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# Exploring the metal-catalyzed reaction of furans with alkyl α-diazomethanesulfonate and α-diazomethanephosphonate: synthesis of ω-acyl-substituted sulfono- and phosphonobutadienes

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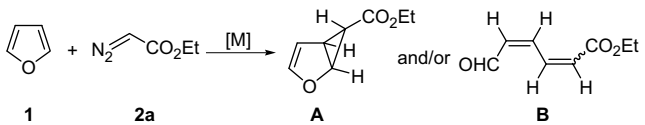
ABSTRACT

The metal-catalyzed reactions of *neo*pentyl α-diazomethanesulfonate (DAMS) and diisopropyl α-diazomethanephosphonate (DIDAMP) with furan, 2-methylfuran and 2-methoxyfuran are reported. The products consist mostly of ω-acyl-substituted sulfono- or phosphonobutadienes and *exo*-cyclopropane derivatives. Treatment of the multicomponent reaction mixtures with iodine afforded exclusively the corresponding (*E*,*E*)-sulfono- and phosphono-ω-acylfunctionalized dienes, thus providing a short and efficient synthetic route to these hitherto unreported classes of compounds.



## 1. Introduction

The metal-catalyzed decomposition of α-diazocarbonyl derivatives with furan and substituted furans to give the corresponding cyclopropane adducts (**A**) and/or the ring opened 1,4-dicarbonyl-1,3-butadienes (**B**), as illustrated in Scheme 1 for the combination furan (**1**)/ethyl diazoacetate (EDA, **2a**), is a well investigated reaction[1] whose products have found several applications in the synthesis of natural products,[2] and in the preparation of compounds of pharmaceutical interest.[3] The intramolecular version of this metal-catalyzed reaction giving rise to functionalized ring systems has also been investigated[4] and applied to the synthesis of natural products.[5]




**Scheme 1.**

## 2. Results and discussion

In the frame of our continuing interest in the chemistry and synthetic applications of diazo compounds, we have recently directed our attention to the hitherto unreported reactions of furan (**1**) and 2-substituted furans (**9** and **16**), with *neo*pentyl α-diazomethanesulfonate (DAMS, **2b**)[6] and diisopropyl α-diazomethanephosphonate (DIDAMP, **2c**),[7] the major aim being the preparation of ring-opened products characterized by a stereodefined conjugated diene motif inserted between an acyl moiety and a sulfonate- or phosphonate group, respectively. Stereodefined conjugated dienes represent a class of valuable synthetic intermediates and are a motif of a variety of natural, biologically interesting products[8] and sulfonic and phosphonic acids play an important role in medicinal chemistry[9] and in other areas of chemical interest, but the preparation of sulfono- and phosphonobutadienes bearing at the ω-position substituents suitable to further synthetic elaborations, such as an acyl moiety, have received little attention. ω-Acyl-substituted sulfonobutadienes, indeed, are still unreported, whereas dimethyl (1*Z*,3*E*)-5-oxo-1,3-hexadien-1-ylphosphonate was prepared in very low yield and photoisomerised into the corresponding (1*E*,3*Z*)- and (1*E*,3*E*)-isomers.[10] A more efficient stereoselective route giving access to (1*Z*,3*E*)-dienylphosphonates has been also reported.[11] In an initial series of experiments, we examined the rhodium(II) acetate dimer ($Rh_2(OAc)_4$)-catalyzed reaction of DAMS (**2b**) and DIDAMP (**2c**) with furan (**1**), under the same reaction conditions already reported for the reaction of **1** with EDA (**2a**).[2a] By rhodium (0.05 mol %)-catalysis, however, DAMS (**2b**) afforded almost exclusively the dimeric di*neo*pentyl (*E*)-ethene-1,2-disulfonate (**3**) rather than the expected derivatives (entry 1, Table 1), whereas the same catalyst load showed to be ineffective in decomposing DIDAMP (**2c**), and it had to be increased to 2 mol % to observe the complete decomposition of **2c** within 48 h, and to 5 mol % in order to observe

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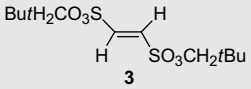
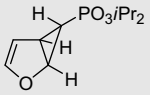
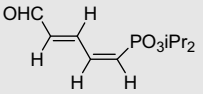
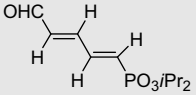
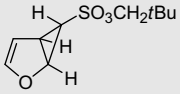
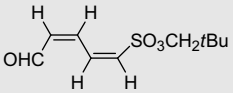
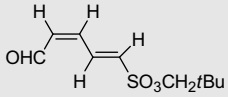
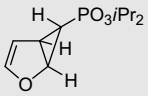
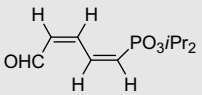
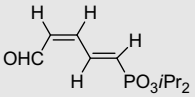
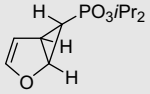
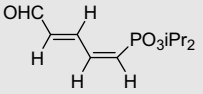
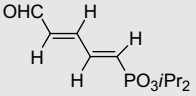
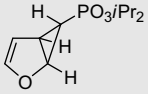
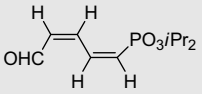
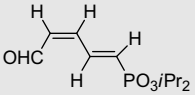
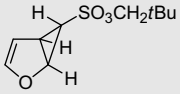
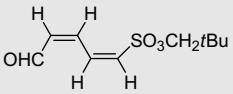
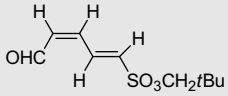
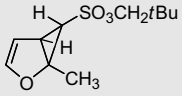
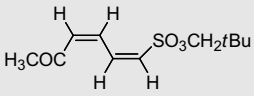
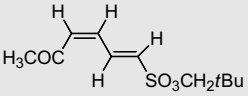
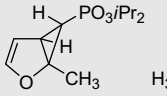
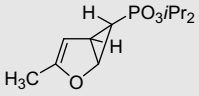
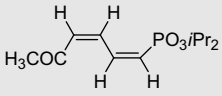
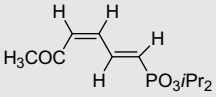
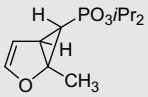
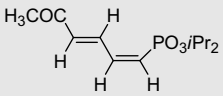
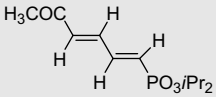
**Table 1**
Metal-catalyzed decomposition of diazo derivatives (**2b**,**c**) in the presence of furan (**1**)[a]

| Entry | Diazo | Catalyst (%) | Time, h | Products | Product ratio[b] | Yield[c] % |
|---|---|---|---|---|---|---|
| 1 | DAMS (**2b**) | $Rh_2(OAc)_4$ (0.05) | 2 |  **3** | — | 95 |
| 2 | DIDAMP (**2c**) | $Rh_2(OAc)_4$ (5) | 0.5 |  **4c**  **5c**  **6c** | **4c**/**5c**/**6c**=1:1.2:3.8 | 81 (**4c**+**5c**, 24; **6c**, 42) |
| 3 | DAMS (**2b**) | CuOTf (0.05) | 3 |  **4b**  **7b**  **8b** | **4b**/**7b**/**8b**=1:0.7:3.7 | 72 (**4b**, 12; **7b**, 4.5; **8b**, 48) |
| 4 | DIDAMP (**2c**) | CuOTf (0.05) | 3 |  **4c**  **7c**  **8c** | **4c**/**7c**/**8c**=1:0.2:1.2 | 85 (**4c**, 31; **7c**, 6; **8c**, 37) |
| 5[d] | DIDAMP (**2c**) | $Rh_2(OAc)_4$ (5) | 0.5 |  **4c**  **5c**  **6c** | **4c**/**5c**/**6c**=1:5.5:17.5 | 80 |
| 6[d] | DIDAMP (**2c**) | CuOTf (1) | 1 |  **4c**  **7c**  **8c** | **4c**/**7c**/**8c**=1:0.4:1.6 | 80 |
| 7[d] | DAMS (**2b**) | CuOTf (0.1) | 0.25 |  **4b**  **7b**  **8b** | **4b**/**7b**/**8b**=1:1.4:4.2 | 84 |

[a] The reactions were carried out on a 1 mmol scale of diazo, see Experimental section for details.
[b] Determined by $^1H$ NMR analysis on the crude mixture.
[c] Calculated by mass recovery on the crude mixture; values in parentheses represent total isolated yield.
[d] Reaction performed in $CH_2Cl_2$.

the diazo disappearance within 0.5 h (entry 2, Table 1). Analysis of the crude reaction mixture by $^1H$ NMR spectroscopy indicated the presence of aliphatic and olefinic signals accounting, respectively, for the presence of a cyclopropyl-derivative and two dienes. Subsequent silica gel column chromatography allowed us to obtain a mixture of diisopropyl *exo*-2-oxabicyclo[3.1.0]hex-3-ene-6-phosphonate (**4c**) and diisopropyl (1*Z*,3*E*)-5-oxopenta-1,3-dienylphosphonate (**5c**) in 24% yield, whereas the major diene **6c**, endowed with (1*E*,3*E*)-configuration, could be isolated as single compound in 42% yield. The stereochemistry of the dienes **5c** and **6c**, as well as the configuration of all the dienes described below, was deduced from the comparison of the H–H coupling constant values and from NOESY analysis, taking advantage of the data reported for 5-oxohexa-1,3-dienylphosphonates.[11] It is worth noting that the two dienes here obtained, do not stereochemically match to those isolated from the reaction of **1** with EDA (**2a**). The reactions were then repeated changing the catalyst from $Rh_2(OAc)_4$ to copper(I) trifluoromethanesulfonate (CuOTf) and a number of interesting differences were observed. In the presence of CuOTf, indeed, the reaction of DAMS (**2b**) with **1** proceeded smoothly affording a mixture of a cyclopropyl derivative and two dienes, which were isolated by silica gel column chromatography and characterized as *neo*pentyl *exo*-2-oxabicyclo[3.1.0]hex-3-ene-6-sulfonate (**4b**) (12%), *neo*pentyl (1*Z*,3*Z*)-5-oxopenta-1,3-diene-1-sulfonate (**7b**) (4.5%) and *neo*pentyl (1*E*,3*Z*)-5-oxopenta-1,3-diene-1-sulfonate (**8b**) (48%) (entry 3, Table 1). CuOTf was also effective in decomposing DIDAMP (**2c**) obtaining along with **4c**, the two dienes complementary in stereochemistry to those obtained by $Rh_2(OAc)_4$-catalyzed reaction, namely diisopropyl (1*Z*,3*Z*)-5-oxopenta-1,3-diene-1-phosphonate (**7c**) and diisopropyl (1*E*,3*Z*)-5-oxopenta-1,3-diene-1-phosphonate (**8c**) (entry 4, Table 1). We also examined the solvent effect on the outcome of the reactions. When the diazo was dissolved in dichloromethane instead of furan, a variation in the product distribution, favouring the formation of the corresponding dienes over the cyclopropane adduct, was observed in all the cases (entries 5–7, Table 1). This trend was particularly evident in the $Rh_2(OAc)_4$-catalyzed DIDAMP reaction (entry 5, Table 1) (4.6-fold higher **5c**/**4c** and **6c**/**4c** ratios in comparison to the corresponding reaction performed in the absence of dichloromethane). It also worth pointing out that the replacement

**Table 2**
Metal-catalyzed decomposition of diazo derivatives (**2b**,**c**) in the presence of 2-methylfuran (**9**)[a]

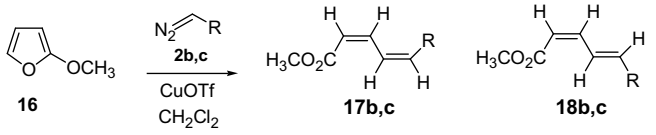
| Entry | Diazo | Catalyst (%) | Time, h | Products | Product ratio[b] | Yield[c] % |
|---|---|---|---|---|---|---|
| 1 | DAMS (**2b**) | CuOTf (0.05) | 1.5 |  **10b**  **11b**  **12b** | **10b**/**11b**/ **12b**=1:1.2:3.8 | 77 (**10b**, 10; **11b**, 13; **12b**, 35) |
| 2 | DIDAMP (**2c**) | CuOTf (0.05) | 1 |  **10c**  **13c**  **11c**  **12c** | **13c**/**10c**/**11c**/ **12c**=1.1:1:2.0:5.8 | 68 (**13c**+**10c**+**11c**, 32; **12c**, 25) |
| 3 | DIDAMP (**2c**) | $Rh_2(OAc)_4$ (5) | 0.25 |  **10c**  **14c**  **15c** | **10c**/**14c**/ **15c**=1:3.9:11 | 89 (**10c**, 5; **14c**, 18; **15c**, 45) |

[a] The reactions were carried out on a 1 mmol scale of diazo, see Experimental section for details.
[b] Determined by $^1H$ NMR analysis on the crude mixture.
[c] Calculated by mass recovery on the crude mixture; values in parentheses represent total isolated yield.

of furan for dichloromethane in dissolving the diazo did not influence the catalytic efficiency of $Rh_2(OAc)_4$ (entry 5, Table 1) whereas the load of CuOTf had to be increased to avoid very long reaction times (entries 6 and 7, Table 1).

Our work went ahead using 2-methylfuran (**9**) as a model unsymmetrical substrate. CuOTf-catalyzed DAMS reaction afforded a mixture of *neo*pentyl *exo*-1-methyl-2-oxabicyclo[3.1.0]hex-3-ene-6-sulfonate (**10b**), and (1*Z*,3*Z*)- and (1*E*,3*Z*)-2-methyl-5-oxopenta-1,3-diene-1-sulfonates (**11b** and **12b**, respectively) in 77% yield (entry 1, Table 2). In comparison to the known analogous rhodium-catalyzed EDA reaction,[2a] **2b** afforded a less complicated array of products showing the complete regioselectivity of the attack in favour of the sterically more congested double bond of the substrate. It is worth noting that this site selectivity is opposite to that previously observed in the reaction of EDA (**1a**), that proceeds on the unsubstituted side of the furan nucleus versus the methylated one in 19:1 ratio. Otherwise no site selectivity was observed with DIDAMP (**2c**) under CuOTf-catalysis (entry 2, Table 2); indeed, equivalent amounts of diisopropyl *exo*-1-methyl-2-oxabicyclo[3.1.0]hex-3-ene-6-sulfonate (**10c**) and diisopropyl *exo*-5-methyl-2-oxabicyclo[3.1.0]hex-3-ene-6-sulfonate (**13c**) were obtained along with diisopropyl (1*E*,3*Z*)-5-oxohexa-1,3-dienylphosphonate (**12c**) and the corresponding (1*Z*,3*Z*)-isomer (**11c**). After silica gel chromatography, only the major component of the mixture, namely **12c** could be isolated as single compound (25%). However, site selectivity was again observed by switching the catalyst from CuOTf to $Rh_2(OAc)_4$ (entry 3, Table 2). Furthermore, as already evidenced with furan (**1**), rhodium- and copper-catalysis furnished dienes endowed with opposite stereochemistry (cf. entries 2 and 3, Table 2).

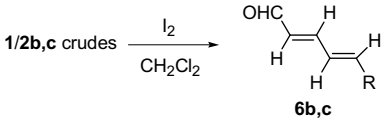
As a third model substrate, we chose 2-methoxyfuran (**16**), known to afford by $Rh_2(OAc)_4$-catalyzed reaction with EDA (**2a**) exclusively the ring-opened products due to the presence of the electron-rich substituent at 2-position. The 0.05 mol % CuOTf-catalyzed reaction of **16** with DAMS (**2b**) gave, after chromatography, methyl (2*Z*,4*Z*)-5-(*neo*pentyloxysulfonyl) penta-2,4-dienoate (**17b**) and the corresponding (2*Z*,4*E*)-isomer **18b** in 18% and 36% yield, respectively (Scheme 2). Analogous results were obtained from the CuOTf-catalyzed reaction of DIDAMP (**2c**). Unexpectedly, the reaction failed to give any identificable product when $Rh_2(OAc)_4$ was used as the catalyst.




b, R = $SO_3CH_2tBu$ (DAMS) **17b,** 18%; **18b**, 36%
c, R = $PO_3iPr_2$ (DIDAMP) **17c**, 20%; **18c,** 41%

**Scheme 2.**

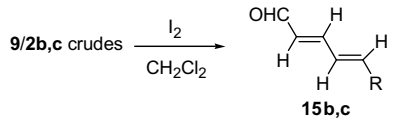
A further interesting facet of this study lies in the possibility to obtain, analogously to that reported by Wenkert for the reactions of furan with **2a**,[1a] a single product per reaction sequence, namely the corresponding (*E*,*E*)-diene, by treatment with iodine of each reaction crude. In particular, *neo*pentyl (1*E*,3*E*)-5-oxopenta-1,3-diene-1-sulfonate (**6b**) and diisopropyl (1*E*,3*E*)-5-oxopenta-1,3-diene-1-phosphonate (**6c**) were, respectively, obtained starting from the furan/DAMS and furan/DIDAMP crudes (Scheme 3).




b, R = $SO_3CH_2tBu$ **6b,** 95%;
c, R = $PO_3iPr_2$ **6c**, 97%

**Scheme 3.**

Analogously, (1*E*,3*E*)-isomers **15b** and **15c** were the compounds we exclusively obtained by the iodine-induced isomerization of 2-methylfuran/DAMS and 2-methylfuran/DIDAMP crudes (Scheme 4). On the other hand, the (2*Z*,4*Z*)- and (2*Z*,4*E*)-dienes (**17b**,**c** and **18b**,**c**), obtained from **16**, were inert towards iodine-promoted isomerization.




b, R = $SO_3CH_2tBu$ **15b,** 96%;
c, R = $PO_3iPr_2$ **15c**, 97%

**Scheme 4.**

## 3. Conclusions

In conclusion, we have developed a route which give access to ω-acylsubstituted sulfono- and -phosphono-butadienes with different and defined geometry by the hitherto unreported metal-catalyzed reaction of alkyl α-diazomethanesulfonate (**2b**) and α-diazomethanephosphonate (**2c**) with furans. The reactions with furan (**1**) and 2-methylfuran (**9**) also furnished, as minor products, oxabicyclo[3.1.0]hex-2-enes (**4b–c**, **10b–c** and **13c**) first substituted at the 6-position with a sulfonate- or phosphonate moiety. From the organic synthesis point of view, particularly interesting is the possibility to obtain a single product per reaction sequence, namely the (1*E*,3*E*)-butadiene, by the iodine-induced isomerization (and destruction of the minor furan products) of a polycomponent crude mixture.

## 4. Experimental

### 4.1. General methods

All reagents were commercially available unless otherwise stated. All reactions were carried out in dried glassware under a dry argon atmosphere. Dichloromethane was distilled over $LiAlH_4$ prior to use. Furan and 2-methylfuran were distilled over NaOH prior to use. Chromatographic purification of the products was accomplished on Merck silica gel (0.040–0.063 mm) using a Biotage SP1 HPCF separation module. 12 M (12 mm×15.0 cm, 9.0 g silica gel) cartridges were used. All new compounds were fully characterized by $^1H$, $^{13}C$ NMR and mass spectra. Nuclear magnetic resonance spectra were acquired on a Bruker AC 200 (200 MHz and 50.3 MHz for $^1H$ and $^{13}C$, respectively) or on a Bruker AC 400 (400 MHz, 100 MHz and 162 MHz for $^1H$, $^{13}C$ and $^{31}P$, respectively) spectrometer at ambient temperature using $CDCl_3$ as solvent. Data for $^1H$ NMR are recorded as follows: chemical shift (δ in ppm), multiplicity (s: singlet; d: doublet; dd: double doublet; ddd: double double doublet; dddd: double double double doublet; t: triplet; dt: double triplet; qt: quartet triplet; br s: broad signal), integration, and coupling constant (Hz). Data for $^{13}C$ NMR are reported in terms of chemical shift (δ in ppm).

GC–MS analyses were carried out with a HP-6850 gas chromatograph (dimethyl silicone column, 12.5 m) equipped with a HP-5975 mass-selective detector.

The following compounds were prepared according to the literature: *neo*pentyl α-diazomethanesulfonate (**2b**);[6b] diisopropil α-diazomethanephosphonate (**2c**).[7a]

### 4.2. Reaction of DAMS (2b) or DIDAMP (2c) with furan (1)

A solution of diazo (**2b** or **2c**, 1.0 mmol) in furan (2.0 mL) was slowly added (0.6 mmol/h) to a magnetically stirred suspension of the catalyst (0.0005–0.05 mmol, see Table 1) in furan (4.0 mL). The reaction was then stirred until the decomposition of the diazo was complete (by TLC and GC analysis). The reaction mixture was evaporated in vacuo, the reaction crude, thus obtained, analyzed by $^1H$ NMR spectroscopy and then submitted to chromatographic purification (20% ethyl acetate/light petroleum for sulfonate analogs and 40% ethyl acetate in light petroleum for phosphonate ones).

### 4.3. Reaction of DAMS (2b) or DIDAMP (2c) with 2-methylfuran (9)

A solution of diazo (**2b** or **2c**, 1.0 mmol) in 2-methylfuran (2.0 mL) was slowly added (0.6 mmol/h) to a magnetically stirred suspension of the catalyst (0.0005–0.05 mmol, see Table 2) in 2-methylfuran (4.0 mL). The reaction was then stirred until the decomposition of the diazo was complete (by TLC and GC analysis). The reaction mixture was evaporated in vacuo, the reaction crude, thus obtained, analyzed by $^1H$ NMR spectroscopy and then submitted to chromatographic purification (20% ethyl acetate/light petroleum for sulfonate analogs and 40% ethyl acetate/light petroleum for phosphonate ones).

### 4.4. Reaction of DAMS (2b) or DIDAMP (2c) with furan (1) in dichloromethane

A solution of diazo (**2b** or **2c**, 1.0 mmol) in dichloromethane (1.0 mL) was slowly added (0.6 mmol/h) to a magnetically stirred suspension of the catalyst (0.0005–0.05 mmol, see Table 1) and furan (50 mmol) in dichloromethane (5 mL). The reaction was then stirred until the decomposition of the diazo was complete (by TLC and GC analysis). The reaction mixture was evaporated in vacuo, the reaction crude, thus obtained, analyzed by $^1H$ NMR spectroscopy and then submitted to chromatographic purification (20% ethyl acetate/light petroleum for sulfonate analogs and 40% ethyl acetate/light petroleum for phosphonate ones).

### 4.5. Reaction of DAMS (2b) or DIDAMP (2c) with 2-methoxyfuran (16) in dichloromethane

A solution of diazo (**2b** or **2c**, 1.0 mmol) in dichloromethane (1.0 mL) was slowly added (0.6 mmol/h) to a magnetically stirred suspension of CuOTf (0.0005 mmol) and 2-methoxyfuran (50 mmol) in dichloromethane (5 mL). The reaction was then stirred until the decomposition of the diazo was complete (by TLC and GC analysis). The reaction mixture was evaporated in vacuo, the reaction crude, thus obtained, analyzed by $^1H$ NMR spectroscopy and then submitted to chromatographic purification (20% ethyl acetate/light petroleum for sulfonate analogs and 40% ethyl acetate/light petroleum for phosphonate ones).

### 4.6. 4-Substituted-(1*E*,3*E*)-butadienes

A solution of the crude reaction mixture (deriving from the furan/DAMS/CuOTf, furan/DIDAMP/CuOTf, furan/DIDAMP/$Rh_2(OAc)_4$, 2-methylfuran/DAMS/CuOTf, 2-methylfuran/DIDAMP/CuOTf or 2-methylfuran/DIDAMP/$Rh_2(OAc)_4$ combination) in dichloromethane (5.0 mL) was treated with two iodine crystals and kept at room temperature for 6 h, and then evaporated in vacuo. A solution of the residue in diethyl ether was washed with 10% sodium thiosulfate solution and with brine, dried and evaporated in vacuo. Filtration through short pad silica gel, gave the corresponding 4-substituted-(1*E*,3*E*)-butadiene as a single compound.

### 4.7. Di*neo*pentyl (*E*)-ethene-1,2-disulfonate (3)

$\delta_H$ (200 MHz) 7.20 (2H, s, 2×C*H*), 3.90 (4H, s, 2×$SO_3CH_2C(CH_3)_3$), 1.08 (18H, s, 2×$C(CH_3)_3$); $\delta_C$ (50 MHz) 25.94, 29.71, 81.73, 136.96.

### 4.8. *Neo*pentyl *exo*-2-oxabicyclo[3.1.0]hex-3-ene-6-sulfonate (4b)

Isolated as a colourless oil. [Found: C, 51.81; H, 6.97. $C_{10}H_{16}O_4S$ requires: C, 51.70; H, 6.94.] $\nu_{max}$ (liquid film) 3000, 1620, 1590, 1060, 1370, 1160 $cm^{-1}$; $\delta_H$ (400 MHz) 6.42 (1H, d, *J* 2.56 Hz, 3-CH), 5.49

(1H, t, *J* 2.62 Hz, 4-CH), 5.04 (1H, dq, *J* 0.65 and 6.14 Hz, 1-CH), 3.92 (2H, s, $SO_3CH_2C(CH_3)_3$), 3.04–3.08 (1H, m, 5-CH), 1.76 (1H, dd, *J* 0.50 and 2.13 Hz, 6-CH), 1.01 (9H, s, $C(CH_3)_3$); $\delta_C$ (100 MHz) 26.44, 29.72, 32.24, 33.55, 64.18, 80.09, 105.23, 148.52; GC–MS (*m*/*z*): 217 (1), [M−$CH_3$], 177 (3), 161 (5), 145 (10), 138 (6), 117 (20), 82 (25), 71 (59), 57 (100).

### 4.9. *Neo*pentyl (1*Z*,3*Z*)-5-oxopenta-1,3-diene-1-sulfonate (7b)

Isolated as a colourless oil. [Found C, 51.79; H, 6.98. $C_{10}H_{16}O_4S$ requires: C, 51.70; H, 6.94.] $\nu_{max}$ (liquid film) 3000, 2720, 1685, 1570, 1370, 1160 $cm^{-1}$; $\delta_H$ (400 MHz) 10.18 (1H, d, *J* 6.0 Hz, CHO), 7.87 (1H, t, *J* 11.64 Hz, 3-CH), 7.72 (1H, t, *J* 11.0 Hz, 2-CH), 6.47 (1H, ddd, *J* 1.18, 1.58 and 11.05 Hz, 1-CH), 6.28 (1H, dddd, 1H, *J* 1.02, 2.54, 6.02 and 11.18 Hz, 4-CH), 3.84 (2H, s, $SO_3CH_2C(CH_3)_3$), 0.98 (9H, s, 9H, $C(CH_3)_3$); $\delta_C$ (100 MHz) 26.43, 32.17, 80.65, 129.94, 133.80, 134.71, 135.68, 189.90; GC–MS (*m*/*z*): 232 (<1), 217 (2), 98 (7), 71 (100), 57 (18).

### 4.10. *Neo*pentyl (1*E*,3*Z*)-5-oxopenta-1,3-diene-1-sulfonate (8b)

Isolated as a colourless oil. [Found C, 51.83; H, 6.95. $C_{10}H_{16}O_4S$ requires: C, 51.70; H, 6.94.] $\nu_{max}$ (liquid film) 3000, 2719, 1684, 1370, 1160 $cm^{-1}$; $\delta_H$ (400 MHz) 10.23 (1H, d, *J* 7.03 Hz, CHO), 8.02 (1H, dd, 1H, *J* 12.08 and 14.80 Hz, 2-CH), 6.96 (1H, t, *J* 11.78 Hz, 3-CH), 6.60 (1H, d, 1H, *J* 14.84 Hz, 1-CH), 6.25 (1H, dd, *J* 7.09 and 11.09 Hz, 4-CH), 3.82 (2H, s, $SO_3CH_2C(CH_3)_3$), 0.98 (9H, s, $C(CH_3)_3$); $\delta_C$ (100 MHz) 26.42, 32.19, 80.66, 132.51, 134.96, 136.15, 139.36, 189.57; GC–MS (*m*/*z*): 232 (<1), 217 (2), 177 (10), 146 (6), 145 (18), 82 (6), 81 (8), 71 (6), 57 (100).

### 4.11. *Neo*pentyl (1*E*,3*E*)-5-oxopenta-1,3-diene-1-sulfonate (6b)

Isolated as a colourless oil. [Found: C, 51.73; H, 6.94. $C_{10}H_{16}O_4S$ requires: C, 51.70; H, 6.94.] $\nu_{max}$ (liquid film) 3000, 2720, 1684, 1370, 1160 $cm^{-1}$; $\delta_H$ (200 MHz) 9.71 (1H, d, 1H, *J* 7.45 Hz, CHO), 7.35 (1H, ddd, *J* 0.65, 11.10 and 14.60 Hz, 2-CH), 7.14 (1H, ddd, *J* 0.59, 11.10 and 14.90 Hz, 3-CH), 6.69 (1H, dt, *J* 0.62 and 14.90 Hz, 1-CH), 6.50 (1H, dd, *J* 7.40 and 15.50 Hz, 4-CH), 3.81 (2H, s, $SO_3CH_2C(CH_3)_3$), 0.98 (9H, s, $C(CH_3)_3$); $\delta_C$ (50 MHz) 25.92, 32.15, 80.17, 131.78, 138.69, 139.78, 143.48, 192.58; GC–MS (*m*/*z*): 217 (1) [M−$CH_3$], 177 (9), 161 (1), 146 (5), 145 (15), 82 (6), 81 (8), 71 (7), 57 (100).

### 4.12. *Neo*pentyl *exo*-1-methyl-2-oxabicyclo[3.1.0]hex-3-ene-6-sulfonate (10b)

Isolated as a colourless oil. [Found: C, 53.85; H, 7.39. $C_{11}H_{18}O_4S$ requires: C, 53.64; H, 7.37.] $\nu_{max}$ (liquid film) 3000, 1620, 1590, 1370, 1160 $cm^{-1}$; $\delta_H$ (400 MHz) 6.38 (1H, d, *J* 2.65 Hz, 3-CH), 5.46 (1H, t, *J* 2.62 Hz, 4-CH), 3.80–4.0 (2H, m, $SO_3CH_2C(CH_3)_3$), 2.92 (1H, t, *J* 3.07 Hz, 5-CH), 1.9 (3H, s, $CH_3$), 1.77 (1H, d, *J* 3.33 Hz, 6-CH), 1.00 (9H, s, $C(CH_3)_3$); $\delta_C$ (100 MHz) 14.67, 26.50, 30.56, 34.43, 39.36, 54.03, 80.17, 105.83, 147.91; GC–MS (*m*/*z*): 246 (6), 96 (8), 95 (100), 94 (11), 71 (2), 57 (4).

### 4.13. *Neo*pentyl (1*Z*,3*Z*)-5-oxohexa-1,3-diene-1-sulfonate (11b)

Isolated as a colourless oil. [Found: C, 53.78; H, 7.36. $C_{11}H_{18}O_4S$ requires: C, 53.64; H, 7.37.] $\delta_H$ (400 MHz) 7.92 (1H, tq, *J* 0.54 and 11.65 Hz, 3-CH), 7.42 (1H, tq, *J* 0.51 and 11.67 Hz, 2-CH), 6.41 (1H, d, *J* 11.45 Hz, 1-CH), 6.31 (1H, d, *J* 11.21 Hz, 4-CH), 3.78 (2H, s, $SO_3CH_2C(CH_3)_3$), 2.30 (3H, s, $COCH_3$), 0.96 (9H, s, $C(CH_3)_3$); $\delta_C$ (100 MHz) 26.44, 32.11, 32.18, 80.24, 128.73, 132.18, 132.76, 137.16, 199.22; GC–MS (*m*/*z*): 246 (<1), 194 (1), 177 (5), 166 (2), 113 (14), 114 (29), 95 (57), 86 (27), 85 (78), 71 (59), 57 (100).

### 4.14. *Neo*pentyl (1*E*,3*Z*)-5-oxohexa-1,3-diene-1-sulfonate (12b)

Isolated as a colourless oil. [Found: C, 53.68; H, 7.38. $C_{11}H_{18}O_4S$ requires: C, 53.64; H, 7.37.] $\nu_{max}$ (liquid film) 3000, 1675, 1590, 1060, 1370, 1160 $cm^{-1}$; $\delta_H$ (400 MHz) 8.15–8.36 (1H, m), 6.35–6.48 (3H, m, 2-CH, 3-CH and 4-CH), 3.80 (2H, s, $SO_3CH_2C(CH_3)_3$), 2.32 (3H, s, $COCH_3$), 0.98 (9H, s, $C(CH_3)_3$); $\delta_C$ (100 MHz) 26.46, 31.99, 32.15, 80.43, 132.07, 133.45, 134.99, 138.78, 199.22; GC–MS (*m*/*z*): 246 (<1), 194 (4), 177 (1), 152 (1), 141 (2), 114 (30), 113 (39), 95 (76), 86 (27), 85 (22), 71 (72), 57 (100).

### 4.15. *Neo*pentyl (1*E*,3*E*)-5-oxohexa-1,3-diene-1-sulfonate (15b)

Isolated as a colourless oil. [Found: C, 53.68; H, 7.37. $C_{11}H_{18}O_4S$ requires: C, 53.64; H, 7.37.] $\nu_{max}$ (liquid film) 3000, 1675, 1590, 1060, 1370, 1160 $cm^{-1}$; $\delta_H$ (400 MHz) 7.25 (1H, ddd, *J* 0.66, 11.19 and 14.92 Hz, 3-CH), 7.11 (1H, ddd, *J* 0.43, 11.54 and 15.31 Hz, 2-CH), 6.61 (1H, dt, *J* 0.55 and 14.85 Hz, 1-CH), 6.52 (1H, d, *J* 15.39 Hz, 4-CH), 3.80 (2H, s, $SO_3CH_2C(CH_3)_3$), 2.32 (3H, s, $COCH_3$), 0.95 (9H, s, $C(CH_3)_3$); $\delta_C$ (100 MHz) 26.44, 28.68, 80.47, 131.43, 136.18, 138.44, 141.24, 197.42; GC–MS (*m*/*z*): 246 (9), 176 (6), 152 (1), 112 (1), 95 (100), 71 (2), 67 (11), 57 (7).

### 4.16. Methyl (2*Z*,4*Z*)-5-[(*neo*pentyloxy)sulfonyl]penta-2,4-dienoate (17b)

[Found: C, 50.41; H, 6.94. $C_{11}H_{18}O_5S$ requires: C, 50.36; H, 6.92.] $\nu_{max}$ (liquid film) 3000, 1720, 1590, 1060, 1370, 1160 $cm^{-1}$; $\delta_H$ (400 MHz) 8.11 (1H, dt, *J* 1.14 and 11.6 Hz, 4-CH), 7.62 (1H, dt, *J* 1.19 and 11.6 Hz, 3-CH), 6.34 (1H, dt, *J* 1.38 and 11.24 Hz, 5-CH), 6.10 (1H, dt, *J* 1.38 and 11.6 Hz, 2-CH), 3.79 (2H, s, $SO_3CH_2C(CH_3)_3$), 3.75 (3H, s, $CO_2CH_3$), 0.97 (9H, s, $C(CH_3)_3$); $\delta_C$ (100 MHz) 26.45, 32.12, 52.22, 80.27, 126.64, 128.44, 135.05, 136.27, 165.98; GC–MS (*m*/*z*): 262 (<1), 247 (<1), 231 (4), 207 (5), 193 (9), 175 (38), 161 (5), 111 (100), 97 (6), 79 (11), 71 (12), 57 (65).

### 4.17. Methyl (2*Z*,4*E*)-5-[(*neo*pentyloxy)sulfonyl]penta-2,4-dienoate (18b)

Isolated as a colourless oil. [Found: C, 50.39; H, 6.92. $C_{11}H_{18}O_5S$ requires: C, 50.36; H, 6.92.] $\nu_{max}$ (liquid film) 3000, 1720, 1590, 1060, 1370, 1160 $cm^{-1}$; $\delta_H$ (400 MHz) 8.35 (1H, dddd, *J* 0.32, 1.00, 11.43 and 15.18 Hz, 4-CH), 6.62 (1H, t, *J* 11.80 Hz, 3-CH), 6.48 (1H, d, *J* 15.18 Hz, 5-CH), 6.10 (1H, d, *J* 11.31 Hz, 2-CH), 3.79 (2H, s, $SO_3CH_2C(CH_3)_3$), 3.78 (3H, s, $CO_2CH_3$), 0.98 (9H, s, $C(CH_3)_3$); $\delta_C$ (100 MHz) 26.44, 32.14, 52.32, 80.40, 127.21, 131.52, 137.74, 138.29, 165.57; GC–MS (*m*/*z*): 247 (<1) [M−$CH_3$], 231 (5), 207 (6), 193 (9), 175 (40), 161 (6), 111 (100), 97 (7), 71 (13), 57 (77).

### 4.18. Diisopropyl *exo*-2-oxabicyclo[3.1.0]hex-3-en-6-ylphosphonate (4c)

Isolated as a colourless oil. [Found: C, 53.67; H, 7.80. $C_{11}H_{19}O_4P$ requires: C, 53.65; H, 7.78.] $\nu_{max}$ (liquid film) 3000, 1620, 1590, 1060, 1050 $cm^{-1}$; $\delta_H$ (200 MHz) 6.32 (1H, br s, 3-CH), 5.51 (1H, t, *J* 0.3 Hz, 4-CH), 4.54–4.448 (2H, m, 2×$CH(CH_3)_2$), 2.53–2.48 (1H, m, 5-CH), 1.38 (12H, 2×s, 2×$CH(CH_3)_2$), 0.27–0.23 (1H, m, 6-CH); $\delta_C$ (50 MHz) 15.71 ($J_{C-P}$ 1.87 Hz), 24.73, 25.82, ($J_{C-P}$ 2.80 Hz), 64.38, 71.24, 107.82, 147.20 ppm; $\delta_P$ (81 MHz) 39.43; GC–MS (*m*/*z*): 246 (1), 204 (4), 189 (7), 175 (2), 163 (16), 162 (51), 145 (12), 133 (30), 115 (5), 99 (4), 81 (100).

### 4.19. Diisopropyl (1*Z*,3*E*)-5-oxopenta-1,3-dienylphosphonate (5c)

Isolated as a colourless oil. [Found: C, 53.63; H, 7.80. $C_{11}H_{19}O_4P$ requires: C, 53.65; H, 7.78.] $\nu_{max}$ (liquid film) 3000, 2720, 1685, 1570, 1050 $cm^{-1}$; $\delta_H$ (200 MHz) 9.72 (1H, d, *J* 7.90 Hz, CHO), 8.29 (1H, dd, *J* 11.37 and 15.54 Hz, 3-CH), 6.95 (1H, dt, *J* 12.73 and 49.01 Hz, 2-CH), 6.25 (1H, dd, *J* 7.97 and 15.5 Hz, 4-CH), 5.99 (1H, t, *J* 13.6 Hz, 1-CH), 4.75–4.71 (2H, m, 2×C*H*$(CH_3)_2$), 1.38 (6H, d, *J* 6.16 Hz, CH(C*H*$_3)_2$), 1.32 (6H, d, *J* 6.16 Hz, CH(C*H*$_3)_2$); $\delta_C$ (100 MHz) 24.82, 71.86, 127.96 ($J_{C-P}$ 1.80 Hz), 137.61, 143.97, 147.07, 194.72; $\delta_P$ (81 MHz) 27.78; GC–MS (*m*/*z*): 246 (7), 231 (37), 203 (8), 189 (57), 162 (62), 144 (4), 123 (17), 107 (10), 82 (60), 81 (100).

### 4.20. Diisopropyl (1*E*,3*E*)-5-oxopenta-1,3-dienylphosphonate (6c)

Isolated as a colourless oil. [Found: C, 53.68; H, 7.80. $C_{11}H_{19}O_4P$ requires: C, 53.65; H, 7.78.] $\nu_{max}$ (liquid film) 3000, 2719, 1685, 1568, 1050 $cm^{-1}$; $\delta_H$ (400 MHz) 9.66 (1H, d, *J* 7.7 Hz, CHO), 7.21–7.15 (2H, m, 2-CH and 3-CH), 6.35 (1H, dd, *J* 7.69 and 15.19 Hz, 4-CH), 6.22 (1H, t, *J* 17.36 Hz, 1-CH), 4.72–4.65 (2H, m, 2×C*H*$(CH_3)_2$), 1.35 (2H, d, *J* 6.16 Hz, CH(C*H*$_3)_2$), 1.29 (6H, d, *J* 6.16 Hz, CH(C*H*$_3)_2$); $\delta_C$ (100 MHz) 24.68, 71.99, 130.03 ($J_{C-P}$ 1.87 Hz), 136.86, 144.02 ($J_{C-P}$ 0.06 Hz), 148.90 ($J_{C-P}$ 0.27 Hz), 193.75; $\delta_P$ (162 MHz) 29.70; GC–MS (*m*/*z*): 246 (<1), 231 (1), 217 (1), 204 (12), 189 (28), 175 (12), 163 (100), 146 (16), 145 (41), 136 (27), 133 (40), 117 (10), 115 (9), 99 (12), 81 (57).

### 4.21. Diisopropyl (1*Z*,3*Z*)-5-oxopenta-1,3-dienylphosphonate (7c)

Isolated as a colourless oil. [Found: C, 53.62; H, 7.79. $C_{11}H_{19}O_4P$ requires: C, 53.65; H, 7.78.] $\nu_{max}$ (liquid film) 3000, 2720, 1685, 1570, 1051 $cm^{-1}$; $\delta_H$ (400 MHz) 10.26 (1H, d, *J* 7.31 Hz, CHO), 8.09 (1H, t, *J* 12.00 Hz, 3-CH), 7.77 (1H, dt, *J* 12.12 and 48.64 Hz, 2-CH), 6.12 (1H, dd, *J* 7.49 and 11.51 Hz, 4-CH), 6.03 (1H, t, *J* 13.54 Hz, 1-CH), 4.76–4.70 (2H, m, 2×C*H*$(CH_3)_2$), 1.38 (6H, d, *J* 6.16 Hz, CH(C*H*$_3)_2$), 1.30 (6H, d, *J* 6.16 Hz, CH(C*H*$_3)_2$); $\delta_C$ (100 MHz) 26.48, 70.50, 127.21 ($J_{C-P}$ 1.80 Hz), 131.58, 138.41, 140.61, 189.86; $\delta_P$ (162 MHz) 12.77; GC–MS (*m*/*z*): 246 (<1), 231 (<1), 217 (2), 204 (5), 189 (7), 1 (19), 175 (4), 163 (16), 162 (82), 145 (20), 133 (100), 117 (101), 115 (18), 99 (12), 81 (56).

### 4.22. Diisopropyl (1*E*,3*Z*)-5-oxopenta-1,3-dienylphosphonate (8c)

Isolated as a colourless oil. [Found: C, 53.66; H, 7.81. $C_{11}H_{19}O_4P$ requires: C, 53.65; H, 7.78.] $\nu_{max}$ (liquid film) 3000, 2720, 1685, 1570, 1050 $cm^{-1}$; $\delta_H$ (400 MHz) 10.27 (1H, d, *J* 7.74 Hz, CHO), 7.91 (1H, ddd, *J* 12.00, 16.67 and 28.57 Hz, 3-CH), 6.96 (1H, t, *J* 11.28 Hz, 2-CH), 6.12–5.98 (2H, m, 1-CH and 4-CH), 4.75–4.71 (2H, m, 2×C*H*$(CH_3)_2$), 1.35 (6H, d, *J* 6.04 Hz, CH(C*H*$_3)_2$), 1.33 (6H, d, *J* 6.13 Hz, CH(C*H*$_3)_2$); $\delta_C$ (100 MHz) 24.42, 71.55, 129.75 ($J_{C-P}$ 1.88 Hz), 132.52, 139.14, 144.35 ($J_{C-P}$ 0.27 Hz), 190.21; $\delta_P$ (162 MHz) 14.69; GC–MS (*m*/*z*): 246 (<1), 231 (1), 217 (1), 189 (28), 1 (19), 175 (12), 163 (100), 146 (16), 145 (41), 136 (27), 133 (38), 117 (10), 99 (12), 81 (55).

### 4.23. Diisopropyl *exo*-3-methyl-2-oxabicyclo[3.1.0]hex-3-en-6-ylphosphonate (13c)

Isolated as a colourless oil. [Found: C, 55.40; H, 8.15. $C_{12}H_{21}O_4P$ requires: C, 55.38; H, 8.13.] $\nu_{max}$ (liquid film) 3000, 1620, 1590, 1060 $cm^{-1}$; $\delta_H$ (400 MHz) 5.16–5.0 (1H, m, 4-CH), 4.70–4.63 (3H, m, 2×C*H*$(CH_3)_2$ and 1-CH), 2.62–4.57 (1H, m, 5-CH), 1.75 (3H, s, $CH_3$), 1.37–1.30 (12H, m, 2×CH(C*H*$_3)_2$), 0.32–0.26 (1H, m, 6-CH); GC–MS (*m*/*z*): 260 (<1), 176 (8), 159 (6), 147 (11), 129 (2), 96 (7), 95 (100), 94 (7).

### 4.24. Diisopropyl *exo*-1-methyl-2-oxabicyclo[3.1.0]hex-3-en-6-ylphosphonate (10c)

Compound detected in mixture with diisopropyl (1*Z*,3*Z*)-5-oxohexa-1,3-dienylphosphonate **11c**. $\delta_H$ (400 MHz) 6.24 (1H, d, *J* 2.56 Hz, 3-CH), 5.26 (1H, t, *J* 2.56 Hz, 4-CH), 4.69–4.65 (2H, m, 2×C*H*$(CH_3)_2$), 2.48 (1H, ddd, *J* 2.55, 4.35 and 15.02 Hz, 5-CH), 2.25 (3H, s, $CH_3$), 1.37–1.30 (12H, m, 2×CH(C*H*$_3)_2$), 0.25 (1H, d, *J* 4.32 Hz, 6-CH); GC–MS (*m*/*z*): 260 (1), 218 (2), 203 (4), 177 (7), 176 (27), 175 (6), 159 (9), 133 (26), 115 (4), 95 (100).

### 4.25. Diisopropyl (1*Z*,3*E*)-5-oxohexa-1,3-dienylphosphonate (14c)

Isolated as a colourless oil. [Found: C, 55.40; H, 8.15. $C_{12}H_{21}O_4P$ requires: C, 55.38; H, 8.13.] $\nu_{max}$ (liquid film) 3000, 1675, 1620, 1570, 1050 $cm^{-1}$; $\delta_H$ (400 MHz) 8.19 (1H, qt, *J* 1.20, 11.26 and 16.00 Hz, 3-CH), 6.94 (1H, ddd, *J* 0.78, 12.81 and 49.34 Hz, 2-CH), 6.19 (1H, 1H, *J* 0.73 and 16.00 Hz, 4-CH), 5.93 (1H, dddd, *J* 0.68, 1.05, 12.81 and 15.13 Hz, 1-CH), 4.70–4.65 (2H, m, 2×C*H*$(CH_3)_2$), 2.40 (3H, s, $COCH_3$), 1.38 (6H, d, *J* 6.16 Hz, CH(C*H*$_3)_2$), 1.30 (6H, d, *J* 6.16 Hz, CH(C*H*$_3)_2$); $\delta_C$ (100 MHz): 24.68, 27.27, 71.66, 126.70 ($J_{C-P}$ 1.81 Hz), 137.50, 139.42, 145.02, 199.93; $\delta_P$ (162 MHz) 24.67; GC–MS (*m*/*z*): 260 (1), 236 (5), 219 (1), 207 (20), 177 (61), 166 (10), 165 (21), 147 (26), 133 (11), 123 (100), 96 (17), 95 (31).

### 4.26. Diisopropyl (1*E*,3*E*)-5-oxohexa-1,3-dienylphosphonate (15c)

Isolated as a colourless oil. [Found: C, 55.37; H, 8.12. $C_{12}H_{21}O_4P$ requires: C, 55.38; H, 8.13.] $\nu_{max}$ (liquid film) 3000, 1675, 1620, 1570, 1050 $cm^{-1}$; $\delta_H$ (400 MHz) 7.11–7.07 (2H, m, 2-CH and 3-CH), 6.36 (1H, d, *J* 13.88 Hz, 4-CH), 6.17–6.13 (1H, m, 1-CH), 4.71–4.67 (2H, m, 2×C*H*$(CH_3)_2$), 2.32 (3H, s, $COCH_3$), 1.37 (6H, d, *J* 6.16 Hz, CH(C*H*$_3)_2$), 1.32 (6H, d, *J* 6.16 Hz, CH(C*H*$_3)_2$); $\delta_C$ (100 MHz) 24.44, 28.27, 71.34, 128.65 ($J_{C-P}$ 1.87 Hz), 135.93, 140.51 ($J_{C-P}$ 0.27 Hz), 144.61 ($J_{C-P}$ 0.06 Hz), 198.71; $\delta_P$ (162 MHz) 15.08; GC–MS (*m*/*z*): 260 (<1), 217 (5), 203 (4), 176 (30), 161 (7), 159 (9), 133 (100), 117 (13), 115 (12), 95 (49).

### 4.27. Diisopropyl (1*Z*,3*Z*)-5-oxohexa-1,3-dienylphosphonate (11c)

Isolated as a colourless oil. [Found: C, 55.38; H, 8.11. $C_{12}H_{21}O_4P$ requires: C, 55.38; H, 8.13.] $\nu_{max}$ (liquid film) 3000, 1675, 1620, 1570, 1050 $cm^{-1}$; $\delta_H$ (400 MHz) 7.92 (1H, dt, *J* 12.01 and 51.00 Hz, 2-CH), 7.53 (1H, t, *J* 11.63 Hz, 3-CH), 6.25 (1H, d, *J* 10.52 Hz, 4-CH), 5.86 (1H, dd, *J* 12.92 and 16.36 Hz, 1-CH), 4.67–4.61 (2H, m, 2×C*H*$(CH_3)_2$), 2.33 (3H, s, $COCH_3$), 1.37 (6H, d, *J* 6.16 Hz, CH(C*H*$_3)_2$), 1.32 (6H, d, *J* 6.16 Hz, CH(C*H*$_3)_2$); $\delta_C$ (100 MHz) 24.63, 32.46, 71.16, 126.44 ($J_{C-P}$ 1.79 Hz), 130.49, 137.15, 142.46, 199.91; $\delta_P$ (162 MHz) 14.35; GC–MS (*m*/*z*): 260 (<1), 245 (1), 218 (4), 203 (89), 177 (16), 176 (40), 175 (11), 160 (8), 159 (15), 133 (37), 117 (5), 115 (6), 95 (100).

### 4.28. Diisopropyl (1*E*,3*Z*)-5-oxohexa-1,3-dienylphosphonate (12c)

Isolated as a colourless oil. [Found: C, 55.41; H, 8.14. $C_{12}H_{21}O_4P$ requires: C, 55.38; H, 8.13.] $\nu_{max}$ (liquid film) 3000, 1675, 1620, 1570, 1050 $cm^{-1}$; $\delta_H$ (400 MHz) 8.05–8.00 (1H, m, 2-CH), 6.37 (1H, dt, *J* 1.05 and 11.63 Hz, 3-CH), 6.21 (1H, dd, *J* 2.12 and 11.18 Hz, 4-CH), 6.01 (1H, dd, *J* 16.96 and 17.68 Hz, 1-CH), 4.70–4.66 (2H, m, 2×C*H*$(CH_3)_2$), 2.24 (3H, s, $COCH_3$), 1.31 (6H, d, *J* 6.16 Hz, CH(C*H*$_3)_2$), 1.29 (6H, d, *J* 6.16 Hz, CH(C*H*$_3)_2$); $\delta_C$ (100 MHz) 24.66, 32.28, 71.70, 129.43 ($J_{C-P}$ 1.89 Hz), 130.60 ($J_{C-P}$ 0.28 Hz), 139.09, 144.97 ($J_{C-P}$

0.06 Hz), 198.92; $\delta_P$ (162 MHz) 15.01; MS ($m/z$): 260 (18), 218 (9), 203 (13), 177 (7), 176 (100), 175 (29), 157 (3), 95 (82), 94 (58).

### 4.29. Methyl (2*Z*,4*Z*)-5-(diisopropoxyphosphoryl)penta-2,4-dienoate (17c)

Isolated as a colourless oil. [Found: C, 52.19; H, 7.68. $C_{12}H_{21}O_5P$ requires: C, 52.17; H, 7.66.] $\nu_{max}$ (liquid film) 3000, 1720, 1630, 1580, 1050 $cm^{-1}$; $\delta_H$ (400 MHz) 8.07 (1H, dddd, *J* 1.09, 11.94, 12.95 and 50.82 Hz, 3-CH), 7.74 (1H, tt, *J* 1.16 and 11.60 Hz, 4-CH), 5.93–5.89 (2H, m, 2-CH and 5-CH), 4.69–4.65 (2H, m, 2×C*H*($CH_3$)$_2$), 3.74 (3H, s, $CO_2CH_3$), 1.33 (6H, d, *J* 6.16 Hz, CH(C*H*$_3$)$_2$), 1.25 (6H, d, *J* 6.17 Hz, CH(C*H*$_3$)$_2$); $\delta_C$ (100 MHz) 24.28, 52.70, 74.05, 123.42, 125.64 ($J_{C-P}$ 1.79 Hz), 139.61, 141.37, 144.86, 166.52; $\delta_P$ (162 MHz) 14.34; GC–MS ($m/z$): 245 (2) [M−$CH_3$], 218 (11), 203 (25), 177 (84), 160 (46), 133 (100), 117 (20), 95 (88).

### 4.30. Methyl (2*Z*,4*E*)-5-(diisopropoxyphosphoryl)penta-2,4-dienoate (18c)

Isolated as a colourless oil. [Found: C, 52.16; H, 7.68. $C_{12}H_{21}O_5P$ requires: C, 52.17; H, 7.66.] $\nu_{max}$ (liquid film) 3000, 1719, 1628, 1580, 1050 $cm^{-1}$; $\delta_H$ (400 MHz) 8.12 (1H, dddd, *J* 0.94, 5.57, 8.80 and 16.81 Hz, 4-CH), 6.60–6.66 (1H, m, 3-CH), 6.03 (1H, dd, *J* 16.93 and 19.03 Hz, 5-CH), 5.90 (1H, dd, *J* 2.97 and 11.37 Hz, 2-CH), 4.69–4.65 (2H, m, 2×C*H*($CH_3$)$_2$), 3.74 (3H, s, $CO_2CH_3$), 1.34 (12H, t, *J* 6.17 Hz, 2×CH(C*H*$_3$)$_2$); $\delta_C$ (100 MHz) 24.38, 52.08, 71.35, 123.65, 128.44 ($J_{C-P}$ 1.89 Hz), 141.30, 142.31, 166.09; $\delta_P$ (162 MHz) 16.33; GC–MS ($m/z$): 218 (4) [M−OCH($CH_3$)$_2$], 203 (10), 176 (36), 160 (10), 133 (43), 95 (100).

## Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2009.06.040.

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