9 (CH) and 78.7 (CH$_2$). Due to peak overlap the phenyl and quaternary =C– signals could not be observed with certainty.

FVP of ylide 9 (70 mg) at 500 °C gave at the furnace exit Ph$_3$PO; δ_P +29.2 and in the cold trap a mixture of:

1-(Tetrahydrofuran-2-yl)but-2-yn-1-one 37 (26%); δ_H (400 MHz) 4.44 (1 H, dd, J 8.6, 5.8), 3.95–3.80 (2 H, m), 2.30–2.00 (4 H, m) and 2.07 (3 H, s); δ_C (75 MHz) 188.8 (CO), 93.7 (C, –C≡), 83.7 (CH), 78.3 (C, –C≡), 69.6 (CH$_2$), 29.3 (CH$_2$), 25.25 (CH$_2$) and 4.3 (CH$_3$) and **4-(tetrahydrofuran-2-yl)but-3-yn-2-one 39** (58%); δ_H (400 MHz) 4.74 (1 H, dd, J 8.0, 4.8), 4.1–3.9 (2 H, m), 2.2–1.8 (4 H, m) and 2.35 (3 H, s); δ_C (75 MHz) 184.3 (CO), 91.0 (C, –C≡), 83.5 (C, –C≡), 68.3 (CH$_2$), 67.6 (CH), 32.7 (CH$_2$), 32.6 (CH$_3$) and 25.34 (CH$_2$).

FVP of ylide 9 (110 mg) at 700 °C gave at the furnace exit Ph$_3$PO; δ_P +29.2 and in the cold trap a mixture of **37** (18%), **39** (33%) data as above, and:

3-Acetylfuran 41 (17%); δ_H (300 MHz) 8.03 (1 H, dd, J 1.5, 0.9), 7.45 (1 H, dd, J 2.0, 1.5), 6.77 (1 H, dd, J 2.0, 0.9) and 2.45 (3 H, s); δ_C (75 MHz) 192.6 (CO), 147.5 (CH), 144.2 (CH), 128.0 (C), 108.5 (CH) and 27.8 (CH$_3$) [good agreement of δ_H and δ_C with lit.[36]].

FVP of ylide 10 (70 mg) at 500 °C gave at the furnace exit Ph$_3$PO; δ_P +29.2 and in the cold trap:

A mixture of **3-phenyl-1-(tetrahydrofuran-2-yl)prop-2-yn-1-one 38** (29%); δ_H (300 MHz) 7.65–7.35 (5 H, m), 4.58 (1 H, dd, J 8.7, 5.7), 4.14–3.85 (2 H, m) and 2.40–1.90 (4 H, m); δ_C (75 MHz) 83.9 (CH), 69.8 (CH$_2$), 29.7 (CH$_2$) and 25.4 (CH$_2$) [due to low intensity and peak overlap, the signals for CO, –C≡ and Ph could not be assigned with certainty] and **1-phenyl-3-(tetrahydrofuran-2-yl)prop-2-yn-1-one 40** (30%); δ_H (300 MHz) 7.65–7.35 (5 H, m), 4.89 (1 H, dd, J 7.8, 4.8), 4.14–3.85 (2 H, m) and 2.40–1.90 (4 H, m); δ_C (75 MHz) 68.4 (CH$_2$), 67.9 (CH), 32.9 (CH$_2$) and 25.4 (CH$_2$) [due to low intensity and peak overlap, the signals for CO, –C≡ and Ph could not be assigned with certainty]. Aromatic CH signals for **38** and **40** were at 134.2, 133.2, 130.9, 129.6, 128.63 and 128 58.

FVP of ylide 10 (50 mg) at 700 °C gave at the furnace exit Ph$_3$PO; δ_P +29.2 and in the cold trap a mixture of **38** (12%), **40** (14%) data as above, and:

3-Benzoylfuran 42 (37%); δ_H (300 MHz) 7.93 (1 H, dd, J 1.5, 0.9), 7.87–7.82 (2 H, m), 7.62–7.56 (1 H, m), 7.51 (1 H, dd, J 1.8, 1.5), 7.50–7.46 (2 H, m) and 6.92 (1 H, dd, J 1.8, 0.9) [good agreement of δ_H with lit.[37]].

FVP of ylide 11 (120 mg) at 500 °C gave at the furnace exit Ph$_3$PO; δ_P +29.2 and in the cold trap a mixture of:

Ethyl 3-(tetrahydrofuran-2-yl)propynoate 45 (42%) (Found 167.0703. C$_9$H$_{11}$O$_3$ (M − H) requires 167.0708); ν_{max}/cm^{-1} 2239 (C≡C), 1717, 1368, 1254, 1052, 1031, 860 and 752; δ_H (400 MHz) 4.73 (1 H, dd, J 8.0, 4.0, 2-H), 4.23 (2 H, q, J 7.0), 3.99–3.92 (1 H, m, 5-H), 3.89–3.80 (1 H, m, 5-H), 2.30–2.20 (1 H, m, 4-H), 2.20–2.00 (2 H, m), 2.00–1.85 (1 H, m) and 1.31 (3 H, t, J 7.0); δ_C (100 MHz) 153.3 (CO), 86.9 (C, –C≡), 76.1 (C, –C≡), 68.3 (CH$_2$), 67.5 (CH), 62.0 (CH$_2$), 32.7 (CH$_2$), 25.3 (CH$_2$) and 13.9 (CH$_3$) and **2-ethynyltetrahydrofuran 18** (16%), data as for FVP of **6**.

FVP of ylide 11 (120 mg) at 750 °C gave at the furnace exit Ph$_3$PO: δ_P +29.2 and in the cold trap a mixture containing low yields of furan, cyclopentadiene and acetaldehyde.

FVP of ylide 15 (100 mg) at 500 °C gave at the furnace exit Ph$_3$PO; δ_P +29.2 and in the cold trap:

Ethyl 3-(tetrahydropyran-4-yl)propynoate 46 (60%) (Found 205.0830. C$_{10}$H$_{14}$O$_3$Na (M + Na) requires 205.0841); ν_{max}/cm^{-1} 2239 (C≡C), 1712, 1260, 1250, 1095, 1021 and 747; δ_H (500 MHz) 4.23 (2 H, q, J 7.0), 3.90 (2 H, ddd, J 11.6, 5.6, 3.6, 2,6-H), 3.51 (2 H, ddd, J 11.8, 8.8, 3.0, 2,6-H), 2.81–2.75 (1 H, m, 4-H), 1.91–1.84 (2 H, m, 3,5-H), 1.79–1.71 (2 H, m, 3,5-H) and 1.32 (3 H, t, J 7.0); δ_C (125 MHz) 153.8 (CO), 90.3 (C, –C≡), 73.8 (C, –C≡), 66.1 (CH$_2$), 62.0 (CH$_2$), 31.0 (CH$_2$), 26.1 (CH) and 14.0 (CH$_3$).

FVP of ylide 15 (100 mg) at 750 °C gave at the furnace exit Ph$_3$PO; δ_P +29.2 and in the cold trap **4-ethynyltetrahydropyran**

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19 (30%) together with cyclopentadiene (20%) and acetaldehyde (25%); data as for FVP of **12**.

FVP of ylide 17 (130 mg) at 600 °C gave at the furnace exit Ph₃PO; δ_P +29.2 and in the cold trap:

A mixture of **ethyl 3-(2,2-dimethyl-1,3-dioxolan-4-yl)propynoate 47** (68%) (Found 221.0782. $C_{10}H_{14}O_4Na$ (M + Na) requires 221.0790); ν_{max}/cm^{-1} 2244 (C≡C), 1716 (C=O), 1374, 1248, 1067 and 846; δ_H (300 MHz) 4.82 (1 H, dd, J 6.6, 5.6, 4-H), 4.24 (2 H, q, J 7.2), 4.21 (1 H, dd, J 8.4, 6.6, 5-H), 4.05 (1 H, dd, J 8.4, 5.6, 5-H), 1.50 (3 H, q, J 0.6), 1.39 (3 H, q, J 0.6) and 1.31 (3 H, t, J 7.2); δ_C (75 MHz) 153.0 (CO), 111.2 (dioxolane C-2), 84.2 (–C≡), 77.0 (–C≡), 69.2 (dioxolane C-5), 64.9 (dioxolane C-4), 62.2 (CH_2CH_3), 26.0 and 25.7 (CMe_2) and 13.9 (CH_2CH_3) and **4-ethynyl-2,2-dimethyl-1,3-dioxolane 48** (9%) (Found 125.0602. $C_7H_9O_2$ (M − H) requires 125.0603); δ_H (300 MHz) 4.72 (1 H, td, J 6.3, 2.1, 4-H), 4.18 (1 H, dd, J 8.1, 6.3, 5-H), 3.95 (1 H, dd, J 8.1, 6.3, 5-H), 2.51 (1 H, d, J 2.1, ≡CH), 1.50 (3 H, q, J 0.6) and 1.39 (3 H, q, J 0.6); δ_C (75 MHz) 110.5 (dioxolane C-2), 85.4 (–C≡), 73.9 (HC≡), 69.8 (dioxolane C-5), 65.2 (dioxolane C-4), 26.1 and 25.8 (CMe_2).

FVP of ylide 17 (120 mg) at 650 °C gave at the furnace exit Ph₃PO; δ_P +29.2 and in the cold trap a mixture of **47** (39%) and **48** (30%), data as above.

Conclusions

Our results show that the tetrahydrofuran, tetrahydropyran and 2,2-dimethyl-1,3-dioxolane rings are generally stable under the conditions required for alkyne formation using the FVP of stabilised phosphonium ylides. Increasing the pyrolysis temperature does lead to observation of new, largely carbene-based, processes in some cases but provided the temperature is carefully controlled the use of this method to construct acetylenic carbohydrate derivatives should be possible and further results on this will be reported shortly.

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