Efficient Diastereoselective Synthesis of Phosphonato Vinylsulfones via a Multicomponent Method

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Abstract: The phosphonato vinylsulfone building block was prepared by a facile three-component reaction of an acetylene, a sulfonyl chloride and a trialkyl phosphite.

Key words: vinylsulfone, dialky acetylenedicarboxylate, trialkyl phosphate, multicomponent reaction, zwitterion

Vinylsulfones, as unsaturated sulfones, are extensively used as intermediates in organic synthesis[1a–e] due to the chemical versatility of the sulfone moiety. Vinyl sulfones are also excellent acceptors in Michael additions and 2π partners in cycloaddition reactions.[1f,g] Several biologically active sulfone molecules, prepared from alkenyl sulfones,[1h–j] and α,β-unsaturated sulfones, have been found to have anticancer[1k] and carcinogenesis-suppressing activity.[1l] Moreover, the sulfone group can be removed at the end of a synthetic sequence by a variety of reductive, alkylative, or oxidative methods.[2] In our investigation, vinylsulfones with phosphonate substituents have been synthesized. Organo phosphonates have been used as substitutes for the corresponding esters and acids with high biological activity;[3a,b] vinylphosphonates have been used as intermediates in the stereoselective synthesis of trisubstituted olefins.[3c–e]

Numerous methods have been developed for the synthesis of vinylsulfones,[4a–g] however, these methods are sometimes complex, do not tolerate sensitive functional groups, and the reagents and starting materials are not always readily available.

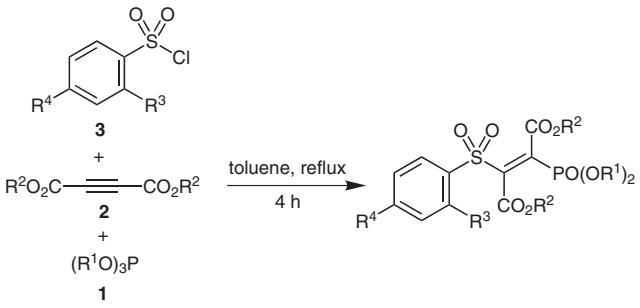
A general way to improve synthetic efficiency and also to address the other criteria is the development of types of multicomponent reactions.[5] Multicomponent reactions (MCRs), by virtue of their convergence, productivity, facile execution, and generally high yields of products, have attracted much attention from the point of view of combinatorial chemistry.[6–8]

We recently reported a new class of multicomponent reactions mediated by zwitterionic intermediates.[9] We were interested in applying this zwitterionic method to the diastereoselective synthesis of (*E*)-phosphonato vinylsulfones using acetylenes and phosphites in the presence of sulfonyl chlorides.

The reaction of trialkyl phosphites **1** with dialkyl acetylenedicarboxylates **2** in the presence of sulfonyl chlorides **3** in toluene under reflux conditions, produced diethyl (*E*)-2-(dialkoxyphosphoryl)-3-(arylsulfonyl)-2-butenedioate derivatives **4** in 83–97% yields after four hours (Table 1).

The IR spectrum of **4a** exhibited absorption bands due to the carbonyl group of esters at 1737 cm^{-1}, the C=C group at 1650 cm^{-1}, and the absorption bands of the sulfone [1338 and 1177 (SO_2) cm^{-1}] and phosphonate [1272 (P=O), 1098 and 1037 (PO–Me), and 856 (P–O) cm^{-1}]

Table 1 Reaction of Trialkyl Phosphites **1** with Dialkyl Acetylenedicarboxylates **2** in the Presence of Sulfonyl Chlorides **3**



4	R^1	R^2	R^3	R^4	Yield of **4** (%)[a]
a	Me	Me	H	H	92
b	Me	Me	H	Me	89
c	Me	Me	H	Et	90
d	Me	Me	Et	H	83
e	Me	Et	H	H	90
f	Me	Et	H	Et	91
g	Me	Et	Et	H	89
h	Et	Et	H	H	94
i	Et	Et	H	Et	90
j	Et	Et	Et	H	84
k	Et	Me	H	H	95
l	Et	Me	H	Me	97
m	Et	Me	H	Et	96
n	Et	Me	Et	H	87

[a] Isolated yield.

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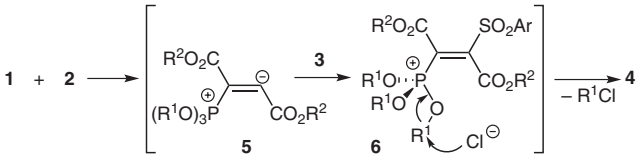
moieties. The ^{1}H NMR spectrum of **4a** exhibited one sharp doublet readily recognized as arising from the methoxy group attached to the phosphorus (δ = 3.79 ppm, $^3J_{H–P}$ = 11.7 Hz), and two sharp singlets arising from the methoxy groups (δ = 3.82 and 3.96 ppm). The aryl moiety exhibited characteristic signals in the aromatic region of the spectrum. The ^{1}H-decoupled ^{13}C NMR spectrum of **4a** showed 11 distinct resonances in agreement with the dimethyl (*E*)-2-(dimethoxyphosphoryl)-3-(phenylsulfonyl)-2-butenedioate structure. The ^{1}H- and ^{13}C-decoupled ^{31}P NMR spectrum of **4a** exhibited one sharp singlet readily recognized as arising from phosphonate (δ = 9.32 ppm). The relative stereochemistry of **4** was determined on the basis of the ^{31}P–^{13}C coupling constants from the vinylphosphonate. Vicinal ^{31}P–^{13}C coupling through a π-bond is a useful tool for assigning *Z*, *E* structure. In general, $^3J_{C–P}$-*trans* coupling is much larger than $^3J_{C–P}$-*cis*.[10] In the ^{13}C NMR spectrum of **4a**, the $^3J_{C–P}$ coupling of 8.5 Hz (δ = 163.23 ppm, *C*O_2Me) was diagnostic for their *E* relationship.[10a] Partial assignment of these resonances is given in the experimental section. The ^{1}H, ^{13}C and ^{31}P NMR spectra of compounds **4b**–**n** were similar to those of **4a** except for the alkoxy group, ester groups and the aryl moiety, which exhibited characteristic signals with appropriate chemical shifts (see Experimental section).

Although we have not established the mechanism of the reaction between the phosphites **1** and the acetylenic esters **2** in the presence of the sulfonyl chloride **3** in an experimental manner, a possible explanation is proposed in Scheme 1.



Scheme 1

On the basis of the well-established chemistry of acetylenic esters,[9a,e,i,11] it is reasonable to assume that the phosphonato vinylsulfone derivatives **4** apparently result from initial addition of the phosphite to the acetylenic ester and subsequent attack of the resulting zwitterion **5** on the sulfonyl chloride **3** to yield ion pair **6**. This intermediate, under the reflux conditions, then suffers attack by the chloride ion to produce the (*E*)-phosphonato vinylsulfone **4** derivatives (Scheme 1).

In summary, the reaction between phosphites and dialkyl acetylenedicarboxylates, in the presence of sulfonyl chlorides, provides a simple one-pot entry into the synthesis of (*E*)-phosphonato vinylsulfone derivatives of potential synthetic and biological interest. The present method carries the advantage of being performed under the neutral conditions and requires no activation or modification of the educts.

Dimethyl and diethyl acetylenedicarboxylates, and trialkyl phosphites were obtained from Merck (Germany) and Fluka (Switzerland) and were used without further purification. Melting points were measured on an Electrothermal 9100 apparatus. Elemental analyses for C, H and N were performed using a Heraeus CHN-O-Rapid analyzer. Mass spectra were recorded on a Finnigan–Matt 8430 mass spectrometer operating at an ionization potential of 70 eV. ^{1}H and ^{13}C NMR spectra were measured as $CDCl_3$ solutions with a Bruker DRX-500 Avance spectrometer at 500.1 and 125.8 MHz, respectively. IR spectra were recorded on a Shimadzu IR-460 spectrometer. Chromatography columns were prepared from Merck silica gel 230–240 mesh.

Dimethyl (*E*)-2-(Dimethoxyphosphoryl)-3-(phenylsulfonyl)-2-butenedioate (4a); Typical Procedure

To a magnetically stirred solution of sulfonyl chloride (0.18 g, 1 mmol) and dimethyl acetylenedicarboxylate (0.14 g, 1 mmol) in toluene (3 mL), was added dropwise a solution of trimethyl phosphite (0.12 g, 1 mmol) in anhydrous toluene (3 mL) at r.t. over 10 min. The reaction mixture was then allowed to stir for 4 h under reflux. The solvent was removed under reduced pressure, and the residue was separated by silica gel column chromatography (silica gel, hexane–EtOAc, 4:1) to give the product **4a**.

Yield: 0.36 g (92%); colorless crystals; mp 119–121 °C.

IR (KBr): 1737 (2 × C=O of CO_2Me), 1650 (C=C), 1594 and 1451 (Ph), 1348 and 1177 (SO_2), 1272 (P=O), 1235 and 1142 (C–O), 1098 and 1037 (POMe), 856 cm^{-1} (P–O).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.79 [6 H, d, $^3J_{H–P}$ = 11.7 Hz, P(OMe)$_2$], 3.82 (3 H, s, OMe), 3.96 (3 H, s, OMe), 7.57 (2 H, t, $^3J_{H–H}$ = 8.1 Hz, 2 × CH of Ph), 7.69 (1 H, t, $^3J_{H–H}$ = 7.5 Hz, CH of Ph), 7.97 (2 H, d, $^3J_{H–H}$ = 7.9 Hz, 2 × CH of Ph).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 53.71 and 53.78 (2 × OMe), 54.28 [d, $^2J_{C–P}$ = 5.3 Hz, P(OMe)$_2$], 129.18 (2 × CH of Ph), 129.53 (2 × CH of Ph), 134.61 (d, $^1J_{C–P}$ = 159.5 Hz, P*C*=C), 134.91 (CH of Ph), 137.81 (*C*$_{ipso}$-SO_2), 148.22 (d, $^2J_{C–P}$ = 6.0 Hz, PC=*C*), 161.61 (d, $^2J_{C–P}$ = 9.8 Hz, *C*O_2Me), 163.23 (d, $^3J_{C–P}$ = 8.5 Hz, *C*O_2Me).

^{31}P NMR (202 MHz, $CDCl_3$): δ = 9.32.

MS: *m*/*z* (%) = 393 (4) [M$^+$ + 1], 361 (52), 327 (3), 296 (100), 281 (57), 207 (18), 155 (14), 125 (41), 109 (48), 93 (27), 77 (72), 59 (10), 45 (3).

Anal. Calcd for $C_{14}H_{17}O_9PS$: C, 42.86; H, 4.37. Found: C, 42.90; H, 4.30.

Dimethyl (*E*)-2-(Dimethoxyphosphoryl)-3-[(4-methylphenyl)sulfonyl]-2-butenedioate (4b)

Yield: 0.36 g (89%); colorless viscous liquid.

IR (KBr): 1730 (2 × C=O of CO_2Me), 1613 (C=C), 1586 and 1429 (Ar), 1333 and 1152 (SO_2), 1275 (P=O), 1198 and 1115 (C–O), 1061 and 1028 (POMe), 852 cm^{-1} (P–O).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.43 (3 H, s, Me), 3.77 [6 H, d, $^3J_{H–P}$ = 11.7 Hz, P(OMe)$_2$], 3.80 (3 H, s, OMe), 3.93 (3 H, s, OMe), 7.34 (2 H, d, $^3J_{H–H}$ = 8.3 Hz, 2 × CH of Ar), 7.81 (2 H, d, $^3J_{H–H}$ = 8.3 Hz, 2 × CH of Ar).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.65 (Me), 53.54 and 53.61 (2 × OMe), 54.13 [d, $^2J_{C–P}$ = 5.4 Hz, P(OMe)$_2$], 129.45 (2 × CH of Ar), 129.76 (2 × CH of Ar), 134.00 (d, $^1J_{C–P}$ = 159.7 Hz, P*C*=C), 134.71 (*C*$_{ipso}$-SO_2), 146.27 (*C*$_{ipso}$-Me), 148.47 (d, $^2J_{C–P}$ =4.6 Hz, PC=*C*), 161.56 (d, $^2J_{C–P}$ = 9.5 Hz, *C*O_2Me), 163.12 (d, $^3J_{C–P}$ = 7.8 Hz, *C*O_2Me).

^{31}P NMR (202 MHz, $CDCl_3$): δ = 9.38.

MS: *m*/*z* (%) = 407 (3) [M$^+$ + 1], 375 (22), 341 (3), 310 (100), 295 (56), 283 (11), 221 (49), 155 (24), 119 (26), 109 (34), 91 (53), 79 (14), 65 (20), 59 (7), 45 (3).

Anal. Calcd for $C_{15}H_{19}O_9PS$: C, 44.34; H, 4.71. Found: C, 44.50; H, 4.60.

Dimethyl (*E*)-2-(Dimethoxyphosphoryl)-3-[(4-ethylphenyl)sulfonyl]-2-butenedioate (4c)

Yield: 0.38 g (90%); colorless viscous liquid.

IR (KBr): 1734 (2 × C=O of CO_2Me), 1620 (C=C), 1586 and 1427 (Ar), 1331 and 1153 (SO_2), 1266 (P=O), 1175 and 1153 (C–O), 1063 and 1022 (PO–Me), 885 cm^{-1} (P–O).

^1H NMR (500 MHz, $CDCl_3$): δ = 1.25 (3 H, t, $^3J_{H-H}$ = 7.6 Hz, CH_2CH_3), 2.72 (2 H, q, $^3J_{H-H}$ = 7.6 Hz, CH_2CH_3), 3.78 [6 H, d, $^3J_{H-P}$ = 11.8 Hz, $P(OMe)_2$], 3.81 (3 H, s, OMe), 3.94 (3 H, s, OMe), 7.37 (2 H, d, $^3J_{H-H}$ = 8.3 Hz, 2 × CH of Ar), 7.85 (2 H, d, $^3J_{H-H}$ = 8.3 Hz, 2 × CH of Ar).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.76 (CH_2CH_3), 28.89 (CH_2CH_3), 53.55 and 53.62 (2 × OMe), 54.15 [d, $^2J_{C-P}$ = 5.1 Hz, $P(OMe)_2$], 128.61 (2 × CH of Ar), 129.60 (2 × CH of Ar), 133.95 (d, $^1J_{C-P}$ = 159.5 Hz, P*C*=C), 134.88 (C_{ipso}-SO_2), 148.50 (d, $^2J_{C-P}$ = 4.7 Hz, PC=*C*), 152.29 (C_{ipso}-Et), 161.57 (d, $^2J_{C-P}$ = 9.7 Hz, *C*O_2Me), 163.13 (d, $^3J_{C-P}$ = 7.8 Hz, *C*O_2Me).

^{31}P NMR (202 MHz, $CDCl_3$): δ = 9.42.

MS: *m*/*z* (%) = 421 (4) [M^+ + 1], 389 (46), 324 (100), 309 (65), 297 (14), 265 (12), 221 (44), 153 (27), 133 (27), 109 (53), 93 (28), 79 (41), 65 (4), 59 (11), 45 (4).

Anal. Calcd for $C_{16}H_{21}O_9PS$: C, 45.72; H, 5.04. Found: C, 45.90; H, 5.10.

Dimethyl (*E*)-2-(Dimethoxyphosphoryl)-3-[(2-ethylphenyl)sulfonyl]-2-butenedioate (4d)

Yield: 0.35 g (83%); colorless viscous liquid.

IR (KBr): 1734 (2 × C=O of CO_2Me), 1621 (C=C), 1586 and 1429 (Ar), 1331 and 1153 (SO_2), 1266 (P=O), 1246 and 1175 (C–O), 1063 and 1020 (PO–Me), 852 cm^{-1} (P–O).

^1H NMR (500 MHz, $CDCl_3$): δ = 1.27 (3 H, t, $^3J_{H-H}$ = 7.4 Hz, CH_2CH_3), 2.97 (2 H, q, $^3J_{H-H}$ = 7.4 Hz, CH_2CH_3), 3.58 (3 H, s, OMe), 3.79 [6 H, d, $^3J_{H-P}$ = 11.6 Hz, $P(OMe)_2$], 3.89 (3 H, s, OMe), 7.33–7.39 (2 H, m, 2 × CH of Ar), 7.58 (1 H, t, $^3J_{H-H}$ = 7.2 Hz, CH of Ar), 7.94 (1 H, d, $^3J_{H-H}$ = 8.1 Hz, CH of Ar).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 15.27 (CH_2CH_3), 25.57 (CH_2CH_3), 53.50 and 53.63 (2 × OMe), 54.15 [d, $^2J_{C-P}$ = 5.1 Hz, $P(OMe)_2$], 126.26, 130.70, 130.94 and 134.93 (4 × CH of Ar), 132.00 (d, $^1J_{C-P}$ = 159.0 Hz, P*C*=C), 135.97 (C_{ipso}-SO_2), 146.11 (C_{ipso}-Et), 149.49 (d, $^2J_{C-P}$ = 4.6 Hz, PC=*C*), 161.13 (d, $^2J_{C-P}$ = 9.7 Hz, *C*O_2Me), 162.77 (d, $^3J_{C-P}$ = 7.8 Hz, *C*O_2Me).

^{31}P NMR (202 MHz, $CDCl_3$): δ = 9.47.

MS: *m*/*z* (%) = 421 (4) [M^+ + 1], 370 (8), 325 (32), 324 (100), 309 (65), 292 (12), 265 (12), 221 (44), 169 (23), 153 (27), 133 (27), 109 (53), 93 (28), 79 (41), 65 (5), 59 (12), 45 (3).

Anal. Calcd for $C_{16}H_{21}O_9PS$: C, 45.72; H, 5.04. Found: C, 45.80; H, 5.00.

Diethyl (*E*)-2-(Dimethoxyphosphoryl)-3-(phenylsulfonyl)-2-butenedioate (4e)

Yield: 0.38 g (90%); colorless crystals; mp 72–74 °C.

IR (KBr): 1726 (2 × C=O of CO_2Et), 1650 (C=C), 1574 and 1459 (Ph), 1332 and 1152 (SO_2), 1263 (P=O), 1109 and 1040 (C–O), 1063 and 1013 (PO–Me), 859 cm^{-1} (P–O).

^1H NMR (500 MHz, $CDCl_3$): δ = 1.21 (3 H, t, $^3J_{H-H}$ = 7.2 Hz, OCH_2CH_3), 1.35 (3 H, t, $^3J_{H-H}$ = 7.2 Hz, OCH_2CH_3), 3.75 [6 H, d, $^3J_{H-P}$ = 11.7 Hz, $P(OMe)_2$], 4.22 (2 H, q, $^3J_{H-H}$ = 7.2 Hz, OCH_2CH_3), 4.39 (2 H, q, $^3J_{H-H}$ = 7.2 Hz, OCH_2CH_3), 7.53 (2 H, t, $^3J_{H-H}$ = 7.7 Hz, 2 × CH of Ph), 7.65 (1 H, t, $^3J_{H-H}$ = 7.5 Hz, CH of Ph), 7.95 (2 H, d, $^3J_{H-H}$ = 7.3 Hz, 2 × CH of Ph).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.44 and 13.61 (2 × OCH_2CH_3), 54.07 [d, $^2J_{C-P}$ = 5.5 Hz, $P(OMe)_2$], 63.04 and 63.22 (2 × OCH_2CH_3), 129.00 (2 × CH of Ph), 129.33 (2 × CH of Ph), 134.48 (d, $^1J_{C-P}$ = 159.0 Hz, P*C*=C), 134.72 (CH of Ph), 137.98 (C_{ipso}-SO_2), 147.97 (d, $^2J_{C-P}$ = 6.0 Hz, PC=*C*), 160.97 (d, $^2J_{C-P}$ = 9.4 Hz, *C*O_2Et), 162.59 (d, $^3J_{C-P}$ = 7.8 Hz, *C*O_2Et).

^{31}P NMR (202 MHz, $CDCl_3$): δ = 8.34.

MS: *m*/*z* (%) = 421 (12) [M^+ + 1], 375 (66), 347 (19), 310 (100), 281 (96), 272 (6), 240 (16), 207 (67), 193 (5), 161 (39), 125 (80), 109 (35), 93 (28), 77 (83), 53 (27).

Anal. Calcd for $C_{16}H_{21}O_9PS$: C, 45.72; H, 5.04. Found: C, 45.80; H, 5.10.

Diethyl (*E*)-2-(Dimethoxyphosphoryl)-3-[(4-ethylphenyl)sulfonyl]-2-butenedioate (4f)

Yield: 0.41 g (91%); colorless viscous liquid.

IR (KBr): 1731 (2 × C=O of CO_2Et), 1650 (C=C), 1586 and 1451 (Ar), 1331 and 1154 (SO_2), 1271 (P=O), 1182 and 1100 (C–O), 1055 and 1023 (PO–Me), 857 cm^{-1} (P–O).

^1H NMR (500 MHz, $CDCl_3$): δ = 1.07 (3 H, t, $^3J_{H-H}$ = 7.4 Hz, CH_2CH_3), 1.27 (3 H, t, $^3J_{H-H}$ = 7.1 Hz, OCH_2CH_3), 1.42 (3 H, t, $^3J_{H-H}$ = 7.1 Hz, OCH_2CH_3), 3.03 (2 H, q, $^3J_{H-H}$ = 7.4 Hz, CH_2CH_3), 3.83 [6 H, d, $^3J_{H-P}$ = 11.5 Hz, $P(OMe)_2$], 4.05 (2 H, q, $^3J_{H-H}$ = 7.1 Hz, OCH_2CH_3), 4.39 (2 H, q, $^3J_{H-H}$ = 7.1 Hz, OCH_2CH_3), 7.40 (2 H, t, $^3J_{H-H}$ = 8.3 Hz, 2 × CH of Ar), 7.92 (2 H, t, $^3J_{H-H}$ = 8.3 Hz, 2 × CH of Ar).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.60 and 13.83 (2 × OCH_2CH_3), 14.92 (CH_2CH_3), 29.02 (CH_2CH_3), 54.13 [d, $^2J_{C-P}$ = 4.9 Hz, $P(OMe)_2$], 63.13 and 63.31 (2 × OCH_2CH_3), 128.62 (2 × CH of Ar), 129.76 (2 × CH of Ar), 132.79 (d, $^1J_{C-P}$ = 147.7 Hz, P*C*=C), 135.22 (C_{ipso}-SO_2), 148.51 (d, $^2J_{C-P}$ = 5.0 Hz, PC=*C*), 152.23 (C_{ipso}-Et), 161.26 (d, $^2J_{C-P}$ = 9.5 Hz, *C*O_2Et), 162.83 (d, $^3J_{C-P}$ = 8.2 Hz, *C*O_2Et).

^{31}P NMR (202 MHz, $CDCl_3$): δ = 8.56.

MS: *m*/*z* (%) = 449 (12) [M^+ + 1], 437 (2), 404 (10), 377 (30), 331 (38), 285 (58), 265 (100), 237 (62), 211 (85), 193 (42), 149 (42), 109 (61), 75 (96), 59 (40), 45 (17).

Anal. Calcd for $C_{18}H_{25}O_9PS$: C, 48.21; H, 5.62. Found: C, 48.20; H, 5.70.

Diethyl (*E*)-2-(Dimethoxyphosphoryl)-3-[(2-ethylphenyl)sulfonyl]-2-butenedioate (4g)

Yield: 0.40 g (89%); colorless viscous liquid.

IR (KBr): 1731 (2 × C=O of CO_2Et), 1650 (C=C), 1586 and 1451 (Ar), 1331 and 1154 (SO_2), 1271 (P=O), 1182 and 1100 (C–O), 1055 and 1023 (PO–Me), 857 cm^{-1} (P–O).

^1H NMR (500 MHz, $CDCl_3$): δ = 1.29 (3 H, t, $^3J_{H-H}$ = 7.5 Hz, CH_2CH_3), 1.32 (3 H, t, $^3J_{H-H}$ = 7.1 Hz, OCH_2CH_3), 1.38 (3 H, t, $^3J_{H-H}$ = 7.1 Hz, OCH_2CH_3), 2.76 (2 H, q, $^3J_{H-H}$ = 7.5 Hz, CH_2CH_3), 3.84 [6 H, d, $^3J_{H-P}$ = 11.5 Hz, $P(OMe)_2$], 4.29 (2 H, q, $^3J_{H-H}$ = 7.1 Hz, OCH_2CH_3), 4.45 (2 H, q, $^3J_{H-H}$ = 7.1 Hz, OCH_2CH_3), 7.36–7.45 (2 H, m, 2 × CH of Ar), 7.61 (1 H, t, $^3J_{H-H}$ = 7.5 Hz, CH of Ar), 8.01 (1 H, d, $^3J_{H-H}$ = 7.9 Hz, CH of Ar).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.41 and 13.74 (2 × OCH_2CH_3), 15.29 (CH_2CH_3), 25.60 (CH_2CH_3), 54.17 [d, $^2J_{C-P}$ = 5.4 Hz, $P(OMe)_2$], 63.08 and 63.18 (2 × OCH_2CH_3), 126.26, 130.86, 130.88 and 134.85 (4 × CH of Ar), 134.06 (d, $^1J_{C-P}$ = 147.7 Hz, P*C*=C), 135.04 (C_{ipso}-SO_2), 146.19 (C_{ipso}-Et), 148.67 (d, $^2J_{C-P}$ = 4.9 Hz, PC=*C*), 160.75 (d, $^2J_{C-P}$ = 9.5 Hz, *C*O_2Et), 162.46 (d, $^3J_{C-P}$ = 8.1 Hz, *C*O_2Et).

^{31}P NMR (202 MHz, $CDCl_3$): δ = 8.51.

MS: *m/z* (%) = 448 (12) [M$^+$], 437 (2), 421 (11), 404 (10), 377 (30), 331 (38), 303 (31), 285 (58), 265 (100), 237 (62), 211 (85), 193 (42), 149 (42), 109 (61), 75 (96), 59 (40), 45 (17).

Anal. Calcd for $C_{18}H_{25}O_9PS$: C, 48.21; H, 5.62. Found: C, 48.10; H, 5.60.

Diethyl (*E*)-2-(Diethoxyphosphoryl)-3-(phenylsulfonyl)-2-butenedioate (4h)
Yield: 0.42 g (94%); colorless viscous liquid.

IR (KBr): 1745 (2 × C=O of CO_2Et), 1697 (C=C), 1580 and 1453 (Ph), 1371 and 1170 (SO_2), 1272 (P=O), 1178 and 1146 (C–O), 1096 and 1019 (PO–Et), 900 cm^{-1} (P–O).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.28 (3 H, t, $^3J_{H-H}$ = 7.6 Hz, OCH_2CH_3), 1.33 [6 H, t, $^3J_{H-H}$ = 7.0 Hz, $P(OCH_2CH_3)_2$], 1.41 (3 H, t, $^3J_{H-H}$ = 7.7 Hz, OCH_2CH_3), 4.14–4.4.22 [4 H, m, $P(OCH_2CH_3)_2$], 4.28 (2 H, q, $^3J_{H-H}$ = 7.7 Hz, OCH_2CH_3), 4.44 (2 H, q, $^3J_{H-H}$ = 7.6 Hz, OCH_2CH_3), 7.58 (2 H, t, $^3J_{H-H}$ = 8.6 Hz, 2 × CH of Ph), 7.70 (1 H, t, $^3J_{H-H}$ = 7.6 Hz, CH of Ph), 8.02 (2 H, d, $^3J_{H-H}$ = 7.8 Hz, 2 × CH of Ph).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.58 and 13.85 (2 × OCH_2CH_3), 16.02 [d, $^3J_{C-P}$ = 6.5 Hz, $P(OCH_2CH_3)_2$], 63.04 and 63.25 (2 × OCH_2CH_3), 64.19 [d, $^2J_{C-P}$ = 6.28 Hz, $P(OCH_2CH_3)_2$], 129.06 (2 × CH of Ph), 129.48 (2 × CH of Ph), 134.70 (CH of Ph), 135.52 (d, $^1J_{C-P}$ = 156.2 Hz, P*C*=C), 138.18 (C_{ipso}-SO_2), 147.48 (d, $^2J_{C-P}$ = 6.2 Hz, PC=*C*), 161.21 (d, $^2J_{C-P}$ = 9.4 Hz, *C*O_2Et), 162.89 (d, $^3J_{C-P}$ = 8.2 Hz, *C*O_2Et).

^{31}P NMR (202 MHz, $CDCl_3$): δ= 7.72.

MS: *m/z* (%) = 448 (2) [M$^+$], 403 (22), 375 (11), 338 (46), 309 (32), 301 (14), 281 (6), 207 (17), 179 (35), 150 (23), 125 (62), 99 (25), 97 (18), 77 (100), 65 (25), 53 (45), 45 (28).

Anal. Calcd for $C_{18}H_{25}O_9PS$: C, 48.21; H, 5.62. Found: C, 48.20; H, 5.50.

Diethyl (*E*)-2-(Diethoxyphosphoryl)-3-[(4-ethylphenyl)sulfonyl]-2-butenedioate (4i)
Yield: 0.43 g (90%); colorless viscous liquid.

IR (KBr): 1736 (2 × C=O of CO_2Et), 1655 (C=C), 1584 and 1454 (Ar), 1360 and 1181 (SO_2), 1268 (P=O), 1141 and 1073 (C–O), 1104 and 1051 (PO–Et), 901 cm^{-1} (P–O).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.00 (3 H, t, $^3J_{H-H}$ = 7.5 Hz, CH_2CH_3), 1.27 (3 H, t, $^3J_{H-H}$ = 7.1 Hz, OCH_2CH_3), 1.31 [6 H, t, $^3J_{H-H}$ = 7.5 Hz, $P(OCH_2CH_3)_2$], 1.38 (3 H, t, $^3J_{H-H}$ = 7.1 Hz, OCH_2CH_3), 2.70 (2 H, q, $^3J_{H-H}$ = 7.5 Hz, CH_2CH_3), 4.07–4.15 [4 H, m, $P(OCH_2CH_3)_2$], 4.27 (2 H, q, $^3J_{H-H}$ = 7.1 Hz, OCH_2CH_3), 4.40 (2 H, q, $^3J_{H-H}$ = 7.1 Hz, OCH_2CH_3), 7.35 (2 H, d, $^3J_{H-H}$ = 8.1 Hz, 2 × CH of Ar), 7.86 (2 H, d, $^3J_{H-H}$ = 8.1 Hz, 2 × CH of Ar).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.55 and 13.81 (2 × OCH_2CH_3), 14.89 (CH_2CH_3), 16.01 [d, $^3J_{C-P}$ = 6.5 Hz, $P(OCH_2CH_3)_2$], 28.94 (CH_2CH_3), 62.92 and 63.13 (2 × OCH_2CH_3), 64.10 [d, $^2J_{C-P}$ = 6.3 Hz, $P(OCH_2CH_3)_2$], 128.55 (2 × CH of Ar), 129.65 (2 × CH of Ar), 133.86 (d, $^1J_{C-P}$ = 156.3 Hz, P*C*=C), 135.30 (C_{ipso}-SO_2), 147.77 (d, $^2J_{C-P}$ = 6.1 Hz, PC=*C*), 152.12 (C_{ipso}-Et), 161.27 (d, $^2J_{C-P}$ = 9.5 Hz, *C*O_2Et), 162.72 (d, $^3J_{C-P}$ = 7.6 Hz, *C*O_2Et).

^{31}P NMR (202 MHz, $CDCl_3$): δ = 5.31.

MS: *m/z* (%) = 476 (4) [M$^+$], 461 (2), 408 (3), 349 (9), 325 (9), 317 (2), 299 (11), 271 (12), 211 (3), 197 (3), 105 (100), 99 (25), 93 (9), 77 (25), 65 (25), 59 (5), 45 (1).

Anal. Calcd for $C_{20}H_{29}O_9PS$: C, 50.42; H, 6.13. Found: C, 50.50; H, 6.00.

Diethyl (*E*)-2-(Diethoxyphosphoryl)-3-[(2-ethylphenyl)sulfonyl]-2-butenedioate (4j)
Yield: 0.40 g (84%); colorless viscous liquid.

IR (KBr): 1736 (2 × C=O of CO_2Et), 1655 (C=C), 1580 and 1454 (Ar), 1360 and 1141 (SO_2), 1387 (P=O), 1180 and 1051 (C–O), 1104 and 1073 (PO–Et), 944 cm^{-1} (P–O).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.21 (3 H, t, $^3J_{H-H}$ = 7.5 Hz, CH_2CH_3), 1.23 (3 H, t, $^3J_{H-H}$ = 7.1 Hz, OCH_2CH_3), 1.27 [6 H, d, $^3J_{H-H}$ = 7.4 Hz, $P(OCH_2CH_3)_2$], 1.38 (3 H, t, $^3J_{H-H}$ = 7.1 Hz, OCH_2CH_3), 2.98 (2 H, q, $^3J_{H-H}$ = 7.5 Hz, CH_2CH_3), 3.98 (2 H, q, $^3J_{H-H}$ = 7.1 Hz, OCH_2CH_3), 4.10–4.18 [4 H, m, $P(OCH_2CH_3)_2$], 4.38 (2 H, q, $^3J_{H-H}$ = 7.1 Hz, OCH_2CH_3], 7.28–7.40 (2 H, m, 2 × CH of Ar), 7.56 (1 H, t, $^3J_{H-H}$ = 7.6 Hz, CH of Ar), 7.94 (1 H, d, $^3J_{H-H}$ = 8.0 Hz, CH of Ar).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.35 and 13.72 (2 × OCH_2CH_3), 15.19 (CH_2CH_3), 16.01 [d, $^3J_{C-P}$ = 6.5 Hz, $P(OCH_2CH_3)_2$], 25.52 (CH_2CH_3), 62.86 and 62.99 (2 × OCH_2CH_3), 64.08 [d, $^2J_{C-P}$ = 6.3 Hz, $P(OCH_2CH_3)_2$], 126.21, 130.74, 130.80 and 134.82 (4 × CH of Ar), 135.42 (d, $^1J_{C-P}$ = 152.6 Hz, P*C*=C), 134.82 (C_{ipso}-SO_2), 146.05 (C_{ipso}-Et), 147.92 (d, $^2J_{C-P}$ = 6.1 Hz, PC=*C*), 160.75 (d, $^2J_{C-P}$ = 9.5 Hz, *C*O_2Et), 162.46 (d, $^3J_{C-P}$ = 7.4 Hz, *C*O_2Et).

^{31}P NMR (202 MHz, $CDCl_3$): δ = 5.35.

MS: *m/z* (%) = 476 (2) [M$^+$], 461 (1), 378 (3), 349 (9), 317 (2), 299 (11), 271 (12), 211 (3), 197 (3), 105 (100), 99 (25), 93 (9), 77 (25), 65 (25), 59 (5), 45 (2).

Anal. Calcd for $C_{20}H_{29}O_9PS$: C, 50.42; H, 6.13. Found: C, 50.50; H, 6.00.

Dimethyl (*E*)-2-(Diethoxyphosphoryl)-3-(phenylsulfonyl)-2-butenedioate (4k)
Yield: 0.40 g (95%); colorless crystals; mp 69–71 °C.

IR (KBr): 1739 (2 × C=O of CO_2Me), 1655 (C=C), 1587 and 1452 (Ph), 1369 and 1173 (SO_2), 1260 (P=O), 1219 and 1173 (C–O), 1097 and 1023 (PO–Et), 896 cm^{-1} (P–O).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.25 [6 H, t, $^3J_{H-H}$ = 7.0 Hz, $P(OCH_2CH_3)_2$], 3.76 (3 H, s, OMe), 3.90 (3 H, s, OMe), 4.08–4.14 [4 H, m, $P(OCH_2CH_3)_2$], 7.15 (2 H, t, $^3J_{H-H}$ = 8.1 Hz, 2 × CH of Ph), 7.64 (1 H, t, $^3J_{H-H}$ = 7.9 Hz, CH of Ph), 7.91 (2 H, d, $^3J_{H-H}$ = 8.6 Hz, 2 × CH of Ph).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 15.99 [d, $^3J_{C-P}$ = 6.5 Hz, $P(OCH_2CH_3)_2$], 53.50 and 53.63 (2 × OMe), 64.29 [d, $^2J_{C-P}$ = 5.5 Hz, $P(OCH_2CH_3)_2$], 129.14 (2 × CH of Ar), 129.41 (2 × CH of Ph), 134.85 (CH of Ph), 135.75 (d, $^1J_{C-P}$ = 158.0 Hz, P*C*=C), 137.98 (C_{ipso}-SO_2), 147.53 (d, $^2J_{C-P}$ = 4.9 Hz, PC=*C*), 161.63 (d, $^2J_{C-P}$ = 9.4 Hz, *C*O_2Me), 163.27 (d, $^3J_{C-P}$ = 7.5 Hz, *C*O_2Me).

^{31}P NMR (202 MHz, $CDCl_3$): δ = 6.15.

MS: *m/z* (%) = 421 (3) [M$^+$ + 1], 390 (3), 389 (15), 378 (3), 361 (7), 324 (100), 309 (30), 223 (9), 207 (5), 129 (23), 125 (47), 109 (29), 77 (67), 65 (11), 51 (13), 45 (4).

Anal. Calcd for $C_{16}H_{21}O_9PS$: C, 45.72; H, 5.04. Found: C, 45.90; H, 5.10.

Dimethyl (*E*)-2-(Diethoxyphosphoryl)-3-[(4-methylphenyl)sulfonyl]-2-butenedioate (4l)
Yield: 0.42 g (97%); colorless viscous liquid.

IR (KBr): 1741 (2 × C=O of CO_2Me), 1604 (C=C), 1502 and 1454 (Ar), 1362 and 1172 (SO_2), 1261 (P=O), 1172 and 1100 (C–O), 1066 and 1034 (PO–Et), 902 cm^{-1} (P–O).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.29 [6 H, t, $^3J_{H-H}$ = 7.0 Hz, $P(OCH_2CH_3)_2$], 2.43 (3 H, s, Me), 3.80 (3 H, s, OMe), 3.93 (3 H, s, OMe), 4.11–4.16 [4 H, m, $P(OCH_2CH_3)_2$], 7.34 (2 H, d, $^3J_{H-H}$ = 8.1 Hz, 2 × CH of Ar), 7.82 (2 H, d, $^3J_{H-H}$ = 8.1 Hz, 2 × CH of Ar).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 15.93 [d, $^3J_{C-P}$ = 6.4 Hz, $P(OCH_2CH_3)_2$], 21.67 (Me), 53.40 and 53.54 (2 × OMe), 64.16 [d, $^2J_{C-P}$ = 5.4 Hz, $P(OCH_2CH_3)_2$], 129.45 (2 × CH of Ar), 129.73 (2 × CH of Ar), 135.10 (d, $^1J_{C-P}$ = 158.2 Hz, P*C*=C), 134.87 (C_{ipso}-SO_2), 146.15 (C_{ipso}-Me), 147.79 (d, $^2J_{C-P}$ = 4.8 Hz, PC=*C*), 161.67 (d, $^2J_{C-P}$ = 9.4 Hz, *C*O_2Me), 163.27 (d, $^3J_{C-P}$ = 7.5 Hz, *C*O_2Me).

^{31}P NMR (202 MHz, $CDCl_3$): δ = 5.10.

MS: *m*/*z* (%) = 435 (22) [M^+ + 1], 403 (34), 389 (6), 375 (4), 338 (100), 323 (36), 311 (6), 235 (11), 139 (54), 119 (21), 109 (30), 91 (86), 81 (23), 65 (39), 53 (9), 45 (5).

Anal. Calcd for $C_{17}H_{23}O_9PS$: C, 47.01; H, 5.34. Found: C, 47.00; H, 5.20.

Dimethyl (*E*)-2-(Diethoxyphosphoryl)-3-[(4-ethylphenyl)sulfonyl]-2-butenedioate (4m)

Yield: 0.43 g (96%); colorless viscous liquid.

IR (KBr): 1732 (2 × C=O of CO_2Me), 1612 (C=C), 1586 and 1427 (Ar), 1330 and 1154 (SO_2), 1257 (P=O), 1186 and 1013 (C–O), 1063 and 1036 (PO–Et), 884 cm^{-1} (P–O).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.24 (3 H, t, $^3J_{H-H}$ = 7.6 Hz, CH_2CH_3), 1.29 [6 H, t, $^3J_{H-H}$ = 7.1 Hz, $P(OCH_2CH_3)_2$], 2.72 (2 H, q, $^3J_{H-H}$ = 7.6 Hz, CH_2CH_3), 3.56 (3 H, s, OMe), 3.80 (3 H, s, OMe), 4.10–4.18 [4 H, m, $P(OCH_2CH_3)_2$], 7.36 (2 H, d, $^3J_{H-H}$ = 8.1 Hz, 2 × CH of Ar), 7.84 (2 H, d, $^3J_{H-H}$ = 8.1 Hz, 2 × CH of Ar).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.84 (CH_2CH_3), 15.98 [d, $^3J_{C-P}$ = 6.6 Hz, $P(OCH_2CH_3)_2$], 28.94 (CH_2CH_3), 53.44 and 53.58 (2 × OMe), 64.22 [d, $^2J_{C-P}$ = 5.4 Hz, $P(OCH_2CH_3)_2$], 128.62 (2 × CH of Ar), 129.63 (2 × CH of Ar), 133.88 (d, $^1J_{C-P}$ = 158.6 Hz, P*C*=C), 135.08 (C_{ipso}-SO_2), 147.86 (d, $^2J_{C-P}$ = 4.8 Hz, PC=*C*), 152.23 (C_{ipso}-Et), 161.74 (d, $^2J_{C-P}$ = 9.4 Hz, *C*O_2Me), 163.31 (d, $^3J_{C-P}$ = 7.7 Hz, *C*O_2Me).

^{31}P NMR (202 MHz, $CDCl_3$): δ = 6.35.

MS: *m*/*z* (%) = 449 (72) [M^+ + 1], 417 (77), 352 (100), 337 (37), 293 (17), 235 (9), 215 (47), 187 (19), 153 (28), 105 (33), 91 (22), 79 (35), 65 (12), 53 (11), 45 (7).

Anal. Calcd for $C_{18}H_{25}O_9PS$: C, 48.21; H, 5.62. Found: C, 48.30; H, 5.50.

Dimethyl (*E*)-2-(Diethoxyphosphoryl)-3-[(2-ethylphenyl)sulfonyl]-2-butenedioate (4n)

Yield: 0.39 g (87%); colorless viscous liquid.

IR (KBr): 1732 (2 × C=O of CO_2Me), 1612 (C=C), 1586 and 1427 (Ar), 1330 and 1186 (SO_2), 1257 (P=O), 1154 and 976 (C–O), 1036 and 1013 (PO–Et), 847 cm^{-1} (P–O).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.26 (3 H, t, $^3J_{H-H}$ = 7.4 Hz, CH_2CH_3), 1.31 [6 H, t, $^3J_{H-H}$ = 7.1 Hz, $P(OCH_2CH_3)_2$], 2.81 (2 H, q, $^3J_{H-H}$ = 7.4 Hz, CH_2CH_3), 3.86 (3 H, s, OMe), 3.93 (3 H, s, OMe), 4.11–4.17 [4 H, m, $P(OCH_2CH_3)_2$], 7.32–7.39 (2 H, m, 2 × CH of Ar), 7.57 (1 H, t, $^3J_{H-H}$ = 7.5 Hz, CH of Ar), 7.93 (1 H, d, $^3J_{H-H}$ = 8.0 Hz, CH of Ar).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 15.27 (CH_2CH_3), 15.98 [d, $^3J_{C-P}$ = 6.6 Hz, $P(OCH_2CH_3)_2$], 25.58 (CH_2CH_3), 53.43 and 53.46 (2 × OMe), 64.20 [d, $^2J_{C-P}$ = 5.3 Hz, $P(OCH_2CH_3)_2$], 126.27, 130.74, 130.91 and 134.91 (4 × CH of Ar), 134.74 (C_{ipso}-SO_2), 135.17 (d, $^1J_{C-P}$ = 162.1 Hz, P*C*=C), 146.12 (C_{ipso}-Et), 148.02 (d, $^2J_{C-P}$ = 4.8 Hz, PC=*C*), 161.27 (d, $^2J_{C-P}$ = 9.4 Hz, *C*O_2Me), 162.94 (d, $^3J_{C-P}$ = 7.7 Hz, *C*O_2Me).

^{31}P NMR (202 MHz, $CDCl_3$): δ = 6.37.

MS: *m*/*z* (%) = 448 (16) [M^+], 418 (14), 352 (100), 325 (7), 293 (17), 235 (9), 215 (47), 187 (19), 153 (28), 105 (33), 91 (22), 79 (35), 65 (12), 53 (11).

Anal. Calcd for $C_{18}H_{25}O_9PS$: C, 48.21; H, 5.62. Found: C, 48.20; H, 5.60.

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