Electrophilic Substitution of β,γ-Unsaturated Esters and Ketones using Phenyl Vinyl Sulphoxide as a Vinyl Cation Synthon

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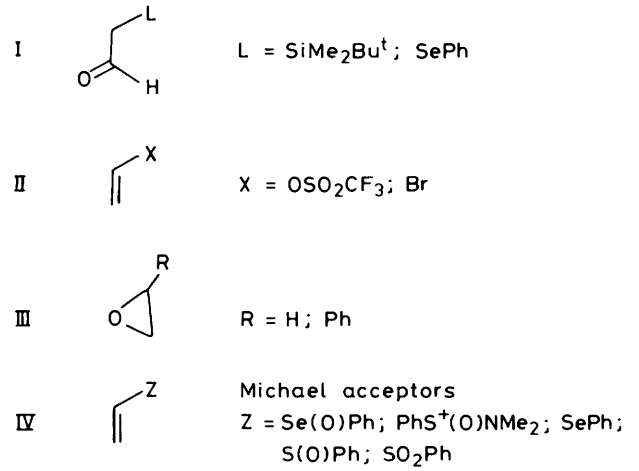
This paper describes a number of examples in which phenyl vinyl sulphoxide is used as a vinyl cation equivalent to react with sterically hindered, charge-stabilized anions derived from α-alkyl-β,γ-unsaturated ketones and esters. With the β,γ-enones(**4**), (**7**), and (**22**), the Michael addition proved to proceed effectively upon using a catalytic amount of base and t-butyl alcohol as solvent. Pyrolysis of the addition product and subsequent distillation *in vacuo* afforded the β,γ;β′,γ′-dienones in good yields. The α,β-enone (**1**) and the β,γ-unsaturated esters (**10**) and (**15**) reactions were performed using sodium hydride as base in benzene. Pyrolysis of the Michael addition products (**2**), (**11**), and (**16**) yielded the β,γ;β′,γ′-dienone (**3**) and the β,γ;β′,γ′-unsaturated esters (**12**) and (**17**). The β,γ;β′,γ′-dienones (**13**), (**14**), (**18**), and (**19**) have been obtained by subsequent saponification of the two esters, conversion of the resulting carboxylic acids into the corresponding acyl chlorides, and reaction of the latter with dimethyl- or diphenyl-cuprate.

Electrophilic vinylation at a tertiary carbon adjacent to the carbonyl group (hereafter referred to as the tertiary α-carbon), of esters or ketones has been developed only to a very limited extent. Most of the methods described suffer from the difficulty of generating vinyl carbenium ions,[1] the limited availability of powerful electrophilic synthons,[2] and the poor nucleophilicity of the carbanion of the carbonyl compound. A variety of types of vinyl cation equivalents have been used (Scheme 1).



Scheme 1. Vinyl cation synthons

Hudrlik[2] introduced the α-silyl aldehydes (synthon I, with L = $SiMe_2Bu^t$). These synthons react smoothly with ketone enolates to yield β-hydroxysilanes, which upon treatment with BF_3·Et_2O yield the desired β,γ-enones. Also α-selenoaldehydes (I, L = SePh)[3] have been used to introduce a vinyl group at the β-position of lithium[3] or zinc[4] enolates.† Reaction of the resulting β-hydroxy selenide intermediate with mesyl chloride in the presence of triethylamine leads to the formation of β,γ-enones in good yields.[3,4] There have been no reported attempts to effect the electrophilic vinylation of β,γ-enones.

The electrophilic vinylation of lithium dienolates using vinyl halogenides (II, X = Br) in the presence of $NiBr_2$ and Bu^nLi has been examined by Rathke.[5] This conversion surprisingly led to γ-substitution in contrast to most other electrophilic reagents which lead to α-substitution.[6]

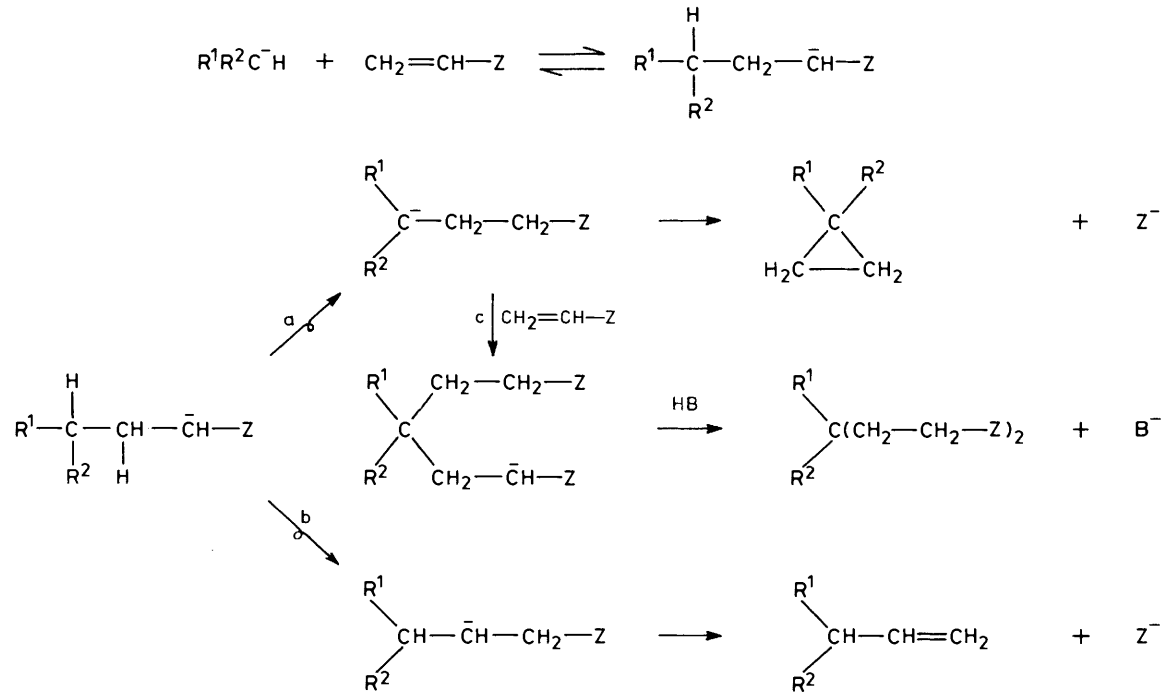
Vinyl substitution using epoxides has only rarely been applied. Epoxides (III) are known to react with dianions of carboxylic acids, but the resulting addition product upon acidification is converted into the corresponding lactone[7,8] instead of the β,γ-unsaturated acid which we wanted.

In view of the highly satisfactory elimination properties of selenoxides, the potential of aryl vinyl selenoxides [IV, Z = Se(O)Ar] was investigated in a Michael addition using lithium enolates.[9] However, intramolecular proton-transfer (Scheme 2) of the 1,4-addition products (also observed in the addition product of the anions of β,γ-enones to phenyl vinyl sulphoxide, see later) leads to a fast elimination of $ArSeO^-$ with formation of cyclopropyl ketones. Johnson[10] examined this type of ethylene transfer to nucleophiles using salts derived from sulphoximines [IV, Z = $PhS^+(O)NMe_2$]. The application of phenyl vinyl selenides appears to be a satisfactory alternative[11] for the cationic vinyl substitution, provided that strong nucleophiles such as alkyl-lithiums are used in the Michael addition.

Ethylenic sulphoxides[12a] and sulphones[13a] proved to be versatile reagents for the introduction of a C_2-fragment,[12b,13b] and are particularly useful vinyl cation synthons.[12c] Therefore, we have studied the ethylinic substitution of the tertiary α-carbon of β,γ-enones for the preparation of the β,γ;β′,γ′-dienones, using phenyl vinyl sulphoxide as a vinyl cation synthon. Although the preparation of these dienones has not previously been reported, their photochemical formation (in low yield) from β,γ;δ,ε-dienones by a 1,3-acyl shift upon direct irradiation at λ 300 nm has been noted.[14]

A practical method to obtain α-alkenyl ketones starting from α-chloro ketones and lithium or Grignard alkynylides has recently been reported by Wender.[15]

† N.B. The β-position of an enolate is the α-position of the derived ketone.



Scheme 2. Michael addition to CH_2=CHZ and subsequent intramolecular proton-transfer followed by elimination of Z^-

Table. Vinylation of β,γ-unsaturated esters and ketones using phenyl vinyl sulphoxide in a Michael addition, subsequent pyrolysis, and conversion into β,γ-enones

Substrate	(Equiv.)	Base	(Equiv.)	Solvent	Sulphoxide addition product (%)	Pyrolysis product (%)	Conversion into β,γ;β′,γ′-dienone (%)
(1)	1.0	NaH	0.10	THF	(2) 0		
	1.0	NaH	0.10	Benzene	92	(3) 61	
(4)	1.0	NaH	0.10	THF	(5) 6		
	1.0	NaH	1.0	THF	≤5		
	1.0	Bu^{t}OK	0.10	THF	5–8		
	1.0	Bu^{t}OK	0.10	Bu^{t}OH	54	(6) 62	
(7)	1.0	Bu^{t}OK	0.10	Bu^{t}OH	(8) 37	(9) 55	
(10)	1.15	NaH	0.15	Benzene	(11) 77	(12) 65	(13) 58
							(14) 43
(15)	1.15	NaH	0.15	Benzene	(16) 78	(17) 64	(18) 62
							(19) 23
(20)	1.0	NaH	0.15	THF	(21) ≤5		
	1.0	Bu^{t}OK	0.15	Bu^{t}OH	5–10		
(22)	1.0	Bu^{t}OK	0.10	Bu^{t}OH	(23) 21	(24) 48	

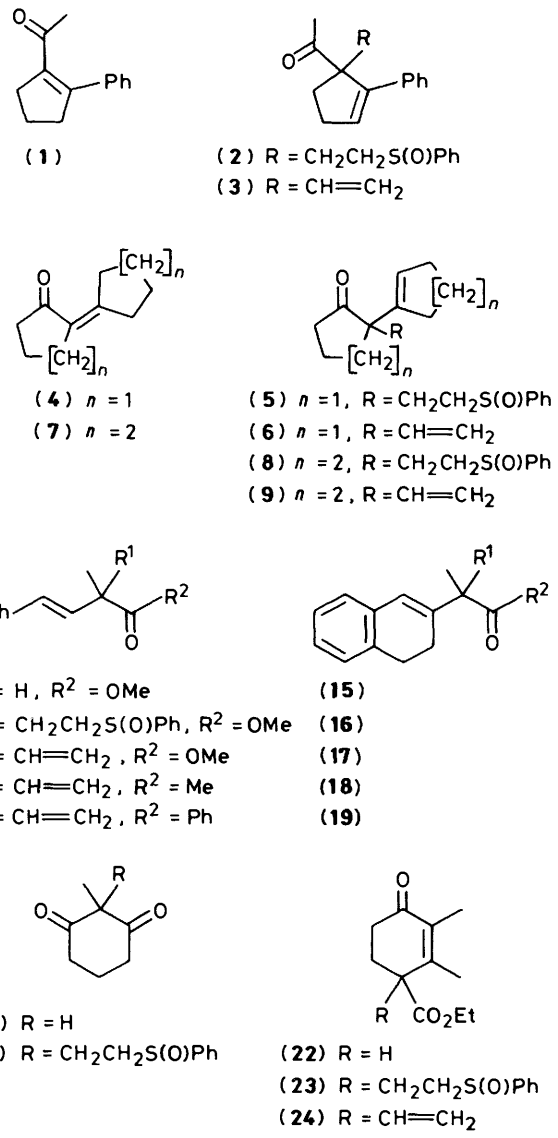
Results and Discussion

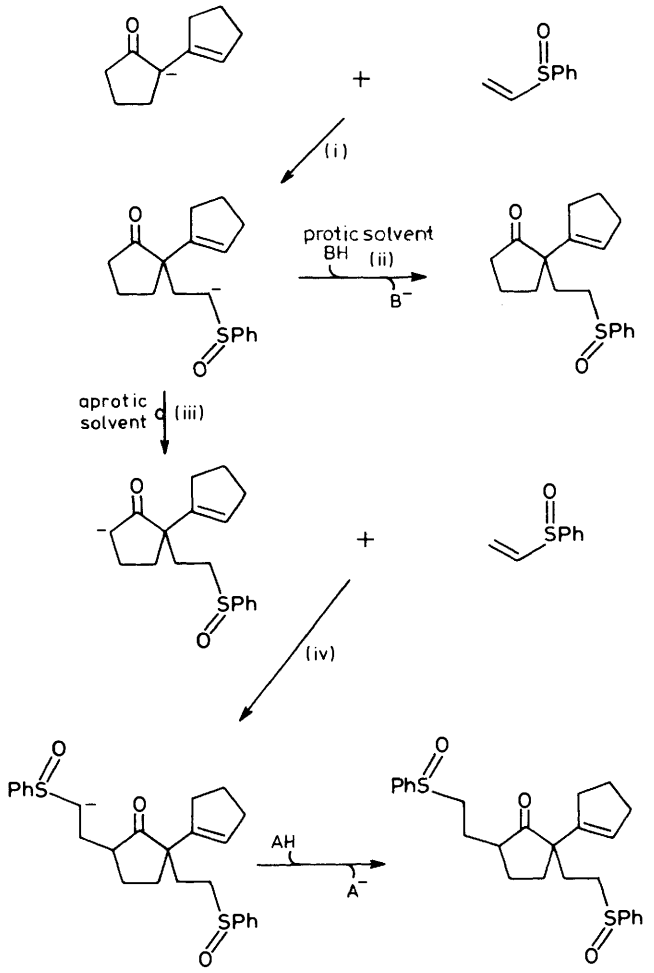
The synthesis of a series of β,γ;β′,γ′-unsaturated ketones and esters, starting from the corresponding β,γ-unsaturated ketones and esters, has been performed using phenyl vinyl sulphoxide (PVSO) as the vinyl cation synthon (Table).

Michael Addition.—Under the conditions described by Tanikaga,[12d] the enone (**1**) was converted into a Michael adduct to give the sulphoxide (**2**) in high yield. However, the dienone (**4**), when subjected to the action of PVSO in a similar way, gave only a low yield of the desired mono-sulphoxide (**5**) in addition to a mixture of some di- and tri-sulphoxides and substantial amounts of unconverted substrate. Clearly in this case proton abstraction from the anion intermediate formed after the Michael addition led to a thermodynamically unequilibrated mixture of anions. As discussed before, intramolecular proton-transfer (Scheme 3, route iii) may also occur and in the presence of PVSO the resulting anions will yield di- and tri-sulphoxides (route iv). The use of 1.0 equiv. instead of 0.1 equiv. of NaH or of catalytic amounts of Bu^{t}OK failed to give a substantial increase in the formation of the desired Michael adduct (see Table), better results being obtained using catalytic amounts of Bu^{t}OK as base in t-butyl alcohol (see also Scheme 3, route ii).

Cyclohexylidenecyclohexanone (**7**) reacted with PVSO in a Michael reaction to yield the adduct (**8**). With this substrate, in contrast to cyclopentylidenecyclopentanone, the solvent also reacts with PVSO to give 2-t-butoxyethyl phenyl sulphoxide (40%). As is seen in the Table, the β,γ-unsaturated esters (**10**) and (**15**) react smoothly with the sulphoxide synthon. The resulting esters (**12**) and (**17**) were used for the preparation of β,γ;β′,γ′-dienones[16] (see later).

Because of its low solubility, 2-methylcyclohexane-1,3-dione





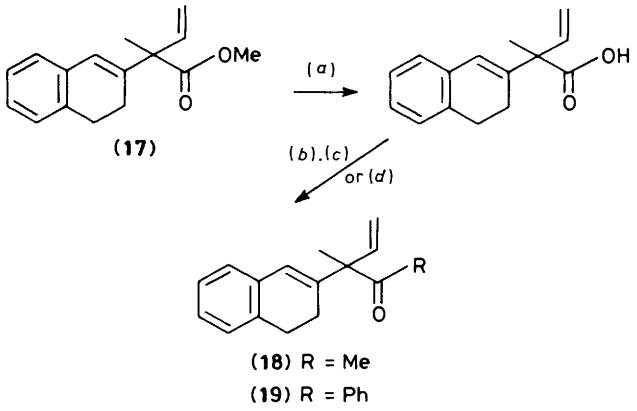
Scheme 3. Michael addition of phenyl vinyl sulphoxide to cyclopentylidenecyclopentanone in protic (BH) and aprotic solvents (AH stands for the substrate and the sulphoxide products)

(**20**) does not react with PVSO in C_6H_6, THF, $CHCl_3$, MeOH, or DME. However, in Bu^{t}OH some addition occurred, the yield being at most 10%. Finally, the enone (**22**) prepared from Hageman's ester[17] with methyl iodide, on reaction with PVSO gave a Michael addition product in low yield. However, the PVSO had acted at a carbon other than that of the initially introduced methyl group, *viz.* at the position γ to the ketonic carbonyl, as was confirmed by pyrolysis of (**23**), to give the γ-vinyl enone (**24**). This result is consistent with that of the alkylation of the ester (**22**) with methylallyl chloride.[17] As to the second substitution, the enhanced reactivity of the γ-position of (**22**) may be explained by the preference of the cyclohexenyl double bond to conjugate with the ketonic rather than with the ester carbonyl bond.

An attempt to synthesize 2,3-dimethyl-4-phenyl-2-vinylcyclohex-3-enone from 3-methyl-4-phenylcyclohex-2-enone failed. Methylation of the anion of the latter ketone with 1 equiv. of methyl iodide[18] led only to a mixture of the starting enone and 2,3,3-trimethyl-4-phenylcyclohex-3-enone, and not to 2,3-dimethyl-4-phenylcyclohex-2- or -3-enone which were both considered appropriate precursors for the preparation of the β,γ;β′,γ′-dienone 2,3-dimethyl-4-phenyl-2-vinylcyclohex-3-enone. The enamine of 3-methyl-4-phenylcyclohex-2-enone failed both to undergo methylation[19] and to react with PVSO.

Pyrolysis of the Sulphoxide Addition Products.—Most of the sulphoxides formed upon Michael addition of ketones and esters to PVSO were contaminated with the starting materials and di- and tri-sulphoxides. In order to avoid the possibility of obtaining a complex thermolysis mixture the addition products were purified using SiO_2 column chromatography. In all cases but one, crystallization of the addition product failed. The purified oils were pyrolysed *in vacuo* at 180—200 °C and the resulting reaction mixture yielded, upon distillation, as the first fraction a colourless oil which proved to contain mainly the desired alkene, and subsequently a yellow viscous oil of diphenyl disulphide with minor amounts of the alkene. The small amount of diphenyl disulphide in the first fraction was removed by column chromatography on SiO_2.

Preparation of β,γ;β′,γ′*-Dienones* (**13**), (**14**), (**18**), *and* (**19**).—The esters (**12**) and (**17**) are suitable precursors for the preparation of β,γ;β′,γ′-dienones (Scheme 4). Their saponification under basic conditions led to the corresponding carboxylic acids which were converted with thionyl chloride into the acyl chlorides. Reaction of these chlorides with a Grignard reagent under the conditions described by Sato[16a] failed to give the



Scheme 4. Preparation of the 3-acyl- (**18**) and 3-benzoyl-1,4-diene (**19**). (*a*) KOH, H_2O, EtOH (reflux); (*b*) $SOCl_2$, benzene (room temp.); (*c*) Me_2CuLi in ether (−78 °C); (*d*) $Ph_2CuMgBr$ in THF (−40 °C).

corresponding dienones, only starting material being recovered. In contrast, reaction both with dimethyl- and diphenyl-cuprate reagent[16b] gave the desired addition with formation, after hydrolysis, of the 3-acyl- [(**13**) and (**14**)] and 3-benzoyl-1,4-dienes [(**18**) and (**19**)] respectively. The somewhat lower yields for the phenylation compared with the methylation (see Table) may be the result of a larger degree of steric repulsion in the addition complex of the acyl chloride and the diphenyl as compared with the dimethyl cuprate.

Experimental

The ^1H n.m.r. spectra were recorded in $CDCl_3$ or CCl_4 as solvent on a Varian A60-D, a Varian XL100-FT, or a Bruker WM-250, using $SiMe_4$ as internal reference. The i.r. spectra were recorded on a Perkin-Elmer 257 grating i.r. spectrometer or a Perkin-Elmer 298 instrument, using a neat film of purified oils or $CHCl_3$ solutions. Microanalyses were performed by the Institute for Organic Chemistry, TNO, Utrecht. The g.l.c. analyses were carried out on a Varian Model-3700 chromatograph and the semi-preparative g.l.c. separations were conducted using a Varian Model 2700 chromatograph. t-Butyl alcohol was distilled from anhydrous potassium carbonate and stored over molecular sieves (4 Å). THF was freshly distilled prior to use from sodium wire with benzophenone as indicator under nitrogen. Benzene was purchased from Merck (pro analysis) and stored over sodium wire. Thionyl chloride and pyridine were purified as described.[20]

Phenyl Vinyl Sulphoxide (PVSO).—To a mixture of Mg (4.71 g, 194 g atom) in THF (40 ml) with two crystals of I_2, pure vinyl bromide (8 g, 75 mmol) was added dropwise. The Grignard reaction started almost immediately and was very exothermic. The reaction mixture was cooled with an ice–water bath and the solution gradually coloured. Then a solution containing vinyl bromide (15 g, 140 mmol) in THF (50 ml) was added at such a rate that the mixture refluxed gently. After the addition was complete and the magnesium had almost completely disappeared, THF (100 ml) was added, the solution was refluxed for 1 h and then cooled to room temperature. The Grignard solution was poured under nitrogen into a dropping funnel and added dropwise with vigorous stirring in 2 h to a solution of ethyl phenylsulphinate (32.1 g, 189 mmol, 1.0 equiv.)[12a] dissolved in anhydrous benzene (250 ml) at a temperature below 25 °C. After the addition the reaction mixture was stirred for a further 2 h and then poured into aqueous NH_4Cl (200 ml). After addition of water (200 ml), the organic layer was separated and the aqueous layer extracted with chloroform (3 × 75 ml). The combined organic layers were subsequently washed with water (2 × 100 ml), brine (100 ml), and dried ($MgSO_4$). The solvents were removed under reduced pressure leaving an oil (25.6 g, 89%) consisting of PVSO with minor amounts of ethyl phenylsulphinate. Column chromatography over SiO_2, eluting initially with dichloromethane, subsequently with a mixture of dichloromethane–ethyl acetate (7:3, v/v; and then 6:4, v/v) afforded an unidentified oil, ethyl phenylsulphinate (2.3 g), and PVSO (20.5 g) as a yellow oil, respectively. The latter material was used for the Michael additions without further purifications; δ (100 MHz; CCl_4): 7.6—7.3 (m, 5 H, Ph), 6.55 (dd, *J* 9, 16 Hz, 1 H, C*H*=CH_2), 6.07 (d, *J* 16 Hz, 1 H, CH=CH_EH), and 5.75 (d, *J* 9 Hz, CH=CH_ZH); $\nu_{max.}$(liq.): 3 060m, 3 010w, 1 600w, 1 580w, 1 475m, 1 445s, 1 365m, 1 310br m, 1 150m, 1 085s, 1 070m, 1 045s, 1 020m, 995m, 965s, 750s, 700s, 690s, 655m, and 620m cm^{-1}.

1-*Acetyl*-1-(2-*phenylsulphinylethyl*)-2-*phenylcyclopent*-2-*ene* (**2**).—1-Acetyl-2-phenylcyclopentene (**1**) (1.25 g, 6.71 mmol) (prepared from 1-phenylcyclopentene and acetic anhydride with $ZnCl_2$ in dichloromethane[21]) in THF (15 ml) was added dropwise over 1 h to a suspension of NaH (32 mg, 1.3 mmol) in THF (10 ml). After the mixture had been stirred for 2 h at room temperature it turned deep yellow, and PVSO (1.0 g, 6.57 mmol) dissolved in THF (10 ml) was added dropwise. The solution gradually coloured to reddish brown and was stored overnight. It was then poured into aqueous NH_4Cl (5%; 150 ml) and extracted with dichloromethane, and the extracts dried ($MgSO_4$) and evaporated under reduced pressure. The remaining viscous oil (2.1 g, 92%) contained the sulphoxide (**2**) which was only slightly contaminated with traces of PVSO (t.l.c.) and traces of solvents; δ (60 MHz; $CDCl_3$) 7.4 (s, 5 H, PhSO), 7.2 (m, 5 H, PhC_q), 6.4 (br t, *J* 3.5 Hz, 1 H, C_q=CH), 3.0—2.4 (m, 2 H, CH_2SO), 2.2—1.7 (m, 6 H, aliphatic H), and 2.1 (s, 3 H, MeCO).

1-*Acetyl*-2-*phenyl*-1-*vinylcyclopent*-2-*ene* (**3**).—The sulphoxide (**2**) was pyrolysed at 180 °C (0.5 mm Hg) to yield a distillate (1.1 g) which contained the dienone (**3**) and diphenyl disulphide. Elution through a SiO_2 column initially with 2—5% CH_2Cl_2 in n-hexane afforded a white crystalline disulphide (300 mg), and subsequent elution with CH_2Cl_2–n-hexane (2:3, v/v) gave (**3**) as a colourless oil (800 mg, 61%). Preparative g.l.c. afforded an analytical sample; δ (60 MHz; CCl_4) 7.5—7.1 (m, 5 H, Ph), 6.7 (dd, *J* 11, 17 Hz, 1 H, C*H*=CH_2), 6.5 (br t, *J* 3 Hz, 1 H, C_q=C*H*CH_2), 5.1 (dd, *J* 2, 11 Hz, 1 H, CH=CH_ZH), 4.9 (dd, *J* 2, 17 Hz, 1 H, CH=CH_EH), 2.7—2.0 (m, 4 H, CH_2CH_2), and 2.0 (s, 3 H, MeCO); $\nu_{max.}$(liq.) 3 080m, 3 060m, 3 020m, 2 950m, 2 930m, 1 705s, 1 630m, 1 600m, 1 580m, 1 500m, 1 450s, 1 415s, 1 305s, 1 230m, 920m, 750s, and 695s, cm^{-1} (Found: C, 84.8; H, 7.6. Calc. for $C_{15}H_{16}O$: C, 84.87; H, 7.60%).

2-*Cyclopent*-1-*enyl*-2-(2-*phenylsulphinylethyl*)*cyclopentanone* (**5**).—To a solution of sodium hydride (50 mg) in THF (40 ml), cyclopentylidenecyclopentanone (**4**) (Aldrich) (1.50 g, 10 mmol) was added dropwise. After 3 h PVSO (1.52 g) was added slowly at reflux temperature and the mixture was left refluxing overnight. The resulting reddish mixture was cooled to room temperature, and aqueous NH_4Cl (5%; 100 ml) was added. The organic layer was separated from the aqueous layer and washed with chloroform (×2). The combined organic layers were washed with water (×2) and then with brine, dried ($MgSO_4$) and the solvent evaporated under reduced pressure to leave a yellow, very viscous oil (2.8 g). Elution of the oil through a SiO_2 column successively with dichloromethane, ethyl acetate–dichloromethane (4:6, v/v) and ethyl acetate–ethanol (1:1, v/v) afforded unchanged enone (800 mg), the addition product (**5**) (0.17 g, 6%), and a mixture of the di-and tri-sulphoxides (1.5 g) respectively. Variation in the amounts of base or enone did not

lead to an increase in the yield of (**5**). The following procedure led to an optimal conversion of cyclopentylidenecyclopentanone. To a solution of Bu^{t}OK (0.55 g) dissolved in Bu^{t}OH (100 ml) cyclopentylidenecyclopentanone (7.3 g) in Bu^{t}OH (50 ml) was added dropwise at room temperature. After the mixture had been stirred for 2 h it was heated under reflux and then a solution of PVSO (7.4 g) in Bu^{t}OH (100 ml) was added slowly over a period of 10 h. The mixture was heated under reflux overnight after which it was cooled, and the Bu^{t}OH removed, in part, under reduced pressure. The mixture was then neutralized with 3% aqueous hydrogen chloride, diluted with water (100 ml), and extracted with chloroform. The organic layer was washed with water (× 2) and brine, and then dried ($MgSO_4$). The solvent of the organic layer was evaporated leaving a viscous yellow oil. Elution of the oil through a SiO_2 column with CH_2Cl_2 and then CH_2Cl_2–ethyl acetate (7:4, v/v) afforded the enone (**4**) (1.8 g) and the sulphoxide (**5**) (7.9 g, 54%); the latter was slightly contaminated with traces of PVSO and ethyl acetate. δ (60 MHz; $CDCl_3$) 7.5 (br s, 5 H, Ph), 5.5—5.3 (m, 1 H, CH=C_q), 3.0—2.5 (m, 2 H, CH_2SO), and 2.4—1.5 (m, 14 H, aliphatic H); $\nu_{max.}$(liq.) 3 000s, 2 970s, 2 880m, 2 860m, 1 770s, 1 760s, 1 660s, 1 450s, 1 050s, and 990s cm^{-1}.

2-*Cyclopent*-1-*enyl*-2-*vinylcyclopentanone* (**6**).—The sulphoxide (**5**) (7.5 g) was pyrolysed *in vacuo* (1 mmHg) at 180—200 °C. Elution of the distillate through SiO_2 with dichloromethane–hexane (1:4, v/v) afforded white crystalline diphenyl disulphide (0.58 g). Subsequent elution with dichloromethane–hexane (1:1, v/v) yielded the dienone (**6**). An analytical sample was obtained by preparative g.l.c.; δ (100 MHz; CCl_4) 5.42 (dd, *J* 10, 17 Hz, 1 H, C*H*=CH_2), 4.85 (br t, *J* 2 Hz, 1 H, CH=C_q), 4.50 (dd, *J* 1.5, 10 Hz, 1 H, CH=CH_ZH), 4.40 (dd, *J* 1.5, 16 Hz, 1 H, CH=CH_EH), and 2.4—1.4 (m, 12 H, aliphatic H); $\nu_{max.}$(liq.) 3 080m, 3 050m, 2 950s, 2 880s, 2 840s, 1 735s, 1 630m, 1 450m, 1 040m, 995m, and 920m cm^{-1} (Found: C, 81.6; H, 9.1. Calc. for $C_{12}H_{16}O$: C, 81.77; H, 9.15%).

2-*Cyclohex*-1-*enyl*-2-(2-*phenylsulphinylethyl*)*cyclohexanone* (**8**).—To a solution of Bu^{t}OK (210 mg, 1.87 mmol) in Bu^{t}OH (80 ml) at reflux temperature was added dropwise in 30 min the enone (**7**) (3.5 g, 19.6 mmol).[22] A solution of PVSO (3.0 g) in Bu^{t}OH (100 ml) was then added slowly (6 h) under reflux, and the refluxing continued overnight. The solution was then cooled, and the solvent partially evaporated and the residue extracted with chloroform. The extract was washed with water, dried (Na_2SO_4), and evaporated under reduced pressure. The residual yellow oil (7.30 g) was eluted through SiO_2 with dichloromethane–ethyl acetate. 5% Ethyl acetate eluted the enone (**7**) (1.8 g) (fraction 1); 25% ethyl acetate eluted the sulphoxide (**8**) (2.4 g, 37%) (fraction 2), and 40% ethyl acetate eluted phenyl 2-t-butoxyethyl sulphoxide (2.0 g 45%), formed by Michael addition of the solvent to the synthon (fraction 3). Fraction 2: (**8**) δ (60 MHz; $CDCl_3$) 7.5 (br s, 5 H, Ph), 5.3 (br s, 1 H, CH=C_q), 3.0—2.5 (m, 2 H, CH_2SO), 2.4—1.4 (m, 18 H, aliphatic H); $\nu_{max.}$(liq.) 2 930s, 2 860m, 2 830m, 1 705s, 1 440s, 1 085m, 1 040s, 745m, and 730s cm^{-1}. Fraction 3: δ (60 MHz; $CDCl_3$) 7.6—7.3 (m, 5 H, Ph), 3.9—3.3 (m, 2 H, CH_2O), 2.7 (dt, 2 H, CH_2SO), and 1.2 (s, 9 H, Me_3C); $\nu_{max.}$(liq.) 3 050w, 2 970s, 2 930m, 2 870m, 1 475m, 1 440s, 1 390m, 1 360m, 1 255m, 1 230m, 1 195s, 1 085s, 1 045s, 750s, and 690s cm^{-1}.

2-*Cyclohex*-1-*enyl*-2-*vinylcyclohexanone* (**9**).—The sulphoxide (**8**) (2.0 g) was subjected to pyrolysis at 200 °C. The distillate was collected *in vacuo* at 130 °C (0.05 mmHg). Elution as described for the dienone (**6**) afforded the dienone (**9**) (680 mg, 55%). An analytical sample was obtained by preparative g.l.c. as a white crystalline compound, m.p. 33—35 °C; δ (100 MHz; $CDCl_3$) 6.07 (dd, *J* 10, 17 Hz, 1 H, C*H*=CH_2); 5.52 (m, 1 H, CH=C_q); 5.11 (dd, *J* 1.5, 11 Hz, CH=CH_ZH); 4.92 (dd, *J* 1.5, 17 Hz, CH=CH_EH); 2.7—1.4 (m, 16 H, aliphatic H); $\nu_{max.}$(liq.) 3 070w, 3 040w, 2 930s, 2 860s, 2 830m, 1 705s, 1 630m, 1 450s, 1 330m, 1 310m, 1 230m, 1 145m, 990m, and 915s cm^{-1} (Found: C, 81.85; H, 9.85. Calc. for $C_{14}H_{20}O$: C, 83.20; H, 9.87%).

Methyl 2-*Methyl*-2-(2-*phenylsulphinylethyl*)-4-*phenylbut*-3-*en*-1-*oate* (**11**).—To a suspension of sodium hydride (400 mg, 55%) in benzene (50 ml) was added dropwise in 30 min a solution of methyl (*E*)-4-phenylbut-3-en-1-oate (**10**) (14.7 g, 1.1 equiv.), containing the 2-methyl homologue (*ca.* 2.2 g),* in benzene (50 ml). After 3 h of stirring at room temperature the solution was refluxed gently and a solution of PVSO (1.0 equiv.) in benzene (100 ml) was added in a period of 3 h. After being refluxed overnight the mixture was cooled, neutralized with 5% aqueous NH_4Cl (200 ml) and diluted with water (100 ml). The organic layer was removed and the aqueous layer washed with chloroform (2 × 75 ml). The combined organic layers were then washed with water (2 × 100 ml) and brine, dried ($MgSO_4$) and evaporated under reduced pressure to leave a reddish viscous oil (25 g). Part of the sulphoxide (**11**) crystallized upon addition of CCl_4 (100 ml). Recrystallization from CCl_4 afforded the pure sulphoxide (**11**) (10.5 g). The residual oil was eluted through SiO_2, first with dichloromethane to yield methyl 2,2-dimethyl-4-phenylbut-3-en-1-oate (2.2 g) as an oil, and then with dichloromethane–ethyl acetate (6:4, v/v) to yield a viscous oil which upon recrystallization afforded the sulphoxide (**11**) (6.8 g, 77%). An analytical sample was obtained by repeated recrystallization from CCl_4 to yield white crystalline material, m.p. 119—123 °C (decomp. 170—180 °C); δ (60 MHz; $CDCl_3$) 7.5 (m, 5 H, PhSO), 7.3 (m, 5 H, PhC), 6.3 (s, 2 H, olefinic H), 3.6 (s, 3 H, OMe), 3.0—2.5 (br m, 2 H, CH_2SO), 2.3—1.8 (m, 2 H, CH_2C_q), and 1.4 (s, 3 H, Me); $\nu_{max.}$(liq.) 3 090w, 3 070w, 3 040m, 3 010s, 2 960m, 1 750s, 1 450s, 1 040s, 970m, 695m, and 670m cm^{-1} (Found: C, 69.7; H, 6.4; S, 9.3. Calc. for $C_{20}H_{22}SO_3$: C, 70.15; H, 6.48; S, 9.36%).

Methyl (E)-2-*Methyl*-4-*phenyl*-2-*vinylbut*-3-*en*-1-*oate* (**12**).—The sulphoxide (**11**) (7.5 g) was heated *in vacuo* (0.05 mmHg) at 180—200 °C. The pyrolysis resulted in the formation of the ester (**12**) and diphenyl disulphide both of which were distilled off at 110—130 °C. The mixture (5.22 g) was purified by passage through SiO_2 with dichloromethane–hexane (1:4, v/v) as eluant to yield the ester (**12**) (3.0 g, 65%). An analytical sample was obtained by preparative g.l.c.: δ (100 MHz; $CDCl_3$) 7.3—7.2 (m, 5 H, Ph), 6.35 (s, 2 H, CH=CH), 6.10 (dd, *J* 10, 18 Hz, 1 H, C*H*=CH_2), 5.13 (dd, *J* 2, 10 Hz, CH=CH_ZH), 5.10 (dd, *J* 2, 18 Hz, 1 H, CH=CH_EH), 3.65 (s, 3 H, OMe), and 1.45 (s, 3 H, Me); $\nu_{max.}$(liq.) 3 100m, 3 070m, 3 030s, 3 020s, 2 960s, 2 950m, 1 750s, 1 630m, 1 600w, 1 580w, 1 500w, 1 450s, 1 440s, 1 420s, 1 380m, 1 250s, 1 230s, 1 210s, 1 115s, 1 005m, 990s, 975s, 930s, and 700s cm^{-1} (Found: C, 77.45; H, 7.2. Calc. for $C_{14}H_{16}O_2$: C, 77.75; H, 7.46%).

(E)-2-*Methyl*-4-*phenyl*-2-*vinylbut*-3-*en*-1-*oic Acid*.—This was obtained by refluxing the ester (**12**) (2.5 g) in a solution of potassium hydroxide (10 g) in water (70 ml) and ethanol (26 ml). Cooling of the reaction mixture and acidification with 5% aqueous HCl to pH 4 gave the acid as a solid; this was then extracted with ether (3 × 100 ml). The combined organic layers were subsequently washed with water (2 × 50 ml), brine, and dried ($MgSO_4$). Removal of the solvents gave the carboxylic

* The esters (**10**) and (**15**) were prepared from methyl (*E*)-4-phenylbut-3-en-1-oate[18b,23] and methyl 2-(1,2-dihydro-3-naphthyl)ethanoate[24] respectively in a way similar to that described for methyl 2-inden-2-ylpropanoate by Stratford.[23] In addition to (**10**) some methyl (*E*)-2,2-dimethyl-4-phenylbut-3-en-1-oate (20—30%) was obtained.

acid (2.2 g, 94%), which recrystallized from hexane to yield an analytical sample, m.p. 81—84 °C. δ (60 MHz; $CDCl_3$) 7.3 (m, 5 H, Ph), 6.4 (s, 2 H, C*H*=C*H*Ph), 6.2 (dd, *J* 10, 17 Hz, 1 H, C*H*=CH_2), 5.2 (dd, *J* 0.5, 10 Hz, 1 H, CH=CH_ZH), 5.2 (dd, *J* 0.5, 17 Hz, 1 H, CH=CH_EH), and 1.6 (s, 3 H, Me); $\nu_{max.}$($CHCl_3$) 3 050br m, 2 650br m, 1 700s, 1 635m, 1 600w, 1 500w, 1 450m, 1 270m, 975m, and 690m cm^{-1} (Found: C, 77.0; H, 7.05. Calc. for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98%).

(E)-3-*Methyl*-1-*phenyl*-3-*vinylpent*-1-*en*-4-*one* (**13**).—The carboxylic acid (1.0 equiv., 120 mg, 0.593 mmol) in benzene (10 ml) was converted into its acyl chloride by stirring it with thionyl chloride (600 mg) overnight at room temperature under nitrogen. Benzene and the excess of thionyl chloride were removed under reduced pressure (0.01 mmHg) to leave a yellow oil which was diluted with anhydrous ether (20 ml); this solution was then injected rapidly into a solution of dimethyl cuprate (1.2 equiv., 0.356 mmol) in ether (50 ml) at −78 °C. The resulting yellow mixture immediately formed a precipitate. The mixture was stirred for another 30 min and then quenched at 0 °C with 5% aqueous ammonium chloride. The aqueous layer, the colour of which changed to blue, was extracted with ether. The organic layer was washed with 5% aqueous ammonium chloride (50 ml), water (3 × 50 ml), brine (50 ml), and dried ($MgSO_4$). The solvents were evaporated under reduced pressure to afford a yellow oil (95 mg), the ^1H n.m.r. spectrum of which indicated the presence of the dienone (**13**), contaminated with 10% of the ester (**12**).[18] Formation of the latter was due to aerial oxidation of the cuprate reagent and subsequent nucleophilic addition of the resulting methoxide ions to the acyl chloride. The oil was eluted through SiO_2 with CH_2Cl_2–hexane (3:7, v/v) as eluant to yield the dienone (**13**) (74 mg, 62%). Purification by preparative g.l.c. yielded a colourless oil; δ (60 MHz: CCl_4) 7.2 (m, 5 H, Ph), 6.4 (s, 2 H, C*H*=C*H*Ph), 6.1 (dd, *J* 10, 17 Hz, 1 H, C*H*=CH_2), 5.2 (dd, *J* 1, 10 Hz, 1 H, CH=CH_ZH), 5.1 (dd, *J* 1, 17 Hz, 1 H, CH=CH_EH), 2.2 (s, 3 H, COMe), and 1.4 (s, 3 H, Me); $\nu_{max.}$(liq.) 3 080w, 3 060w, 2 980s, 2 940m, 1 720s, 1 630m, 1 600w, 1 500m, 1 450s, 1 350s, 980s, 920s, 750s, and 700s cm^{-1} (Found: C, 83.65; H, 8.0. Calc. for $C_{14}H_{16}O$: C, 83.96; H, 8.05%).

(E)-3-*Benzoyl*-3-*methyl*-1-*phenylpenta*-1,4-*diene* (**14**).—A mixture containing THF (5 ml), Mg (100 mg), and a crystal of iodine was treated with bromobenzene (650 mg, 1.1 equiv.) at 50 °C. When the Grignard reaction started the solution refluxed gently and an additional amount of THF (5 ml) was added. After cooling to room temperature the Grignard solution was diluted with THF (10 ml). Of the resulting solution, 5 ml was added dropwise to a solution of $Cu^{I}I$ (100 mg, 0.55 equiv.) in dry ether (20 ml) at −30 °C. The mixture was warmed up to −5 °C and stirred for 1 h to yield the organic cuprate complex and the magnesium salt as a black precipitate. The heterogeneous reaction mixture was cooled to −40 °C and a solution of the acyl chloride prepared from the carboxylic acid (200 mg, 1.0 equiv.) (see before) was injected rapidly leading to the formation of a new precipitate. The mixture was stirred for an additional 40 min, aqueous NH_4Cl (50 ml, 5%) was added and the reaction mixture poured into ether (100 ml). The organic layer was separated and the aqueous layer extracted with ether (2 × 25 ml). The combined organic layers were subsequently washed with 3% aqueous NH_4Cl to remove the Cu^{I} ions [the aqueous layer coloured blue as a result of aerial oxidation of Cu^{I} ions to Cu^{II} ions followed by complexation by NH_3 with formation of $Cu(NH_3)_4^{2+}$], with water (50 ml) and brine (50 ml). The solution was dried (Na_2SO_4) and evaporated under reduced pressure to leave an oil (120 mg) which merely consisted of the dienone (**14**). The oil was purified by passage through SiO_2 with dichloromethane as eluant and subsequent preparative g.l.c.; δ (60 MHz; CCl_4) 8.1—7.8 (m, 2 H, ArH), 7.7—7.0 (m, 8 H, ArH), 6.70 (d, *J* 16 Hz, 1 H, PhC*H*), 6.35 (d, *J* 16 Hz, 1 H, CH–C*H*C_6), 6.35 (dd, *J* 10, 16 Hz, 1 H, C*H*=CH_2), 5.20 (dd, *J* 1, 17 Hz, 1 H, CH=CH_EH), 5.20 (dd, *J* 1, 10 Hz, 1 H, CH=CH_ZH), and 1.5 (s, 3 H, Me); $\nu_{max.}$(liq.) 3 080m, 3 050m, 3 020m, 2 980m, 2 930m, 2 860w, 1 675s, 1 630w, 1 600m, 1 575m, 1 490m, 1 445s, 1 405w, 1 365m, 1 230s, 1 180m, 970s, 920s, 800m, 745s, and 690s cm^{-1} (Found: C, 86.7; H, 6.9. Calc. for $C_{19}H_{18}O$: C, 86.99; H, 6.92%).

Methyl 2-(1,2-*Dihydro*-3-*naphthyl*)-2-(2-*phenylsulphinylethyl*)*propanoate* (**16**).—The preparation of the sulphoxide (**16**) was carried out as described for (**11**) using methyl 2-(1,2-dihydro-3-naphthyl)propanoate (**15**)[25] (25 g) and PVSO (17.6 g). The resulting addition product (**16**) (33.5 g, 78%) was slightly contaminated with traces of the solvents. Attempts to recrystallize the very viscous oil failed, and no analytically pure sample was obtained; δ (60 MHz; $CDCl_3$) 7.5—7.4 (m, 5 H, PhSO), 7.0 (m, 4 H, ArH), 6.3 (br s, 1 H, olefinic H), 3.6 (s, 3 H, OMe), 3.0—2.5 (m, 4 H, aliphatic H), 2.4—1.9 (m, 4 H, aliphatic H), and 1.4 (s, 3 H, Me).

Methyl 2-*Methyl*-2-(1,2-*dihydro*-3-*naphthyl*)*but*-3-*en*-1-*oate* (**17**).—Pyrolysis of the sulphoxide (**16**) (28.0 g) was carried out as described for (**11**) to afford the dienoate (**17**) (11.8 g, 64%). An analytical sample was obtained by preparative g.l.c. to yield a colourless oil; δ (60 MHz, $CDCl_3$) 7.0 (s, 4 H, C_6H_4), 6.2 (br s, 1 H, C_6H_4C*H*), 6.2 (dd, *J* 10, 18 Hz, 1 H, C*H*=CH_2), 5.2 (dd, *J* 1.5, 10 Hz, 1 H, CH=CH_ZH), 5.1 (dd, *J* 1.5, 18 Hz, 1 H, CH=CH_EH), 3.7 (s, 3 H, OMe), 2.7 (m, 2 H, CH_2), 2.1 (m, 2 H, CH_2), and 1.5 (s, 3 H, Me); $\nu_{max.}$(liquid) 3 090w, 3 060w, 2 990m, 2 890m, 2 830m, 1 735s, 1 635m, 1 600w, 1 450m, 1 430m, 1 240s, 1 110s, 920m, and 750s cm^{-1} (Found: C, 78.9; H, 7.45. Calc. for $C_{16}H_{18}O_2$: C, 79.31; H, 7.49%).

2-(1,2-*Dihydro*-3-*naphthyl*)-2-*methylbut*-3-*en*-1-*oic acid*.—This was prepared from the ester (**17**) (11.0 g) as described before; yield 10.2 g (98%). Recrystallization from hexane afforded an analytically pure sample, m.p. 85—88 °C. δ (60 MHz, $CDCl_3$) 11.8 (br s, 1 H, OH), 7.1 (s, 4 H, C_6H_4), 6.4 (br s, 1 H, C_6H_4C*H*), 6.3 (dd, *J* 10, 18 Hz, 1 H, C*H*=CH_2), 5.3 (dd, *J* 1, 10 Hz, 1 H, CH=CH_ZH), 5.2 (dd, *J* 1, 18 Hz, 1 H, CH=CH_EH), 3.0—2.6 (m, 2 H, CH_2), 2.4—2.0 (m, 2 H, CH_2), and 1.5 (s, 3 H, Me); $\nu_{max.}$($CHCl_3$) 3 300—2 800br m, 2 940m, 2 890m, 1 705s, 1 635w, 1 485w, 1 450w, 1 270m, and 925m cm^{-1} (Found: C, 78.6; H, 7.05. Calc. for $C_{15}H_{16}O_2$: C, 78.92; H, 7.06%).

3-(1,2-*Dihydro*-3-*naphthyl*)-3-*methylpent*-4-*en*-2-*one* (**18**).—The preceding carboxylic acid (1.5 g) was converted into its acyl chloride which was then subjected to the action of dimethyl cuprate, in a manner similar to that described for the preparation of (**13**) to yield the dienone (**18**) (935 mg, 65%). Upon purification by preparative g.l.c., an analytical sample was obtained as a colourless oil; δ (250 MHz; $CDCl_3$) 7.2—7.0 (m, 4 H, C_6H_4), 6.45 (s, 1 H, C_6H_4C*H*), 6.35 (dd, *J* 10, 17 Hz, 1 H, C*H*=CH_2), 5.30 (dd, *J* 1.5, 10 Hz, 1 H, CH=CH_ZH), 5.15 (dd, *J* 1.5, 17 Hz, CH=CH_EH), 2.75 (m, 2 H, CH_2), 2.20 (s, 3 H, COMe), 2.15 (m, 2 H, CH_2), and 1.40 (s, 3 H, Me); $\nu_{max.}$(liquid) 3 060w, 3 020w, 2 980m, 2 930m, 2 880w, 2 820w, 1 720s, 1 630w, 1 485m, 1 450m, 1 350m, 920m, 760m, and 750s cm^{-1} (Found: C, 85.15; H, 8.0. Calc. for $C_{16}H_{18}O$: C, 84.91; H, 8.02%).

2-(1,2-*Dihydro*-3-*naphthyl*)-2-*methyl*-1-*phenylbut*-3-*en*-1-*one* (**19**).—To a mixture of ether (5 ml), Mg (420 mg, 17.3 mg-atom), and a crystal of iodine, a solution of bromobenzene (2.75 g, 17.5 mmol) in ether (3 ml) was added dropwise at reflux temperature. After the Grignard reaction had started the reaction mixture was diluted with ether (3 ml). The mixture was refluxed under nitrogen for 1 h and then cooled to room temperature. From

this solution (in total 6 ml) 3 ml were taken and added to a solution of Cu^{I} I (420 mg, 2.21 mmol) in dry ether (20 ml) at −30 °C. After the addition the mixture was warmed to −5 °C. The diphenyl cuprate was formed (yellow-green solution) together with a black precipitate of the magnesium salt. A solution of the acyl chloride prepared from the carboxylic acid (425 mg) in dry ether was then added at −40 °C to form a new precipitate. The solution was stirred for 40 min, after which it was poured into 5% aqueous NH_4Cl (100 ml) and extracted with ether (2 × 100 ml). The combined organic layers were washed with 3% aqueous NH_4Cl to remove the copper salts, with water, and finally with brine. The solution was then dried (Na_2SO_4) and evaporated under reduced pressure to leave a yellow oil. The enone (**19**) was purified by passage through SiO_2 with dichloromethane as eluant (yield 125 mg). Subsequent purification by preparative g.l.c. afforded an analytical sample; δ (250 MHz, $CDCl_3$) 8.05 (d, *J* 8 Hz, 2 H, 2-H + 6-H of PhCO), 7.45 (m, 1 H, 4-H of PhCO), 7.32 (t, *J* 7.5 Hz, 2 H, 3-H + 5-H of PhCO), 7.22—7.00 (m, 4 H, C_6H_4), 6.57 (s, 1 H, C_6H_4CH), 6.55 (dd, *J* 10, 17 Hz, 1 H, CH=CH_2), 5.26 (d, *J* 0.5, 10 Hz, 1 H, CH=CH_ZH), 5.21 (dd, *J* 0.5, 17 Hz, 1 H, CH=CH_EH), 2.67 (t, *J* 7.5 Hz, 2 H, $C_6H_4CH_2CH_2$), 2.26 (quint, *J* 7.5 Hz, 1 H, $C_6H_4CH_2CH_\alpha H$), 2.09 (quint, *J* 7.5 Hz, 1 H, $C_6H_4CH_2CH_\beta H$), and 1.54 (s, 3 H, Me); $\nu_{max.}$(liquid) 3 080w, 3 060m, 3 020m, 2 980m, 2 930m, 2 880m, 2 830m, 1 675s, 1 630m, 1 600m, 1 485m, 1 445m, 1 365m, 1 230s, 1 180s, 960s, 925m, 850m, 760s, 750s, 715s, 700s, and 685s cm^{-1} (Found: C, 87.35; H, 6.95. Calc. for $C_{21}H_{20}O$: C, 87.46; H, 6.99%).

4-Ethoxycarbonyl-2,3-dimethyl-4-(2-phenylsulphinylethyl)-cyclohex-2-enone (**23**).—To a solution of Bu^tOK (3.43 g) in Bu^tOH (100 ml) was added dropwise a solution of 4-ethoxycarbonyl-2,3-dimethylcyclohex-2-enone (**22**); the mixture immediately became yellow and then reddish, and finally black; it was then stirred for 2 h. Subsequently the mixture was heated under reflux and a solution of PVSO (4.7 g) in Bu^tOH (30 ml) was added dropwise; the colour of the solution changed slowly to dark-red. After being refluxed overnight, the solution was cooled and the Bu^tOH, in part, removed under reduced pressure. The resulting mixture was poured into 3% aqueous hydrogen chloride (100 ml) and extracted with ether (3 × 100 ml). The organic layer was washed successively with water (75 ml) and brine (100 ml), dried ($MgSO_4$), and the solvents removed under reduced pressure. The viscous yellow oil was eluted through SiO_2 to yield four fractions. The first (4.0 g), eluted with dichloromethane, contained starting enone (**22**), slightly contaminated with 4-ethoxycarbonyl-3,4-dimethylcyclohex-2-enone [already present in (**22**) as a minor by-product from the methylation of the Hageman's ester[17]]. The second fraction, obtained with dichloromethane–ethyl acetate (7:3, v/v), upon pyrolysis *in vacuo* afforded a mixture of unidentified sulphoxides (2.2 g) and traces of the γ-substituted sulphoxide (**23**). With a 1:1 (v/v) mixture of the same two solvents the sulphoxide (**23**) (2.2 g, 21%) was isolated. The fourth fraction, eluted with a 1:4 (v/v) mixture of the same solvents contained a mixture of disulphoxides (1.5 g), which were not identified. Fraction 3, which was slightly contaminated with traces of Bu^tOH, was used as such for the pyrolysis (see below): δ (60 MHz; $CDCl_3$) 7.6—7.3 (m, 5 H, Ph), 4.1 (dq, *J* 7 Hz, 2 H, OCH_2CH_3), 3.0—1.8 (m, 8 H, aliphatic H), 1.1 (dt, *J* 7 H, 3 H, OCH_2CH_3); $\nu_{max.}$(liquid) 3 020w, 2 980m, 2 960s, 2 880m, 1 670s, 1 570w, 1 440s, 1 385m, 1 355m, 1 200s, 1 080s, 1 045s, 750s, and 705m cm^{-1}.

4-Ethoxycarbonyl-2,3-dimethyl-4-vinylcyclohex-2-enone (**24**).—The sulphoxide (**23**) (1.9 g) was pyrolysed at 180 °C and the product distilled at 120—130 °C at 0.04 mmHg. Elution of the latter through SiO_2 with hexane afforded diphenyl disulphide (320 mg). With dichloromethane–hexane (3:1, v/v) as eluant, the dienone (**24**) (580 mg, 48%) was obtained, an analytical sample of which was obtained by preparative g.l.c.; δ (60 MHz; CCl_4) 6.2 (dd, *J* 11, 18 Hz, 1 H, CH=CH_2), 5.3 (dd, *J* 1.5, 11 Hz, 1 H, CH=CH_ZH), 4.9 (dd, *J* 1.5, 18 Hz, 1 H, CH=CH_EH), 4.2 (q, *J* 8 Hz, 2 H, OCH_2CH_3), 2.5—1.9 (m, 4 H, aliphatic H), 1.8 (s, 6 H, Me–C=C–Me), and 1.2 (t, *J* 8 Hz, 3 H, OCH_2CH_3); $\nu_{max.}$(liquid) 3 080w, 2 980m, 2 960m, 2 930m, 2 870m, 1 730s, 1 670s, 1 630m, 1 445m, 1 370m, 1 340m, 1 310m, 1 300m, 1 230s, 1 190m, 1 175m, 1 130m, 1 090m, 1 055m, 1 020m, 995m, and 920m cm^{-1} (Found: C, 70.1; H, 8.15. Calc. for $C_{13}H_{18}O_3$: C, 70.24; H, 8.16%).

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