[3 + 2]-Annulation using Allylidene(triphenyl)phosphoranes: a One-Step Synthesis of Cyclopentadienes

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A convenient method for the synthesis of substituted cyclopentadienes has been developed using allylidene(triphenyl)phosphoranes. (3-Ethoxycarbonyl-2-substituted-2-propenylidene)triphenylphosphoranes **1** reacted with α-halogenoketones under very mild reaction conditions to undergo a [3 + 2]-annulation leading to the regioselective formation of tri- or tetra-substituted cyclopentadienes in good to excellent yields. Allylidenephosphoranes **1** also reacted with *S*-ethyl bromoethanethioate to yield 4-ethylthiocyclopentadienes, which was readily converted into a cyclopentenone.

Five-membered carbocyclic ring formation has been much studied recently,[1] particularly with respect to intramolecular Wittig reactions. Several phosphoranes including (1-ethoxycarbonylcyclopropyl)triphenylphosphonium salts,[2] (phenyliminovinylidene)triphenylphosphorane[3] and (bromoacetylmethylene)triphenylphosphorane[4] have been developed for this purpose, the compounds acting as bifunctional reagents in the annulations. Allylidenephosphoranes may also function in this way, reacting with various electrophiles at the positions α or γ to the phosphorus atom.[5] However, the synthetic utility of

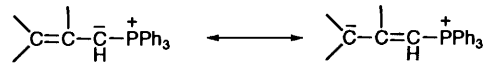


Fig. 1

phosphoranes in annulations has been little explored, except for cyclohexadiene formation with α,β-unsaturated aldehydes.[6] We have previously reported cyclopentene formation from glyoxals and cephalosporin 3'-triphenylphosphonium ylide, which is a highly resonance-stabilized allylidene(triphenyl)phosphorane.[7] The reaction takes place by way of an initial aldol condensation at the 2-position of the cephalosporin followed by an intramolecular Wittig reaction to give the tricyclic cephalosporin bearing the five-membered ring between C-2 and C-4. This finding suggests the possibility of five-membered ring formation by allowing allylidenephosphorane to react with ketones having an appropriate leaving group at the α-position.

In a previous communication we described that the stabilized allylidenephosphorane **1** reacted with α-halogenocarbonyl compounds to give substituted cyclopentadienes.[8] This paper describes the detail and the scope of this [3 + 2]-annulation.

Results and Discussion

We chose (2-substituted 3-ethoxycarbonylprop-2-enylidene)-triphenylphosphoranes **1a–c** as stabilized allylidenephosphoranes. The precursors, the phosphonium salts **2a** and **2c**, were prepared in the form of a *ca.* 1 : 1 mixture of the *E*- and *Z*-isomers according to the literature method,[9] and **2b** was prepared in the *Z* form from ethyl (*Z*)-4-bromo-3-phenylbut-2-enoate.

Because of the paucity of literature precedents,[10] the alkylation of allylidenephosphorane with alkyl halides gives an uncertain pattern of regioselectivity. In order to examine this feature of the reactions, **2a** was treated with Bu^{t}OK in THF to generate the phosphorane **1a**, which was subsequently treated with iodomethane to give the γ-methylated phosphonium

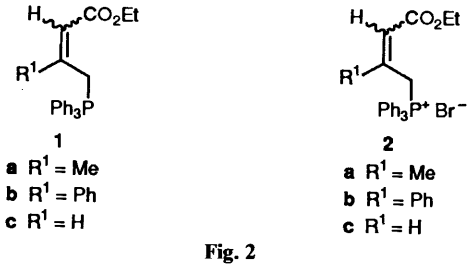
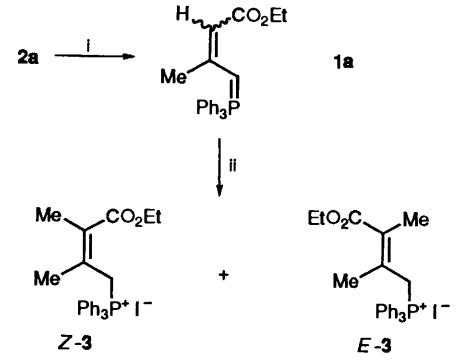


Fig. 2



Scheme 1 *Reagents and conditions:* i, Bu^{t}OK, THF; ii, MeI, THF

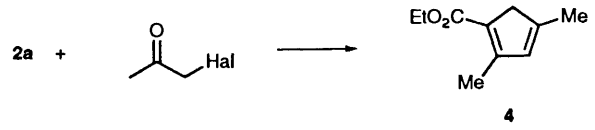
iodide **3** (75%); no other α-methylation product was detected. The ^{1}H NMR spectra showed that the γ-methylation product **3** was a *ca.* 3 : 1 mixture of two isomers, in which the major isomer was isolated in pure crystalline form. The 2-methyl protons and the ester O-methylene protons of the major isomer appeared to higher field than those of the minor isomer, indicating that the major and minor isomers have the structures *Z*-**3** and *E*-**3**, respectively. This is analogous to the observation of Howe for the conformers of the phosphonium bromide **2a**.[9] The 3-methyl protons of the major isomer resonated at 2.02 ppm as a double of triplet by long-range couplings with the phosphorus atom (*J* 4.0 Hz) and the 1-methylene protons (*J* 1.1 Hz). Thus, alkylation of the allylidenephosphorane **1a** was found to occur exclusively at the γ-position to the phosphorus atom.

Next, reaction of the phosphorane **1a** with an α-halogenoketone was examined. When a mixture of the phosphonium bromide **2a** and bromoacetone was stirred in dichloromethane in the presence of diisopropylethylamine, the desired cyclopentadiene **4** was obtained (66%). Some of the reaction conditions examined are listed in Table 1. Although the reaction

Table 1 Reaction of **2a** and halogenoacetone under various conditions

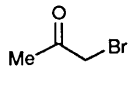
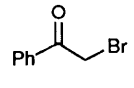
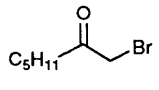
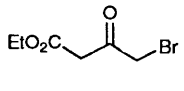
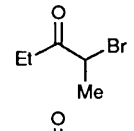
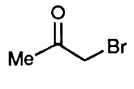
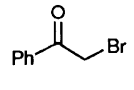
	Halogenoacetone	Reaction conditions[a]		Yield[b] of **4**
Entry	Hal	Base	Solvent	(%)
1	Br	Pr^i_2NEt	CH_2Cl_2	66
2	Br	Pr^i_2NEt	DMF	42
3	Br	K_2CO_3	MeCN	25
4	Br	$NaHCO_3$	CH_2Cl_2/H_2O	96
5	I	$NaHCO_3$	CH_2Cl_2/H_2O	62
6	Cl	$NaHCO_3$	CH_2Cl_2/H_2O	72

[a] All reactions were carried out at room temperature for 12 h. [b] Isolated yield based on the phosphonium bromide **2a**.



Scheme 2

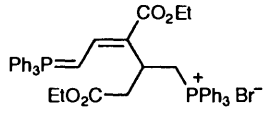
Table 2 Preparation of cyclopentadienes[a]

	Phosphonium		Cyclopentadiene	
Entry	bromide	Halogenoketone	No.	Yield[b] (%)
1	**2a**		**4**	96
2	**2a**		**5**	78
3	**2a**		**6**	71
4	**2a**		**7**	50
5	**2a**		**8**	72
6	**2b**		**9**	48
7	**2b**		**10**	23

[a] All reactions were carried out at room temperature for 12 h in a heterogeneous medium of CH_2Cl_2 and aqueous $NaHCO_3$. [b] Isolated yield based on the phosphonium bromide.

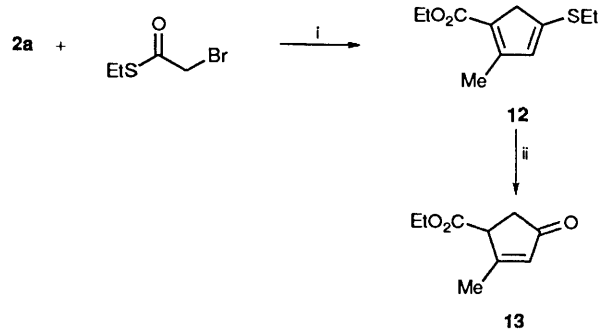
proceeds under anhydrous conditions using diisopropylethylamine and K_2CO_3 as the base, the best results were obtained in a heterogeneous medium of dichloromethane and saturated aqueous $NaHCO_3$, at room temperature under nitrogen, in which the annulation might be promoted by a phase-transfer reaction. Of the halogeno-acetones used, bromoacetone gave the highest yield of **4** (entry 4). The low yield with iodoacetone seems to be due to the instability of the iodide under the reaction conditions.

As can be seen from Table 2, the annulation is applicable to the preparation of the variety of cyclopentadienes. Primary bromides reacted with **2a** to give excellent yields of the corresponding cyclopentadienes (entries 1–4). A secondary bromide also underwent annulation with **2a** to give the tetrasubstituted cyclopentadiene **8** (72%) (entry 5). It is noteworthy that no competitive elimination of the halide was observed because of the very mild conditions. The 2-phenyl phosphonium bromide **2b** reacted with bromoacetone and bromoacetophenone to afford the 2-phenylcyclopentadienes **9** and **10**, respectively, although in lower yield compared with **2a**. This may be the result of the reduced reactivity of **2b** for steric and electronic reasons. The phosphonium bromide **2c** having no substituent at the 2-position failed to undergo annulation with bromoacetone. The easy dimerization of **2c** has been reported[11] to form the dimer **11**, which was, in fact, detected upon exposure of **2c** in the heterogeneous medium.



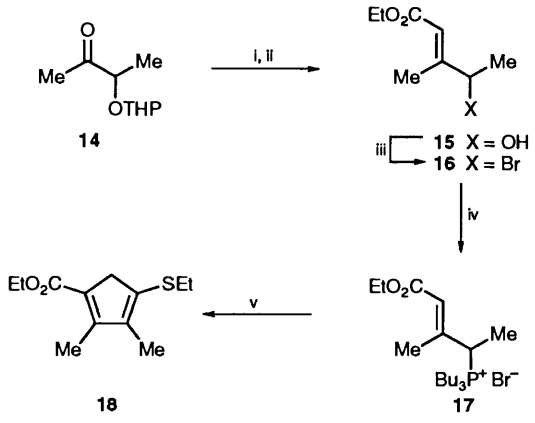
11

It has been reported that thioesters undergo an intramolecular Wittig reaction to produce cyclic thioenol ethers.[12] When *S*-ethyl bromoethanethioate was allowed to react with **2a**, the expected 4-ethylthiocyclopentadiene **12** was obtained (51%). The latter was converted by treatment with titanium tetrachloride[13] into the cyclopentenone **13** (75%).



Scheme 3 *Reagents and conditions:* i, $NaHCO_3$, CH_2Cl_2, H_2O; ii, $TiCl_4$, CH_2Cl_2, AcOH, then H_2O

To explore further the scope of the annulation, we prepared the secondary phosphonium bromide **17** from acetoin tetrahydropyranyl ether **14** by a straightforward sequence (Scheme 4) consisting of a Wittig–Horner reaction with triethyl phosphonoacetate, deprotection, bromination and then treatment



Scheme 4 *Reagents and conditions:* i, $(EtO)_2P(O)CH_2CO_2Et$, NaH, THF; ii, $HClO_4$, THF, H_2O; iii, PBr_3, CH_2Cl_2; iv, Bu_3P, benzene; v, Bu^{t}OK, $BrCH_2COSEt$, THF

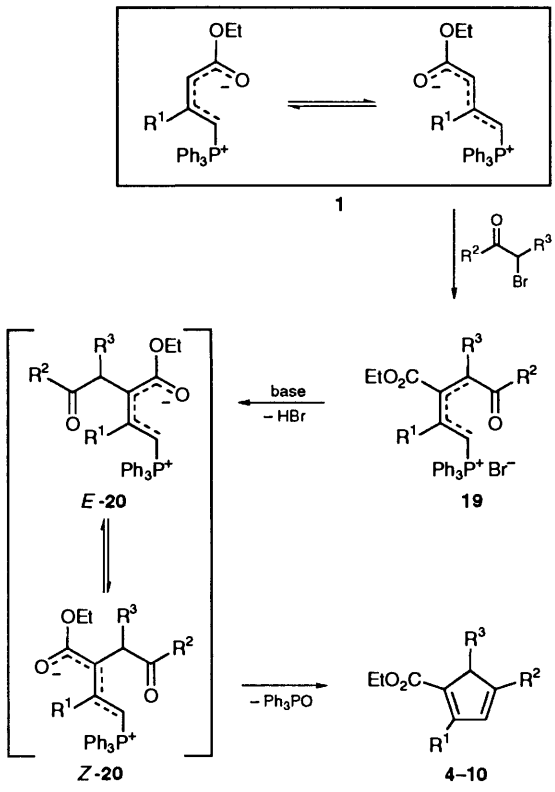
with tributylphosphine.* Attempted reaction of the phosphonium bromide **17** with *S*-ethyl bromoethanethioate in dichloromethane and saturated aqueous $NaHCO_3$ gave none of the expected cyclopentadiene **18**. Instead isolation of *S*-ethyl ethylthioethanethioate from the reaction mixture shows attendant hydrolysis of the bromide in the aqueous medium. The desired compound **18** was obtained under anhydrous conditions. Thus, the phosphonium bromide **17** was treated with an equivalent of Bu^{t}OK in THF and then *S*-ethyl bromoethanethioate. After disappearance of the yellow colour of the phosphorane the mixture was treated slowly with an additional equivalent of Bu^{t}OK to give **18** (23%). The resulting ethylthiocyclopentadiene **18** might be a precursor of methylenomycin.[14]

Although cyclopentadienes are known to undergo ready 1,5-sigmatropic migration,[15] those prepared above have the double bonds fixed at the 1- and 3-positions. Notable spectroscopic features are as follows: (1) UV absorption maxima appear in the region 285–302 nm for the 4-alkyl substituted cyclopentadienes **4** and **6–9**, and 331–340 for 4-phenyl- and 4-ethylthio-cyclopentadienes **5**, **10**, **12** and **18** due to the conjugated dienoic acid ester.

(2) In the ^1H NMR spectra of the 2-methyl series **4–8**, **12** and **18**, the homoallylic coupling (*J* 2.3–2.5) between the 5-protons and the 2-methyl protons was observed and the allylic coupling (*J* 0.7–1.0) between the 5-protons and 3-proton was also observed in many cases. The homoallylic coupling disappeared in 2-phenylcyclopentadienes **9** and **10**, in which the 5-methylene protons appeared as a doublet (*J* 1.0).

(3) The 5-methyl protons of **8** resonated at 1.22 ppm as a doublet (*J* 7.4). The cyclopentadienes are stable to 1,5-sigmatropic migration and unchanged when left at room temperature for several weeks. Furthermore, there was no migration of the double bonds of compound **4** when it was heated in refluxing toluene.

A plausible mechanism for the annulation is outlined in Scheme 5; it appears to proceed stepwise. The first step is nucleophilic substitution of the halides by the C-3 carbanion of the 1,4-dipole resonance form of **1**, leading to regioselective formation of the alkylated phosphonium salts **19**. Regeneration of the phosphorane **20** from **19** takes place smoothly by way of a phase-transfer reaction, a subsequent intramolecular Wittig reaction furnishing the cyclpentadienes **4–10**. The intermediate



Scheme 5

phosphorane would be a mixture of the two conformers *E*-**20** and *Z*-**20** as found in the γ-methylated phosphonium salt **3**. The formation of cyclopentadiene in high yield can be explained by ready interconversion of the conformers.†

In conclusion, we have developed an efficient [3 + 2] annulation for the regioselective synthesis of substituted cyclopentadienes in a single operation under very mild reaction conditions.

Experimental

All m.p.s were measured on a Gallenkamp micro melting point apparatus and are uncorrected. IR spectra were recorded on a Hitachi 260–10 spectrometer. ^1H NMR spectra were measured at 90 MHz on a Hitachi R-90H spectrometer or at 360 MHz on a Bruker AM-360 spectrometer, using $SiMe_4$ as the internal standard. ^{13}C NMR were recorded at 90 MHz on a Bruker AM-360 spectrometer or at 75 MHz on a Bruker MSL-300 spectrometer. Solvent peak ($CDCl_3$: δ_C 77.0) was used for the internal standard. Mass spectra were recorded on a Hitachi M-80B spectrometer.

Allyltriphenylphosphonium Bromides **2a–c**.—(3-Ethoxycarbonyl-2-methylprop-2-enyl)triphenylphosphonium bromide **2a** and (3-ethoxycarbonylprop-2-enyl)triphenylphosphonium bromide **2c** were prepared according to the literature method[9] as a mixture of the *E*- and *Z*-geometrical isomers and used without separation of the isomers. (*Z*)-(3-Ethoxycarbonyl-2-phenylprop-2-enyl)triphenylphosphonium bromide **2b** was prepared from ethyl (*Z*)-4-bromo-3-phenylbut-2-enoate[16] (366 mg, 1.36 mmol) by treatment with triphenylphosphine (360 mg, 1.37 mmol) in dry benzene (10 cm^3) for 3 days at 40 °C under N_2. The precipitates were filtered off and recrystallized from dichloromethane–benzene to give the phosphonium bromide (530 mg, 73%) as colourless crystals, m.p. 190–192 °C (decomp.) (Found: C, 67.6; H, 5.0; Br, 14.9. $C_{30}H_{28}BrO_2P$ requires C, 67.80; H, 5.31; Br, 15.04%); ν_{max}(Nujol)/cm^{-1} 1701, 1630, 1450, 1197, 1111, 761 and 698; δ_H(90 MHz; $CDCl_3$) 7.54–7.80 (15 H, m, Ph), 7.26 (5 H, br s, 2-Ph), 6.12 (2 H, d, *J* 17.4, PCH_2), 6.07 (1 H,

* Triphenylphosphine gave poor yield of the corresponding phosphonium bromide.

† Howe has reported that the allylidenetriphenylphosphorane **1a** and **1c** exist mainly as two conformers depicted in Scheme 5 in rapid equilibrium.[9]

d, *J* 5.5, =CHP), 3.90 (2 H, q, *J* 7.0, OCH_2CH_3) and 1.13 (3 H, t, *J* 7.0, OCH_2CH_3).

(3-Ethoxycarbonyl-2,3-dimethylprop-2-enyl)triphenylphosphonium Iodide **3**.—Potassium *tert*-butoxide (1.0 mol dm^{-3} in THF; 1.0 cm^3, 1.0 mmol) was added dropwise to a stirred suspension of **2a** (470 mg, 1.0 mmol) in dry THF at 0 °C under N_2 and the mixture was stirred for a further 30 min. To this cooled mixture was added iodomethane (0.1 cm^3, 1.6 mmol). The mixture was stirred for 2 days at room temperature. The precipitate was filtered off and dissolved in dichloromethane. Filtration and evaporation of the dichloromethane solution gave white crystals of the title compound (360 mg, 75%). An analytical sample was obtained by recrystallization from MeCN–ethyl acetate, m.p. 100–105 °C (decomp.) (Found: C, 59.3; H, 5.2. $C_{26}H_{28}IO_2P$ requires C, 58.88; H, 5.32%); δ_H(90 MHz; $CDCl_3$) 7.56–8.02 (15 H, m, Ph), 5.24 (2 H, d, *J* 17, PCH_2), 3.80 (2 H, q, *J* 7.1, OCH_2CH_3), 2.02 (3 H, dt, *J* 4.0 and 1.1, 3-Me), 1.81 (3 H, d, *J* 6.7, 2-Me) and 1.07 (3 H, q, *J* 7.1, OCH_2CH_3).

Ethyl 2,4-Dimethylcyclopenta-1,3-diene-1-carboxylate **4**: *General Procedure.—Method A*. Saturated aq. $NaHCO_3$ (10 cm^3) was layered on a solution of (3-ethoxycarbonyl-2-methylprop-2-enyl)triphenylphosphonium bromide **2a** (470 mg, 1.0 mmol) in dichloromethane (10 cm^3). To this well-stirred mixture was added a solution of bromoacetone (150 mg, 1.1 mmol) in dichloromethane (2 cm^3) and the mixture was stirred at room temperature for 12 h under N_2. The aqueous layer was separated and extracted with dichloromethane. The combined organic layers were washed with water, dried ($MgSO_4$), and evaporated under reduced pressure. The residue was passed through a short column of SiO_2 (eluent: hexane–ether, 1:1 v/v) and further purified by flash chromatography on SiO_2 to give the title compound as an oil (160 mg, 96%), b.p. 80 °C/0.2 mmHg (bath temp.) (Found: M^+, 166.100 79. $C_{10}H_{14}O_2$ requires *M*, 166.0993); ν_{max}(neat)/cm^{-1} 1703, 1630, 1560, 1190, 1078, 751 and 693; δ_H(360 MHz; $CDCl_3$) 6.05 (1 H, br s, 3-H), 4.20 (2 H, q, *J* 7.1, OCH_2CH_3), 3.22 (2 H, dq, *J* 0.8, 2.5, 5-H), 2.30 (3 H, t, *J* 2.5, 2-Me), 2.07 (3 H, d, *J* 1.6, 4-Me) and 1.30 (3 H, t, *J* 7.1, OCH_2CH_3); δ_C(90 MHz; $CDCl_3$) 164.96, 156.22, 150.86, 133.21, 126.71, 59.24, 45.96, 16.31, 15.41 and 14.54; λ_{max}(MeOH)/nm 285 (ε/dm^3 mol^{-1} cm^{-1} 13 300) and 229 (22 100); *m/z* 166 (M^+, 31%), 137 (8), 121 (30) and 93 (95).

Method B. To a solution of **2a** (470 mg, 1.0 mmol) in dichloromethane (10 cm^3) was added Pr^i_2NEt (0.5 cm^3, 2.3 mmol) and then bromoacetone (150 mg, 1.1 mmol) under N_2. The mixture was stirred for 12 h and concentrated under reduced pressure. The residue was purified by chromatography in a similar manner to that described above to give the title compound (109 mg, 66%).

Ethyl 2-Methyl-4-phenylcyclopenta-1,3-diene-1-carboxylate **5**.—In the same manner as described for the preparation (method A) of **4**, the phosphonium bromide **2a** (470 mg, 1.0 mmol) was treated with 2-bromoacetophenone (220 mg, 1.1 mmol) to give the title compound as needles (180 mg, 78%); m.p. 37–38 °C (hexane–ethyl acetate) (Found: C, 78.9; H, 6.8. $C_{15}H_{16}O_2$ requires C, 78.92; H, 7.06%); ν_{max}(Nujol)/cm^{-1} 1705, 1380, 1220, 1186, 1075 and 750; δ_H(360 MHz; $CDCl_3$) 7.28–7.57 (5 H, m, Ph), 6.75 (1 H, br s, 3-H), 4.25 (2 H, q, *J* 7.1, OCH_2CH_3), 3.70 (2 H, dq, *J* 0.8, 2.4, 5-H), 2.35, (3 H, t, *J* 2.4, 2-Me) and 1.35 (3 H, t, *J* 7.1, OCH_2CH_3); δ_C(75 MHz; $CDCl_3$) 165.08, 155.75, 150.53, 134.88, 131.87, 128.72, 128.04, 127.95, 125.60, 59.55, 42.08, 15.57 and 14.52; λ_{max}(MeOH)/nm 331 (ε/dm^3 mol^{-1} cm^{-1} 14 100) and 225 (10 400); *m/z* 228 (M^+, 71%), 199 (7) and 155 (100).

Ethyl 2-Methyl-4-pentylcyclopenta-1,3-diene-1-carboxylate **6**.—In the same manner as described for the preparation (method A) of **4**, the phosphonium bromide **2a** (470 mg, 1.0 mmol) was treated with 1-bromoheptan-2-one (210 mg, 1.1 mmol) to give the title compound as an oil (160 mg, 71%) (Found: M^+, 222.1591. $C_{14}H_{22}O_2$ requires *M*, 222.1619); ν_{max}(neat)/cm^{-1} 1700, 1622, 1558, 1077, 893 and 750; δ_H(360 MHz; $CDCl_3$) 6.06 1 H, br s, 3-H), 4.20 (2 H, q, *J* 7.0, OCH_2CH_3), 3.22 (2 H, dq, *J* 0.7, 2.5, 5-H), 2.38 (2 H, dt, *J* 1.2, 7.5, 4-CH_2), 2.31 (3 H, t, *J* 2.5, 2-Me), 1.54 (2 H, m, $CH_2CH_2CH_2CH_2CH_3$), 1.31 (3 H, t, *J* 7.0, OCH_2CH_3), 1.30 (4 H, m, $CH_2CH_2CH_2CH_2CH_3$) and 0.89 [3 H, t, *J* 7.1, $(CH_2)_4$-CH_3]; δ_C(75 MHz; $CDCl_3$) 165.17, 156.10, 156.05, 132.07, 126.51, 59.28, 44.34, 31.65, 30.92, 29.01, 22.53, 15.52, 14.54 and 14.02; λ_{max}(MeOH)/nm 291 (ε/dm^3 mol^{-1} cm^{-1} 11 500); *m/z* 222 (M^+, 36%) and 149 (15).

Ethyl 4-Ethoxycarbonyl-3-methylcyclopenta-1,3-dienylacetate **7**.—In the same manner as described for the preparation (method A) of **4**, the phosphonium bromide **2a** (470 mg, 1.0 mmol) was treated with ethyl 4-bromo-3-oxobutanoate (230 mg, 1.1 mmol) to give the title compound as an oil (100 mg, 50%) Found: C, 66.1; H, 7.0. $C_{13}H_{16}O_4$ requires C, 66.09; H, 6.83%); ν_{max}(neat)/cm^{-1} 1738, 1700, 1627, 1559, 1072, 900 and 750; δ_H(360 MHz; $CDCl_3$) 6.26 (1 H, br s, 3-H), 4.21 (2 H, q, *J* 7.0, OCH_2CH_3), 4.17 (2 H, q, *J* 7.1, OCH_2CH_3), 3.42 (2 H, d, *J* 1.4, 4-CH_2), 3.37 (2 H, dq, *J* 1.0, 2.4, 5-H), 2.32 (3 H, t, *J* 2.4, 2-Me), 1.31 (3 H, t, *J* 7.0, OCH_2CH_3) and 1.27 (3 H, t, *J* 7.1, OCH_2CH_3); λ_{max}(MeOH)/nm 285 (ε/dm^3 mol^{-1} cm^{-1} 10 700); *m/z* 238 (M^+, 65%), 193 (29) and 165 (47).

Ethyl 4-Ethyl-2,5-dimethylcyclopenta-1,3-diene-1-carboxylate **8**.—In the same manner as described for the preparation (method A) of **4**, the phosphonium bromide **2a** (470 mg, 1.0 mmol) was treated with 2-bromopentan-3-one (180 mg, 1.1 mmol) to give the title compound as an oil (140 mg, 72%) (Found: C, 73.9; H, 9.1. $C_{12}H_{15}O_2$ requires C, 74.19; H, 9.34%); ν_{max}(neat)/cm^{-1} 1695, 1619, 1552, 1074, 848 and 774; δ_H(360 MHz; $CDCl_3$) 5.96 (1 H, br s, 3-H), 4.14–4.31 (2 H, m, OCH_2CH_3), 3.20 (1 H, qq, *J* 7.5, 2.3, 5-H), 2.22–2.42 (2 H, m, 4-CH_2CH_3), 2.30 (3 H, 3, *J* 2.3, 2-Me), 1.32 (3 H, t, *J* 7.1, OCH_2CH_3), 1.22 (3 H, d, *J* 7.5, 5-Me) and 1.14 (3 H, t, *J* 7.4, 4-CH_2CH_3); δ_C(75 MHz; $CDCl_3$) 165.03, 163.50, 154.76, 132.63, 128.89, 59.18, 49.39, 22.09, 15.70, 14.77, 14.56 and 12.93; λ_{max}(MeOH)/nm 293 (ε/dm^3 mol^{-1} cm^{-1} 9800); *m/z* 194 (M^+, 91%), 149 (29) and 121 (100).

Ethyl 4-Methyl-2-phenylcyclopenta-1,3-diene-1-carboxylate **9**.—In the same manner as described for the preparation (method A) of **4**, the phosphonium bromide **2b** (540 mg, 1.0 mmol) was treated with bromoacetone (150 mg, 1.1 mmol) to give the title compound as an oil (114 mg, 50%) (Found: M^+, 228.1173. $C_{15}H_{16}O_2$ requires *M*, 228.1149); ν_{max}(neat)/cm^{-1} 1710, 1672, 1558, 1220, 1168, 898, 750 and 701; δ_H(360 MHz; $CDCl_3$) 7.27–7.50 (5 H, m, Ph), 6.28 (1 H, br s, 3-H), 4.11 (2 H, q, *J* 7.1, OCH_2CH_3), 3.45 (2 H, d, *J* 1.0, 5-H), 2.13 (3 H, d, *J* 1.5, 4-Me) and 1.17 (3 H, t, *J* 7.1, OCH_2CH_3); λ_{max}(MeOH)/nm 302 (ε/dm^3 mol^{-1} cm^{-1} 7400) and 232 (12 400); *m/z* 228 (M^+, 100%), 183 (33) and 155 (88).

Ethyl 2,4-Diphenylcyclopenta-1,3-diene-1-carboxylate **10**.—In the same manner as described for the preparation (method A) of **4**, the phosphonium bromide **2b** (540 mg, 1.0 mmol) was treated with 2-bromoacetophenone (220 mg, 1.1 mmol) to give the title compound as needles (67 mg, 23%), m.p. 88.5–89.2 °C (hexane–ethyl acetate) Found: C, 82.4; H, 6.1. $C_{20}H_{18}O_2$ requires C, 82.73; H, 6.25%); ν_{max}(Nujol)/cm^{-1} 1699, 1202, 1085, 778 and 741; δ_H(90 MHz; $CDCl_3$) 7.21–7.80 (10 H, m, Ph), 6.97 (1 H, t, *J*

0.9, 3-H), 4.17 (2 H, q, *J* 7.1, OCH_2CH_3), 3.95 (2 H, d, *J* 0.9, 5-H) and 1.21 (3 H, t, *J* 7.1, OCH_2CH_3); λ_{max}(MeOH)/nm 340 (ε/dm^3 mol^{-1} cm^{-1} 15 200) and 262 (16 600); *m*/*z* 290 (M^+, 100%), 245 (17) and 217 (97).

Ethyl 4-Ethylthio-2-methylcyclopenta-1,3-diene-1-carboxylate **12**.—In the same manner as described for the preparation (method A) of **4**, the phosphonium bromide **2a** (470 mg, 1.0 mmol) was treated with *S*-ethyl bromoethanethioate (200 mg, 1.1 mmol) to give the title compound as an oil (110 mg, 51%) (Found: M^+, 212.0855. $C_{11}H_{16}O_2S$ requires *M*, 212.0870); ν_{max}(neat)/cm^{-1} 1698, 1607, 1497, 1240, 1072, 892 and 750; δ_H(360 MHz; $CDCl_3$) 6.05 (1 H, br s, 3-H), 4.20 (2 H, q, *J* 7.0, OCH_2CH_3), 3.43 (2 H, t, *J* 2.4, 5-H), 2.90 (2 H, q, *J* 7.4, SCH_2CH_3), 2.31 (3 H, t, *J* 2.4, 2-Me), 1.36 (3 H, t, *J* 7.4, SCH_2CH_3) and 1.30 (3 H, t, *J* 7.0, OCH_2CH_3); δ_C(75 MHz; $CDCl_3$) 164.48, 155.93, 149.64, 129.24, 125.54, 59.34, 44.92, 26.62, 15.44, 14.52 and 13.90; λ_{max}(MeOH)/nm 335 (ε/dm^3 mol^{-1} cm^{-1} 9300); *m*/*z* 212 (M^+, 79%), 183 (14), 167 (29) and 139 (75).

Ethyl 2-Methyl-4-oxocyclopent-2-ene-1-carboxylate **13**.—Titanium tetrachloride (0.1 cm^3, 0.9 mmol) was added to a stirred solution of **12** (88 mg, 0.42 mmol) in a mixture of dry dichloromethane (7 cm^3) and acetic acid (7 cm^3) at 0 °C and the mixture was further stirred for 30 min at 0 °C. To this mixture water (0.04 cm^3, 2.2 mmol) was added and the mixture was stirred for 12 h at room temperature. The reaction mixture was poured into ice–water. The organic layer was separated and the aqueous layer was extracted with dichloromethane. The combined organic layers were washed successively with water, saturated aq. $NaHCO_3$ and brine, dried ($MgSO_4$), and evaporated under reduced pressure. The residue was purified by flash chromatography (eluent: hexane–ether, 3:1 v/v) to give the title compound as an oil (50 mg, 73%), which showed spectral data identical with those reported.[17]

Ethyl (E)-4-*Hydroxy-3-methylpent-2-enoate* **15**.—Sodium hydride (60% dispersion in mineral oil; 3.0 g, 75 mmol) was added portionwise to a solution of triethyl phosphonoacetate (13.3 g, 59.4 mmol) in dry THF (30 cm^3) and the mixture was further stirred for 30 min. To this mixture was added a solution of **14**[18] (9.7 g, 57 mmol) in dry THF (20 cm^3). The mixture was stirred for 24 h at room temperature and then poured into saturated aq. NH_4Cl (30 cm^3) and extracted with ethyl acetate. The extract was washed with brine, dried ($MgSO_4$), and evaporated under reduced pressure. The residue was purified by chromatography on SiO_2 to give ethyl (*E*)-4-[(tetrahydro-2*H*-pyran-2-yl)oxy]-3-methylpent-2-enoate as an oil (10.2 g, 74%).

The whole product was dissolved in THF (100 cm^3) and treated with a mixture of perchloric acid (*ca.* 70%; 4 cm^3) and water (20 cm^3). The mixture was stirred for 6 h at room temperature. The THF was evaporated under reduced pressure and the remaining residue was extracted with ethyl acetate. The extract was washed with brine, dried ($MgSO_4$), and evaporated under reduced pressure. The residue was distilled under reduced pressure to give the title compound as a colourless oil (6.0 g, 67%), b.p. 95–105 °C/0.3 mmHg (lit.,[19] b.p. 72–75 °C/0.1 mmHg).

Ethyl 4-Bromo-3-methylpent-2-enoate **16**.—Phosphorus tribromide (3.2 g, 11.8 mmol) was added to a solution of **15** (4.77 g, 30 mmol) in dichloromethane (30 cm^3) at 0 °C and the mixture was further stirred for 20 h at room temperature before being poured into saturated aq. $NaHCO_3$ (30 cm^3). The organic layer was separated and the aqueous layer was extracted with dichloromethane. The combined organic layers were washed with brine, dried ($MgSO_4$), and evaporated under reduced pressure. The residue was distilled under reduced pressure to give the title compound (3.1 g, 47%), b.p. 75 °C/2 mmHg (Found: M^+, 220.0081. $C_8H_{13}BrO_2$ requires *M*, 220.0099); ν_{max}(neat)/cm^{-1} 1715, 1642, 1221 and 1158; δ_H(90 MHz; $CDCl_3$) 5.91 (1 H, q, *J* 1.0, 2-H), 4.65 (1 H, q, *J* 7.0, 4-H), 4.17 (2 H, q, *J* 7.0, OCH_2CH_3), 2.27 (3 H, d, *J* 1.3, 3-Me), 1.80 (3 H, d, *J* 7.0, 5-H) and 1.28 (3 H, t, *J* 7.0, OCH_2CH_3).

(1-Ethoxycarbonyl-2-methylbut-1-en-3-yl)tributylphosphonium Bromide **17**.—Tributylphosphine (2.0 g, 10 mmol) was added to a solution of **16** (2.0 g, 9.0 mmol) in dry benzene (30 cm^3) under N_2 and the mixture was refluxed for 10 h. The solvent was evaporated under reduced pressure and the residue was purified by chromatography on SiO_2 (eluent: ethyl acetate–MeOH, 10:1 v/v) to give the title compound as an oil (3.78 g, 96%); ν_{max}(neat)/cm^{-1} 1710, 1641, 1471, 1227 and 1164; δ_H(300 MHz; $CDCl_3$) 6.16 (1 H, m), 4.48 (1 H, dq, *J* 17.1, 7.4, 1-H), 4.18 (2 H, q, *J* 7.0, OCH_23H_3), 2.62–2.40 (6 H, m, PCH_2), 2.29 (3 H, d, *J* 2.9, 2-Me), 1.70–1.48 (15 H, m, 1-Me, $PCH_2CH_2CH_2$), 1.28 (3 H, t, *J* 7.2, OCH_2CH_3) and 0.98 ([9 H, t, *J* 6.9, $P(CH_2)_3CH_3$]; *m*/*z* (FAB) 343 (M^+ − Br).

Ethyl 4-Ethylthio-2,3-dimethylcyclopenta-1,3-diene-1-carboxylate **18**.—Potassium *tert*-butoxide (1.0 mol dm^{-3} in THF; 1.0 cm^3, 1 mmol) was added slowly to a stirred suspension of **17** (430 mg, 1.0 mmol) in dry THF (20 cm^3) at 0 °C under N_2 and allowed to warm to room temperature over 1 h. To this yellow suspension was added *S*-ethyl bromoethanethioate (210 mg, 1.1 mmol) and the mixture was stirred for 2 h until the yellow colour disappeared. To the suspension was added slowly Bu^{t}OK (1.0 mol dm^{-3} in THF; 1.0 ml, 1 mmol) over 2 h and the mixture was further stirred for 1 d. The mixture was poured into water and extracted with ether. The extract was washed with brine, dried ($MgSO_4$), and evaporated under reduced pressure. The residue was purified by flash chromatography on SiO_2 (eluent: hexane–ether) to give the title compound as an oil (52 mg, 23%) (Found: M^+, 226.0990. $C_{12}H_{18}O_2S$ requires *M*, 226.1027); ν_{max}(neat)/cm^{-1} 1699, 1537, 1380, 1230 and 1062; δ_H(90 MHz; $CDCl_3$) 4.22 (2 H, q, *J* 7.0, OCH_2CH_3), 3.36 (2 H, br s, 5-H), 2.90 (2 H, q, *J* 7.0, SCH_2CH_3), 2.29 (3 H, t, *J* 2.4, 2-Me), 1.90 (3 H, br s, 3-Me), 1.31 (3 H, t, *J* 7.0, SCH_2CH_3) and 1.27 (3 H, t, *J* 7.0, OCH_2CH_3); λ_{max}(MeOH)/nm 339 (ε/dm^3 mol^{-1} cm^{-1} 7200).

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