A new synthesis of π-electron conjugated phosphonates and phosphonic bis(diethylamides) and their SHG activities

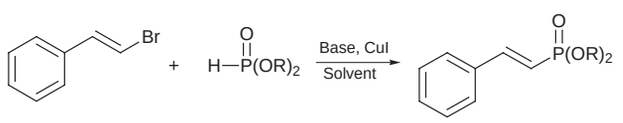
Takuji Ogawa,*,† Naoya Usuki and Noboru Ono

Department of Chemistry, Faculty of Science, Ehime University, Matsuyama 790, Japan

A series of vinylic and arylic phosphonates and phosphonic bis(diethylamides) were prepared by copper promoted substitution of the corresponding bromides. These π-electron conjugated phosphonates and phosphonic bis(diethylamides) were investigated to elucidate their optical and second harmonic generation (SHG) properties; it was found that diphenyl 2-(4-dimethylaminophenyl)ethenylphosphonate exhibited strong SHG activity, the efficiency being 13 times greater than that of urea.

Dialkyl vinyl- and aryl-phosphonates and vinyl- and aryl-phosphonic bis(dialkylamides) have been attracting interest as versatile intermediate reagents in organic synthesis, and have been synthesized *via* multi-step methods or palladium catalysed reactions from dialkyl phosphonates and vinyl bromides.[1–4] Here we report that these compounds can be prepared by the copper promoted reaction which we have been using for the synthesis of a series of vinylic substituted compounds;[5–9] some of these prepared π-electron conjugated phosphonates have relatively strong second harmonic generation (SHG) activities together with good transparency to light.

The reaction for their preparation is simple and straightforward as shown in Scheme 1; the corresponding vinylic bromides were heated with phosphonates in the presence of a base and copper(I) iodide. The reaction conditions were optimized by using reactions of 1-bromo-2-phenylethene with phosphonates in the presence of copper(I) iodide. The results are collected in Table 1.



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Scheme 1

Hexamethylphosphoric triamide (HMPA) as the solvent and KH as the base afforded the best yields in the shortest reaction time (Runs 1, 2, 4, 5, 7, 8, 10 and 11), however because of the potential carcinogenicity of HMPA, we recommend to use other solvents like tetramethylurea (TMU) (Run 12), dimethylformamide (DMF) (Run 13) or tetrahydrofuran (THF) (Runs 3, 6, 9, 14 and 15) although the yields were generally diminished and a longer reaction time was required with these solvents when compared with HMPA. Less basic triethylamine was also effective as the base for these reactions (Runs 3, 6, 9 and 15).

The reaction is essentially stereospecific and the *E*:*Z* ratio of the starting bromides was retained in the products although a little isomerization of *Z* to *E* was observed with prolonged heating.

The reaction was successful not only with alkyl phosphonates (Runs 1–9), but also with phenyl phosphonate, to afford the corresponding 2-phenylethenylphosphonate in good yields (Runs 10–15). The substitution reaction proceeded well with phenyl bromide, 2-arylethenyl bromides, and 4-phenylbuta-1,3-dienyl bromide to give the corresponding phosphonates in moderate to good yields (Table 2).

† *Present address:* Institute for Fundamental Research of Organic Chemistry, Kyushu University, Fukuoka, 812-81, Japan.

Table 1 Reaction conditions for the preparation of 2-phenylethenylphosphonates **1** by the copper-promoted reaction

Run	Bromide *E*:*Z*[a]	Phosphonate R group	Base[b]	Solvent[c]	*T*/°C	*t*/h[d]	Product (%)[e]	Product *E*:*Z*[a]
1	84:16	Me	KH	HMPA	120	2	**1a** (78)	86:14
2	19:81	Me	KH	HMPA	120	2	**1a** (65)	38:64
3	>99:1	Me	TEA	THF	reflux	24	**1a** (51)	>99:1
4	84:16	Et	KH	HMPA	120	2	**1b** (82)	84:16
5	19:81	Et	KH	HMPA	120	2	**1b** (66)	27:73
6	>99:1	Et	TEA	THF	reflux	24	**1b** (65)	>99:1
7	84:16	Pr^i	KH	HMPA	120	2	**1c** (99)	84:16
8	19:81	Pr^i	KH	HMPA	120	2	**1c** (80)	20:80
9	>99:1	Pr^i	TEA	THF	reflux	24	**1c** (65)	>99:1
10	84:16	Ph	KH	HMPA	120	2	**1d** (92)	98:2
11	19:81	Ph	KH	HMPA	120	2	**1d** (72)	21:79
12	>99:1	Ph	KH	TMU	120	4	**1d** (76)	>99:1
13	>99:1	Ph	KH	DMF	120	24	**1d** (46)	>99:1
14	>99:1	Ph	KH	THF	reflux	24	**1d** (86)	>99:1
15	>99:1	Ph	TEA	THF	reflux	24	**1d** (76)	>99:1

[a] The *E*:*Z* ratios were determined by ^{1}H NMR spectroscopy. [b] KH, potassium hydride; TEA, triethylamine. [c] HMPA, hexamethylphosphoric triamide; TMU, tetramethylurea; DMF, dimethylformamide; THF, tetrahydrofuran. [d] Reactions were terminated when the starting bromide was consumed. [e] Yields refer to the isolated values and not optimized.

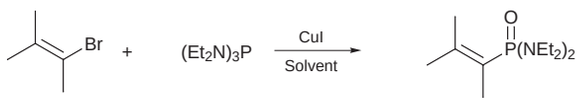
Table 2 Yields and physical properties of π-electron conjugated phosphonates, phosphonic bis(ethylamides) and related compounds

Compounds	Yield (%)	Mp or bp/°C
1a	78[a]	*ca.* 90 (0.01 mmHg)
1b	82[a]	*ca.* 100 (0.1 mmHg)
1c	99[a]	*ca.* 110 (0.05 mmHg)
1d	92[a]	110–111
2	59[b]	60 (0.05 mmHg)
3a	27[c]	*ca.* 100 (0.05 mmHg)
3b	40[c]	95–97
4	40[c]	125–127[f]
5a	37[c]	97–99[g]
5b	15[c]	88–89[f]
5c	65[d]	89–91[f]
5d	38[c]	125–127[f]
5e	83[c]	121–123[h]
5f	62[d]	104–106[i]
6	39[d]	86–88
7	83[d]	133–134[f]
8	27[e]	*ca.* 90 (0.1 mmHg)
9	49[e]	113–115[f]

[a] KH, HMPA, 120 °C, 2 h. [b] Et_3N, TMU, 120 °C, 4 h. [c] Et_3N, THF, reflux, 24 h. [d] Et_3N, DMF, 120 °C, 24 h. [e] $(Et_2N)_3P$, CuI, DMF, 120 °C, 40 h. [f] For the (*E*)-isomer which crystallized out. [g] For the mixture of *E*:*Z* = 12:88. [h] For the mixture of *E*:*Z* = 67:33. [i] For the mixture of *E*:*Z* = 97:3.

Generally the copper promoted arylic or vinylic substitution reactions show significant solvent effects; the reaction proceeded smoothly only in solvents with a strong coordinating ability like HMPA, TMU, DMF, or dimethyl sulfoxide (DMSO); in less coordinating solvents such as THF or chlorinated hydrocarbons no reaction occurred at all.[5–9] Therefore it is noteworthy that with the present reactions they proceeded readily even in THF to give the products in moderate to good yields. Probably the phosphonates or their anions themselves coordinated to the copper promoter to activate the reaction.

Because the previously reported methods for preparation of phosphonic bis(ethylamides) requires tedious procedures[10–13] we tried a more direct vinyl Arbuzov type reaction of tris(diethylamino)phosphine with phenyl and vinyl bromides in the presence of copper(I) iodide and succeeded in obtaining the substituted products in moderate yields (Scheme 2).



Scheme 2

Organic nonlinear optical materials have been attracting much attention as promising second or third harmonic generation materials because of their large hyperpolarizabilities, ultra fast response times, and synthetic flexibility which permits modification of their molecular parameters.[14–17] Most of the compounds are based on charge transfer transition states with strong electron acceptors such as nitro groups, and strong electron donors like amino groups, linked by π-electron conjugated systems. However, a recent theoretical paper suggests that the maximum molecular first hyperpolarizability, β, could be achieved by using less strong donor and acceptor groups having an electronegativity similar to that of the linking π-electron conjugated system.[18] Phosphonates and phosphonic bis(ethylamides) are good candidates for being such moderately strong electron acceptor groups. With this in mind we studied optical and second harmonic generation (SHG) activities of π-conjugated phosphonates and phosphonic bis(ethylamides) prepared by the present method.[19]

Calculated second order hyperpolarizabilities (β_{calc}) of π-electron conjugated phosphonates and phosphonic bis(ethylamides) by the semi-empirical molecular orbital method[20] were in the order of 1.6–24 × 10^{-30} esu as shown in Table 3. *para*-Amino substituted arylvinylphosphonates **5d** and **5e** showed relatively high β_{calc} values (15 and 24 × 10^{-30} esu) compared with the corresponding nitro compound **11** (6 × 10^{-30} esu). Actually the phosphonate **5d** exhibited strong SHG activity, the efficiency being 13 times that of urea (will be abbreviated as 13U) when measured by powder method at 532 nm with a Nd-YAG laser (1064 nm).[21] The corresponding nitro compound **11** showed no SHG activity with the powder method (Table 3).

Other phosphonates having comparable or higher β_{calc} values than **5d** did not always show strong SHG activities; the efficiency being 0.13U for **1d** (β_{calc} = 3 × 10^{-30} esu), 0.7U for **5b** (β_{calc} = 6 × 10^{-30} esu) and 0.7U for **7** (β_{calc} = 15 × 10^{-30} esu) and no activity observed for **4** (β_{calc} = 3 × 10^{-30} esu), **5c** (β_{calc} = 9 × 10^{-30} esu), **5e** (β_{calc} = 24 × 10^{-30} esu), **5f** (β_{calc} = 8 × 10^{-30} esu) and **6** (β_{calc} = −2 × 10^{-30} esu). These non-SHG active crystals probably have centrosymmetric space groups since the second order macroscopic coefficient of optical susceptibility $\chi^{(2)}$ will vanish in these space group crystals.[22–24] The phosphonate **5d** with SHG activity of 13U had the non-centrosymmetric $Pca2_1$ space group.

Theoretical and experimental studies revealed that polarizabilities α, β and γ can be expressed in terms of the bond length alternation (BLA) and the π-electron bond order alternating (BOA) structural parameters.[25–29] BLA of the phosphonate **5d** was found to be 0.127 Å as measured by X-ray crystallographic analysis (Table 4) (see Fig. 1 for X-ray structure), which is significantly smaller than that of the parent 2-phenylethenylphosphonic acid (0.157 Å).[30] The result is consistent with the theoretical prediction that with increasing donor and/or acceptor strength the ground state structure of the bridge

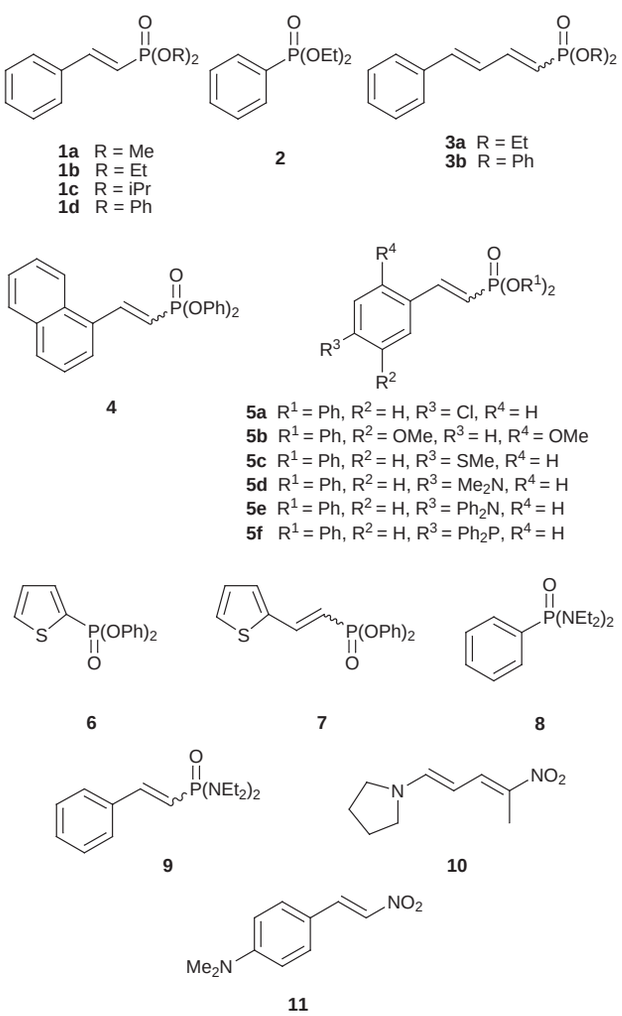


Table 3 Optical properties of π-electron conjugated phosphonates, phosphonic bis(ethylamides) and related compounds

Compound (E:Z)[a]	β_{calc}[b]/ 10^{-30} esu	SHG Efficiency[c]	$\lambda_{max}(\lambda_{cutoff})$/nm	
			Benzene	Acetonitrile
1d (98:2)	3.115	0.13	278.5 (310)	262.5 (320)
4 (11:89)	3.209 (E)	0	304.0 (368)	299.5 (364)
	1.647 (Z)			
5b (100:0)	6.414 (E)	0.7	345.5 (407)	345.5 (402)
5c (100:0)	8.702 (E)	0	313.5 (354)	318.0 (368)
5d (100:0)	15.448 (E)	13	349.0 (400)	351.0 (415)
5e (67:33)	24.093 (E)	0	369.5 (432)	363.0 (452)
5f (97:3)	8.483 (E)	0	306.0 (381)	305.0 (385)
6	−1.922	0	233.0 (285)	232.0 (287)
7 (100:0)	15.086 (E)	0.7	294.0 (338)	298.0 (359)
10	20.352 (E)	2.5[d]	422.0 (528)	436.5 (590)
11	6.409 (E)	0		452.0 (500)

[a] E:Z ratio of the measured sample. [b] MOPAC ver. 6.01.[49] [c] Measured by the powder method using a Nd-YAG laser (1064 nm). Values are relative to urea. [d] Data from Ref. 5.

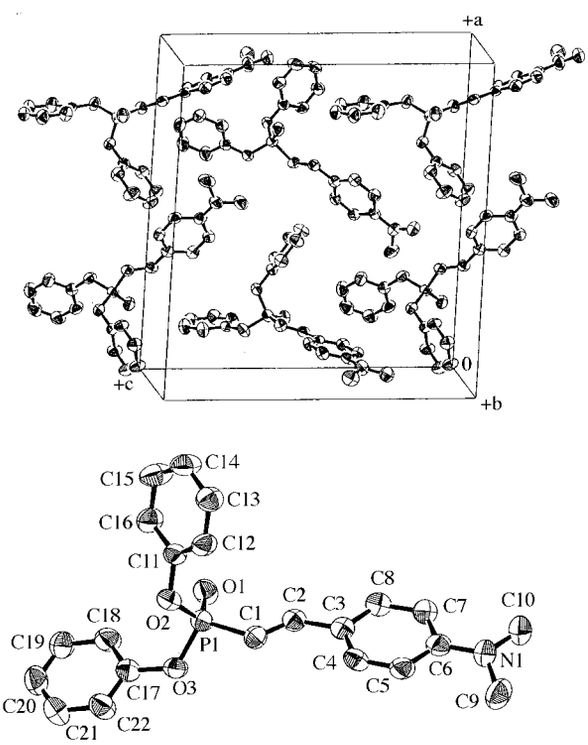


Fig. 1 Single crystal X-ray structure of compound **5d**

becomes both more delocalized and dipolar, *i.e.* it changes towards a fully delocalized structure.[25]

Judging from the acidity of nitro and phosphonate groups, the nitro group is a stronger acceptor than the phosphonate group. Therefore 1-nitro-2-arylethenes should have more delocalized structures and small BLA parameters according to the theoretical prediction. However, in reality the phosphonate compounds have a more delocalized structure than the corresponding nitro compounds; BLA of 1-nitro-2-phenylethene was 0.179 Å[31] and that of 1-(2-chloro-4-dimethylaminophenyl)-2-nitroethene was 0.147 Å,[32] both are larger than those of the corresponding phosphonate compounds. Probably the larger orbitals of the phosphine atom, relative to the nitrogen atom, enable a more efficient delocalization of the π-electrons. This indicates that by using heavier elements than second row elements as donor and/or acceptor groups, the BLA and therefore polarizabilities α, β, and γ can be tuned most efficiently.

Worthy to note with these π-electron conjugated phosphonates as optical materials is that they have better transparency at shorter wavelength than nitro compounds. For example nitro compound **11** had a cut-off wavelength at about 500 nm, while

Table 4 Selected bond distances (Å) and bond angles (°) for phosphonate **5d** with estimated standard deviations in parentheses

Bond distances	
P(1)–C(1)	1.760(7)
C(1)–C(2)	1.324(9)
C(2)–C(3)	1.458(9)
C(3)–C(8)	1.395(9)
C(8)–C(7)	1.378(10)
C(7)–C(6)	1.410(9)
C(3)–C(4)	1.378(8)
C(4)–C(5)	1.360(9)
C(5)–C(6)	1.40(1)
Bond angles	
P(1)–C(1)–C(2)	119.3(5)
C(1)–C(2)–C(3)	129.0(6)
C(2)–C(3)–C(8)	118.9(6)
C(2)–C(3)–C(4)	124.4(6)

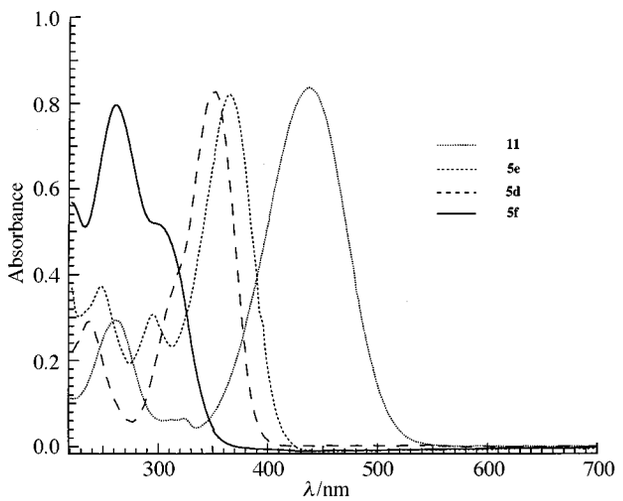


Fig. 2 Absorption spectra of 1-nitro-2-(4-dimethylaminophenyl)-ethene **11**, and diphenyl 2-(4-dimethylaminophenyl)ethenylphosphonate **5d**, diphenyl 2-(4-diphenylaminophenyl)ethenylphosphonate **5e** and diphenyl 2-(4-diphenylphosphinophenyl)ethenylphosphonate **5f** in acetonitrile

that of the corresponding phosphonate **5d** was about 415 nm; about 85 nm shorter wavelength. When the diphenylamino group of **5d** was substituted with a diphenylphosphino group as in compound **5f**, the cut-off wavelength became even shorter and light of wavelength longer than *ca.* 385 nm could be transmitted (Fig. 2).

Usually the SHG efficiency–transparency trade off has been the most serious problem for conjugated and polar molecules possessing CT characteristics; large hyperpolarizability inevitably leads to a loss of transparency as depicted in Eqn. (1);[14] where β_{CT} is the CT component of β, $\hbar\omega$ is the laser fundamental photon energy, W is the energy gap, f is the oscillator strength of the CT transition in the molecule, and $\Delta\mu$ is the change in the dipole moment.[33] In order to increase β_{CT}, the energy gap W should be small; as a consequence the absorption band will shift to longer wavelength.

$$\beta_{CT} = \frac{3e^2\hbar^2 W f \Delta\mu}{2m[W^2 - (2\hbar\omega)^2][W^2 - (\hbar\omega)^2]} \quad (1)$$

The π-electron conjugated phosphonates surmounted this trade-off problem; even though the β_{calc} was larger for phosphonate **5d** than nitro compound **11**, the transparency of **5d** was better than **11**. The reason for this is that the π-electron conjugated phosphonates have a small degree of CT character as can be seen in their solvent dependent absorption; the lowest energy absorption of phosphonates did not shift to longer wavelength in acetonitrile compared with that in benzene

solution (Table 3). It is an important finding that compounds with little CT character such as **5d** can exhibit relatively large SHG character.

Here we have exhibited that π-electron conjugated phosphonates and phosphonic bis-amides having moderate electron withdrawing ability can be good candidates for non-linear optical materials.[34]

Experimental

Mps were measured on a Yanaco micro melting point apparatus and are uncorrected. ^{1}H NMR Spectra were measured on a JEOL JNM-GSX270 or JNM-EX 400 spectrometer and *J* values are given in Hz. IR and UV–VIS spectra were recorded with a Hitachi 270-30 and Shimadzu UV-2200 spectrometer, respectively. Mass spectra were taken on a Hitachi M-80B instrument. The cyclic voltammetry was carried out at room temperature under nitrogen using a Yanagimoto P-1100 machine.

1-Bromo-2-phenylethene was purchased from Tokyo Chemical Industry Co., Ltd. and distilled prior to use. (1*E*,3*E*)/(1*Z*,3*E*)-1-Bromo-4-phenylbutadiene,[35] 1-bromo-2-(4-dimethylaminophenyl)ethene,[36] and 1-bromo-2-(4-chlorophenyl)-ethene[37] were prepared by the literature methods. 1-Bromo-2-(4-methylthiophenyl)ethene was prepared by modification of the reported method.[35] 1-Bromo-2-(4-diphenylaminophenyl)-ethene was prepared from 4-diphenylaminobenzaldehyde[38] by a similar method to the reported one.[35] 1-Bromo-2-(4-diphenylphosphophenyl)ethene was prepared from 4-diphenylphosphobenzaldehyde[39] by a similar method to the reported one.[35]

Preparation of π-electron conjugated phosphonates from the corresponding bromides and di-alkyl and -aryl phosphonates by the copper promoted reaction

Typical procedure for the reactions in hexamethylphosphoric triamide (HMPA) using potassium hydride as base

Dimethyl 2-phenylethenylphosphonate 1a. To the solution of the anion generated from dimethyl phosphonate (660 mg, 6 mmol) and KH (684 mg, 17.1 mmol) in hexamethylphosphoric triamide (HMPA) (4 cm^3), were added copper(I) iodide (1.14 g, 6 mmol) and 1-bromo-2-phenylethene (*E*:*Z* = 84:16) (366 mg, 2 mmol) under a nitrogen atmosphere. The solution was heated at 120 °C for 2 h until the starting bromide was consumed completely. Benzene (30 cm^3) and brine (30 cm^3) were added to the reaction mixture and the organic layer was separated and washed with *ca.* 10% aqueous sodium hydrogen sulfate (30 cm^3), brine (30 cm^3 × 5), and dried with sodium sulfite. The solvent was evaporated and the residue was purified by silica gel column chromatography with hexane–dichloromethane as the eluents to give the phosphonate **1a** (*E*:*Z* = 86:14) (662 mg, 78%) as a colourless oil (lit.,[40] mp 29–30 °C) which was further purified by bulb to bulb distillation *in vacuo* for further analysis (Found: C, 56.65; H, 6.3. $C_{10}H_{13}O_3P$ requires C, 56.6; H, 6.2%); ν_{max}(NaCl)/cm^{-1} 2980, 2930, 2830 and 1240; δ_H($CDCl_3$) (*E*)-isomer: 3.77 (d, 6H, *J* 11.0, $POCH_3$), 6.22 (dd, 1H, *J* 17.7 and 14.3, C=C*H*–P), 7.21 (d, 1H, *J* 14.3, Ph–C*H*=C) and 7.35–7.66 (m, 5H); (*Z*)-isomer: 3.62 (d, 6H, *J* 11.3, $POCH_3$), 5.77 (dd, 1H, *J* 14.3 and 15.6, C=C*H*–P), 7.35–7.66 (m, 6H, *Ph*–C*H*=C); *m*/*z* (EI) 212 (M$^+$, 24%) and 117 (100).

Diethyl 2-phenylethenylphosphonate 1b. Reaction of 1-bromo-2-phenylethene (*E*:*Z* = 84:16) with diethyl phosphonate, according to the typical procedure in HMPA using KH as the base, led to diethyl 2-phenylethenylphosphonate **1b** (*E*:*Z* = 84:16) (82%) as a colourless oil (lit.,[41] bp 156–158 °C/3 mm Hg) (Found: C, 59.8; H, 7.3. $C_{12}H_{17}O_3P$ requires C, 60.0; H, 7.1%); ν_{max}(KBr)/cm^{-1} 2950 and 1220; δ_H($CDCl_3$) (*E*)-isomer: 1.35 (t, 6H, *J* 7.1, OCH_2CH_3), 4.13 (dq, 4H, *J* 7.0 and 7.1, $POCH_2CH_3$), 6.26 (dd, 1H, *J* 17.5 and 17.5, C=C*H*–P) and 7.34–7.70 (m, 6H, *Ph*–C*H*=C); (*Z*)-isomer: 1.18 (t, 6H, *J* 7.0, OCH_2CH_3), 3.99 (dq, 4H, *J* 7.3 and 7.5, $POCH_2CH_3$), 5.80 (dd, 1H, *J* 14.3 and 15.6, C=C*H*–P), 7.19 (d, 1H, *J* 14.3, Ph–C*H*=C), 7.34–7.70 (m, 5H, Ph); *m*/*z* (EI) 240 (M$^+$, 14%) and 131 (100).

Diisopropyl 2-phenylethenylphosphonate 1c. Reaction of 1-bromo-2-phenylethene (*E*:*Z* = 84:16) with diisopropyl phosphonate, according to the typical procedure, in HMPA using KH as the base, led to diisopropyl 2-phenylethenylphosphonate **1c** (*E*:*Z* = 84:16) (99%) as a colourless oil (lit.,[42] bp 122 °C/0.06 mmHg) (Found: C, 62.3; H, 8.0. $C_{14}H_{21}O_3P$ requires C, 62.7; H, 7.9%); ν_{max}(KBr)/cm^{-1} 2960 and 1225; δ_H($CDCl_3$) (*E*)-isomer: 1.35 (dd, 12H, *J* 6.1 and 13.1, $POCHCH_3$), 4.71 (m, 2H, $POCHCH_3$), 6.27 (dd, 1H, *J* 17.4 and 17.4, C=C*H*–P) and 7.33–7.74 (m, 6H, *Ph*–C*H*=C); (*Z*)-isomer: 1.21 (dd, 6H, *J* 6.1 and 27.2, $OCHCH_3$), 4.68 (m, 2H, $POCHCH_3$), 5.82 (dd, 1H, *J* 14.5 and 15.1, C=C*H*–P), 7.33–7.74 (m, 6H, *Ph*–C*H*=C); *m*/*z* (EI) 268 (M$^+$, 18%), 209 (14) and 104 (100).

Diphenyl 2-phenylethenylphosphonate 1d. Reaction of 1-bromo-2-phenylethene (*E*:*Z* = 84:16) with diphenyl phosphonate, according to the typical procedure, in HMPA using KH as the base, led to diphenyl 2-phenylethenylphosphonate **1d** (*E*:*Z* = 98:2) (92%) as colourless crystals, mp 111 °C (lit.,[43] 109 °C) (Found: C, 71.0; H, 5.1. $C_{20}H_{17}O_3P$ requires C, 71.4; H, 5.1%); ν_{max}(KBr)/cm^{-1} 3000 and 1180; δ_H($CDCl_3$) (*E*)-isomer: 6.47 (dd, 1H, *J* 17.4 and 19.2, C=C*H*–P), 7.13–7.52 (m, 15H, Ph) and 7.69 (dd, 1H, *J* 17.4 and 23.2, Ph–C*H*=C); *m*/*z* (EI) 336 (M$^+$, 57%) and 149 (100).

Typical procedure for the reactions using triethylamine as the base in solvents other than HMPA

Diethyl phenylphosphonate 2. To the solution of the anion generated from diethyl phosphonate (829 mg, 6 mmol) and triethylamine (*ca.* 1.0 g, 9.88 mmol) in tetramethylurea (TMU) (4 cm^3), were added copper(I) iodide (1.14 g, 6 mmol) and bromobenzene (314 mg, 2 mmol) under a nitrogen atmosphere. The solution was heated to 120–140 °C for 24 h until the starting bromide was consumed completely. Benzene (30 cm^3) and brine (30 cm^3) were added to the reaction mixture and the organic layer was separated and washed with *ca.* 10% aqueous sodium hydrogen sulfate (30 cm^3), brine (30 cm^3 × 5), and dried with sodium sulfite. The solvent was evaporated and the residue was purified by silica gel column chromatography with hexane–dichloromethane as the eluents to give the phosphonate **2** (253 mg, 59%) as a colourless oil (lit.,[44] bp 90 °C/0.2 mmHg) which was further purified by bulb to bulb distillation *in vacuo* for further analysis; δ_H($CDCl_3$) 1.33 (t, *J* 6.4, OCH_2CH_3), 4.11 (m, 4H, OCH_2CH_3) and 7.47–7.85 (m, 5H, aromatic); *m*/*z* (EI) 214 (M$^+$, 28%) and 77 (100).

Diethyl 4-phenylbuta-1,3-dienylphosphonate 3a. Reaction of 1-bromo-4-phenylbuta-1,3-diene (1*E*:1*Z* = 25:75; 3*E*:3*Z* > 99:1) with diethyl phosphonate, according to the typical procedure in THF using triethylamine as the base, led to diethyl 4-phenylbuta-1,3-dienylphosphonate **3a** (27%) as a pale yellow oil (lit.,[45] bp 125–126 °C/0.05 mmHg) (Found: C, 62.8; H, 7.3. $C_{14}H_{19}O_3P$ requires C, 63.15; H, 7.2%); ν_{max}(KBr)/cm^{-1} 2950 and 1220; *m*/*z* (EI) 266 (M$^+$, 12%) and 128 (100).

Diphenyl 4-phenylbuta-1,3-dienylphosphonate 3b. Reaction of 1-bromo-4-phenylbuta-1,3-diene (1*E*:1*Z* = 25:75; 3*E*:3*Z* > 99:1) with diphenyl phosphonate, according to the typical procedure in THF using triethylamine as the base, led to diphenyl 4-phenylbuta-1,3-dienylphosphonate **3b** (40%) as colourless crystals, mp 95–97 °C (Found: C, 73.0; H, 5.3. $C_{22}H_{19}O_3P$ requires C, 72.9; H, 5.3%); ν_{max}(KBr)/cm^{-1} 2950 and 1220; *m*/*z* (EI) 362 (M$^+$, 23%) and 326 (100).

Diphenyl 2-(1-naphthyl)ethenylphosphonate 4. Reaction of 1-bromo-2-(1-naphthyl)ethene (*E*:*Z* = 8:92) with diphenyl phosphonate, according to the typical procedure in THF using triethylamine as the base, led to diphenyl 2-(1-naphthyl)-ethenylphosphonate **4** (*E*:*Z* = 11:89) (61%) as colourless crystals, mp 97 °C (Found: C, 74.5; H, 5.0. $C_{24}H_{19}O_3P$ requires

C, 74.6; H, 5.0%); ν_{max}(KBr)/cm^{-1} 2980 and 1180; δ_H($CDCl_3$) (*E*)-isomer: 6.60 (dd, 1H, *J* 17.1 and 18.9, C=C*H*–P) and 6.87–8.17 (m, 18H, *Ph*–C*H*=C); (*Z*)-isomer: 6.32 (dd, 1H, *J* 13.7 and 17.1, C=C*H*–P) and 6.87–8.17 (m, 18H, aromatic and Ar–C*H*=C); *m*/*z* (EI) 386 (M^+, 25%) and 152 (100).

Diphenyl 2-(4-chlorophenyl)ethenylphosphonate 5a. Reaction of 1-bromo-2-(4-chlorophenyl)ethene (*E*:*Z* = 9:91) with diphenyl phosphonate, according to the typical procedure in THF using triethylamine as the base, led to diphenyl 2-(4-chlorophenyl)ethenylphosphonate **5a** (*E*:*Z* = 12:88) (37%) as colourless crystals, mp 99 °C (Found: C, 65.2; H, 4.7. $C_{20}H_{16}ClO_3P$ requires C, 64.8; H, 4.4%); ν_{max}(KBr)/cm^{-1} 3000 and 1180; δ_H($CDCl_3$) (*E*)-isomer: 6.44 (dd, 1H, *J* 17.6 and 18.8, C=C*H*–P) and 7.06–7.69 (m, 15H, *Ph*–C*H*=C); (*Z*)-isomer: 6.02 (dd, 1H, *J* 14.0 and 17.1, C=C*H*–P) and 7.06–7.69 (m, 15H, aromatic and Ar–C*H*=C); *m*/*z* (EI) 372 (M^+ + 2, 35%), 370 (M^+, 100) and 277 (100).

Diphenyl 2-(2,5-dimethoxyphenyl)ethenylphosphonate 5b. Reaction of 1-bromo-2-(2,5-dimethoxyphenyl)ethene (*E*:*Z* = 15:85) with diphenyl phosphonate, according to the typical procedure in dimethylformamide using triethylamine as the base, led to diphenyl 2-(2,5-dimethoxyphenyl)ethenylphosphonate **5b** (*E*:*Z* > 99:1) (15%) as colourless crystals, which were recrystallized from methanol to give pure (*E*)-isomer, mp 89 °C (Found: C, 66.2; H, 5.25. $C_{22}H_{21}O_5P$ requires C, 66.7; H, 5.3%); ν_{max}(KBr)/cm^{-1} 3000, 2900 and 1180; δ_H($CDCl_3$) 3.78 (s, 3H, OMe), 3.82 (s, 3H, OMe), 6.55 (dd, 1H, *J* 17.7 and 21.4, C=C*H*–P) and 6.86–7.39 (m, 13H, aromatic) and 7.95 (dd, 1H, *J* 17.7 and 25.0, Ar–C*H*=C); *m*/*z* (EI) 396 (M^+, 55%), 303 (80) and 162 (100).

Diphenyl 2-(4-methylthiophenyl)ethenylphosphonate 5c. Reaction of 1-bromo-2-(4-methylthiophenyl)ethene (*E*:*Z* = 7:93) with diphenyl phosphonate, according to the typical procedure in dimethylformamide using triethylamine as the base, led to diphenyl 2-(4-methylthiophenyl)ethenylphosphonate **5c** (*E*:*Z* = 65:35) (65%) as colourless crystals, which were recrystallized to give pure (*E*)-isomer, mp 91 °C (Found: C, 65.5; H, 5.0. $C_{21}H_{19}O_3PS$ requires C, 66.0; H, 5.0%); ν_{max}(KBr)/cm^{-1} 3050 and 1210; δ_H($CDCl_3$) (*E*)-isomer: 2.48 (s, 3H, SMe), 6.39 (dd, 1H, *J* 17.4 and 19.5, C=C*H*–P) and 6.78–7.71 (m, 15H, *Ph*–C*H*=C and *Ph*O); (*Z*)-isomer: 2.47 (s, 3H, SMe), 5.90 (dd, 1H, *J* 14.2 and 17.6, C=C*H*–P) and 6.78–7.71 (m, 15H, aromatic and Ar–C*H*=C); *m*/*z* (EI) 382 (M^+, 100%) and 288 (40).

Diphenyl 2-(4-dimethylaminophenyl)ethenylphosphonate 5d. Reaction of 1-bromo-2-(4-dimethylaminophenyl)ethene (*E*:*Z* = 18:82) with diphenyl phosphonate, according to the typical procedure in THF using triethylamine as the base for 48 h, led to diphenyl 2-(4-dimethylaminophenyl)ethenylphosphonate **5d** (71%) as colourless crystals, which were recrystallized to give pure (*E*)-isomer, mp 127 °C (Found: C, 69.65; H, 5.9; N, 3.9. $C_{22}H_{22}NO_3P$ requires C, 69.65; H, 5.8; N, 3.7%); ν_{max}(KBr)/cm^{-1} 3000, 2900 and 1160; δ_H($CDCl_3$) (*E*)-isomer: 3.00 (s, 6H, Me_2N), 6.12 (dd, 1H, *J* 17.2 and 20.0, C=C*H*–P) and 6.62–7.40 (m, 14H, aromatic); *m*/*z* (EI) 379 (M^+, 100%).

Diphenyl 2-(4-diphenylaminophenyl)ethenylphosphonate 5e. Reaction of 1-bromo-2-(4-diphenylaminophenyl)ethene (*E*:*Z* = 19:81) with diphenyl phosphonate, according to the typical procedure in DMF using triethylamine as the base for 48 h, led to diphenyl 2-(4-diphenylaminophenyl)ethenylphosphonate **5e** (*E*:*Z* = 67:33) (83%) as colourless crystals, mp 123 °C (Found: C, 76.4; H, 5.2; N, 3.2. $C_{32}H_{26}NO_3P$ requires C, 76.3; H, 5.2; N, 2.8%); ν_{max}(KBr)/cm^{-1} 3050 and 1190; δ_H($CDCl_3$) (*E*)-isomer: 6.24 (dd, 1H, *J* 17.4 and 19.8, C=C*H*–P) and 6.77–7.68 (m, 25H, aromatic and Ar–C*H*=C); (*Z*)-isomer: 5.76 (dd, 1H, *J* 14.0 and 17.7, C=C*H*–P) and 6.77–7.68 (m, 25H, aromatic and Ar–C*H*=C); *m*/*z* (EI) 379 (M^+, 100%).

Diphenyl 2-(4-diphenylphosphinophenyl)ethenylphosphonate 5f. Reaction of 1-bromo-2-(4-diphenylphosphinophenyl)ethene (*E*:*Z* = 23:77) with diphenyl phosphonate, according to the typical procedure in DMF using triethylamine as the base for 48 h, led to colourless crystals of mp 120 °C, which are dissolved in dichloromethane and washed with 10% aqueous ammonia. As the aqueous solution turned blue indicating the presence of copper, the crystals might be the copper salt complex of diphenyl 2-(4-diphenylphosphinophenyl)-ethenylphosphonate. The organic layer was washed with water until the aqueous solution became neutral, dried with sodium sulfate, evaporated and purified by silica gel column chromatography to give diphenyl 2-(4-diphenylphosphinophenyl)-ethenylphosphonate **5f** (*E*:*Z* = 97:3) (62%) as colourless crystals, mp 106 °C (Found: C, 73.6; H, 5.1. $C_{32}H_{26}O_3P_2$ requires C, 73.8; H, 5.0%); ν_{max}(KBr)/cm^{-1} 3000 and 1180; δ_H($CDCl_3$) (*E*)-isomer: 6.46 (dd, 1H, *J* 17.4 and 19.2, C=C*H*–P), 7.16–7.47 (m, 24H, aromatic) and 7.67 (dd, 1H, *J* 17.4 and 23.8, Ar–C*H*=C); *m*/*z* (EI) 520 (M^+, 100%) and 427(5).

Diphenyl 2-thienylphosphonate 6. Reaction of 2-bromothiophene with diphenyl phosphonate, according to the typical procedure in DMF using triethylamine as the base for 24 h, led to diphenyl 2-thienylphosphonate **6** (39%) as colourless crystals, mp 88 °C (lit.,[46] 75 °C) (Found: C, 61.0; H, 4.2. $C_{16}H_{13}O_3PS$ requires C, 60.8; H, 4.1%); ν_{max}(KBr)/cm^{-1} 3080 and 1266; δ_H($CDCl_3$) 7.13–7.34 (m, 11H) and 7.73–7.80 (m, 2H); *m*/*z* (EI) 316 (M^+, 100%) and 223 (58).

Diphenyl 2-(2-thienyl)ethenylphosphonate 7. Reaction of 1-bromo-2-(4-diphenylaminophenyl)ethene (*E*:*Z* = 22:78) with diphenyl phosphonate, according to the typical procedure in DMF using triethylamine as the base for 48 h, led to diphenyl 2-(2-thienyl)ethenylphosphonate **7** (*E*:*Z* = 43:57) (83%) as colourless crystals, which were recrystallized from methanol to give pure (*E*)-isomer, mp 134 °C (Found: C, 63.0 H, 4.35. $C_{18}H_{15}O_3PS$ requires C, 63.15; H, 4.4%); ν_{max}(KBr)/cm^{-1} 3100 and 1194; δ_H($CDCl_3$) (*E*)-isomer: 6.19 (dd, 1H, *J* 17.2 and 18.7, C=C*H*–P) and 6.78–8.83 (m, 14H, aromatic and Ar–C*H*=C); (*Z*)-isomer: 5.74 (dd, 1H, *J* 14.3 and 16.7, C=C*H*–P) and 6.78–8.83 (m, 14H, aromatic and Ar–C*H*=C); *m*/*z* (EI) 342 (M^+, 53%), 249 (56), 173 (68) and 97 (100).

The copper-promoted Arbuzov type vinylic substitution reaction to give π-electron conjugated phosphonates and phosphinamides

Typical procedure. Preparation of diethyl 2-phenylethenylphosphonate 1b. A mixture of copper(I) iodide (10.26 g, 54 mmol), triethyl phosphite (8.97 g, 54 mmol) and 1-bromo-2-phenylethene (*E*:*Z* = 84:16) (3.29 g, 18 mmol) in tetramethylurea (15 cm^3) was heated at 120 °C under a nitrogen atmosphere with stirring for 24 h. To the cooled reaction mixture was added benzene (30 cm^3) and brine (30 cm^3), and the organic layer was separated, washed with *ca.* 10% aqueous sodium hydrogen sulfate (30 cm^3) and brine (30 cm^3 × 5), and dried with sodium sulfite. The solvent was evaporated and the residue was purified by silica gel column chromatography with hexane–dichloromethane as the eluents to give the phosphonate **1b** (*E*:*Z* = 86:14) (3.50 g, 81%) as a colourless oil.

Using this method phosphonates **1a**, **1c** and **1d** were prepared in 35, 53 and 25% isolated yields respectively.

N,*N*,*N*′,*N*′-Tetraethyl-*P*-phenylphosphonic diamide 8

Reaction of bromobenzene with tris(diethylamino)phosphine, according to the typical procedure in DMF for 40 h, led to diamide **8** (27%) as a colourless oil, bp *ca.* 90 °C/0.1 mmHg (lit.,[47] 95 °C/0.5 mmHg); ν_{max}(KBr)/cm^{-1} 2920 and 1180; δ_H($CDCl_3$) 1.04 (t, 12H, *J* 7.2, NCH_2CH_3), 3.03–3.14 (m, 8H, NCH_2CH_3), 7.4–7.5 (m, 3H) and 7.73–7.82 (m, 2H); *m*/*z* (EI) 268 (M^+, 20%) and 196 (100).

N,*N*,*N*′,*N*′-Tetraethyl-*P*-(2-phenylethenyl)phosphonic diamide 9

Reaction of 1-bromo-2-phenylethene (*E*:*Z* = 84:16) with tris-(diethylamino)phosphine, according to the typical procedure in DMF for 40 h, led to diamide **9** (*E*:*Z* = 84:16), which was recrystallized from methanol to give pure (*E*)-isomer (49%) as colourless crystals, mp 113–115 °C (lit.,[10] 103.5 °C) (Found:

C, 65.6; H, 9.6; N, 9.5. $C_{16}H_{27}N_2OP$ requires C, 65.3; H, 9.2; N, 9.5%); ν_{max}(KBr)/cm^{-1} 2900 and 1160; δ_H($CDCl_3$) (*E*)-isomer: 1.11 (t, 12H, *J* 7.0, NCH_2CH_3), 3.04–3.13 (m, 8H, NCH_2CH_3), 6.35 (dd, 1H, *J* 17.4 and 18.3, C=C*H*–P) and 7.34–7.53 (m, 6H, *Ph*–C*H*=C); *m*/*z* (EI) 294 (M^+, 16%) and 222 (100).

X-Ray crystallographic study of 5d

Crystal data. $C_{22}H_{22}NO_3P$, $M = 379.39$. Orthorhombic, $a = 19.611(1)$, $b = 5.745(8)$, $c = 17.667(6)$ Å, $V = 1990(1)$ Å^3 (by least-squares refinement on diffractometer angles for 25 carefully centred reflections in the range $20.41 < 2\theta < 29.80°$, $\lambda = 0.71069$ Å), space group $Pca2_1$ (No. 29), $Z = 4$, $D_{calc} = 1.266$ g cm^{-3}, colourless prism $0.62 \times 0.22 \times 0.12$ mm, μ(Mo-Kα) = 1.59 cm^{-1}.

Data collection and processing. A Rigaku AFC5R diffractometer with graphite-monochromated Mo-Kα radiation was used: $\omega - 2\theta$ scan technique to a maximum 2θ value of 55.0°. Scans of $(1.47 + 0.30 \tan \theta)°$ were made at a speed of 16.0 min^{-1} (in omega). A total of 2669 reflections were collected. The intensities of three representative reflections which were measured after every 150 reflections declined by −1.80%. A linear correction factor was applied to the data to account for this phenomenon.

Structure solution and refinement. The structure was solved by direct methods (SIR92). The non-hydrogen atoms were refined anisotropically. The final cycle of full-matrix least-squares refinement was based on 1284 observed reflections [$I > 1.00\sigma(I)$] and 245 variable parameters and converged (largest parameter shift was 0.01 times its esd). Neutral atom-scattering factors were taken from Cromer and Waber.[48] Anomalous dispersion effects were included in F_{calc};[49] the values for $\Delta f'$ and $\Delta f''$ were those of Cromer.[48] Final $R = 0.052$, $R_w = 0.055$, goodness of fit = 1.10. The final ΔF synthesis showed no peaks outside the range from −0.23 to +0.21 e Å^{-3}.

All the calculations were performed using the TEXSAN[50] crystallographic software package of Molecular Structure Corporation. The ORTEP programmes were used to obtain Fig. 1.

Full crystallographic details, excluding structure factor tables, have been deposited at the Cambridge Crystallographic Data Centre (CCDC). For details of the deposition scheme, see 'Instructions for Authors', *J. Chem. Soc.*, *Perkin Trans. 1*, available *via* the RSC Web page (http://www.rsc.org/authors). Any request to the CCDC for this material should quote the full literature citation and the reference number 207/244.

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