# Convenient synthesis of substituted cyclopentenones *via* [3 + 2] annulation of allylidenetriphenylphosphorane with 1,2-diacylethylenes: application to synthesis of (±)-methyl dehydrojasmonate

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**(3-Alkoxycarbonyl-2-ethoxyprop-2-enylidene)triphenylphosphoranes 1 and 2 undergo [3 + 2] annulation with 1,2-diacylethylenes 3 to give 2-ethoxycyclopentadienes 6 as mixtures of the 1,3- and 1,4-diene. The mixtures are conveniently converted upon mild acid treatment into cyclopentenones 7 in a single form. Annulation of phosphorane 1 with acylmethylenemalonates 10 affords cyclopenta-1,3-dienes 11 in a highly regioselective fashion, which are readily converted into substituted cyclopentenones 12 in excellent yields. Phosphorane 1 also undergoes annulation with 1,2-acylacetylene 14 to give the fulvene 15, which is transformed into the exomethylenecyclopentenone 16. Furthermore, an application of the annulation to the synthesis of (±)-methyl dehydrojasmonate is described.**

## Introduction

Allylidenetriphenylphosphorane acts as a bidental 1,3-construction unit in annulations, including cyclopentadiene formation with α-halogeno ketones[1] and cyclohexadiene formation with α,β-unsaturated aldehydes.[2,3] The phosphorane has two nucleophilic centres at the α- and γ-position of the electron-delocalized structure. The first nucleophilic attack occurs predominantly at the γ-position as demonstrated by the above annulations.[4] Taking advantage of the nature of the phosphorane, we have described recently an additional [3 + 2] annulation between the phosphorane and 1,2-diacylethylenes which generates substituted cyclopentadienes without accompanying formation of other possible cyclohexadienes.[5] In order to extend the scope and the utility of this annulation, we investigated synthesis of substituted cyclopentenones with [2-ethoxy-3-(ethoxycarbonyl)prop-2-enylidene]triphenylphosphorane **1** in a similar manner to the previously reported synthesis of cyclopentenones from ethoxyphosphorane **1** and α-halogeno ketones,[1b] because construction of cyclopentenones has been intensively studied in recent years.[6] However, the annulation of the allylidenephosphorane with 1,2-diacylethylenes generally affords mixtures of the double-bond isomers involving cyclopenta-1,3- and -1,4-dienes and hence the difficulty of the present work would be associated with conversion of the resulting isomeric mixtures of 2-ethoxycyclopentadienes into cyclopentenones in a single form. We found that the conversion was accomplished through an equilibrium process by treatment with weak acid. In addition, excellent results are obtained by use of acylmethylenemalonates as substrates which lead to exclusive formation of the 2-ethoxycyclopenta-1,3-dienes and then the corresponding cyclopentenones after mild acid treatment. We report here details of an efficient access to substituted cyclopentenones from 2-ethoxyphosphorane and 1,2-diacylethylenes including acylmethylenemalonates and, furthermore, details of an application of the method to the synthesis of (±)-methyl dehydrojasmonate **20**.[7]

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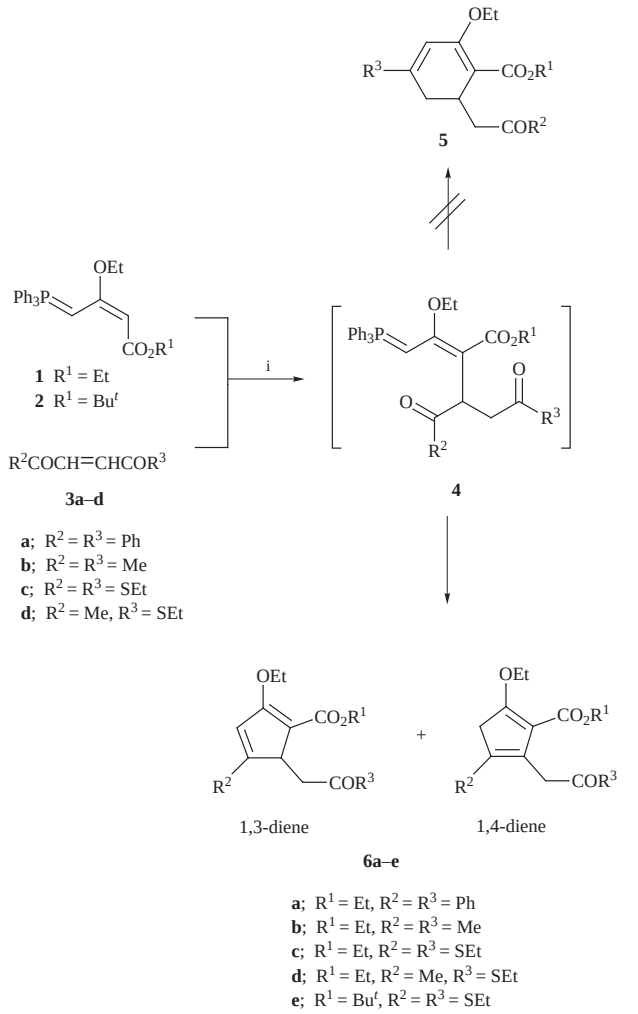
**Table 1** Ethoxycyclopentadienes **6** and cyclopentenones **7** from allylidenephosphorane and 1,2-diacylethylenes

| Entry | Ylide | Substrate | Cyclopentadiene (%)[a] | Cyclopentenone (%)[b] |
|---|---|---|---|---|
| 1 | **1** | **3a** | **6a** (94) | **7a** (60) |
| 2 | **1** | **3b** | **6b** (51) | **7b** (60) |
| 3 | **1** | **3c** | **6c** (80) | **7c** (73) |
| 4 | **1** | **3d** | **6d** (58) | **7d** (56) |
| 5 | **2** | **3c** | **6e** (83) | **7e** (78) |

[a] The cyclopentadienes were obtained as mixtures of the 1,3- and 1,4-diene. Total yields are those obtained after flash chromatography. [b] Yields are those obtained after flash chromatography.

## Results and discussion

When the phosphorane **1** was allowed to react with 1,2-dibenzoylethylene **3a** in THF at −30 °C to room temperature, [3 + 2] annulation occurred smoothly and the cyclopentadiene **6a** was obtained in 94% yield without accompanying formation of [3 + 3] annulation product **5a** (Scheme 1). The cyclopentadiene **6a** was an inseparable mixture of the 1,3- and 1,4-dienes in a 1:1 ratio, as indicated from the $^1$H NMR spectrum. The mixture may arise from the initially formed 1,3-diene through an equilibrium process under the weakly basic reaction conditions as described previously.[1b] Phosphorane **1** underwent [3 + 2] annulation with various other diacylethylenes **3** to afford the corresponding cyclopentadienes **6** as mixtures of the 1,3- and 1,4-dienes and the results are illustrated in Table 1. Diacetylethylene **3b** gave compound **6b** in 51% yield, and diethyl dithiofumarate **3c** gave compound **6c** in 80% yield, each as a 1:1 isomeric mixture. When the unsymmetrical ethylene *S*-ethyl 4-oxopent-2-enethioate **3d** was allowed to react with the phosphorane **1** in a similar manner, compound **6d** was obtained in 58% yield as a 1:2 mixture of the 1,3- and 1,4-diene and no other regioisomers were detected. This indicates that the Michael addition occurs at the 3-position of substrate **3d** in a highly regioselective fashion and successive Wittig reaction leads to product **6d**. Phosphorane *tert*-butyl ester **2** also underwent annulation with thioester **3c**, to afford compound **6e** as

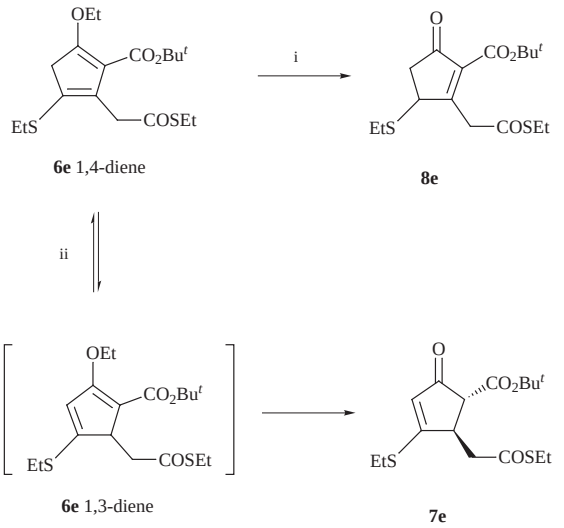



**Scheme 1** (see Table 1) *Reagents and conditions*: i, THF, −30 °C to room temp., 2 days

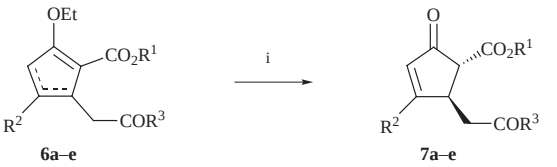
a 1:1 mixture of the 1,3- and 1,4-diene in 83% yield. Thus, annulations with 1,2-diacylethylenes gave mixtures of the cyclopenta-1,3- and -1,4-dienes in all cases.

Problems were encountered during the attempted conversion of these cyclopentadienes into cyclopentenones. As anticipated, hydrolysis of the cyclopentadiene **6a** in the form of a 1:1 mixture of 1,3- and 1,4-diene with aq. 2 M HCl–$CHCl_3$ led to the formation of a 1:1 mixture of the corresponding 2-oxocyclopent-3-enecarboxylate **7a** and 5-oxocyclopent-1-enecarboxylate **8a**. Therefore, hydrolysis of the 1,4-diene isomer of compound **6e**, which was isolated in a pure form by crystallization, was examined under various conditions and it was eventually found that the cyclopenta-1,4-diene could be converted into the cyclopentenone **7e** in 78% yield when treated with aq. AcOH in THF at room temperature for 2 days (Scheme 2). On the other hand, hydrolysis of the cyclopenta-1,4-diene with aq. 2 M HCl–$CHCl_3$ gave the alternative cyclopentenone **8e** in 97% yield. Apparently, the cyclopenta-1,4-diene must be in equilibrium with the 1,3-isomer in the weak acidic medium and the latter is slowly hydrolyzed to give the cyclopentenone **7e** predominantly. When the cyclopentadiene **6e** in the form of a 1:1 mixture of the 1,3- and 1,4-isomer was subjected to hydrolysis under the same conditions, the cyclopentenone **7e** was obtained in 78% yield as the sole product. In this way, the cyclopentadienes **6a**–**d** in the form of isomeric mixtures could be converted into the corresponding cyclopentenones **7a**–**d** (Scheme 3) and the results are listed in Table 1. Thus, the two-step sequence for the preparation of cyclopentenones **7** from the phosphorane and 1,2-diacylethylenes was accomplished.

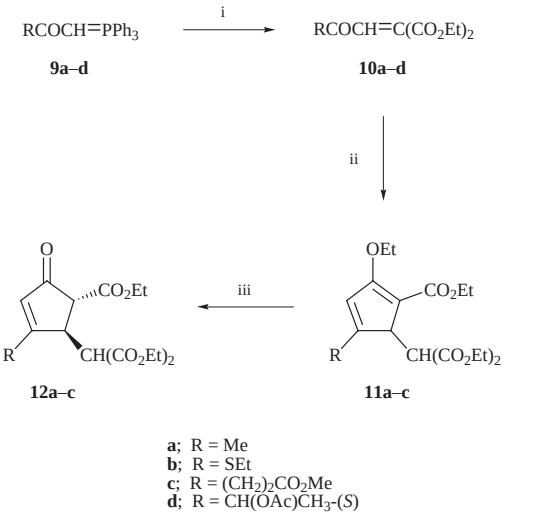
In a search for suitable substrates, we found that acylmethylenemalonates **10** give excellent results. The acylmethylenemalonates **10a**–**d** were readily prepared by Wittig reaction of the corresponding phosphoranes **9a**–**d** with diethyl oxomalonate. When phosphorane **1** was allowed to react with diethyl 2-oxopropylidenemalonate **10a**, annulation proceeded nicely to give a 94% yield of 1,3-diene **11a** exclusively (Scheme 4, Table 2). In contrast to the annulation with 1,2-diacyl-




**Scheme 2** *Reagents and conditions*: i, aq. 2 M HCl, $CHCl_3$, room temp., 12 h; ii, aq. AcOH, THF, room temp., 2 days




**Scheme 3** (see Table 1) *Reagents and conditions*: i, aq. AcOH, THF, room temp., 2 days



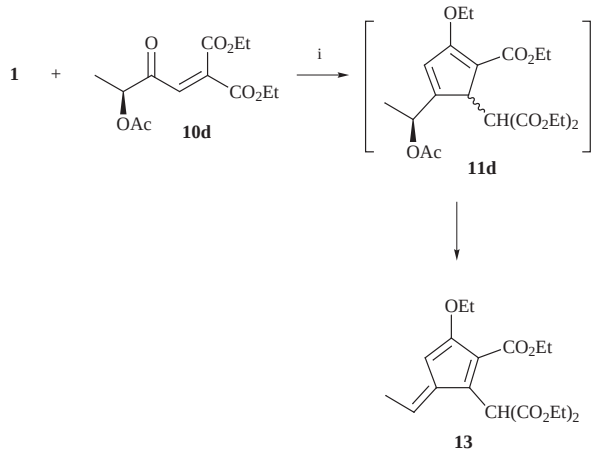

**Scheme 4** *Reagents and conditions*: i, diethyl oxomalonate, $CHCl_3$, room temp., 48 h; ii, **1**, THF, −30 °C to room temp., 2 days; iii, aq. 2 M HCl, $CHCl_3$, room temp., 12 h

**Table 2** 2-Ethoxycyclopenta-1,3-dienes **11** and cyclopentenones **12** from allylidenephosphorane **1** and acylmethylenemalonate **10**

| Entry | Substrate | Cyclopentadiene (%)[a] | Cyclopentenone (%)[a] |
|---|---|---|---|
| 1 | **10a** | **11a** (94) | **12a** (90) |
| 2 | **10b** | **11b** (87) | **12b** (94) |
| 3 | **10c** | **11c** (81) | **12c** (95) |

[a] Yields are those obtained after flash chromatography.

ethylenes **3**, no formation of the corresponding 1,4-diene was observed. In fact, 1,3-diene **11a** did not undergo base-induced isomerization to the 1,4-diene under the reaction conditions. The reason for this may be that formation of the cyclopentadienyl anion is prevented because of preferential anion formation at the neighbouring malonate moiety. Treatment of 1,3-diene **11a** with aq. 2 M HCl–$CHCl_3$ furnished the cyclopentenone **12a** in 90% yield. Ethylthiocarbonyl derivative **10b** also underwent annulation, to give the 1,3-diene **11b** in 87% yield as a single product. Similarly, the substrate **10c**, having a longer substituent, smoothly gave the cyclopentadiene **11c** in 81% yield. These cyclopentadienes **11b** and **11c** could be converted in a similar manner into cyclopentenones **12b** and **12c** in 94 and 95% yield, respectively. Thus, the annulation of phosphorane **1** with acylmethylenemalonates **10** provides an excellent route to substituted cyclopentenones in a regioselective fashion. However, when substrate **10d** was subjected to annulation with phosphorane **1** in an attempt to prepare an optically active cyclopentadiene, the fulvene **13** was obtained in 90% yield as the sole product‡ and the expected cyclopentadiene **11d** was not detected (Scheme 5). Compound **13** may come from compound



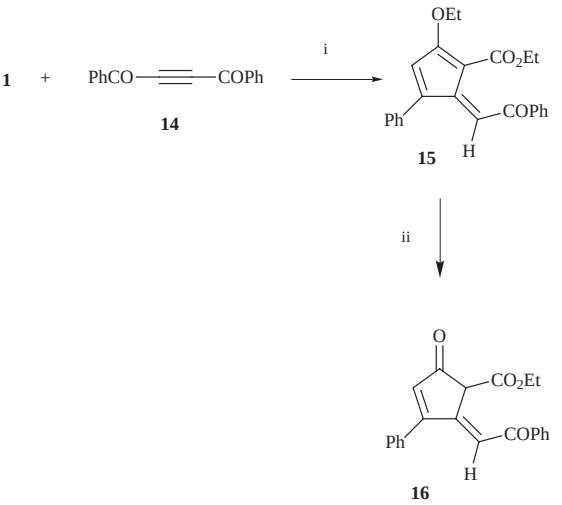

**Scheme 5** *Reagents and conditions*: i, THF, −30 °C to room temp., 2 days

**11d** or its 1,4-diene isomer as an intermediate *via* elimination of acetic acid.

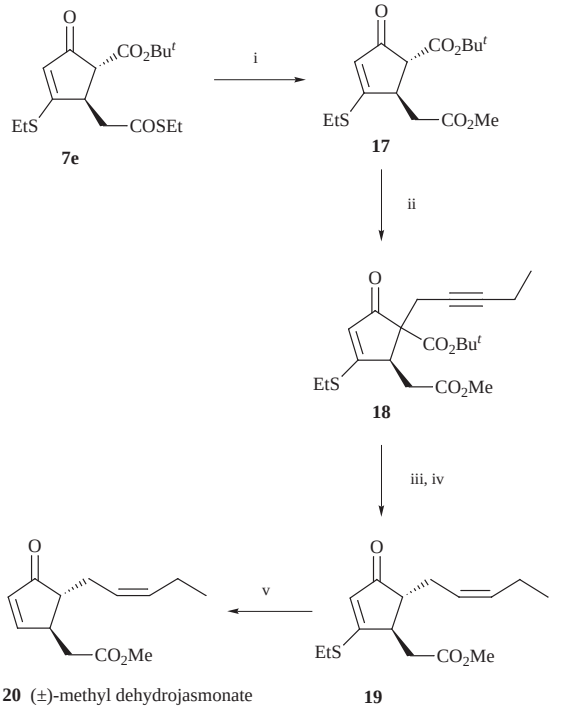
Another fulvene could be prepared directly by annulation with a 1,2-diacylacetylene.[7b] When phosphorane **1** was allowed to react with dibenzoylacetylene **14** in THF at −20 °C to room temperature for 48 h, the fulvene **15** was obtained in 92% yield as a single, *Z*-isomer (Scheme 6). The *Z*-orientation of the benzoyl group was estimated on the basis of the chemical shift ($\delta$ 6.76) of the exocyclic vinyl proton in comparison with those of analogous fulvene derivatives prepared previously.[7b] Treatment of the fulvene **15** with aq. 2 M HCl–$CHCl_3$ gave the cyclopentenone **16** in 97% yield, providing access to exomethylene cyclopentenones.

An application of the annulation to the synthesis of (±)-methyl dehydrojasmonate **20**[8] was next examined starting from the 3-(ethylthio)cyclopent-2-enone **7e** (Scheme 7). Treatment of compound **7e** with NaOH in methanol at 0 °C gave methyl ester **17** in 74% yield. Alkylation of β-keto ester **17** with 1-bromopent-2-yne proceeded smoothly to give compound **18** in 94% yield. Decarboxylation of compound **18** with TFA followed by partial hydrogenation afforded *cis* olefin **19** in 90% yield.

‡ The geometry of the exocyclic double bond of the fulvene **13** was confirmed by the observation of cross-peaks between the allylic methyl protons and the C-4 vinyl proton and between the exocyclic vinyl proton and the C-2 methine proton in the NOESY spectra.




**Scheme 6** *Reagents and conditions*: i, THF, −30 °C to room temp., 2 days; ii, aq. 2 M HCl, $CHCl_3$, room temp., 12 h




**Scheme 7** Synthesis of (±)-methyl dehydrojasmonate. *Reagents and conditions*: i, NaOH, MeOH, 0 °C, 1 h; ii, NaHDMS, 1-bromopent-2-yne, THF, 0 to 60 °C; iii, $CF_3CO_2H$ (TFA), anisole; iv, $H_2$, Pd–C, EtOH; v, $NiCl_2$, $NaBH_4$, aq. EtOH.

Finally, desulfurization of compound **19** was achieved with nickel borate to furnish (±)-methyl dehydrojasmonate **20** in 47% yield, with 32% recovery of unchanged starting material **19** (69% conversion).

## Conclusions

We have demonstrated that the annulation of [2-ethoxy-3-(ethoxycarbonyl)prop-2-enylidene]triphenylphosphorane with diacylethylenes provides a convenient route to substituted cyclopentenones. In particular, acylmethylenemalonates may be used as suitable substrates, which lead to high-yielding preparations of cyclopenta-1,3-dienes in most cases and then cyclopentenones after subsequent hydrolysis in a regioselective fashion. In addition, annulation of the phosphorane with 1,2-diacylacetylene provides access to an alternative type of cyclopentenone.

## Experimental

All mps were measured on a Mettler FP62 apparatus and are uncorrected. UV spectra were recorded on a JASCO V-550 spectrometer. IR spectra were recorded on a JASCO FT/IR-5300 spectrometer. $^1$H NMR spectra were measured at 300 MHz in $CDCl_3$ on a Varian Gemini 300BB spectrometer, using $SiMe_4$ as the internal standard. *J*-Values are given in Hz. $^{13}$C NMR spectra were recorded at 75 MHz on the same spectrometer, and solvent peak ($CDCl_3$: $\delta_C$ 77.0) was used for the internal standard. Mass spectra were recorded on a Hitachi M-80B spectrometer. Optical rotations were measured with a JASCO DIP-1000 polarimeter, with $[\alpha]_D$-values given in units of $10^{-1}$ deg cm$^{-1}$ g$^{-1}$. Flash chromatography was performed on Wakogel C-300. Extracts were dried over $MgSO_4$ and evaporated under reduced pressure. THF was distilled from sodium benzophenone ketyl. Petroleum spirit refers to the fraction with distillation range 60–70 °C.

### Ethyl 5-(benzoylmethyl)-2-ethoxy-4-phenylcyclopenta-1,3- and -1,4-dienecarboxylate 6a

A solution of 1,2-dibenzoylethylene **3a** (260 mg, 1.1 mmol) in THF (2 cm$^3$) was added to a stirred solution of phosphorane **1** (413 mg, 1.0 mmol) in THF (20 cm$^3$) at −30 °C under nitrogen. The mixture was stirred at room temperature for 48 h, and was then evaporated under reduced pressure. The residue was purified by flash chromatography [hexane–ethyl acetate (5:1)] to give the *cyclopentadiene* **6a** (353 mg, 94%) as an oil (Found: M$^+$, 376.1667. $C_{24}H_{24}O_4$ requires *M*, 376.1673); $\nu_{max}$(neat)/cm$^{-1}$ 1690, 1611 and 1576; $\delta_H$(300 MHz; $CDCl_3$) 8.03 (2 × ½ H, br d, *J* 8.5, COPh), 7.88 (2 × ½ H, br d, *J* 8.5, COPh), 7.57–7.19 (8 H, m, Ph), 6.81 (1 × ½ H, s, 3-H), 4.69 (1 × ½ H, dd, *J* 6 and 3.5, 5-H), 4.35 (2 × ½ H, s, $CH_2$), 4.36–3.93 (4 H, m, OC*H*$_2$CH$_3$), 3.60 (2 × ½ H, s, $CH_2$), 3.45 (1 × ½ H, dd, *J* 16.5 and 6, COC*H*$_2$), 3.12 (1 × ½ H, dd, *J* 16.5 and 3.5, COC*H*$_2$), 1.47 (3 H, t, *J* 7, OCH$_2$C*H*$_3$), 1.05 (3 × ½ H, t, *J* 7, OCH$_2$C*H*$_3$) and 1.03 (3 × ½ H, t, *J* 7, OCH$_2$C*H*$_3$); $\delta_C$(75 MHz; $CDCl_3$) 198.0, 197.9, 173.2, 167.8, 163.8, 158.8, 137.2, 137.1, 136.3, 133.6, 133.4, 132.9, 129.6, 128.9, 128.8, 128.5, 128.5, 128.3, 128.2, 128.1, 128.1, 127.9, 127.0, 126.6, 119.6, 110.2, 67.1, 59.4, 59.2, 43.7, 40.7, 38.9, 38.6, 15.2, 15.1, 14.2 and 14.1.

### Ethyl 2-ethoxy-4-methyl-5-(2-oxopropyl)cyclopenta-1,3- and -1,4-dienecarboxylate 6b

In the same manner as described for the preparation of compound **6a**, phosphorane **1** (412 mg, 1.0 mmol) was treated with hex-3-ene-2,5-dione **3b** (121 mg, 1.1 mmol) to give the cyclopentadiene **6b** (128 mg, 51%) as an oil, $\delta_H$(300 MHz; $CDCl_3$) 6.20 (1 × ½ H, br s, 3-H), 4.30–4.00 (4 H, m, OC*H*$_2$CH$_3$), 3.66 (1 × ½ H, ddd, *J* 7.5, 4 and 1, 5-H), 3.59 (2 × ½ H, s, $CH_2$), 3.12 (2 × ½ H, s, $CH_2$), 3.02 (1 × ½ H, dd, *J* 16.5 and 4, COC*H*$_2$), 2.72 (1 × ½ H, dd, *J* 16.5 and 7.5, COC*H*$_2$), 2.18 (3 × ½ H, s, COC*H*$_3$), 2.15 (3 × ½ H, s, COC*H*$_3$), 1.99 (3 × ½ H, d, *J* 1.5, 4-Me), 1.85 (3 × ½ H, s, 4-Me) and 1.40–1.10 (6 H, t, *J* 7, OCH$_2$C*H*$_3$). This compound was unstable and was used immediately in the next step.

### Ethyl 2-ethoxy-4-ethylthio-5-(ethylthiocarbonylmethyl)cyclopenta-1,3- and -1,4-dienecarboxylate 6c

In the same manner as described for the preparation of compound **6a**, phosphorane **1** (412 mg, 1.0 mmol) was treated with diethyl dithiofumarate **3c** (224 mg, 1.1 mmol) to give the *cyclopentadiene* **6c** (196 mg, 80%) as an oil (Found: M$^+$, 344.1118. $C_{16}H_{24}O_4S_2$ requires *M*, 344.1115); $\nu_{max}$(neat)/cm$^{-1}$ 1694, 1597 and 1553; $\delta_H$(300 MHz; $CDCl_3$) 6.08 (1 × ½ H, s, 3-H), 4.25–4.09 (4 H, m, OC*H*$_2$CH$_3$), 4.02 (2 × ½ H, s, C*H*$_2$), 3.79 (1 × ½ H, dd, *J* 7.5 and 4, 5-H), 3.35 (2 × ½ H, s, C*H*$_2$), 3.17 (1 × ½ H, dd, *J* 15.5 and 4, one of COC*H*$_2$), 2.99 (1 × ½ H, dd, *J* 15.5 and 7.5, one of COC*H*$_2$), 2.93–2.80 (6 × ½ H, m, SC*H*$_2$CH$_3$), 2.65 (2 × ½ H, q, *J* 7.5, SC*H*$_2$CH$_3$), 1.46 (3 × ½ H, t, *J* 7, OCH$_2$C*H*$_3$), 1.41 (3 × ½ H, t, *J* 7, OCH$_2$C*H*$_3$), 1.36 (3 × ½ H, t, *J* 7.5, SCH$_2$C*H*$_3$), 1.29 (3 × ½ H, t, *J* 7, OCH$_2$C*H*$_3$), 1.28 (3 × ½ H, t, *J* 7, OCH$_2$C*H*$_3$), 1.23 (3 × ½ H, t, *J* 7.5, SCH$_2$C*H*$_3$) and 1.21 (6 × ½ H, t, *J* 7.5, SCH$_2$C*H*$_3$); $\delta_C$(75 MHz; $CDCl_3$) 196.9, 196.6, 173.4, 168.0, 163.1, 158.8, 141.7, 121.5, 115.7, 110.1, 106.0, 102.9, 67.3, 67.0, 59.7, 59.0, 47.6, 44.8, 43.4, 42.1, 29.4, 26.8, 23.4, 23.2, 15.2, 15.1, 14.9, 14.6, 14.5, 14.2, 14.1 and 13.2.

The pure 1,4-isomer was isolated by repeated flash chromatography as an oil (Found: M$^+$, 344.1070); $\nu_{max}$(neat)/cm$^{-1}$ 1700, 1604 and 1560; $\delta_H$(300 MHz; $CDCl_3$) 4.20 (2 H, q, *J* 7, OC*H*$_2$CH$_3$), 4.13 (2 H, q, *J* 7, OC*H*$_2$CH$_3$), 4.02 (2 H, s, C*H*$_2$), 3.35 (2 H, s, C*H*$_2$), 2.84 (2 H, q, *J* 7.5, SC*H*$_2$CH$_3$), 2.65 (2 H, q, *J* 7.5, SC*H*$_2$CH$_3$), 1.46 (3 H, t, *J* 7, OCH$_2$C*H*$_3$), 1.28 (3 H, t, *J* 7, OCH$_2$C*H*$_3$) and 1.21 (6 H, t, *J* 7.5, SCH$_2$C*H*$_3$); $\delta_C$(75 MHz; $CDCl_3$) 197.0, 173.5, 163.1, 141.7, 121.5, 110.1, 67.3, 59.7, 43.4, 42.1, 29.4, 23.2, 15.2, 14.9, 14.7 and 14.2; $\lambda_{max}$(MeOH)/nm 319 ($\varepsilon$/dm$^3$ mol$^{-1}$ cm$^{-1}$ 5200).

### Ethyl 2-ethoxy-5-(ethylthiocarbonylmethyl)-4-methylcyclopenta-1,3- and -1,4-dienecarboxylate 6d

In the same manner as described for the preparation of analogue **6a** phosphorane **1** (412 mg, 1.0 mmol) was treated with *S*-ethyl 4-oxopent-2-enethioate **3d** (174 mg, 1.1 mmol) to give the *cyclopentadiene* **6d** (173 mg, 58%) as an oil (Found: M$^+$, 298.1169. $C_{15}H_{22}O_4S$ requires *M*, 298.1238); $\nu_{max}$(neat)/cm$^{-1}$ 1692, 1624 and 1559; $\delta_H$(300 MHz; $CDCl_3$) 6.20 (1 × ⅔ H, br s, 3-H), 4.28–4.02 (4 H, m, OC*H*$_2$CH$_3$), 3.73 (2 × ⅓ H, s, C*H*$_2$), 3.57 (1 × ⅔ H, dd, *J* 4 and 7.5, 5-H), 3.18 (1 × ⅔ H, dd, *J* 4 and 15, COC*H*$_2$), 3.12 (2 × ⅓ H, s, C*H*$_2$), 2.98 (1 × ⅔ H, dd, *J* 7.5 and 15, COC*H*$_2$), 2.83 (2 × ⅔ H, q, *J* 7.5, SC*H*$_2$CH$_3$), 2.82 (2 × ⅓ H, q, *J* 7.5, SC*H*$_2$CH$_3$), 2.06 (3 × ⅔ H, d, *J* 1.5, 4-Me), 1.90 (3 × ⅓ H, s, 4-Me), 1.43 (3 × ⅓ H, t, *J* 7, OCH$_2$C*H*$_3$), 1.40 (3 × ⅔ H, t, *J* 7, OCH$_2$C*H*$_3$), 1.31 (3 × ⅔ H, t, *J* 7, OCH$_2$C*H*$_3$), 1.28 (3 × ⅓ H, t, *J* 7, OCH$_2$C*H*$_3$) and 1.21 (3 H, t, *J* 7.5, SCH$_2$C*H*$_3$); $\delta_C$(75 MHz; $CDCl_3$) 197.9, 197.1, 171.3, 168.4, 163.7, 163.5, 157.9, 129.6, 126.8, 121.0, 106.2, 66.9, 66.8, 59.4, 59.0, 48.1, 42.9, 42.0, 41.7, 23.4, 23.1, 16.1, 15.1, 15.0, 14.6, 14.5, 14.2 and 13.0.

The pure 1,3-isomer was isolated by repeated flash chromatography as an oil (Found: M$^+$, 298.1197); $\nu_{max}$(neat)/cm$^{-1}$ 1692, 1671, 1624 and 1559; $\delta_H$(300 MHz; $CDCl_3$; assignments were assisted by a $^1$H–$^1$H COSY experiment) 6.20 (1 H, br s, 3-H), 4.28–4.14 (4 H, m, OC*H*$_2$CH$_3$), 3.58 (1 H, dd, *J* 4 and 7.5, 5-H), 3.18 (1 H, dd, *J* 4 and 15, COC*H*$_2$), 2.98 (1 H, dd, *J* 7.5 and 15, COC*H*$_2$), 2.83 (2 H, q, *J* 7.5, SC*H*$_2$CH$_3$), 2.06 (3 H, d, *J* 1.5, 4-Me), 1.40 (3 H, t, *J* 7, OCH$_2$C*H*$_3$), 1.31 (3 H, t, *J* 7, OCH$_2$C*H*$_3$) and 1.21 (3 H, t, *J* 7.5, SCH$_2$C*H*$_3$); $\delta_C$(75 MHz; $CDCl_3$) 197.0, 168.3, 163.4, 157.9, 121.0, 106.2, 66.8, 59.0, 48.1, 42.9, 23.4, 16.1, 15.1, 14.6 and 14.5; $\lambda_{max}$(MeOH)/nm 309.0 ($\varepsilon$/dm$^3$ mol$^{-1}$ cm$^{-1}$ 6600) and 233.0 (7300).

### *tert*-Butyl 2-ethoxy-4-ethylthio-5-(ethylthiocarbonylmethyl)-cyclopenta-1,3- and -1,4-dienecarboxylate 6e

In the same manner as described for the preparation of compound **6a**, phosphorane **2** (440 mg, 1.0 mmol) was treated with diethyl dithiofumarate **3c** (224 mg, 1.1 mmol) to give the cyclopentadiene **6e** (309 mg, 83%) as an oil (Found: M$^+$, 372.1385. $C_{18}H_{28}O_4S_2$ requires *M*, 372.1428); $\nu_{max}$(neat)/cm$^{-1}$ 1676, 1591 and 1553; $\delta_H$(300 MHz; $CDCl_3$) 6.08 (1 × ½ H, s, 3-H), 4.20 (2 × ½ H, t, *J* 7, OC*H*$_2$CH$_3$), 4.11 (2 × ½ H, t, *J* 7, OC*H*$_2$CH$_3$), 4.02 (2 × ½ H, s, C*H*$_2$), 3.72 (1 × ½ H, dd, *J* 3.5 and 7.5, 5-H), 3.32 (2 × ½ H, s, C*H*$_2$), 3.18 (1 × ½ H, dd, *J* 3.5 and 15.5, COC*H*$_2$), 2.96 (1 × ½ H, dd, *J* 7.5 and 15.5, COC*H*$_2$), 2.89 (2 × ½ H, q, *J* 7.5, SC*H*$_2$CH$_3$), 2.86 (2 × ½ H, q, *J* 7.5, SC*H*$_2$CH$_3$), 2.83 (2 × ½ H, q, *J* 7.5, SC*H*$_2$CH$_3$), 2.64 (2 × ½ H, q, *J* 7.5, SC*H*$_2$CH$_3$), 1.51 (9 × ½ H, s, Bu$^t$), 1.49 (9 × ½ H, s, Bu$^t$), 1.45 (3 × ½ H, t, *J* 7, OCH$_2$C*H*$_3$), 1.41 (3 × ½ H, t, *J* 7, OCH$_2$C*H*$_3$), 1.36 (3 × ½ H, t, *J* 7.5, SCH$_2$C*H*$_3$), 1.23 (3 × ½ H, t, *J* 7.5,

$SCH_2CH_3$), 1.21 ($3 \times \frac{1}{2}$ H, t, *J* 7.5, $SCH_2CH_3$) and 1.21 ($3 \times \frac{1}{2}$ H, t, *J* 7.5, $SCH_2CH_3$); $\delta_C$(75 MHz; $CDCl_3$) 196.9, 196.4, 172.6, 167.4, 162.4, 162.3, 157.8, 141.5, 121.2, 115.7, 111.3, 107.2, 80.2, 78.9, 66.9, 66.7, 47.6, 44.7, 43.1, 41.8, 29.1, 28.4, 28.1, 26.6, 23.2, 23.0, 15.0, 15.0, 14.8, 14.5 and 13.1.

Trituration of the resulting oil in ethyl acetate–hexane gave the pure 1,4-*isomer* as needles, mp 89.0–90.0 °C (from hexane–ethyl acetate) (Found: H, 7.83; C, 58.04; S, 17.42. $C_{18}H_{28}O_4S_2$ requires H, 7.58; C, 58.03; S, 17.21%); $\nu_{max}$(Nujol)/$cm^{-1}$ 1674, 1589 and 1553; $\delta_H$(300 MHz; $CDCl_3$) 4.11 (2 H, t, *J* 7, $OCH_2CH_3$), 4.02 (2 H, s, $CH_2$), 3.32 (2 H, s, $CH_2$), 2.83 (2 H, q, *J* 7.5, $SCH_2CH_3$), 2.64 (2 H, q, *J* 7.5, $SCH_2CH_3$), 1.49 (9 H, s, Bu$^t$), 1.45 (3 H, t, *J* 7, $OCH_2CH_3$), 1.21 (3 H, t, *J* 7.5, $SCH_2CH_3$) and 1.21 (3 H, t, *J* 7.5, $SCH_2CH_3$); $\delta_C$(75 MHz; $CDCl_3$) 196.9, 172.6, 162.4, 141.5, 121.2, 111.3, 80.2, 66.9, 43.1, 41.8, 29.1, 28.1, 23.0, 15.0, 14.8 and 14.5; $\lambda_{max}$(MeOH)/nm 312.5 ($\varepsilon$/$dm^3$ $mol^{-1}$ $cm^{-1}$ 3900) and 261.0 (11 700).

**Hydrolysis of compound 6a with aq. HCl**

Aq. HCl (2 M, 20 $cm^3$) was layered on a solution of the cyclopentadiene **6a** (53 mg, 0.14 mmol) in chloroform (20 $cm^3$). The mixture was vigorously stirred for 12 h at room temperature. The aqueous layer was extracted with chloroform. The combined organic layers were washed with aq. $NaHCO_3$, dried and evaporated. The mixture containing a 1:1 mixture of cyclopentenones **7a** and **8a** was purified by flash chromatography [hexane–ethyl acetate (5:1)] within 10 min to give ethyl 2-(benzoylmethyl)-5-oxo-3-phenylcyclopent-3-enecarboxylate **7a** (20 mg, 41%) as prisms and ethyl 2-(benzoylmethyl)-5-oxo-3-phenylcyclopent-1-enecarboxylate **8a** (5 mg, 9%) as an oil, which decomposed readily on silica gel.

*Compound* **7a**: mp 97.6–99.1 °C (from hexane–diethyl ether) (Found: H, 5.76; C, 75.72%; $M^+$, 348.1337. $C_{22}H_{20}O_4$ requires H, 5.79; C, 75.84%; *M*, 348.1360); $\nu_{max}$(neat)/$cm^{-1}$ 1732, 1696 and 1599; $\delta_H$(300 MHz; $CDCl_3$; assignments were assisted by a $^1H$–$^1H$ COSY experiment) 7.87 (2 H, br d, *J* 8.5, COPh), 7.63–7.35 (8 H, m, Ph), 6.47 (1 H, d, *J* 1.5, 4-H), 4.47 (1 H, br d, *J* 11, 2-H), 4.34–4.27 (2 H, m, $OCH_2CH_3$), 3.49 (1 H, dd, *J* 18.5 and 2.5, $COCH_2$), 3.27 (1 H, d, *J* 2, 1-H), 3.03 (1 H, dd, *J* 18.5 and 11, $COCH_2$) and 1.36 (3 H, t, *J* 7, $OCH_2CH_3$); $\delta_C$(75 MHz; $CDCl_3$) 200.4, 197.1, 177.5, 168.5, 136.1, 133.6, 132.7, 131.4, 129.3, 128.7, 128.0, 127.4, 127.4, 61.8, 60.5, 42.5, 40.6 and 14.2; $\lambda_{max}$(MeOH)/nm 281.5 ($\varepsilon$/$dm^3$ $mol^{-1}$ $cm^{-1}$ 20 000) and 246.5 (20 500).

*Compound* **8a**: (Found: $M^+$, 348.1329. $C_{22}H_{20}O_4$ requires *M*, 348.1360); $\nu_{max}$(neat)/$cm^{-1}$ 1746, 1715, 1628 and 1599; $\delta_H$(300 MHz; $CDCl_3$; assignments were assisted by a $^1H$–$^1H$ COSY experiment) 7.86 (2 H, br d, *J* 8.5, COPh), 7.60–7.10 (8 H, m, Ph), 4.79 (1 H, d, *J* 17, $COCH_2$), 4.29 (2 H, q, *J* 7, $OCH_2CH_3$), 4.34–4.26 (1 H, m, 3-H), 3.75 (1 H, d, *J* 17, $COCH_2$), 3.12 (1 H, dd, *J* 19 and 7.5, 4-$CH_2$), 2.57 (1 H, dd, *J* 19 and 2.5, 4-$CH_2$) and 1.25 (3 H, t, *J* 7, $OCH_2CH_3$); $\delta_C$(75 MHz; $CDCl_3$) 202.3, 194.1, 181.5, 162.8, 139.7, 136.2, 134.5, 133.7, 129.3, 128.7, 128.2, 127.9, 127.8, 61.1, 48.6, 45.2, 40.0 and 14.1; $\lambda_{max}$(MeOH)/nm 404.0 ($\varepsilon$/$dm^3$ $mol^{-1}$ $cm^{-1}$ 3500) and 246.0 (11 000).

**Hydrolysis of compound 6a with aq. AcOH**

A solution of the cyclopentadiene **6a** (223 mg, 0.59 mmol) in THF–AcOH–water (5:1:5; 22 $cm^3$) was stirred at 0 °C to room temperature for 48 h. The mixture was concentrated under reduced pressure and the remaining solution was extracted with diethyl ether. The extract was washed with aq. $NaHCO_3$, dried, and evaporated. The residue was purified by flash chromatography [hexane–ethyl acetate (5:1)] to give the cyclopentenone **7a** (124 mg, 60%) as prisms.

**Hydrolysis of 1,4-isomer of compound 6e with aq. HCl**

In the same manner as described for hydrolysis of compound **6a** with aq. HCl, the 1,4-isomer of compound **6e** (100 mg, 0.27 mmol) was hydrolyzed to give tert-*butyl* 3-*ethylthio*-2-(*ethylthiocarbonylmethyl*)-5-*oxocyclopent*-1-*enecarboxylate* **8e** (90 mg, 97%) as an oil (Found: $M^+$, 344.1138. $C_{16}H_{24}O_4S_2$ requires *M*, 344.1115); $\nu_{max}$(neat)/$cm^{-1}$ 1744, 1721 and 1582; $\delta_H$(300 MHz; $CDCl_3$; assignments were assisted by an $^1H$–$^1H$ COSY experiment) 4.31 (1 H, d, *J* 15.5, $COCH_2$), 4.11 (1 H, d, *J* 15.5, $COCH_2$), 4.00 (1 H, dd, *J* 2 and 7, 3-H), 3.01 (1 H, dd, *J* 7 and 19.5, one of 4-H), 2.92 (2 H, q, *J* 7.5, $SCH_2CH_3$), 2.62 (1 H, dd, *J* 2 and 19.5, one of 4-H), 2.51–2.38 (2 H, m, $SCH_2CH_3$), 1.54 (9 H, s, Bu$^t$), 1.27 (3 H, t, *J* 7.5, $SCH_2CH_3$) and 1.23 (3 H, t, *J* 7.5, $SCH_2CH_3$); $\delta_C$(75 MHz; $CDCl_3$) 200.2, 193.2, 172.7, 161.2, 136.7, 82.8, 45.3, 44.0, 43.9, 28.1, 23.9, 14.5 and 14.4.

**Ethyl 3-methyl-5-oxo-2-(2-oxopropyl)cyclopent-3-enecarboxylate 7b**

In the same manner as described for hydrolysis of compound **6a** with aq. AcOH, the cyclopentadiene **6b** (128 mg, 0.51 mmol) was hydrolyzed to give the *cyclopentenone* **7b** (68 mg, 60%) as an oil (Found: $M^+$, 224.1044. $C_{12}H_{16}O_4$ requires *M*, 224.1048); $\nu_{max}$(neat)/$cm^{-1}$ 1703 and 1622; $\delta_H$(300 MHz; $CDCl_3$; assignments were assisted by a $^1H$–$^1H$ COSY experiment) 5.92 (1 H, br s, 4-H), 4.25 (2 H, q, *J* 7, $OCH_2CH_3$), 3.56 (1 H, br d, *J* 10, 2-H), 3.03 (1 H, d, *J* 2.5, 1-H), 2.97 (1 H, dd, *J* 18 and 4, $COCH_2$), 2.49 (1 H, dd, *J* 18 and 10, $COCH_2$), 2.20 (3 H, s, $COCH_3$), 2.12 (3 H, s, 3-Me) and 1.32 (3 H, t, *J* 7, $OCH_2CH_3$); $\delta_C$(75 MHz; $CDCl_3$) 205.4, 200.8, 179.5, 168.7, 129.6, 61.6, 59.8, 45.3, 43.8, 30.0, 17.3 and 14.2; $\lambda_{max}$(MeOH)/nm 231.0 ($\varepsilon$/$dm^3$ $mol^{-1}$ $cm^{-1}$ 10 700).

**Ethyl 3-ethylthio-2-(ethylthiocarbonylmethyl)-5-oxocyclopent-3-enecarboxylate 7c**

In the same manner as described for hydrolysis of compound **6a** with aq. AcOH, the cyclopentadiene **6c** (600 mg, 1.74 mmol) was hydrolyzed to give the *cyclopentenone* **7c** (550 mg, 73%) as an oil (Found: H, 6.41; C, 53.18; S, 20.09%; $M^+$ 316.0787. $C_{14}H_{20}O_4S_2$ requires H, 6.37; C, 53.14; S, 20.27%; *M*, 316.0802); $\nu_{max}$(neat)/$cm^{-1}$ 1733, 1690 and 1542; $\delta_H$(300 MHz; $CDCl_3$) 5.87 (1 H, br s, 4-H), 4.23 (2 H, q, *J* 7, $OCH_2CH_3$), 3.86–3.79 (1 H, m, 2-H), 3.33 (1 H, d, *J* 3, 1-H), 3.11 (1 H, dd, *J* 16 and 4, $COCH_2$), 2.95 (2 H, q, *J* 7.5, $SCH_2CH_3$), 2.90 (2 H, q, *J* 7.5, $SCH_2CH_3$), 2.68 (1 H, dd, *J* 16 and 10, $COCH_2$), 1.40 (3 H, t, *J* 7.5, $SCH_2CH_3$), 1,30 (3 H, t, *J* 7, $OCH_2CH_3$) and 1.25 (3 H, t, *J* 7.5, $SCH_2CH_3$); $\delta_C$(75 MHz; $CDCl_3$) 196.2, 196.0, 181.9, 168.3, 122.1, 61.7, 58.9, 46.8, 44.4, 27.4, 23.6, 14.6, 14.2 and 13.0; $\lambda_{max}$(MeOH)/nm 283.5 ($\varepsilon$/$dm^3$ $mol^{-1}$ $cm^{-1}$ 16 300) and 236.5 (5700).

**Ethyl 2-(ethylthiocarbonylmethyl)-3-methyl-5-oxocyclopent-3-enecarboxylate 7d**

In the same manner as described for hydrolysis of compound **6a** with aq. AcOH, the cyclopentadiene **6d** (171 mg, 0.57 mmol) was hydrolyzed to give the *cyclopentenone* **7d** (87 mg, 56%) as an oil (Found: $M^+$, 270.0947. $C_{13}H_{18}O_4S$ requires *M*, 270.0925); $\nu_{max}$(neat)/$cm^{-1}$ 1736, 1705 and 1622; $\delta_H$(300 MHz; $CDCl_3$; assignments were assisted by a $^1H$–$^1H$ COSY experiment) 5.93 (1 H, br s, 4-H), 4.23 (2 H, q, *J* 7, $OCH_2CH_3$), 3.68–3.58 (1 H, m, 2-H), 3.28 (1 H, d, *J* 3, 1-H), 3.02 (1 H, dd, *J* 15.5 and 4.5, $COCH_2$), 2.90 (2 H, q, *J* 7.5, $SCH_2CH_3$), 2.63 (1 H, dd, *J* 15.5 and 9.5, $COCH_2$), 2.15 (3 H, s, 3-Me), 1.30 (3 H, t, *J* 7, $OCH_2CH_3$) and 1.25 (3 H, t, *J* 7.5, $SCH_2CH_3$); $\delta_C$(75 MHz; $CDCl_3$) 200.3, 196.6, 178.9, 168.4, 129.8, 61.7, 58.6, 45.1, 23.7, 17.4, 14.7 and 14.2; $\lambda_{max}$(MeOH)/nm 232.0 ($\varepsilon$/$dm^3$ $mol^{-1}$ $cm^{-1}$ 11 600).

***tert*-Butyl 3-ethylthio-2-(ethylthiocarbonylmethyl)-5-oxocyclopent-3-enecarboxylate 7e**

In the same manner as described for hydrolysis of compound **6a** with aq. AcOH, the cyclopentadiene **6e** (618 mg, 1.6 mmol) was hydrolyzed to give the *cyclopentenone* **7e** (446 mg, 78%) as an oil (Found: $M^+$, 344.1112. $C_{16}H_{24}O_4S_2$ requires *M*, 344.1115); $\nu_{max}$(neat)/$cm^{-1}$ 1728, 1692 and 1547; $\delta_H$(300 MHz; $CDCl_3$) 5.86

(1 H, br s, 4-H), 3.77 (1 H, br d, *J* 10, 2-H), 3.22 (1 H, d, *J* 3, 1-H), 3.09 (1 H, dd, *J* 4 and 16, COC$H_2$), 2.94 (2 H, q, *J* 7.5, SC$H_2$CH$_3$), 2.90 (2 H, q, *J* 7.5, SC$H_2$CH$_3$), 2.65 (1 H, dd, *J* 10 and 16, COC$H_2$), 1.49 (9 H, s, Bu$^t$), 1.39 (3 H, t, *J* 7.5, SCH$_2$C$H_3$) and 1.26 (3 H, t, *J* 7.5, SCH$_2$C$H_3$); $\delta_C$(75 MHz; $CDCl_3$) 196.6, 196.2, 181.7, 167.5, 122.2, 82.1, 59.9, 46.9, 44.5, 28.0, 27.4, 23.6, 14.7 and 13.1; $\lambda_{max}$(MeOH)/nm 283.5 ($\varepsilon$/dm$^3$ mol$^{-1}$ cm$^{-1}$ 19 000) and 234.0 (8600).

**Diethyl (2-ethylthiocarbonylmethylene)propanedioate 10b**

A solution of *S*-ethyl (triphenylphosphoranylidene)ethanethionate (3.1 g, 8.5 mmol) and diethyl oxomalonate (1.4 g, 8.1 mmol) in chloroform (50 cm$^3$) was stirred at room temperature for 48 h. The mixture was evaporated under reduced pressure. The residue was purified by flash chromatography [hexane–ethyl acetate (5:1)] to give *title compound* **10b** (1.78 g, 85%) as an oil (Found: H, 6.15; C, 50.67; S, 12.10. $C_{11}H_{16}O_5S$ requires H, 6.20; C, 50.75; S, 12.32%); $\nu_{max}$(neat)/cm$^{-1}$ 1736 and 1672; $\delta_H$(300 MHz; $CDCl_3$) 7.01 (1 H, s, C*H*=), 4.38 (2 H, q, *J* 7, OC$H_2$CH$_3$), 4.30 (2 H, q, *J* 7, OC$H_2$CH$_3$), 3.01 (2 H, q, *J* 7.5, SC$H_2$CH$_3$), 1.35 (3 H, t, *J* 7, OCH$_2$C$H_3$), 1.32 (3 H, t, *J* 7, OCH$_2$C$H_3$) and 1.30 (3 H, t, *J* 7.5, SCH$_2$C$H_3$); $\delta_C$(75 MHz; $CDCl_3$) 187.4, 164.4, 162.4, 134.3, 133.9, 62.5, 62.0, 24.1, 14.2, 13.9 and 13.8.

**1′,1′-Diethyl 5′-methyl 3-oxopent-1-ene-1,1,5-tricarboxylate 10c**

The starting phosphorane **9c** was prepared in 83% overall yield by modification of the literature procedure *via* acylation[9a] of (*tert*-butoxycarbonylmethylene)triphenylphosphorane with 3-(methoxycarbonyl)propionyl chloride followed by decarboxylation.[9b] The phosphorane **9c** was purified by flash chromatography [ethyl acetate–methanol (10:1)] to give an oil, which was used without further purification: $\delta_H$(300 MHz; $CDCl_3$) 7.78–7.40 (15 H, m, Ph), 3.72 (1 H, d, *J* 26, CH=P), 3.66 (3 H, s, OMe) and 2.67 (2 H, br s, $CH_2CH_2$).

In the same manner as described for the preparation of compound **10b**, phosphorane **9c** (400 mg, 1.0 mmol) was treated with diethyl oxomalonate (200 mg, 1.1 mmol) to give *title compound* **10c** (288 mg, 98%) as an oil (Found: M$^+$, 276.1077. $C_{13}H_{18}O_7$ requires *M*, 276.0763); $\nu_{max}$(neat)/cm$^{-1}$ 1739, 1707 and 1632; $\delta_H$(300 MHz; $CDCl_3$) 7.17 (1 H, s, C*H*=), 4.36 (2 H, q, *J* 7, OC$H_2$CH$_3$), 4.31 (2 H, q, *J* 7, OC$H_2$CH$_3$), 3.69 (3 H, s, OC$H_3$), 2.95 (2 H, t, *J* 6.5, CH$_2$C$H_2$), 2.66 (2 H, t, *J* 6.5, CH$_2$C$H_2$), 1.33 (3 H, t, *J* 7, OCH$_2$C$H_3$) and 1.33 (3 H, t, *J* 7, OCH$_2$C$H_3$); $\delta_C$(75 MHz; $CDCl_3$) 196.7, 172.7, 164.7, 162.8, 135.8, 135.0, 62.5, 62.0, 51.9, 38.1, 27.4, 13.8 and 13.7.

**(*S*)-Diethyl 4-acetoxy-3-oxopent-1-ene-1,1-dicarboxylate 10d**

In the same manner as described for the preparation of compound **10b**, phosphorane **9d**[9b] (730 mg, 1.9 mmol) was treated with diethyl oxomalonate (326 mg, 1.9 mmol) to give *title compound* **10d** (530 mg, 99%) as an oil (Found: M + H$^+$, 287.1135. $C_{13}H_{19}O_7$ requires *m*/*z*, 277.1130); $[\alpha]_D^{25}$ −31.8 (*c* 0.24, MeOH); $\nu_{max}$(neat)/cm$^{-1}$ 1742, 1717 and 1630; $\delta_H$(300 MHz; $CDCl_3$) 7.25 (1 H, s, C*H*=), 5.25 (1 H, q, *J* 7, COCH), 4.36 (2 H, q, *J* 7, OC$H_2$CH$_3$), 4.31 (2 H, q, *J* 7, OC$H_2$CH$_3$), 2.15 (3 H, s, COC$H_3$), 1.45 (3 H, d, *J* 7, C$H_3$CH), 1.34 (3 H, t, *J* 7, OCH$_2$C$H_3$) and 1.33 (3 H, t, *J* 7, OCH$_2$C$H_3$); $\delta_C$(75 MHz; $CDCl_3$) 195.6, 170.2, 164.5, 162.5, 138.0, 131.4, 74.3, 62.6, 62.1, 20.5, 15.6, 13.8 and 13.7.

**Ethyl 5-[bis(ethoxycarbonyl)methyl]-2-ethoxy-4-methylcyclopenta-1,3-dienecarboxylate 11a**

In the same manner as described for the preparation of compound **6a**, phosphorane **1** (412 mg, 1.0 mmol) was treated with compound **10a** (235 mg, 1.1 mmol) to give the *cyclopentadiene* **11a** (333 mg, 94%) as needles, mp 33.5–35.0 °C (from hexane–diethyl ether) (Found: H, 7.25; C, 60.73%; M$^+$, 354.1678. $C_{18}H_{26}O_7$ requires H, 7.39; C, 61.00%; *M*, 354.1677); $\nu_{max}$(neat)/cm$^{-1}$ 1734, 1701, 1665, 1624 and 1559; $\delta_H$(300 MHz; $CDCl_3$) 6.22 (1 H, br s, 3-H), 4.71 (1 H, d, *J* 3.5, 5-CH), 4.30–4.14 (6 H, m, OC$H_2$CH$_3$), 4.10–4.01 (2 H, m, OC$H_2$CH$_3$), 3.92 (1 H, d, *J* 3.5, 5-H), 2.09 (3 H, d, *J* 1.5, 4-Me), 1.39 (3 H, t, *J* 7, OCH$_2$C$H_3$), 1.31 (3 H, t, *J* 7, OCH$_2$C$H_3$), 1.30 (3 H, t, *J* 7, OCH$_2$C$H_3$) and 1.17 (3 H, t, *J* 7, OCH$_2$C$H_3$); $\delta_C$(75 MHz; $CDCl_3$) 169.5, 169.0, 167.2, 163.5, 158.1, 121.9, 104.1, 66.9, 61.7, 60.9, 59.2, 50.9, 49.9, 17.2, 15.1, 14.5, 14.1 and 14.0; $\lambda_{max}$(MeOH)/nm 308.0 ($\varepsilon$/dm$^3$ mol$^{-1}$ cm$^{-1}$ 7800).

**Ethyl 5-[bis(ethoxycarbonyl)methyl]-2-ethoxy-4-ethylthiocyclopenta-1,3-dienecarboxylate 11b**

In the same manner as described for the preparation of compound **6a**, phosphorane **1** (412 mg, 1.0 mmol) was treated with compound **10b** (286 mg, 1.1 mmol) to give the *cyclopentadiene* **11b** (348 mg, 87%) as needles, mp 78.5–80.0 °C (from hexane–diethyl ether) (Found: H, 6.92; C, 57.08; S, 7.76%; M$^+$, 400.1561. $C_{19}H_{28}O_7S$ requires H, 7.05; C, 56.98; S, 8.01%; *M*, 400.1554); $\nu_{max}$(neat)/cm$^{-1}$ 1736, 1701, 1659 and 1597; $\delta_H$(300 MHz; $CDCl_3$) 6.09 (1 H, s, 3-H), 4.62 (1 H, d, *J* 4, 5-CH), 4.32–4.04 (9 H, m, OC$H_2$CH$_3$ and 5-H), 2.90 (2 H, q, *J* 7.5, SC$H_2$CH$_3$), 1.40 (3 H, t, *J* 7, OCH$_2$C$H_3$), 1.37 (3 H, t, *J* 7.5, SCH$_2$C$H_3$), 1.32 (3 H, t, *J* 7, OCH$_2$C$H_3$), 1.29 (3 H, t, *J* 7, OCH$_2$C$H_3$) and 1.18 (3 H, t, *J* 7, OCH$_2$C$H_3$); $\delta_C$(75 MHz; $CDCl_3$) 168.9, 168.7, 166.5, 163.0, 158.4, 116.5, 103.5, 67.0, 61.6, 60.8, 59.1, 52.0, 49.9, 27.1, 15.0, 14.5, 14.0, 14.0 and 13.0; $\lambda_{max}$(MeOH)/nm 345.0 ($\varepsilon$/cm$^3$ mol$^{-1}$ cm$^{-1}$ 12 700) and 233.5 (13 700).

**Ethyl 5-[bis(ethoxycarbonyl)methyl]-2-ethoxy-4-[2-(methoxycarbonyl)ethyl]cyclopenta-1,3-dienecarboxylate 11c**

In the same manner as described for the preparation of compound **6a**, phosphorane **1** (412 mg, 1.0 mmol) was treated with compound **10c** (315 mg, 1.1 mmol) to give the *cyclopentadiene* **11c** (345 mg, 81%) as needles, mp 58.3–59.6 °C (from diethyl ether–hexane) (Found: H, 7.15; C, 59.26. $C_{21}H_{30}O_9$ requires H, 7.09; C, 59.14%); $\nu_{max}$(KBr)/cm$^{-1}$ 1732, 1663, 1622 and 1557; $\delta_H$(300 MHz; $CDCl_3$; assignments were assisted by a $^1$H–$^1$H COSY experiment) 6.23 (1 H, br s, C*H*=), 4.70 (1 H, d, *J* 3.5, 5-CH), 4.36–4.00 (8 H, m, OC$H_2$CH$_3$), 4.31 (1 H, dd, *J* 3.5 and 1, 5-H), 3.67 (3 H, s, OC$H_3$), 2.85–2.51 (4 H, m, 4-C$H_2$C$H_2$), 1.39 (3 H, t, *J* 7, OCH$_2$C$H_3$), 1.32 (3 H, t, *J* 7, OCH$_2$C$H_3$), 1.30 (3 H, t, *J* 7, OCH$_2$C$H_3$) and 1.16 (3 H, t, *J* 7, OCH$_2$C$H_3$); $\delta_C$(75 MHz; $CDCl_3$) 173.1, 169.5, 168.5, 167.2, 163.6, 160.1, 121.1, 104.7, 66.9, 61.8, 60.9, 59.2, 51.6, 51.0, 48.8, 32.7, 25.9, 14.9, 14.4, 13.9 and 13.8; $\lambda_{max}$(MeOH)/nm 305.0 ($\varepsilon$/dm$^3$ mol$^{-1}$ cm$^{-1}$ 8800) and 230.0 (5500).

**Ethyl 2-[bis(ethoxycarbonyl)methyl]-3-methyl-5-oxocyclopent-3-enecarboxylate 12a**

In the same manner as described for hydrolysis of compound **6a** with aq. HCl, the cyclopentadiene **11a** (167 mg, 0.47 mmol) was hydrolyzed to give the *cyclopentenone* **12a** (138 mg, 90%) as an oil (Found: M$^+$, 326.1342. $C_{16}H_{22}O_7$ requires *M*, 326.1364); $\nu_{max}$(neat)/cm$^{-1}$ 1736, 1709 and 1626; $\delta_H$(300 MHz; $CDCl_3$) 5.96 (1 H, br s, 4-H), 4.24 (2 H, q, *J* 7, OC$H_2$CH$_3$), 4.22 (2 H, q, *J* 7, OC$H_2$CH$_3$), 4.16 (2 H, q, *J* 7, OC$H_2$CH$_3$), 3.87 (2 H, m, 2-H and 2-CH), 3.71 (1 H, d, *J* 2.5, 1-H), 2.18 (3 H, s, 3-Me), 1.32 (3 H, t, *J* 7, OCH$_2$C$H_3$), 1.27 (3 H, t, *J* 7, OCH$_2$C$H_3$) and 1.22 (3 H, t, *J* 7, OCH$_2$C$H_3$); $\delta_C$(75 MHz; $CDCl_3$) 200.2, 176.7, 168.6, 167.6, 166.9, 130.7, 62.1, 62.0, 61.8, 56.2, 51.4, 47.3, 17.5, 14.2, 14.0 and 14.0.

**Ethyl 2-[bis(ethoxycarbonyl)methyl]-3-ethylthio-5-oxocyclopent-3-enecarboxylate 12b**

In the same manner as described for hydrolysis of compound **6a** with aq. HCl, the cyclopentadiene **11b** (200 mg, 0.5 mmol) was hydrolyzed to give the *cyclopentenone* **12b** (175 mg, 94%) as an oil (Found: H, 6.62; C, 54.98; S, 8.53%; M$^+$, 372.1214. $C_{17}H_{24}O_7S$ requires H, 6.50; C, 54.82; S, 8.61%; *M*, 372.1241); $\nu_{max}$(neat)/cm$^{-1}$ 1736, 1699, 1549 and 1449; $\delta_H$(300 MHz;

$CDCl_3$) 5.91 (1 H, d, *J* 1.5, 4-H), 4.24 (2 H, q, *J* 7, $OCH_2CH_3$), 4.21 (2 H, q, *J* 7, $OCH_2CH_3$), 4.17 (2 H, q, *J* 7, $OCH_2CH_3$), 4.04 (1 H, ddd, *J* 1.5, 3 and 4.5, 2-H), 3.92 (1 H, d, *J* 4.5, 2-CH), 3.84 (1 H, d, *J* 3, 1-H), 2.96 (2 H, q, *J* 7.5, $SCH_2CH_3$), 1.39 (3 H, t, *J* 7.5, $SCH_2CH_3$), 1.31 (3 H, t, *J* 7, $OCH_2CH_3$), 1.27 (3 H, t, *J* 7, $OCH_2CH_3$) and 1.23 (3 H, t, *J* 7, $OCH_2CH_3$); $\delta_C$(75 MHz; $CDCl_3$) 196.0, 179.2, 168.6, 167.4, 166.4, 123.0, 62.2, 61.8, 56.2, 52.4, 46.6, 27.5, 14.2, 14.0, 13.9 and 13.0.

**Ethyl 2-[bis(ethoxycarbonyl)methyl]-3-[2-(methoxycarbonyl)-ethyl]-5-oxocyclopent-3-enecarboxylate 12c**

In the same manner as described for hydrolysis of compound **6a** with aq. HCl, the cyclopentadiene **11c** (100 mg, 0.23 mmol) was hydrolyzed to give the *cyclopentenone* **12c** (89 mg, 95%) as an oil (Found: $M^+$, 398.1608. $C_{19}H_{26}O_9$ requires *M*, 398.1575); $\nu_{max}$(neat)/$cm^{-1}$ 1738, 1709 and 1620; $\delta_H$(300 MHz; $CDCl_3$; assignments were assisted by a $^1H$–$^1H$ COSY experiment) 5.94 (1 H, br s, C*H*=), 4.24 (2 H, *J* 7, $OCH_2CH_3$), 4.22 (2 H, *J* 7, $OCH_2CH_3$), 4.16 (2 H, *J* 7, $OCH_2CH_3$), 3.91 (2 H, br s, 2-H and 2-CH), 3.73 (1 H, d, 2.5, 1-H), 3.72 (3 H, s, $OCH_3$), 2.88–2.61 (4 H, m, 3-$CH_2CH_2$), 1.31 (3 H, t, *J* 7, $OCH_2CH_3$), 1.27 (3 H, t, *J* 7, $OCH_2CH_3$) and 1.22 (3 H, t, *J* 7, $OCH_2CH_3$); $\delta_C$(75 MHz; $CDCl_3$) 200.0, 178.7, 172.3, 168.5, 167.7, 166.9, 129.0, 62.1, 62.0, 61.8, 56.0, 52.0, 51.3, 46.4, 31.1, 26.1, 14.0, 13.9 and 13.8.

**(*E*)-Ethyl 2-[bis(ethoxycarbonyl)methyl]-5-ethoxy-3-ethylidene-cyclopenta-1,4-dienecarboxylate 13**

In the same manner as described for the preparation of compound **6a**, phosphorane **1** (412 mg, 1.0 mmol) was treated with compound **10d** (303 mg, 1.1 mmol) to give the *fulvene* **13** (329 mg, 90%) as an oil (Found: $M^+$, 366.1706. $C_{19}H_{26}O_7$ requires *M*, 366.1677); $\nu_{max}$(neat)/$cm^{-1}$ 1732, 1638 and 1601; $\delta_H$(300 MHz; $CDCl_3$; assignments were assisted by $^1H$–$^1H$ COSY and NOESY experiments) 6.56 (1 H, qd, *J* 7.5 and 1, C*H*=), 5.50 (1 H, s, 2-CH), 5.46 (1 H, d, *J* 1, 4-H), 4.29 (2 H, q, *J* 7, 1-$CO_2CH_2CH_3$), 4.20 (4 H, q, *J* 7, $CO_2CH_2CH_3$), 4.01 (2 H, q, *J* 7, 5-$OCH_2CH_3$), 2.09 (3 H, d, *J* 7.5, $CH_3CH$=), 1.42 (3 H, d, *J* 7, 5-$OCH_2CH_3$), 1.33 (3 H, t, *J* 7, 1-$CO_2CH_2CH_3$) and 1.24 (6 H, t, *J* 7, $CO_2CH_2CH_3$); $\delta_C$(75 MHz; $CDCl_3$) 168.1, 163.9, 160.3, 140.8, 136.5, 134.8, 128.7, 89.6, 65.6, 61.7, 60.5, 49.5, 16.6, 14.3, 14.0 and 13.9; $\lambda_{max}$(MeOH)/nm 375 ($\varepsilon$/$dm^3$ $mol^{-1}$ $cm^{-1}$ 600), 289 (10 400) and 233 (15 100).

**(*Z*)-Ethyl 5-benzoylmethylene-2-ethoxy-4-phenylcyclopenta-1,3-dienecarboxylate 15**

In the same manner as described for the preparation compound **6a**, phosphorane **1** (412 mg, 1.0 mmol) was treated with 1,4-diphenylbut-2-yne-1,4-dione **14** (121 mg, 1.1 mmol) to give *title compound* **15** (344 mg, 92%) as purple prisms, mp 131.5–133.0 °C (from hexane–ethyl acetate) (Found: H, 5.98; C, 76.69. $C_{24}H_{22}O_4$ requires H, 5.92; C, 76.99%); $\nu_{max}$(Nujol)/$cm^{-1}$ 1717, 1667 and 1586; $\delta_H$(300 MHz; $CDCl_3$; assignments were assisted by $^1H$–$^1H$ COSY and NOESY experiments) 7.94 (2 H, br d, *J* 8.5, COPh), 7.54–7.41 (8 H, m, Ph), 6.76 (1 H, s, =C*H*COPh), 6.56 (1 H, s, 3-H), 4.37 (2 H, q, *J* 7, $OCH_2CH_3$), 3.81 (2 H, q, *J* 7, $OCH_2CH_3$), 1.47 (3 H, t, *J* 7, $OCH_2CH_3$) and 0.92 (3 H, t, *J* 7, $OCH_2CH_3$); $\delta_C$(75 MHz; $CDCl_3$) 194.0, 171.3, 163.1, 147.7, 142.7, 137.0, 133.5, 133.4, 133.1, 129.5, 129.0, 128.7, 128.6, 128.6, 120.1, 98.9, 67.5, 59.2, 15.3 and 13.9; $\lambda_{max}$(MeOH)/nm 458.0 ($\varepsilon$/$dm^3$ $mol^{-1}$ $cm^{-1}$ 2200), 424.5 (2200), 290.5 (13 500) and 241.0 (19 100).

**(*E*)-Ethyl 2-benzoylmethylene-5-oxo-3-phenylcyclopent-3-ene-carboxylate 16**

In the same manner as described for hydrolysis of compound **6a** with aq. HCl, the cyclopentadiene **15** (215 mg, 0.57 mmol) was hydrolyzed to give the *cyclopentenone* **16** (192 mg, 97%) as purple needles, mp 120.9–121.7 °C (from hexane–diethyl ether) (Found: H, 5.20; C, 76.09. $C_{22}H_{18}O_4$ requires H, 5.24; C, 76.29%); $\nu_{max}$(Nujol)/$cm^{-1}$ 1736, 1705, 1659 and 1603; $\delta_H$(300 MHz; $CDCl_3$; assignments were assisted by $^1H$–$^1H$ COSY and NOESY experiments) 7.87 (2 H, br d, *J* 8.5, COPh), 7.60–7.42 (8 H, m, Ph), 7.27 (1 H, dd, *J* 0.5 and 1.5, =C*H*COPh), 6.60 (1 H, d, *J* 0.5, 4-H), 4.66 (1 H, d, *J* 1.5, 1-H), 4.28 (2 H, q, *J* 7, $OCH_2CH_3$) and 1.33 (3 H, t, *J* 7, $OCH_2CH_3$); $\delta_C$(75 MHz; $CDCl_3$) 197.9, 189.8, 171.4, 165.8, 150.2, 137.9, 135.0, 133.3, 132.1, 130.7, 129.1, 128.7, 128.3, 128.2, 119.8, 61.9, 57.2 and 14.2; $\lambda_{max}$(MeOH)/nm 302.0 ($\varepsilon$/$dm^3$ $mol^{-1}$ $cm^{-1}$ 27 300).

**Methyl (5-*tert*-butoxycarbonyl-2-ethylthio-4-oxocyclopent-2-enyl)acetate 17**

Aq. NaOH (0.01 M; 24 $cm^3$, 2.4 mmol) was added to an ice-cooled solution of thioester **7e** (800 mg, 2.3 mmol) in MeOH (160 $cm^3$) and the mixture was stirred for 1 h at 0 °C. It was then neutralized with 1 M aq. HCl, and concentrated under reduced pressure. The remaining solution was extracted with diethyl ether and the extract was washed with water, dried and evaporated. The residue was purified by flash chromatography [hexane–ethyl acetate (5:1)] to give *title compound* **17** (538 mg, 74%) as needles, mp 54.5–55.2 °C (from diethyl ether–petroleum spirit) (Found: H, 6.99; C, 57.46; S, 9.97. $C_{15}H_{22}O_5S$ requires H, 7.05; C, 57.30; S, 10.20%); $\nu_{max}$(neat)/$cm^{-1}$ 1736, 1699 and 1549; $\delta_H$(300 MHz; $CDCl_3$) 5.86 (1 H, d, *J* 1.5, 3-H), 3.73–3.69 (1 H, br s, 1-H), 3.70 (3 H, s, $OCH_3$), 3.20 (1 H, d, *J* 3, 5-H), 2.94 (2 H, q, *J* 7.5, $SCH_2CH_3$), 2.89 (1 H, dd, *J* 16.5 and 4, $COCH_2$), 2.44 (1 H, dd, *J* 16.5 and 10, $COCH_2$), 1.49 (9 H, s, Bu$^t$) and 1.39 (3 H, t, *J* 7.5, $SCH_2CH_3$); $\delta_C$(75 MHz; $CDCl_3$) 196.7, 181.6, 171.1, 167.7, 122.2, 82.1, 60.3, 52.0, 44.2, 37.8, 28.0, 27.4 and 13.1.

**Methyl [5-*tert*-butoxycarbonyl-2-ethylthio-4-oxo-5-(pent-2-ynyl)-cyclopent-2-enyl]acetate 18**

A solution of sodium bis(trimethylsilyl)amide (NaHDMS) (1 M in THF; 2.6 $cm^3$) was added to a solution of the cyclopentenone **17** (670 mg, 2.13 mmol) in THF (40 $cm^3$) at −30 °C under nitrogen and the mixture was stirred for 2 h at 0 °C. A solution of 1-bromopent-2-yne (410 mg, 2.79 mmol) in THF (1 $cm^3$) was added and the mixture was stirred for 3 h at room temperature and then for 12 h at 60 °C. The cooled reaction mixture was poured into saturated aq. $NH_4Cl$ and extracted with diethyl ether. The extract was dried and evaporated. The residue was purified by flash chromatography [hexane–ethyl acetate (5:1)] to give *title compound* **18** (766 mg, 94%) as needles, mp 76.1–77.3 °C (from hexane) (Found: H, 7.36; C, 62.94; S, 8.33. $C_{20}H_{28}O_5S$ requires H, 7.42; C, 63.13; S, 8.43%); $\nu_{max}$(neat)/$cm^{-1}$ 1732, 1694 and 1551; $\delta_H$(300 MHz; $CDCl_3$) 5.98 (1 H, d, *J* 1.5, 3-H), 3.87 (1 H, ddd, *J* 1.5, 6 and 9, 1-H), 3.71 (3 H, s, OMe), 2.96 (2 H, q, *J* 7.5, $SCH_2CH_3$), 2.90–2.70 (4 H, m, 1- and 5-$CH_2$), 2.07 (2 H, tq, *J* 2.5 and 7.5, $CH_2CH_3$), 1.42 (3 H, t, *J* 7.5, $SCH_2CH_3$), 1.40 (9 H, s, Bu$^t$) and 1.03 (3 H, t, *J* 7.5, $CH_2CH_3$); $\delta_C$(75 MHz; $CDCl_3$) 199.9, 181.3, 171.7, 168.2, 122.9, 84.0, 82.7, 74.1, 62.6, 52.0, 47.4, 34.7, 27.8, 27.3, 23.6, 14.1, 13.1 and 12.4.

**Methyl [2-ethylthio-4-oxo-5-(pent-2-enyl)cyclopent-2-enyl]-acetate 19**

A solution of compound **18** (433 mg, 1.14 mmol), anisole (0.4 $cm^3$) and TFA (4 $cm^3$) in benzene (20 $cm^3$) was stirred at 0 °C for 1 h and then at 40 °C. After the starting material had disappeared completely (TLC, *ca.* 3 h), the reaction mixture was evaporated under reduced pressure at 60 °C. The residue was purified by flash chromatography [hexane–ethyl acetate (3:1)] to give *methyl* [2-*ethylthio*-4-*oxo*-5-(*pent*-2-*ynyl*)*cyclopent*-2-*enyl*]*acetate* (286 mg, 90%) as an oil (Found: $M^+$, 280.1128. $C_{15}H_{20}O_3S$ requires *M*, 280.1132); $\nu_{max}$(neat)/$cm^{-1}$ 1738, 1692 and 1545; $\delta_H$(300 MHz; $CDCl_3$) 5.93 (1 H, br s, 3-H), 3.71 (3 H, s, $OCH_3$), 3.35–3.29 (1 H, m, 1-H), 2.93 (2 H, q, *J* 7.5, $SCH_2CH_3$), 2.86 (1 H, dd, *J* 5 and 16.5, one of $COCH_2$), 2.67–2.35 (4 H, m, 5-H, 5-$CH_2$ and one of $COCH_2$), 2.10 (2 H, tq,

*J* 7.5 and 2.5, $CH_2CH_3$), 1.39 (3 H, t, *J* 7.5, $SCH_2CH_3$) and 1.06 (3 H, t, *J* 7.5, $CH_2CH_3$); $\delta_C$(75 MHz; $CDCl_3$) 203.7, 181.2, 171.5, 123.3, 83.5, 75.2, 51.8, 51.3, 45.5, 38.0, 27.0, 20.2, 14.1, 13.1 and 12.3.

The oil (140 mg, 0.5 mmol) was dissolved in EtOH (5 $cm^3$) and the solution was stirred with Pd/C (10%, 200 mg) under hydrogen (1 atm) for 2 h at room temperature. After filtration, the filtrate was evaporated under reduced pressure. The residue was purified by flash chromatography [hexane–ethyl acetate (3:1)] to give *title compound* **19** (141 mg, 100%) as an oil (Found: H, 8.05; C, 63.72; S, 11.30%; $M^+$, 282.1283. $C_{15}H_{22}O_3S$ requires H, 7.85; C, 63.80; S, 11.35%; *M*, 282.1288); $\nu_{max}$(neat)/$cm^{-1}$ 1738, 1692 and 1547; $\delta_H$(300 MHz; $CDCl_3$; assignments were assisted by a $^1H$–$^1H$ COSY experiment) 5.90 (1 H, br s, 3-H), 5.64–5.38 (1 H, m, 5-$CH_2CH$=C*H*), 5.34–5.18 (1 H, m, 5-$CH_2CH$=CH), 3.71 (3 H, s, $OCH_3$), 3.12–3.01 (1 H, m, 1-H), 2.92 (2 H, q, *J* 7.5, $SCH_2CH_3$), 2.78 (1 H, dd, *J* 5.5 and 16, one of $COCH_2$), 2.56–2.30 (4 H, m, 5-H, 5-$CH_2$ and one of $COCH_2$), 2.14–1.94 (2 H, m, $CH_2CH_3$), 1.38 (3 H, t, *J* 7.5, $SCH_2CH_3$) and 0.96 (3 H, t, *J* 7.5, $CH_2CH_3$); $\delta_C$(75 MHz; $CDCl_3$) 205.0, 180.9, 171.6, 134.6, 124.2, 123.4, 52.6, 51.9, 45.6, 38.8, 28.4, 27.1, 20.6, 14.2 and 13.1.

**(±)-Methyl [4-oxo-5-(pent-2-enyl)cyclopent-2-enyl]acetate [(±)-methyl dehydrojasmonate] 20**

Sodium borohydride (0.24 g, 6.3 mmol) was slowly added to a stirred solution of nickel chloride hexahydrate (0.71 g, 3.0 mmol) in EtOH (100 $cm^3$) and water (3 $cm^3$) at 0 °C over a period of 15 min, and the mixture was stirred for 10 min at room temperature. To the resulting black suspension was added a solution of compound **19** (72 mg, 0.26 mg) in EtOH (2 $cm^3$) and the mixture was stirred at room temperature for 2 h and then heated under reflux for 24 h. The cooled reaction mixture was filtered through Celite and the filtrate was evaporated under reduced pressure. After the residue had been shaken with brine and chloroform, the chloroform layer was dried and evaporated. The residue was purified by flash chromatography [hexane–ethyl acetate (3:1)] to give starting material **19** (23 mg, 32% recovery) and title compound **20** (27 mg, 47%) which showed spectral data consistent with those reported[9] for *(±)-methyl dehydrojasmonate,* $\delta_H$(300 MHz; $CDCl_3$; assignments were assisted by $^1H$–$^1H$ COSY experiment) 7.63 (1 H, dd, *J* 2.5 and 5.5, 2-H), 6.18 (1 H, dd, *J* 2 and 5.5, 3-H), 5.62–5.40 (1 H, m, 5-$CH_2CH$=C*H*), 5.36–5.20 (1 H, m, 5-$CH_2CH$=CH), 3.71 (3 H, s, $OCH_3$), 3.10–2.98 (1 H, m, 1-H), 2.64–2.20 (5 H, m, 1-$CH_2$, 5-H and 5-$CH_2$), 2.11–1.96 (2 H, m, $CH_2CH_3$) and 0.96 (3 H, t, *J* 7.5, $CH_2CH_3$); $\delta_C$(75 MHz; $CDCl_3$) 210.2, 171.8, 165.3, 134.5, 133.8, 124.4, 51.8, 51.0, 43.2, 38.2, 27.7, 20.6 and 14.2.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## References


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