



Flash vacuum pyrolysis of stabilised phosphorus ylides. Part 16.¹ Model studies for the construction of conjugated polymers.

R. Alan Aitken,* Martin J. Drysdale, Lawrence Hill, Keith W. Lumbard,
James R. MacCallum and Shirley Seth

School of Chemistry, University of St. Andrews, North Haugh, St. Andrews, Fife, UK KY16 9ST

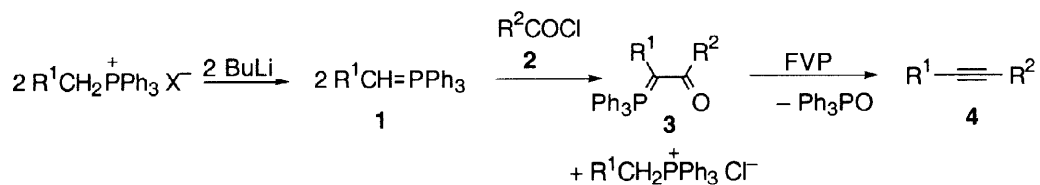
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Abstract

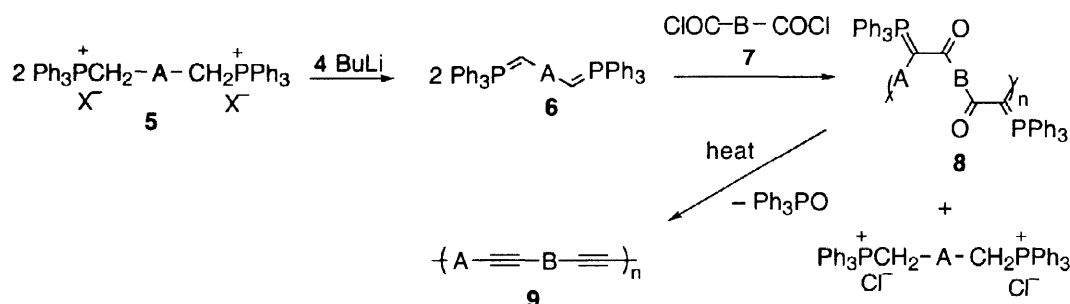
Reaction of a range of bis(ylides) with acid chlorides has been used to prepare the bis(oxoylides) **11–15**. Similarly a range of simple ylides react with bis(acid chlorides) to give bis(oxoylides) **19–27** with the isomeric structure. Flash vacuum pyrolysis (FVP) of one example of the first type results in extrusion of Ph₃P rather than the expected Ph₃PO while six examples of the second type do extrude Ph₃PO upon FVP at 500 °C to afford the bis(alkynes) **28**. Examples of the corresponding bis(tributylphosphonium ylides) have also been prepared but attempts to construct a tetrakis(oxoylide) **31** using a stepwise approach were unsuccessful. Fully assigned ¹³C NMR spectra are presented for six of the bis(oxoylides). © 1999 Elsevier Science Ltd. All rights reserved.

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In previous parts of this series we have used thermal extrusion of Ph₃PO from stabilised ylides **3** using the technique of flash vacuum pyrolysis (FVP) to prepare a variety of alkynes **4**. Since the ylides **3** are readily formed by acylation of simple ylides **1** with acid chlorides **2**, this represents a convenient and general method for synthesis of alkynes. In Parts 4² and 8,³ acetylenic acid chlorides **2** (R² = RC≡C) were used to extend the method to the preparation of 1,3-diynes and in one case a 1,3,5-triyn. There has been considerable recent interest in conjugated oligo- and poly-yne because of their potentially useful electrical and

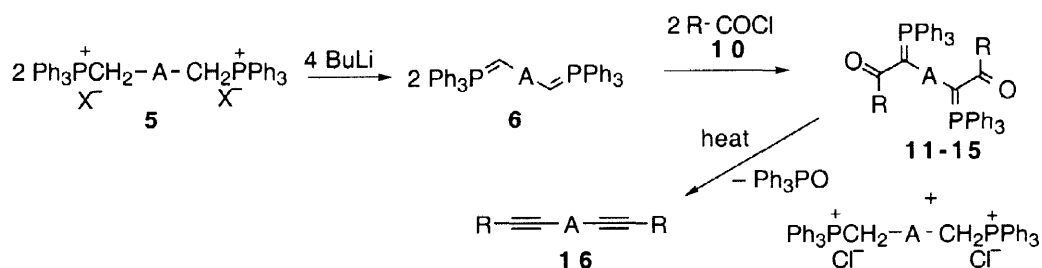


non-linear optical properties.⁴ A range of poly(aryleneethynes), (–Ar¹–C≡C–Ar²–C≡C–)_n have been reported,⁵ and several different approaches to the linear allotrope of carbon, (–C≡C–)_n have recently been described.⁶ We envisaged that the poly(oxoylides) **8** could be formed by reaction of bis(ylides) **6** with bis(acid chlorides) **7** as shown, and that these might be soluble precursor polymers which, upon extrusion of Ph₃PO, would provide access to a variety of polyynes **9**. No polymers of this type have been reported before although there is



one report of poly(oxoylides) with phosphorus incorporated in the main chain.⁷ Before embarking on the synthesis of the poly(oxoylides) **8** we thought it wise to confirm that the chemistry was amenable to construction of oligo(oxoylides) by means of a model study. In this paper we describe the results of this work, including synthesis of the necessary monomers **6** and **7**, which has not only shown that the method is likely to be viable, but has also provided a framework of spectroscopic data for later reference in the polymer formation.

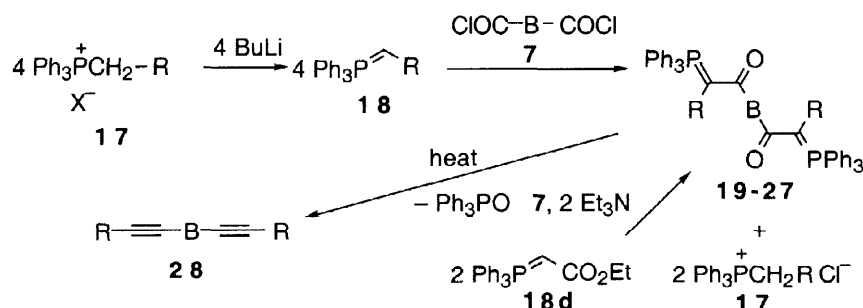
We first prepared, using known methods, the two bis(phosphonium salts) **5** suitable for generation of the bis(ylides) **6**. In forming **5a** and **5b** it was found to be essential to use DMF since reaction in less polar solvents such as toluene led to precipitation of the mono(phosphonium salts) which did not react further. The formation of polyenes using the Wittig reaction by treatment of bis(ylides) with dialdehydes has already been described.⁸ Reaction of the salts **5** with butyllithium to give bis(ylides) **6** followed by treatment with 1 equiv. of the acid chlorides **10** resulted in the required acylation accompanied by transylidation⁹ to give the bis(oxoylides) **11–15** in moderate yield (Table 1). The products were high melting point crystalline solids which showed ³¹P NMR signals in the expected region. In their EI mass spectra, even at 20 eV, only peaks for M⁺-Ph₃PO were seen but the use of FAB readily gave parent ion signals for **12–15**. By using phenylpropynoyl chloride, ylide **13**, the potential precursor to a tetrayne, was obtained while the chloromethyl groups in **14** and **15** would allow attachment of further ylide functions (see later).



In a complementary approach a range of mono ylides **18** derived from simple phosphonium salts **17** were reacted in a 4:1 ratio with the bis(acid chlorides) **7** to give the isomeric bis(oxoylides) **19–23** with similar properties to **11–15** (Table 1). In Part 8³ we described the preparation of bis(oxoylides) by reaction of ylides with oxalyl chloride (**7**, B = —) in the same way. A series of four bis(oxoylides) **24–27** were also prepared using a different method which involved treating the ylide **18d** with the bis(acid chlorides) **7** and triethylamine. These four ylides with an extra stabilising group present gave ³¹P NMR signals at a somewhat higher frequency (Table 1) and the ¹³C NMR spectra of the bis(oxoylides) **19**, **22** and **24–27** provide ready confirmation of the structures and form a highly consistent pattern (Table 2). The preparation of **24** and **25** and their conversion to the corresponding diynes using conventional pyrolysis have been briefly reported before but with few details.¹⁰

Table 1 Formation and Properties of Bis-oxoylides

Cpd No.	A or B	R	Reacting Components	Yield (%)	mp (°C)	δ_p
11	1,4-C ₆ H ₄	Ph	5a 10a	51	259–261	14.2
12	biphenyl-4,4'-diyl	Ph	5b 10a	26	264–266	14.6
13	1,4-C ₆ H ₄	PhC≡C	5a 10b	55	214–216	15.95
14	1,4-C ₆ H ₄	4-ClCH ₂ C ₆ H ₄	5a 10c	64	192–195	13.8
15	1,4-C ₆ H ₄	3-ClCH ₂ C ₆ H ₄	5a 10d	43	205–207	14.7
19	1,4-C ₆ H ₄	Ph	17a 7a	60	270–274	14.8
20	thiophene-2,5-diyl	Ph	17a 7b	10	257–260	15.8
21	thiophene-2,5-diyl	2-thienyl	17b 7b	22	>250	16.65
22	biphenyl-4,4'-diyl	Ph	17a 7c	38	272–276	15.1
23	1,4-C ₆ H ₄	4-MeC ₆ H ₄	17c 7a	79	282–284	14.4
24	1,4-C ₆ H ₄	CO ₂ Et	18d 7a	82	241–243	19.4
25	1,3-C ₆ H ₄	CO ₂ Et	18d 7d	100	—	19.6
26	biphenyl-4,4'-diyl	CO ₂ Et	18d 7c	99	232–233	19.3
27	thiophene-2,5-diyl	CO ₂ Et	18d 7b	70	238–240	19.2
33	—	—	32 10a	36	175–180	17.2
35	1,4-C ₆ H ₄	—	34 7a	50	177–180	16.9
36	biphenyl-4,4'-diyl	—	34 7c	29	161–163	17.2



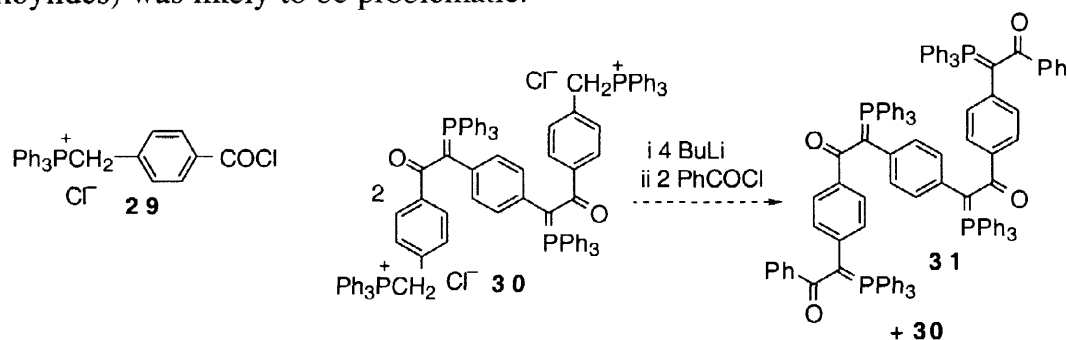
In an attempt to construct higher oligo(oxoylides), two separate approaches to the bis(phosphonium salt) **30** were examined. Treatment of the bis(oxoylide) **14** bearing chloromethyl groups with triphenylphosphine did give a product in 73% yield (mp 173–174 °C) whose spectroscopic data were in agreement with expectation [δ_{H} 8.1–6.8 (72 H, m) and 6.7–6.4 (4 H, m); δ_{P} +22.3 and 14.0] but this could not be obtained in pure form. The alternative approach of acylating the bis(ylide) from **5a** with the phosphonio acid chloride **29** gave an oily solid which did not contain the required material (δ_{P} +31.5). The crude sample of **30** obtained from **14** was treated with butyllithium and benzoyl chloride in an attempt to form the tetrakis(oxoylide) **31** but this produced mainly Ph₃PO although minor components

Table 2 ^{13}C NMR spectra [δ_{C} ($J_{\text{P-C}}$)] of the bis(oxoylides) **19**, **22** and **24–27**

	P=C	C=O	P-phenyl			
			C-1	C-2	C-3	C-4
19	73.2 (108)	184.6 (5)	127.2 (90)	133.5 (9)	128.0 (13)	131.5 (2)
22	74.9 (107)	183.5	126.4 (91)	133.4 (10)	128.4 (12)	131.5
24	68.9 (112)	192.9 (5)	126.3 (93)	133.3 (10)	128.5 (12)	131.7 (2)
25	69.1 (113)	192.7 (5)	126.3 (93)	133.4 (10)	128.5 (12)	131.7 (2)
26	69.0 (110)	193.0 (6)	126.3 (93)	133.3 (10)	128.6 (12)	131.8 (2)
27	69.4 (113)	183.7 (6)	126.5 (94)	133.3 (10)	128.8 (13)	131.9 (2)

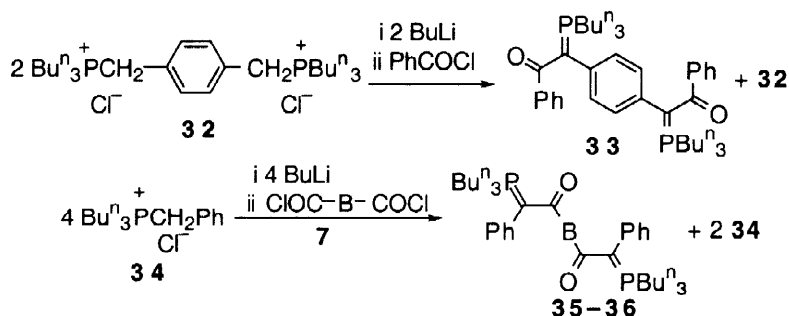
	B signals	R signals
19	141.1 (12), 127.3 (4 C)	137.7(12), 134.7 (4), 131.2 (4 C), 124.4 (2 C)
22	140.3 (2 C), 139.8 (12), 127.5 (4 C), 125.6 (4 C)	137.4 (11), 134.6 (4), 129.1 (4 C), 125.0 (2 C)
24	144.0 (9), 127.5	167.7 (15), 58.6, 13.8
25	141.8 (9), 130.0 (2 C), 129.1, 125.9	167.6 (15), 58.6, 13.7
26	142.1, 142.0 (9), 128.9 (4 C), 126.1 (4 C)	167.6 (14), 58.5, 13.6
27	149.3 (10), 129.9	167.5 (14), 58.8, 13.9

with ^{31}P NMR signals in the expected region (δ_{P} +14.2–15.3) were present which may have been the required product. It was clear however that the stepwise synthesis of higher oligo(oxoylides) was likely to be problematic.

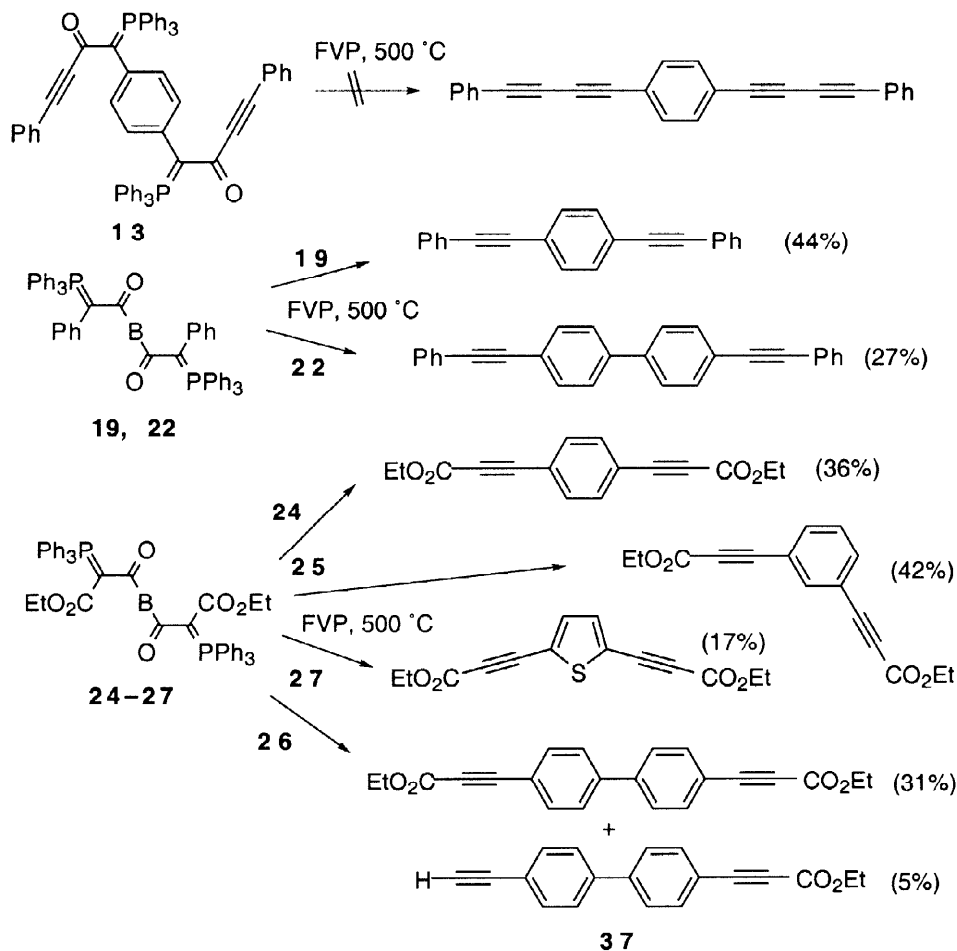


As a result of other studies, we were aware that by changing from triphenylphosphonium to tributylphosphonium ylides the temperature required for extrusion of the phosphine oxide is dramatically reduced. As an example, extrusion from $\text{Bu}_3\text{P}=\text{C}(\text{Pr})\text{COPh}$ was essentially complete upon FVP at 300 °C as compared to the temperature of 500 °C required for the triphenyl analogue. This may be greatly beneficial in the thermal conversion of the proposed poly(oxoylides) which has to be done under conventional conditions where higher temperatures may favour undesired side-reactions of the target polyynes **9**. With this in mind, the bis(oxoylides) **33**, **35** and **36** were prepared as

shown from the bis(phosphonium salt) **32** and benzoyl chloride, and from the salt **34** with bis(acid chlorides) **7a** and **7c**. As compared to the triphenyl analogues these had significantly lower melting points and slightly higher ^{31}P NMR chemical shifts (Table 1). Unfortunately satisfactory analytical data could not be obtained for **19** or **36** but their spectroscopic data showed them to consist overwhelmingly of the desired material.



Selected examples of the bis(oxylides) were now subjected to FVP at $500\text{ }^\circ\text{C}$ and 10^{-2} Torr. The compound **13** underwent complete reaction but the main phosphorus-containing product was triphenylphosphine and there was no evidence for formation of the expected 1,4-bis(phenylbutadiynyl)benzene. In contrast both **19** and **22** did undergo reaction in the desired sense to give the expected diynes **28** in moderate yield after preparative TLC. The four bis(oxylides) **24-27** with additional stabilising ester groups also behaved well and afforded



the bis(acetylenic esters) **28** in moderate yield after chromatographic purification. The yield of 67% quoted from conventional pyrolysis of **24**¹⁰ refers to impure product and the yields of the two pyrolysis methods are probably comparable. In the case of **26** the major bis(acetylenic ester) **28** was accompanied by a minor product which was identified as the monoester **37** in which one ester group had been lost. The occurrence of this process at 750 °C as well as its mechanism was discussed fully in Part 4 of this series.²

In conclusion, this study has shown that a range of monomers **6** and **7** required for the construction of the poly(oxoylides) **8** are readily prepared and that they react in the desired sense in the formation of model bis(oxoylides). However the failure of the Ph₃PO extrusion in the case of **13** and our inability to construct the tetrakis(oxoylide) **31** using a stepwise approach have highlighted some potential problems in applying this method to polymer synthesis. The results of our studies on the poly(oxoylides) **8** will be reported shortly.

Experimental

Melting points were recorded on a Reichert hot-stage microscope and are uncorrected. Infra red spectra were recorded for solids as Nujol mulls and for liquids as thin films unless otherwise indicated, on a Perkin Elmer 1420 instrument. NMR spectra were obtained for ¹H at 300 MHz and for ¹³C at 75 MHz on a Bruker AM300 instrument, and for ³¹P at 32 MHz using a Varian CFT 20 instrument. All spectra were run on solutions in CDCl₃ unless otherwise indicated, with internal Me₄Si as reference for ¹H and ¹³C and external 85% H₃PO₄ as reference 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 an A. E. I. MS-902 spectrometer using electron impact at 70 eV or, where noted, using FAB on a Fisons VG Autospec instrument. Dry toluene was prepared by storing over sodium wire and dry THF was freshly distilled from potassium benzophenone ketyl.

Starting Phosphonium salts

1,4-Bis(triphenylphosphoniomethyl)benzene dichloride 5a. This was prepared by heating a mixture of 1,4-bis(chloromethyl)benzene (26.25 g, 0.15 mol) and triphenylphosphine (78.6 g, 0.3 mol) in DMF (250 cm³) under reflux for 4 h. This gave the product as colourless crystals (100 g, 95%), mp >340 °C (lit.,¹¹ >400 °C); δ_H (CD₃SOCD₃) 8.0–7.5 (30 H, m), 6.81 (4 H, s) and 5.18 (4 H, br d, *J* 15); δ_P(CD₃SOCD₃) +22.8.

4,4'-Bis(triphenylphosphoniomethyl)biphenyl dibromide 5b. This was prepared as for **5a** using 4,4'-bis(bromomethyl)biphenyl¹² to give colourless crystals (8.6 g, 80%), mp 302–304 °C (lit.,¹³ 300 °C) (Found: C, 67.8; H, 4.8. C₅₀H₄₂Br₂P₂·H₂O requires C, 68.0; H, 5.0%); δ_H (CD₃SOCD₃) 8.0–7.5 (34 H, m), 7.2–7.0 (4 H, m) and 5.26 (4 H, br d, *J* 16); δ_H (CDCl₃) 8.0–7.4 (30 H, m), 7.02 and 6.80 (8 H, AB pattern, *J* 8) and 5.63 (4 H, br d, *J* 15); δ_P (CD₃SOCD₃) +22.4; δ_P (CDCl₃) +23.1.

(2-Thienylmethyl)triphenylphosphonium bromide 17b. This was prepared by heating a mixture of 2-bromomethylthiophene (freshly prepared from 2-hydroxymethylthiophene by treatment with PBr₃) with 1 equiv. of triphenylphosphine in toluene under reflux for 4 h to give light brown crystals (33.0 g, 91%), mp 265–275 °C dec. (lit.,¹⁴ 262 °C); δ_H 7.8–7.5 (15 H, m), 7.2 (2 H, m), 6.9 (1 H, m) and 5.75 (2 H, d, *J* 14); δ_P +21.3.

(4-Methylbenzyl)triphenylphosphonium chloride 17c. Reaction as for **17b** using 4-methylbenzyl bromide gave colourless crystals (16.45 g, 41%), mp 248–254 °C (lit.,¹⁵ 240–241 °C); δ_{H} 7.9–7.6 (15 H, m), 6.94 (4 H, s), 5.31 (2 H, d, *J* 14) and 2.24 (3 H, d, *J* 3); δ_{P} +22.2.

1,4-Bis(tributylphosphoniomethyl)benzene dichloride 32. Reaction as for **5a** using 1,4-bis(chloromethyl)benzene and tributylphosphine gave colourless crystals (36.9 g, 94%), mp 271–273 °C (Found: C, 66.1; H, 10.6. $\text{C}_{32}\text{H}_{62}\text{Cl}_2\text{P}_2$ requires C, 66.3; H, 10.8%); ν_{max} / cm^{-1} 1512, 1412, 1314, 1280, 1230, 1100, 968, 918, 860, 807 and 722; δ_{H} (CD_3SOCD_3) 7.47 (4 H, s), 4.03 (4 H, br d, *J* 15), 2.5–2.0 (12 H, m), 1.6–1.2 (24 H, m) and 0.90 (18 H, t, *J* 7); δ_{P} (CD_3SOCD_3) +33.4.

Benzyltributylphosphonium chloride 34 Reaction as for **17b** using benzyl chloride and tributylphosphine gave colourless crystals (35.4 g, 87%), mp 164–165 °C; ν_{max} / cm^{-1} 1287, 1098, 1078, 968, 916, 899, 724 and 705; δ_{H} 7.55–7.25 (5 H, m), 4.32 (2 H, d, *J* 16), 2.65–2.25 (6 H, m), 1.6–1.3 (12 H, m) and 0.91 (9 H, t, *J* 7); δ_{P} +31.6.

(4-Chlorocarbonylbenzyl)triphenylphosphonium chloride 29. Reaction as for **17b** using 4-chloromethylbenzoic acid gave (4-carboxybenzyl)triphenylphosphonium chloride as colourless crystals (5.0 g, 39%); δ_{H} (CD_3SOCD_3) 8.0–7.6 (17 H, m), 7.3–7.1 (2 H, m) and 6.57 (2 H, d, *J* 16); δ_{P} (CD_3SOCD_3) +23.0. This was treated with thionyl chloride under reflux for 2 h followed by evaporation to give colourless crystals (>90%); δ_{H} 8.1–7.4 (19 H, m) and 5.88 (2 H, d, *J* 16). This material was used immediately for preparation of **30** since it was found to decompose upon storage.

Acid chlorides

Thiophene-2,5-dicarbonyl chloride 7b. Oxidation of 2-acetyl-5-methylthiophene with KMnO_4 in aqueous NaOH ¹⁶ gave thiophene-2,5-dicarboxylic acid; δ_{H} 9.8 (2 H, br s) and 7.74 (2 H, s). This was treated with thionyl chloride (2 equiv.) and pyridine (2 equiv.) in toluene under reflux for 12 h to give, after filtration, evaporation and distillation the diacid chloride (? g, 87%), mp 42–44 °C (lit.,¹⁷ 45–46 °C); δ_{H} 7.98 (2 H, s).

Biphenyl-4,4'-dicarbonyl chloride 7c. Stepwise oxidation of 4,4'-dimethylbiphenyl using chromium trioxide in acetic acid followed by KMnO_4 in aqueous NaOH gave biphenyl 4,4'-dicarboxylic acid **18**. This was treated with 2 equiv. PCl_5 in POCl_3 under reflux for 6 h to give the dichloride as colourless crystals (? g, 60%), mp 180–182 °C (lit.,¹⁹ 184 °C); δ_{H} 8.25 and 7.78 (8 H, AB pattern, *J* 9).

4-Chloromethylbenzoyl chloride 10c. A mixture of 4-chloromethylbenzoic acid (5.0 g) and thionyl chloride (20 cm^3) was heated under reflux for 2 h. Evaporation and Kugelrohr distillation of the residue gave a colourless low melting solid (5.3 g, 96%), b.p. (oven temp.) 120 °C at 0.2 mmHg (lit.,²⁰ 126–128 °C at 6 mmHg); δ_{H} 8.12 and 7.57 (4 H, AB pattern, *J* 8) and 4.65 (2 H, s).

Preparation of ylides 11–15 and 33

A suspension of the bis(phosphonium salt) **5** (6.25 mmol) was stirred in dry THF (75 cm^3) under N_2 at RT while butyllithium in hexane (12.5 mmol) was added, followed after 30 min. by the acid chloride **10** (6.25 mmol) in dry THF (5 cm^3). After stirring for a further 12 h,

the mixture was added to water and extracted with ether. Drying and evaporation of the ether extract gave the products as follows:

1,4-Bis[(benzoyl)(triphenylphosphoranylidene)methyl]benzene 11. From bis(phosphonium salt) **5a** and benzoyl chloride **10a** as yellow crystals (1.33 g, 51%), mp 260 °C (Found: C, 82.8; H, 5.2. $C_{58}H_{44}O_2P_2$ requires C, 83.4; H, 5.3%); ν_{max}/cm^{-1} 1497, 1432, 1350, 1187, 1120, 1100, 973, 745, 720 and 690; δ_H 7.7–7.0 (40 H, m), and 6.40 (4 H, m); δ_P +14.2; m/z 556 (M^+-Ph_3PO , 8%), 479 (1), 296 (2), 278 (100), 277 (90), 262 (8), 201 (12), 199 (10), 185 (6) and 183 (15).

4,4'-Bis[(benzoyl)(triphenylphosphoranylidene)methyl]biphenyl 12. From bis(phosphonium salt) **5b** and benzoyl chloride **10a** as yellow crystals (0.74 g, 26%), mp 264–266 °C (HRMS: found $M+H^+$, 911.3189. $C_{64}H_{48}O_2P_2$ requires $M+H$, 911.3208); ν_{max}/cm^{-1} 1575, 1430, 1260, 1172, 1100, 1020, 997, 963, 850, 810, 782, 743, 718 and 694; δ_H 8.0–6.75 (48 H, m); δ_P +14.6; m/z (FAB) 911 (M^++H , 42%), 650 (15), 633 (M^++H-Ph_3PO , 33), 547 (7), 354 (25), 279 (93), 262 (25) and 77 (100).

1,4-Bis(2-oxo-4-phenyl-1-triphenylphosphoranylidenebut-3-ynyl)benzene 13. From bis(phosphonium salt) **5a** and phenylpropynoyl chloride **10b** as orange crystals (1.52 g, 55%), mp 214–216 °C (HRMS: found $M+H^+$, 883.2872. $C_{62}H_{44}O_2P_2$ requires $M+H$, 883.2895); ν_{max}/cm^{-1} 2194, 1435, 1340, 1262, 1207, 1098, 968, 750, 722 and 686; δ_H 7.65–7.05 (40 H, m) and 6.86 (4 H, s); δ_P +15.95; m/z (FAB) 883 (M^++H , 24%), 605 (M^++H-Ph_3PO , 26), 326 (15), 315 (12), 183 (78) and 69 (100).

1,4-Bis[(4-chloromethylbenzoyl)(triphenylphosphoranylidene)methyl]benzene 14. From bis(phosphonium salt) **5a** and 4-chloromethylbenzoyl chloride **10c** as yellow crystals (1.86 g, 64%), mp 192–195 °C (HRMS: found $M+H^+$, 931.2463. $C_{60}H_{46}Cl_2O_2P_2$ requires $M+H$, 931.2428); ν_{max}/cm^{-1} 1490, 1433, 1355, 1260, 1122, 1102, 968, 842, 750, 718 and 689; δ_H 7.7–7.0 (38 H, m), 6.54 (4 H, s) and 4.50 (4 H, s); δ_P +13.8; m/z (FAB) 931 (M^++H , 7%), 669 (60), 279 (35) and 183 (100).

1,4-Bis[(3-chloromethylbenzoyl)(triphenylphosphoranylidene)methyl]benzene 15. From bis(phosphonium salt) **5a** and 3-chloromethylbenzoyl chloride **10d** as yellow crystals (1.25 g, 43%), mp 205–207 °C (HRMS: found $M+H^+$, 931.2392. $C_{60}H_{46}Cl_2O_2P_2$ requires $M+H$, 931.2428); ν_{max}/cm^{-1} 1490, 1432, 1255, 1203, 1100, 1021, 970, 740, 713 and 688; δ_H 7.7–7.0 (38 H, m), 6.43 (4 H, s) and 4.48 (4 H, s); δ_P +14.7; m/z (FAB) 931 (M^++H , 15%), 669 (65), 279 (100) and 183 (56).

1,4-Bis[(benzoyl)(tributylphosphoranylidene)methyl]benzene 33. From bis(phosphonium salt) **32** and benzoyl chloride **10a** as yellow crystals (0.80 g, 36%), mp 175–180 °C (Found: C, 77.05; H, 9.9. $C_{46}H_{68}O_2P_2$ requires C, 77.3; H, 9.6%); ν_{max}/cm^{-1} (film) 2920, 1668, 1594, 1575, 1494, 1477, 1403, 1375, 1215, 1142, 1090, 997, 964, 902, 783, 743, 710 and 690; δ_H 7.4–7.2 (4 H, m), 7.15–6.97 (6 H, m), 6.85 (4 H, s), 2.2–1.8 (12 H, m), 1.65–1.25 (24 H, m) and 0.92 (18 H, t, J 7); δ_P +17.2; m/z (20 eV or FAB) no signal observed above 218 (Bu_3PO).

Preparation of ylides 19–23, 35 and 36

A suspension of the phosphonium salt **17** (16 mmol) was stirred in dry THF (75 cm³) under N₂ at RT while butyllithium in hexane (16 mmol) was added, followed after 30 min. by the bis(acid chloride) **7** (4 mmol) in dry THF (5 cm³). After stirring for a further 12 h, the mixture was added to water and extracted with ether. Drying and evaporation of the ether extract gave the products as follows:

1,4-Bis[(phenyl)(triphenylphosphoranylidene)acetyl]benzene 19. From benzyltriphenylphosphonium chloride **17a** and terephthaloyl chloride **7a** as yellow crystals (2.00 g, 60%), mp 270–274 °C (Found: C, 81.85; H, 5.25. C₅₈H₄₄O₂P₂ requires C, 83.4; H, 5.3%); ν_{\max} /cm⁻¹ 1506, 1495, 1438, 1348, 1252, 1139, 1102, 964, 758, 728 and 695; δ_{H} 7.75–7.35 (34 H, m) and 6.80 (10 H, m); δ_{C} see Table 2; δ_{P} +14.8; m/z 556 (M⁺–Ph₃PO, 11%), 379 (1), 279 (30), 278 (100), 277 (90), 262 (8), 205 (11), 201 (34), 199 (24), 185 (17) and 183 (27).

2,5-Bis[(phenyl)(triphenylphosphoranylidene)acetyl]thiophene 20. From benzyltriphenylphosphonium chloride **17a** and thiophene-2,5-dicarbonyl chloride **7b** as yellow crystals (0.34 g, 10%), mp 257–260 °C (Found: C, 79.9; H, 4.9. C₅₆H₄₂O₂P₂S requires C, 80.0; H, 5.0%); ν_{\max} /cm⁻¹ 1492, 1430, 1360, 1308, 1242, 1100, 997, 960, 822, 750, 728 and 690; δ_{H} 7.65–7.2 (30 H, m), 6.91 (10 H, s) and 6.37 (2 H, s); δ_{P} +15.8; m/z 562 (M⁺–Ph₃PO, 22%), 490 (1), 476 (3), 379 (48), 351 (1), 285 (14), 284 (66), 278 (54), 277 (100), 262 (24), 211 (16), 201 (30), 199 (24), 185 (18) and 183 (48).

2,5-Bis[(2-thienyl)(triphenylphosphoranylidene)acetyl]thiophene 21. From (2-thienylmethyl)triphenylphosphonium bromide **17b** and thiophene-2,5-dicarbonyl chloride **7b** as orange crystals (0.75 g, 22%), mp >300 °C (Found: C, 72.8; H, 4.7%; M+H⁺, 853.1610. C₅₂H₃₈O₂P₂S₃ requires C, 73.2; H, 4.5%; M+H, 853.1587); ν_{\max} /cm⁻¹ 1490, 1430, 1360, 1320, 1230, 1174, 1100, 1022, 993, 890, 838, 727, 708 and 687; δ_{H} 7.7–7.2 (30 H, m), 7.0–6.4 (6 H, m) and 6.75 (2 H, s); δ_{P} +16.65; m/z (FAB) 853 (M⁺+H, 40%), 833 (10), 575 (M⁺–Ph₃PO, 3), 385 (15), 296 (26), 278 (15), 201 (16), 183 (36) and 65 (100).

4,4'-Bis[(phenyl)(triphenylphosphoranylidene)acetyl]biphenyl 22. From benzyltriphenylphosphonium chloride **17a** and biphenyl-4,4'-dicarbonyl chloride **7c** as yellow crystals (1.38 g, 38%), mp 272–276 °C (Found: C, 84.0; H, 5.35. C₆₄H₄₈O₂P₂ requires C, 84.4; H, 5.3%); ν_{\max} /cm⁻¹ 1430, 1250, 1170, 1118, 1092, 1018, 990, 960, 840, 740 and 690; δ_{H} 7.8–7.2 (38 H, m) and 6.91 (10 H, s); δ_{C} see Table 2; δ_{P} +15.1; m/z 632 (M⁺–Ph₃PO, 0.5%), 355 (10), 354 (35), 313 (2), 298 (12), 281 (22), 278 (40), 277 (100), 253 (20), 201 (50), 199 (40), 185 (18), 183 (40) and 152 (60).

1,4-Bis[(4-methylphenyl)(triphenylphosphoranylidene)acetyl]benzene 23. From 4-methylbenzyltriphenylphosphonium chloride **17c** and terephthaloyl chloride **7a** as yellow crystals (2.72 g, 79%), mp 282–284 °C (HRMS: found M+H⁺, 863.3245. C₆₀H₄₈O₂P₂ requires M+H, 863.3208); ν_{\max} /cm⁻¹ 1500, 1482, 1440, 1260, 1242, 1132, 1107, 978, 865, 753, 730 and 694; δ_{H} 7.75–7.2 (30 H, m), 7.17 (4 H, s), 6.63 (8 H, s) and 2.16 (6 H, s); δ_{P} (CD₂Cl₂) +14.4; m/z (FAB) 863 (M⁺+H, 36%), 585 (M⁺+H–Ph₃PO, 6), 393 (12), 306 (10), 279 (13), 201 (12), 183 (23) and 69 (100).

1,4-Bis[(phenyl)(tributylphosphoranylidene)acetyl]benzene 35. From benzyltributylphosphonium chloride **34** and terephthaloyl chloride **7a** as yellow crystals (1.43 g, 50%), mp 177–180 °C (Found: C, 77.1; H, 9.6. C₄₆H₆₈O₂P₂ requires C, 77.3; H, 9.6%); ν_{\max} /cm⁻¹ (film) 1670, 1593, 1494, 1458, 1448, 1402, 1310, 1270, 1227, 1202, 1150, 1110, 998, 965, 900, 818, 780, 718, 695 and 650; δ_{H} 7.1–6.9 (14 H, m), 2.2–1.85 (12 H, m), 1.55–1.2 (24 H, m) and 0.88 (18 H, t, *J* 7); δ_{P} +16.9; *m/z* (20 eV) no signal observed above 218 (Bu₃PO).

4,4'-Bis[(phenyl)(tributylphosphoranylidene)acetyl]biphenyl 36. From benzyltributylphosphonium chloride **34** and biphenyl-4,4'-dicarbonyl chloride **7c** as yellow crystals (0.92 g, 29%), mp 161–163 °C; ν_{\max} /cm⁻¹ 1600, 1490, 1414, 1347, 1280, 1225, 1174, 1096, 1078, 965, 913, 899, 815, 722 and 702; δ_{H} 7.4–7.1 (18 H, m), 2.3–1.85 (12 H, m), 1.65–1.25 (24 H, m) and 0.91 (18 H, t, *J* 7); δ_{P} +17.2; *m/z* (20 eV or FAB) no signal observed above 218 (Bu₃PO).

Preparation of ylides 24–27

A solution of the bis(acid chloride) **7** (15 mmol) in dry toluene (20 cm³) was added to a solution of (ethoxycarbonylmethylene)triphenylphosphorane **18d** (10.26 g, 30 mmol) and dry triethylamine (3.0 g, 30 mmol) in dry toluene (180 cm³) over 15 min. The mixture was stirred at room temperature for 12 h and then evaporated. The residue was taken up in dichloromethane which was washed with water, dried and evaporated to give the products as follows:

1,4-Bis[(ethoxycarbonyl)(triphenylphosphoranylidene)acetyl]benzene 24. From terephthaloyl chloride **7a** as a light yellow solid (9.93 g, 82%), mp 241–243 °C (lit.,¹⁰ 252–253 °C); δ_{H} 7.85–7.7 (12 H, m), 7.70 (4 H, s), 7.5–7.35 (18 H, m), 3.70 (4 H, q, *J* 7) and 0.65 (6 H, t, *J* 7); δ_{C} see Table 2; δ_{P} +19.4.

1,3-Bis[(ethoxycarbonyl)(triphenylphosphoranylidene)acetyl]benzene 25. From isophthaloyl chloride **7d** as a yellow solid (12.03 g, 100%); δ_{H} 8.07 (1 H, m), 7.8–7.55 (12 H, m), 7.55–7.35 (18 H, m), 7.3–7.15 (3 H, m), 3.68 (4 H, q, *J* 7) and 0.62 (6 H, t, *J* 7); δ_{C} see Table 2; δ_{P} +19.6. This was used without further purification for the synthesis of **28**.

4,4'-Bis[(ethoxycarbonyl)(triphenylphosphoranylidene)acetyl]biphenyl 26. From biphenyl-4,4'-dicarbonyl chloride **7c** as a yellow powder (12.86 g, 99%), mp 232–233 °C (HRMS: found *M*+*H*⁺, 903.2969. C₅₈H₄₈O₆P₂ requires *M*+*H*⁺, 903.3004); ν_{\max} /cm⁻¹ 1666, 1517, 1290, 1104, 1080, 746, 722 and 691; δ_{H} 7.80 and 7.60 (8 H, AB pattern, *J* 9), 7.8–7.7 (12 H, m), 7.55–7.4 (18 H, m), 3.70 (4 H, q, *J* 7) and 0.62 (6 H, t, *J* 7); δ_{C} see Table 2; δ_{P} +19.3; *m/z* (FAB) 903 (*M*+*H*⁺, 100%), 857 (56), 831 (6), 579 (20), 375 (50), 303 (86) and 277 (82).

2,5-Bis[(ethoxycarbonyl)(triphenylphosphoranylidene)acetyl]thiophene 27. From thiophene-2,5-dicarbonyl chloride **7b** as a yellow foam (8.74 g, 70%), mp 238–240 °C (Found: C, 72.2; H, 4.8. C₅₀H₄₂O₆P₂S requires C, 72.1; H, 5.1%); ν_{\max} /cm⁻¹ 1673, 1543, 1316, 1238, 1104, 1078 and 723; δ_{H} 7.8–7.7 (14 H, m), 7.55–7.35 (18 H, m), 3.75 (4 H, q, *J* 7) and 0.75 (6 H, t, *J* 7); δ_{C} see Table 2; δ_{P} +19.2; *m/z* (FAB) 833 (*M*+*H*⁺, 42%), 787 (22), 509 (6), 413 (5), 375 (100) and 303 (40).

FVP of bis(oxoylides)

The apparatus used was as described previously.²¹ All pyrolyses were conducted at 500 °C and at 10⁻² Torr and were complete within 2 h. Under these conditions the contact time in the hot zone was estimated to be ≈10 ms.

FVP of the bis(ylide) **13** (0.1 g) at gave a yellow solid in which Ph₃P (δ_P -5.4) was the main phosphorus compound present with no evidence for the expected 1,4-bis(4-phenylbuta-1,3-diyanyl)benzene.

FVP of the bis(ylide) **19** (0.40 g) followed by preparative TLC (silica, EtOAc) gave 1,4-bis(phenylethynyl)benzene (59 mg, 44%) as yellow crystals, mp 182–184 °C (lit.,²² 184–186 °C) (Found: M⁺, 278.1109. C₂₂H₁₄ requires M, 278.1096); δ_H 7.75–7.40 (14 H, m); δ_C 131.6 (4 C), 131.5 (4 C), 128.45 (2 C), 128.38 (4 C), 123.1 (2 C, 4ry), 123.04 (2 C, 4ry), 91.2 (2 C, -C≡) and 89.1 (2 C, -C≡); *m/z* 278 (M⁺, 100%), 275 (27), 250 (4), 224 (6), 200 (7), 150 (11), 139 (72), 125 (27) and 113 (24).

FVP of the bis(ylide) **22** (0.41 g) followed by preparative TLC (silica, EtOAc) gave 4,4'-bis(phenylethynyl)biphenyl (43 mg, 27%) as yellow crystals, mp 252–254 °C (lit.,²³ 253–254 °C) (Found: M⁺, 354.1399. C₂₈H₁₈ requires M, 354.1408); δ_H 7.7–7.2 (18 H, m); *m/z* 354 (M⁺, 40%), 177 (100), 163 (18), 156 (8), 150 (28) and 137 (10).

FVP of the bis(ylide) **24** (9.0 g) followed by chromatography (silica, CH₂Cl₂–light petrol, 2:3) gave 1,4-bis(ethoxycarbonylethynyl)benzene (1.07 g, 36%) as an off-white solid, mp 90–92 °C (lit.,¹⁰ 90–91 °C); $\nu_{\max}/\text{cm}^{-1}$ 2209 (C≡C), 1696 (C=O), 1281, 1192, 1104, 1024, 849, 746 and 723; δ_H 7.58 (4 H, s), 4.31 (4 H, q, *J* 7) and 1.36 (6 H, t, *J* 7); δ_C 153.6 (CO), 132.9 (4 C), 121.8 (2 C, 4ry), 84.4 (-C≡), 82.9 (-C≡), 62.3 and 14.1; *m/z* 270 (M⁺, 35%), 225 (65), 198 (60), 153 (60) and 126 (100).

FVP of the bis(ylide) **25** (2.12 g) followed by chromatography (silica, CH₂Cl₂–light petroleum, 1:1) gave 1,3-bis(ethoxycarbonylethynyl)benzene (0.29 g, 42 %) as colourless crystals, mp 52–54 °C (lit.,¹⁰ 52–53 °C); $\nu_{\max}/\text{cm}^{-1}$ 2220 (C≡C), 1697 (C=O), 1303, 1216, 1025, 746, 722 and 686; δ_H 7.8–7.35 (4 H, m), 4.31 (4 H, q, *J* 7) and 1.37 (6 H, t, *J* 7); δ_C 153.8 (CO), 138.8, 134.6 (2 C), 129.0, 120.5 (2 C, 4ry), 83.9 (-C≡), 81.6 (-C≡), 62.3 and 14.0; *m/z* 270 (M⁺, 45 %), 225 (96), 198 (75), 153 (58) and 126 (100).

FVP of the bis(ylide) **26** (10.06 g) followed by chromatography (silica, CH₂Cl₂–light petroleum, 2:1) gave 4,4'-bis(ethoxycarbonylethynyl)biphenyl as colourless crystals (1.20 g, 31%) mp 122–123 °C; (Found: C, 76.3; H, 5.2. C₂₂H₁₈O₄ requires C, 76.3; H, 5.2%); $\nu_{\max}/\text{cm}^{-1}$ 2205 (C≡C), 1696 (C=O), 1302, 1290, 1191, 1177, 1032 and 746; δ_H 7.68 and 7.62 (8 H, AB pattern, *J* 9), 4.32 (4 H, q, *J* 7) and 1.37 (6 H, t, *J* 7); δ_C 154.0 (CO), 141.9 (4ry), 133.6 (4 C), 127.2 (4 C), 119.4 (4ry), 85.6 (-C≡), 81.7 (-C≡), 62.2 and 14.1; *m/z* 346 (M⁺, 90%), 322 (20), 301 (50), 274 (46), 231 (36), 202 (100), 159 (35) and 132 (92).

A minor product was found to be 4-(ethoxycarbonylethynyl)-4'-ethynylbiphenyl **37** as colourless crystals (0.15 g, 5%) mp 104–105 °C; (HRMS: found M⁺, 274.0987. C₁₉H₁₄O₂ requires M, 274.0994); $\nu_{\max}/\text{cm}^{-1}$ 3300 (≡C–H), 2206 (C≡C), 1696 (C=O), 1522, 1289, 1192, 1177 and 821; δ_H 7.7–7.5 (8 H, m), 4.32 (2 H, q, *J* 7), 3.16 (1 H, s, ≡CH) and 1.36 (3 H, t, *J* 7); δ_C 154.0 (CO), 142.3 (4ry), 140.1 (4ry), 133.5 (2 C), 132.7 (2 C), 127.1 (2 C), 127.0 (2 C), 121.9 (4ry), 118.8 (4ry), 85.7 (-C≡), 83.2 (-C≡), 78.4 (≡CH), 78.1 (-C≡), 62.2 and 14.1; *m/z* 274 (M⁺, 66%), 250 (72), 229 (45), 205 (60), 202 (100) and 176 (26).

FVP of the bis(ylide) **27** (2.01g) followed by chromatography (silica, CH₂Cl₂–light petroleum, 1:1) gave 2,5-bis(ethoxycarbonylethynyl)thiophene as colourless crystals (0.11 g, 17%), mp 121–122 °C (Found: C, 61.2; H, 4.5. C₁₄H₁₂O₄S requires C, 60.9; H, 4.4%); $\nu_{\max}/\text{cm}^{-1}$ 2210 (C≡C), 1702 (C=O), 1282, 1195, 1171, 814, 744 and 722; δ_{H} 7.38 (2 H, s), 4.30 (4 H, q, *J* 7) and 1.36 (6 H, t, *J* 7); δ_{C} 153.6 (CO), 136.2 (CH), 124.3 (4ry), 86.3 (–C≡), 78.0 (–C≡), 62.5 and 14.1; *m/z* 276 (M⁺, 67%), 231 (70), 204 (80), 159 (64) and 132 (100).

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