The α-Vinylation of β-Dicarbonyl Compounds by Alk-1-enyl-lead Triacetates

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Treatment of (E,E)-distyrylmercury (1) with lead tetra-acetate gave a mixture of (E)-styrylmercury acetate (3) and (E)-styryl-lead triacetate (2), which decomposed to (E)-styryl acetate (4) and lead(II) acetate. The vinyl-lead compound (2), generated in this way, reacted rapidly with β-keto ester (5) to give the α-(E)-styryl derivative (6) in synthetically useful yield. This procedure for the α-vinylation of (5) has been applied to the divinylmercury compounds (7)—(13), and to the synthesis of the α-(E)-styryl β-dicarbonyl compounds (28), (30), (32), and (34). Compounds (6), (28), (30), (32), and (34). Compounds (6), (28), (30), (32), and (34) have also been produced by reaction with lead compound (2) generated by reaction of tributyl-(E)-styrylstannane (36) and lead tetra-acetate. Isolation of the relatively stable cyclopent-1-enyl-lead triacetate (21b), and its reaction with keto ester (5) to give a quantitative yield of compound (18), provided evidence that vinyl-lead triacetates are the vinylating species.

Although the synthetic utility of vinyl anions is well established,[1] the value of vinyl cations has not been so widely appreciated in synthesis, and it is only in recent years that a number of methods have been developed for the vinylation of substrates using vinyl cation synthetic equivalents. In this work, which has concentrated to a large extent on the synthesis of α-vinyl carbonyl compounds of biological importance, two distinct approaches have been used. The most widely applied method involves the reaction of an enolate anion with an electrophile containing an appropriately masked vinyl group. The electrophiles have included iron complexes of alkynes[2] and enol ethers,[3] (phenylseleno)acetaldehyde,[4] α-trialkylsilyl aldehydes,[5] phenyl vinyl sulphoxide,[6] and (E)-2-chlorovinyl phenyl sulphone.[7]

The other approach, which is relevant to the present study, involves the direct introduction of the vinyl group. Except for the dihalogenovinylation of enolates by trichloroethylene[8] and trifluoroethylene,[9] reactions which proceed by nucleophilic addition to the intermediate dihalogenoacetylenes, these reactions involve organometallic intermediates. They include the palladium-catalysed replacement of bromine in vinyl bromides by Reformatsky enolates[10] and by tin enolates,[11] and a similar nickel-catalysed reaction of lithium enolates of esters.[12]

Our successful use of aryl-lead triacetates as efficient C-arylating agents of a wide range of soft carbon nucleophiles[13] led us to explore the possibility of extending this work to C-vinylation by vinyl-lead triacetates. Such compounds had not been isolated, and were expected to be relatively unstable since alkyl-lead triacetates are stated to be 'too unstable to permit their isolation.'[14] The latter compounds have often been proposed as reactive intermediates,[15] and their instability would appear to be due to the ease of breakdown to an alkyl cation and lead(II) acetate (see Scheme 1). Vinyl-lead triacetates

$$R-Pb(OAc)_3 \longrightarrow R^+ + Pb(OAc)_2 + AcO^-$$
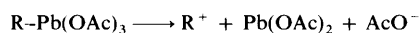
Scheme 1.

were first reported as possible intermediates by Corey and Wollenberg[16] in an acetylene synthesis, which involved the reaction of a tributyl(vinyl)stannane with lead tetra-acetate (see Scheme 2). Subsequently, Larock et al.[17] showed that treatment of vinylmercury compounds with lead tetra-acetate afforded a stereospecific route to enol acetates. Although no mechanism was proposed for this reaction, it would appear likely that a vinyl-lead compound is initially produced. Since we had found that mercury–lead exchange on treatment of diarylmercury
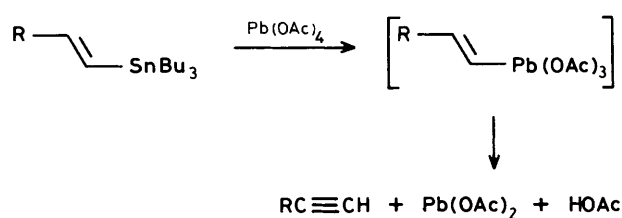
Scheme 2.

compounds with lead tetra-acetate[18] is considerably faster than the corresponding tin–lead exchange for aryltrialkyl-stannanes,[19] and lends itself to the in situ generation of aryl-lead triacetates, we first examined the reaction of vinylmercury compounds with lead tetra-acetate for the production of vinyl-lead triacetates.[20]

Early evidence for the proposed formation of vinyl-lead triacetates was obtained from an n.m.r. spectroscopic study of the reaction between (E,E)-distyrylmercury (1) and lead tetra-acetate in deuteriochloroform. A rapid reaction occurred to give initially a mixture of (E)-styrylmercury acetate (3), and a species with two vinylic protons which resonated in the aromatic region. The signals due to this second compound gradually decreased with time, while at the same time signals due to (E)-styryl acetate (4) appeared in the spectrum, and after 23 h only signals due to (3) and (4) were present. The formulation of the unstable intermediate as (E)-styryl-lead triacetate (2) is consistent with these observations, and thus the reaction can be represented as in Scheme 3.*

In an attempt to explore the potential of (E)-styryl-lead triacetate (2) as an electrophilic vinylating agent, a rapidly stirred chloroform solution of the divinylmercury compound (1) was treated with lead tetra-acetate at room temperature, and after 1 minute the β-keto ester (5) was added. The mixture was stirred overnight to afford the α-(E)-styryl β-keto ester (6) in 65% yield (see Scheme 3; entry 1, Table 1). The above method of in situ generation of a vinyl-lead triacetate, followed by reaction with the β-keto ester (5), has been examined for the divinyl-mercury compounds (7)—(13), and the results are presented in Table 1. For all except the divinylmercury compound (13), which afforded 11% of the α-vinylated compound (20) (entry 9,

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* Further evidence for the intermediacy of (2) and for other vinyl-lead triacetates will be presented in a future paper.[21]

Table 1. Reaction of keto ester (5) with a mixture of divinylmercury compounds and lead tetra-acetate (LTA) as in Scheme 3[a]

| | | Reaction conditions | | | | | |
| | | Time[b] (min) | R_2Hg^c (mol equiv.) | Py[c] (mol equiv.) | LTA[c] (mol equiv.) | Product | % Yield[d] |
Entry	R_2Hg						
1	(1)	1	1.1	0	1.1	(6)	65
2	(7)	3	0.5	40	1	(14)	52
3	(8)	15	1	0	1	(15)	59
4	(9)	5	1.5	20	2	(16)	46
5	(10)	3	2	50	2	(17)	51
6	(11)	5	2	20	2	(18)	65
7	(12)	15	2	5	2	(19)	80
8	(12)	5	2	5	2	(19)	54
9	(13)	5	1	20	1	(20)	11

[a] See Experimental section for the general method. [b] The time allowed for the mercury–lead exchange before addition of the keto ester (5). [c] Relative to the keto ester. [d] Isolated yield.

Scheme 3.

(7) $R^1 = H$, $R^2 = p - MeOC_6H_4$

(8) $R^1 = R^2 = Ph$

(9) $R^1 = R^2 = Me$

(10) $R^1 = Me$, $R^2 = Ph$

(11) $n = 1$

(12) $n = 2$

(13)

(14) $R^1 = p - MeOC_6H_4$, $R^2 = H$

(15) $R^1 = R^2 = Ph$

(16) $R^1 = R^2 = Me$

(17) $R^1 = Ph$, $R^2 = Me$

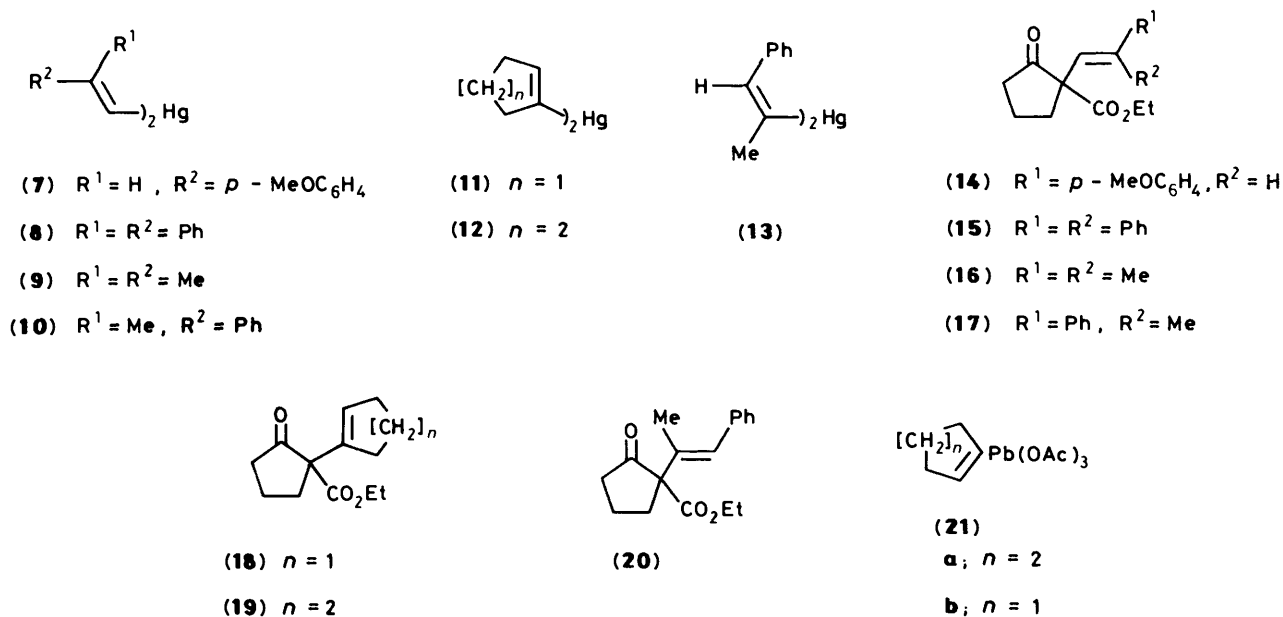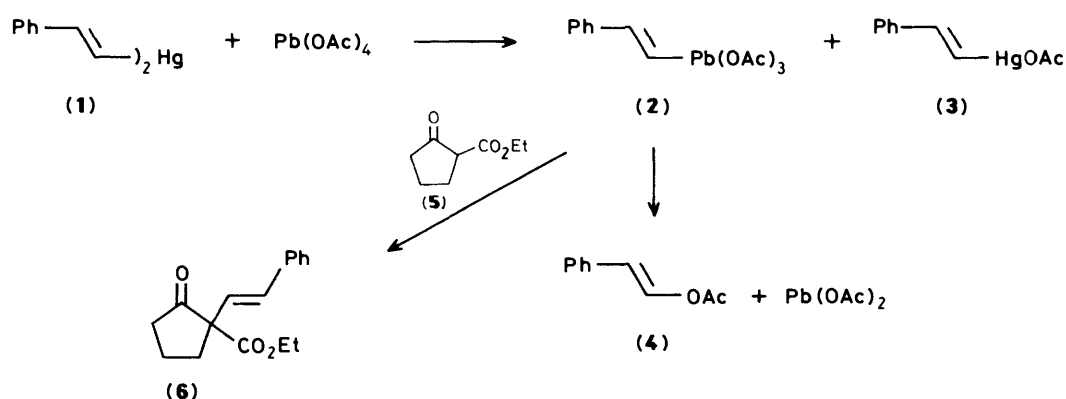(18) $n = 1$

(19) $n = 2$

(20)

(21)

a; $n = 2$

b; $n = 1$

Table 1), yields of the corresponding α-vinyl β-keto esters (14)—(19) were moderate to good (45—80%) (entries 2—8, Table 1).

From Table 1 it can be seen that it was not possible to produce a standard set of conditions for the vinylation reaction. This was due to the different rates of the various mercury–lead exchange reactions, and to the differing stabilities of the intermediate vinyl-lead triacetates. The optimum time for the mercury–lead exchange was determined in each case by [1]H n.m.r. spectroscopy, while the solvent system reported in Table 1 was that which gave the highest yield of the product. Although

the reactions proceeded in chloroform without added base, in all but two cases (entries 1 and 3, Table 1) the addition of pyridine resulted in a higher yield of the α-vinylated product.

Indirect support for our proposal that an unstable intermediate is the vinylating agent in these reactions is to be found in the reactions of bis(cyclohex-1-enyl)mercury (12) (entries 7 and 8, Table 1). In this case it was possible to extend the time for the mercury–lead exchange reaction due to the higher stability of cyclohex-1-enyl-lead triacetate (21a),[21] resulting in a marked improvement in the yield of the product (19).

In the absence of a detailed examination of the stereochemical features of the reaction, there is little that can be said about this aspect of the vinylation at this stage. As would be expected, the (E)-configuration in the mercury compounds (1) and (7) is retained in the products (6) and (14) respectively. The reactions of the mercury compounds (10) and (13), which were expected to yield useful information on this point, led in fact to conflicting results. In the case of compound (10) with the (E)-configuration, only the E-isomer (17)* was produced in the reaction; however, in the reaction of the (Z,Z)-divinylmercury compound (13), the only product isolated was the E-isomer (20) (entry 9, Table 1) in significantly lower yield than obtained in the other examples included in Table 1.

(22) R = Ph

(23) R = Me

(24) R¹ = R³ = Ph , R² = H

(25) R¹ = R² = Me , R³ = Ph

(26) R¹ = R² = Ph , R³ = Me
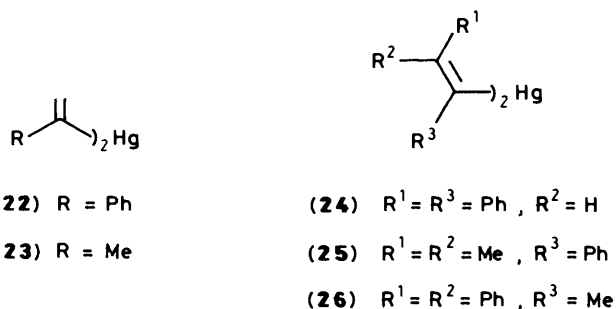
Not all of the divinylmercury compounds that were studied were found to produce α-vinylated products with the β-keto ester (5). The low reactivity of compound (13) has already been noted (entry 9, Table 1), and this would appear to be associated with the presence of a substituent α to the mercury, since compounds (22)—(26) failed to yield any of the corresponding α-vinyl β-keto ester. In the case of mercury compounds (22)—(24), this could be due to a relatively slow mercury–lead exchange;[21] however, the reason for non-reactivity of compounds (25) and (26) is less clear, since they are known to undergo a rapid metal–metal exchange with lead tetra-acetate.[21]

Two other approaches to the above vinylation of β-dicarbonyl compounds were examined; however, neither proved to be as synthetically useful as the above procedure. In the first of these, which is outlined in Scheme 4, the vinyl-lead
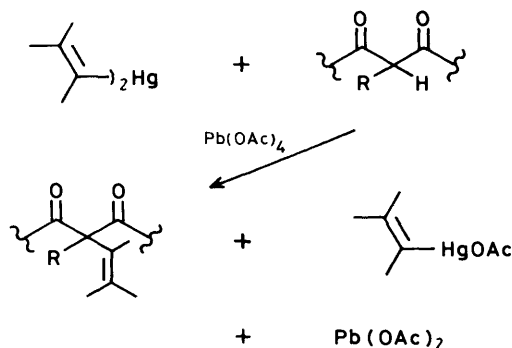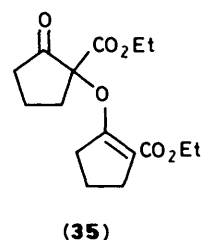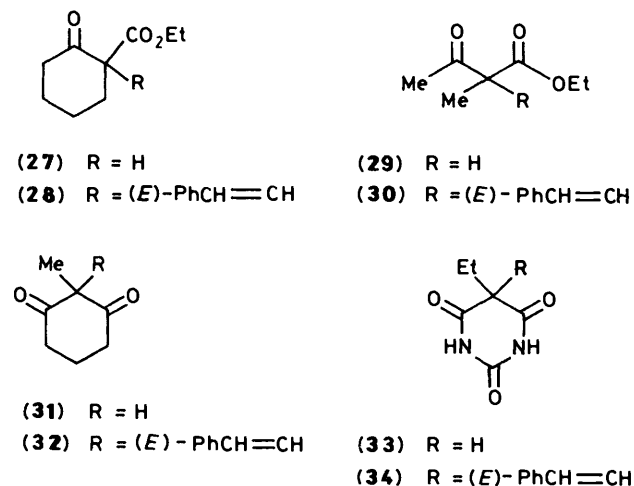

Scheme 4.

Table 2. Reaction of a mixture of di[(E)-styryl]mercury (1) and β-dicarbonyl compounds with lead tetra-acetate (LTA) in dimethyl sulphoxide–acetic acid

| | | Reaction conditions | | | |
| | | Compound (1)[a] | LTA[a] | | |
Entry	β-Dicarbonyl	(mol equiv.)	(mol equiv.)	Product	% Yield[b]
1	(5)	1.1	2.2	(6)	66
2	(27)	1.0	2.4	(28)	57
3	(29)	1.0	1.9	(30)	52
4	(31)	2.0	4.1	(32)	15
5	(33)	1.1	2.0	(34)	66

[a] Relative to the β-dicarbonyl compound. [b] Determined by ¹H n.m.r. spectroscopy.

compound was generated from a divinylmercury compound in the presence of a β-dicarbonyl compound. The method was successfully employed with (E,E)-distyrylmercury (1) and the β-dicarbonyl compounds (5), (27), (29), (31), and (33), to yield the α-(E)-styryl β-dicarbonyl compounds (6), (28), (30), (32), and (34) respectively. Best yields were obtained with a dimethyl sulphoxide–acetic acid solvent system, and these are listed in Table 2. As can be seen, yields were comparable to those obtained by the previous method, except for entry 4 where the poor yield of (32) is attributed to the low solubility of the diketone (31). Isolation of the products was not as readily achieved as in the first method due to the presence of products resulting from oxidation of the dicarbonyl compound by lead tetra-acetate. For example, the dimeric compound (35)[22] was

(27) R = H
(28) R = (E)-PhCH=CH

(29) R = H
(30) R = (E)-PhCH=CH

(31) R = H
(32) R = (E)-PhCH=CH

(33) R = H
(34) R = (E)-PhCH=CH

(35)

* The configuration followed from the absence of an n.O.e. of the vinyl proton signal at δ_H 5.85 in the n.m.r. spectrum, on irradiation at δ_H 2.05 (the chemical shift of the methyl group).

Table 3. Reaction of β-dicarbonyl compounds with a mixture of tributyl[(E)-styryl]stannane (36) and lead tetra-acetate (LTA) in chloroform-pyridine

| | | Reaction conditions | | |
| | | Compound (36)[a] | LTA[a] | | |
Entry	β-Dicarbonyl	(mol equiv.)	(mol equiv.)	Product	% Yield[b]
1	(5)	1.0	1.1	(6)	55
2	(27)	1.0	1.1	(28)	66
3	(29)	1.0	1.5	(30)	24
4[c]	(31)	1.0	1.0	(32)	53
5[c]	(33)	1.0	1.0	(34)	84

[a] Relative to the β-dicarbonyl compound. [b] Determined by ^{1}H n.m.r. spectroscopy. [c] Solubility of the dicarbonyl compound was improved by adding 2 drops of dimethyl sulphoxide.

produced in the first reaction recorded in Table 2 (entry 1). Because of this competing oxidation reaction the method cannot be applied to those divinylmercury compounds which undergo slow mercury–lead exchange with lead tetra-acetate.

The last approach involved the use of tin–lead exchange, a method analogous to that developed by us for the synthesis of aryl-lead triacetates.[19] The compound examined was tributyl-[(E)-styryl]stannane (36), which underwent a rapid metal–metal exchange when stirred with lead tetra-acetate in chloroform at room temperature to yield initially a solution of (E)-styryl-lead triacetate (2) and tributylstannyl acetate (by ^{1}H n.m.r. spectroscopy). When this mixture was treated after 5 minutes with the β-keto ester (5) in the presence of pyridine, the α-vinylated compound (6) was produced in similar yield to that obtained by the above methods (Scheme 5). The lead compound
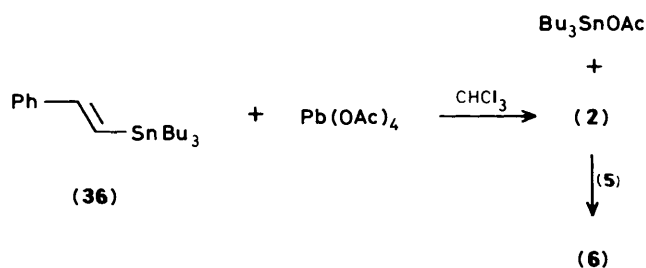
Scheme 5.

(2) generated in this way was also allowed to react with the β-dicarbonyl compounds (27), (29), (31), and (33) to give the α-vinyl β-dicarbonyls (28), (30), (32), and (34) in fair to good yields (see Table 3). Although this approach avoids vinyl group wastage inherent in the use of divinylmercury compounds, a serious limitation to this method was the difficulty experienced in separating the product from tributylstannyl acetate.

The tin–lead exchange reaction illustrated for the vinyl-stannane (36) was useful in providing definite evidence that vinyl-lead triacetates were the reactive vinylating agents in this work. Since it appeared that the instability of vinyl-lead triacetates was due to a breakdown to lead(II) acetate and a vinyl cation as in Scheme 1, the isolation of cyclopent-1-enyl-lead triacetate (21b) was attempted. It was reasoned that the high energy of the cyclopent-1-enyl cation[23] may result in a more stable vinyl-lead compound. In fact, when a mixture of tributyl(cyclopent-1-enyl)stannane (37) and lead tetra-acetate in dry chloroform was treated with dry light petroleum, the lead compound (21b) was precipitated. Although very sensitive to moisture, it could be collected and freed from tributylstannyl

acetate by washing with light petroleum in a dry bag. Attempted purification by crystallisation resulted in decomposition of (21b); however, the freshly precipitated material reacted with the β-keto ester (5) in chloroform–pyridine to afford the α-vinylated compound (18) in quantitative yield.

Synthesis of Divinylmercury Compounds.—The previously unreported divinylmercury compounds (7), (9), (10), (25), and (26) were produced by a standard procedure from the corresponding vinyl bromide. The bromide was converted *via* the Grignard reagent to the vinylmercury bromide, which was treated with tin(II) chloride or potassium iodide to give the divinylmercury compound. Compound (13) was obtained directly from the reaction of the corresponding Grignard reagent with mercury(II) bromide. 1-Bromo-2-methyl-1-phenyl-propene (38) and the vinylmercury bromides (39)—(44) are also reported for the first time in this work. The bromide (38) was readily obtained from the corresponding alkene by bromination followed by dehydrobromination.

(37)

(38)
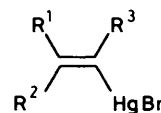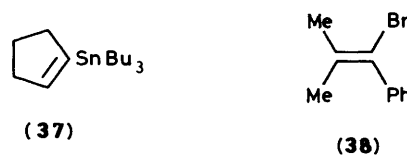
(39) R^1 = p - MeOC$_6$H$_4$, R^2 = R^3 = H

(40) R^1 = H , R^2 = R^3 = Ph

(41) R^1 = R^2 = Me , R^3 = Ph

(42) R^1 = R^2 = Ph , R^3 = Me

(43) R^1 = Ph , R^2 = Me , R^3 = H

(44) R^1 = H , R^2 = Ph , R^3 = Me

Experimental

For general experimental procedures see our earlier paper.[22]

1-*Bromo-2-methyl-1-phenylpropene* (38).—2-Methyl-1-phenylprop-1-ene[24] (5 g) was treated at 0 °C with a solution of bromine (1.8 ml) in carbon tetrachloride (15 ml), and the solution was kept at room temperature overnight. The solvent was evaporated off and the crude dibromide was treated with potassium hydroxide (2.1 g) in absolute ethanol (80 ml) at reflux for 30 min. The reaction mixture was worked up in the usual way and the crude product was distilled (Kugelrohr), 90—100 °C at 0.8 mmHg to give the *title compound* (38) as a liquid (4.5 g, 56%) (Found: C, 56.3; H, 5.0. C$_{10}$H$_{11}$Br requires C, 56.9; H, 5.3%); λ$_{max.}$(cyclohexane) 246 nm (ε 3 800); δ(CDCl$_3$) 1.67 (3 H, s, Me), 2.00 (3 H, s, Me), and 7.18 (5 H, m, ArH); *m/z* 131 (*M* − Br, 100%).

Synthesis of Vinylmercury Bromides.—The vinyl bromide (10 drops) and ethylene dibromide (3 drops) were added to tetrahydrofuran (THF) (10 ml) containing magnesium turnings (1.5 mol equiv.). Once initiation occurred, the remainder of the vinyl bromide (3—10 mmol) in THF (30 ml) was added during 1 h at reflux under nitrogen. The mixture was refluxed for a further 1 h,

and the solution was then transferred dropwise (double-ended needle) to a solution of mercury(II) bromide (1.1 mol equiv.) in THF (30 ml) at reflux. The resulting mixture was heated at reflux for 1 h, and then stirred at room temperature overnight. The mixture was filtered, the precipitate washed with THF (3 × 30 ml), and the filtrate evaporated. The product was crystallised from the solvent indicated.

The following compounds were prepared according to the above general method.

(a) Isopropenylmercury bromide (59%), m.p. 160—162 °C (from cyclohexane) (lit.,[25] 167 °C); $\delta(CDCl_3)$ 2.12 (3 H, dd, J_1 1.5, J_2 1.5 Hz, Me), 5.00 (1 H, dq, J 1.5, 0.3 Hz, [199]Hg satellites gave $J_{2.Hg}$ 281 Hz, CHH cis to Hg), and 5.66 (1 H, dq, J 1.5, 0.3 Hz, [199]Hg satellites gave $J_{2.Hg}$ 601 Hz, CHH trans to Hg).

(b) 1-Phenylvinylmercury bromide (22%), m.p. 89—90 °C (from cyclohexane–light petroleum) (lit.,[26] 89.5—90.5 °C); $\lambda_{max.}$-(CH$_3$CN) 252 nm (ε 11 500); $\delta(CDCl_3)$ 5.44 (1 H, d, J 0.4 Hz, [199]Hg satellites gave $J_{2.Hg}$ 288 Hz, CHH cis to Hg), 6.09 (1 H, d, J 0.4 Hz, [199]Hg satellites gave $J_{2.Hg}$ 582 Hz, CHH trans to Hg), and 7.10—7.58 (5 H, m, ArH).

(c) (E)-Styrylmercury bromide (36%), m.p. 203—204 °C (from ethanol) (lit.,[27] 202—203 °C); $\delta([^2H_6]DMSO)$ 6.77 (1 H, d, J 18.0 Hz, [199]Hg satellites gave $J_{1.Hg}$ 246 Hz, PhCH), 6.85 (1 H, d, J 18.0 Hz, [199]H satellites gave $J_{2.Hg}$ 297 Hz, HgCH), and 7.15—7.50 (5 H, m, ArH).

(d) (E)-p-Methoxystyrylmercury bromide (39) (33%), m.p. 220—222 °C (Found: C, 26.4; H, 2.4. C_9H_9BrHgO requires C, 26.1; H, 2.2%); $\lambda_{max.}$(dioxane) 235 and 284 nm (ε 12 700 and 24 300); $\delta(CDCl_3-[^2H_6]DMSO)$ 3.79 (3 H, s, OMe), 6.59 (1 H, d, J 17.5 Hz, [199]Hg satellites gave $J_{1.Hg}$ 248 Hz, HgCH), 6.79 (1 H, d, J 17.5 Hz, [199]Hg satellites gave $J_{2.Hg}$ 284 Hz, PhCH), and 6.85 and 7.31 (4 H, AA'BB', m-H and o-H, respectively).

(e) 2-Methylprop-1-enylmercury bromide (29%), m.p. 89—94 °C (from light petroleum) (lit.,[28] 91—93.5 °C); $\lambda_{max.}$(cyclohexane) 232 nm (ε 5 100); $\delta(CDCl_3)$ 1.93 (3 H, d, J 1.2 Hz, Me), 1.98 (3 H, s, [199]Hg satellites gave $J_{Me.Hg}$ 34 Hz, Me), and 5.56 (1 H, m, [199]Hg satellites gave $J_{1.Hg}$ 284 Hz, 1-H).

(f) (Z)-1,2-Diphenylvinylmercury bromide (40) (38%), m.p. 157—158 °C (from cyclohexane–light petroleum) (Found: C, 36.2; H, 2.6. $C_{14}H_{11}BrHg$ requires C, 36.6; H, 2.4%); $\lambda_{max.}$-(dioxane) 232 and 292 nm (ε 16 200 and 15 500); $\delta(CDCl_3-[^2H_6]DMSO)$ 6.98—7.82 (10 H, m, ArH) and 7.75 (1 H, s, [199]Hg satellites gave $J_{2.Hg}$ 544 Hz, β-H).

(g) 2-Methyl-1-phenylprop-1-enylmercury bromide (41) (20%), m.p. 83—85 °C (from cyclohexane–light petroleum) (Found: C, 29.2; H, 2.8. $C_{10}H_{11}BrHg$ requires C, 29.2; H, 2.7%); $\lambda_{max.}$(cyclohexane) 235 and 248 nm (ε 14 000 and 7 300); $\delta(CDCl_3)$ 1.76 (3 H, s, [199]Hg satellites gave $J_{Me.Hg}$ 22 Hz, Me trans to Hg), 2.12 (3 H, s, [199]Hg satellites gave $J_{Me.Hg}$ 37 Hz, Me cis to Hg), and 6.92—7.50 (5 H, m, ArH). [1]H N.m.r. n.O.e. difference spectroscopy showed a 1.5% enhancement of ArH integral on irradiation at δ 1.76, but no effect on irradiation at δ 2.12.

(h) 1,1-Diphenyl-1-propen-2-ylmercury bromide (42) (31%), m.p. 161—166 °C (from cyclohexane) (Found: C, 37.7; H, 2.7. $C_{15}H_{13}BrHg$ requires C, 38.0; H, 2.8%); $\lambda_{max.}$(cyclohexane) 267 nm (ε 11 500); $\delta(CDCl_3)$ 2.16 (3 H, s, [199]Hg satellites gave $J_{Me.Hg}$ 202 Hz, Me) and 7.08—7.46 (10 H, m, ArH).

(i) (E)-2-Phenylprop-1-enylmercury bromide (43) (26%), m.p. 175—176 °C (from cyclohexane–light petroleum) (Found: C, 27.1; H, 2.3. C_9H_9BrHg requires C, 27.2; H, 2.3%); $\lambda_{max.}$-(cyclohexane) 263 nm (ε 9 100); $\delta(CDCl_3-[^2H_6]DMSO)$ 2.4 (3 H, s, Me), 6.28 (1 H, s, [199]Hg satellites gave $J_{1.Hg}$ 230 Hz, α-H), and 7.13—7.57 (5 H, m, ArH).

(j) (Z)-1-Phenylprop-1-en-2-ylmercury bromide (44) was obtained after crystallisation from cyclohexane–light petroleum, followed by chromatography on triethylamine-deactivated silica gel in chloroform–light petroleum, as yellow crystals (2%),

m.p. 99—100 °C (Found: C, 27.3; H, 2.5%); $\lambda_{max.}$(cyclohexane) 234 and 264 nm (ε 7 200 and 7 000); $\delta(CDCl_3)$ 2.24 (3 H, d, J 1.8 Hz, [199]Hg satellites gave $J_{Me.Hg}$ 185 Hz, Me), 7.20—7.56 (5 H, m, ArH), and 7.42 (1 H, s, [199]Hg satellites gave $J_{1.Hg}$ 538 Hz, α-H).

The major product from this reaction was bis[(Z)-α-methylstyryl]mercury (13), which was also produced during the chromatographic purification of compound (44) (see below).

(k) Cyclopent-1-enylmercury bromide (34%), m.p. 200—203 °C (lit.,[29] 182—184 °C) (Found: C, 17.6; H, 1.9. Calc. for C_5H_7BrHg: C, 17.3; H, 2.0%); $\lambda_{max.}$(cyclohexane) 234 nm (ε 3 200); $\delta(CDCl_3$; at 70 °C) 1.66—2.10 (2 H, m, CH$_2$), 2.20—2.70 (4 H, m, 2 × CH$_2$), and 5.83 (1 H, m, [199]Hg satellites gave $J_{2.Hg}$ 150 Hz, 2-H).

Cyclohex-1-enylmercury Bromide.—The previously reported method[30] was used to prepare the title compound, m.p. 173—175 °C (lit.,[30] 174—175 °C); $\lambda_{max.}$(EtOH) 228 nm (ε 6 800); $\delta(CDCl_3)$ 1.40—1.90 and 2.10—2.50 (8 H, m, 4 × CH$_2$) and 5.66 (1 H, m, [199]Hg satellites gave $J_{2.Hg}$ 298 Hz, 2-H).

2,2-Diphenylvinylmercury Bromide.—The title compound was prepared (35%) by the method of Sokolov et al.,[31] m.p. 152—155 °C (from cyclohexane) (lit.,[31] 157 °C); $\lambda_{max.}$(CHCl$_3$) 248 and 268 nm (ε 10 100 and 13 000); $\delta(CDCl_3$ 6.40 (1 H, s, [199]Hg satellites gave $J_{1.Hg}$ 258 Hz, α-H), 7.30 (5 H, br s, ArH), and 7.38 (5 H, br s, ArH).

Synthesis of Divinylmercury Compounds.—(Method A) A solution of tin(II) chloride (0.4 g) in water (5 ml) was added to a solution of sodium hydroxide (0.9 g) in water (4 ml), and a suspension of the vinylmercury bromide (0.5 g) in ethanol (5 ml) and water (5 ml) was added to the stirred mixture during 1 h. The solution was stirred at room temperature overnight, diluted with water (10 ml), and extracted with ether (3 × 20 ml). The extract was dried (Na$_2$SO$_4$), filtered, and the solvent evaporated off to give the crude product. Purification was achieved by Kugelrohr distillation or crystallisation.

(Method B) A solution of potassium iodide (4 g) in acetone (60 ml) and water (7 ml) was added to a solution of the vinylmercury bromide (1 g) in acetone (50 ml). The product precipitated almost immediately, and the mixture was stirred for a further 3 h. The product was collected at the pump and purified by crystallisation.

The above procedures were used to prepare the following compounds.

(a) (E,E)-Distyrylmercury[32] (1), (56%, Method B), m.p. 136—140 °C (from heptane) (Found: C, 47.7; H, 3.3. Calc. for $C_{16}H_{14}Hg$: C, 47.2; H, 3.5%); $\lambda_{max.}$(dioxane) 272 nm (ε 23 000); $\delta(CDCl_3)$ 6.79 (1 H, d, J 19.6 Hz, [199]Hg satellites gave $J_{2.Hg}$ 144 Hz, β-H), 7.13 (1 H, d, J 19.6 Hz, [199]Hg satellites gave $J_{1.Hg}$ 114 Hz, α-H), and 7.10—7.44 (5 H, m, ArH).

(b) Bis[(E)-p-methoxystyryl]mercury (7) (59%, Method B), m.p. 172—176 °C (from toluene) (Found: C, 46.2; H, 3.9. $C_{18}H_{18}HgO_2$ requires C, 46.3; H, 3.9%); $\lambda_{max.}$(dioxane) 288 nm (ε 39 600); $\delta([^2H_8]dioxane$; 70 °C) 3.75 (3 H, s, OMe), 6.69 (1 H, d, J 19.2 Hz, [199]Hg satellites gave $J_{2.Hg}$ 143 Hz, β-H), 6.91 (1 H, d, J 19.2 Hz, [199]Hg satellites gave $J_{1.Hg}$ 116 Hz, α-H), and 6.83 and 7.27 (4 H, AA'BB', m-H and o-H respectively).

(c) Bis(2,2-diphenylvinyl)mercury (8) (60%, Method A), m.p. 135—135.5 °C (lit.,[33] 140.5 °C); $\lambda_{max.}$(dioxane) 245 and 288 nm (ε 19 200 and 23 200); $\delta(CDCl_3)$ 6.67 (1 H, s, [199]Hg satellites gave $J_{1.Hg}$ 116 Hz, 1-H), 7.23 (5 H, m, ArH), and 7.27 (5 H, m, ArH).

(d) Bis(2-methylprop-1-enyl)mercury (9) (94%, Method A), b.p. 150 °C at 1 mmHg (Found: C, 30.9; H, 4.6. $C_8H_{14}Hg$ requires C, 30.9; H, 4.5%); $\delta(CDCl_3)$ 1.89 (3 H, d, J 1.2 Hz, [199]Hg satellites gave $J_{Me.Hg}$ 59 Hz, Me), 1.92 (3 H, s, [199]Hg

satellites gave $J_{Me,Hg}$ 17 Hz, Me), and 5.86 (1 H, s, ^{199}Hg, satellites gave $J_{1,Hg}$ 118 Hz, 1-H).

(e) *Bis*[(E)-2-*phenylprop*-1-*enyl*]*mercury* (**10**) (84%, Method B), m.p. 141—143 °C (from cyclohexane–light petroleum) (Found: C, 49.6; H, 4.0. $C_{18}H_{18}Hg$ requires C, 49.7; H, 4.2%); λ_{max} (cyclohexane) 280 nm (ε 22 700); δ(CDCl$_3$) 2.41 (3 H, d, J 0.5 Hz, ^{199}Hg satellites gave $J_{Me,Hg}$ 18 Hz, Me), 6.63 (1 H, d, J 0.5 Hz, ^{199}Hg satellites gave $J_{1,Hg}$ 105 Hz, 1-H), and 6.93—7.34 (5 H, m, ArH).

(f) Bis(cyclopent-1-enyl)mercury (**11**) (84%, Method B), b.p. 190—200 °C at 1 mmHg; m.p. 60—63 °C (lit.,^{34} 63.5—64.5 °C); λ_{max} (cyclohexane) 238 nm (ε 9 200); δ(CDCl$_3$) 1.54—1.98 (2 H, m, CH$_2$), 2.14—2.64 (4 H, m, 2 × CH$_2$), and 5.73 (1 H, m, ^{199}Hg satellites gave $J_{2,Hg}$ 79 Hz, 2-H).

(g) Bis(cyclohex-1-enyl)mercury (**12**) (90%, Method A), b.p. 160—170 °C at 0.6 mmHg (lit.,^{30} 170 °C at 10 mmHg); λ_{max}. 225 nm (ε 8 700); δ(CDCl$_3$) 1.34—1.82 (4 H, m, 2 × CH$_2$), 1.86—2.50 (4 H, m, 2 × CH$_2$), and 5.49 (1 H, m, ^{199}Hg satellites gave $J_{2,Hg}$ 136 Hz, 2-H).

(h) Bis(1-phenylvinyl)mercury (**22**) (75%, Method B), m.p. 46—48 °C (unstable solid from light petroleum–absolute ethanol) (lit.,^{26} 68—69 °C); λ_{max} (cyclohexane) 241 nm (ε 22 000); δ(CDCl$_3$) 5.28 (1 H, d, J 2.0 Hz, ^{199}Hg satellites gave $J_{2,Hg}$ 143 Hz, 2-H *cis* to Hg), 6.11 (1 H, d, J 2.0 Hz, ^{199}Hg satellites gave $J_{2,Hg}$ 243 Hz, 2-H *trans* to Hg), and 7.10—7.44 (5 H, m, ArH).

(i) Di-isopropenylmercury (**23**) (44%, Method A), b.p. 30—40 °C at 0.4 mmHg (lit.,^{25} 69—70 °C at 13 mmHg); δ(CDCl$_3$) 2.02 (3 H, dd, J_1 1.6, J_2 1.6 Hz, ^{199}Hg satellites gave $J_{Me,Hg}$ 88 Hz, Me), 4.86 (1 H, m, ^{199}Hg satellites gave $J_{1,Hg}$ 128 Hz, C*H*H *cis* to Hg), 5.60 (1 H, m, ^{199}Hg satellites gave $J_{1,Hg}$ 257 Hz, CH*H* *trans* to Hg).

(j) Bis[(Z)-1,2-diphenylvinyl]mercury (**24**) (Method B), m.p. 240—243 °C (toluene) (lit.,^{35} 243—244 °C); λ_{max} (dioxane) 240 and 280 nm (ε 20 900 and 19 000); δ([^{2}H$_8$]dioxane; 70 °C) 7.07—7.65 (10 H, m, ArH) and 8.00 (1 H, s, ^{199}Hg satellites gave $J_{2,Hg}$ 242 Hz, 2-H).

(k) *Bis*(2-*methyl*-1-*phenylprop*-1-*enyl*)*mercury* (**25**) (77%, Method B), m.p. 91—92 °C (from light petroleum) (Found: C, 51.9; H, 5.05. $C_{20}H_{22}Hg$ requires C, 51.9; H, 4.8%); λ_{max} (cyclohexane) 246 nm (ε 30 600); δ(CDCl$_3$) 1.78 (3 H, s, ^{199}Hg satellites gave $J_{Me,Hg}$ 11 Hz, Me), 2.11 (3 H, s, ^{199}Hg satellites gave $J_{Me,Hg}$ 19 Hz, Me), 6.80—7.40 (5 H, m, ArH).

(l) *Bis*(1,1-*diphenylprop*-1-*en*-2-*yl*)*mercury* (**26**) (57%, Method B), m.p. 188—190 °C (from cyclohexane) (Found: C, 61.7; H, 4.55. $C_{30}H_{26}Hg$ requires C, 61.4; H, 4.5%); λ_{max} (cyclohexane) 273 nm (ε 20 500); δ(CDCl$_3$) 1.90 (3 H, s, ^{199}Hg satellites gave $J_{Me,Hg}$ 99 Hz, Me) and 7.00—7.44 (10 H, m, ArH).

Bis[(Z)-*phenylprop*-1-*en*-2-*yl*]*mercury* (**13**).—This compound was obtained in 16% yield directly from the Grignard reaction used to prepare the corresponding vinylmercury bromide (**44**). Chromatography on a triethylamine-deactivated silica gel column in chloroform–light petroleum, followed by crystallisation from cyclohexane–light petroleum, gave the *title compound* (**13**), m.p. 125—128 °C (Found: C, 50.1; H, 4.45. $C_{18}H_{18}Hg$ requires C, 49.7; H, 4.2%); λ_{max} (cyclohexane) 235 and 262 nm (ε 12 800 and 11 800); δ(CDCl$_3$) 2.10 (3 H, d, J 1.6 Hz, ^{199}Hg satellites gave $J_{Me,Hg}$ 92 Hz, Me), 7.08—7.50 (5 H, m, ArH), and 7.64 (1 H, d, J 1.6 Hz, ^{199}Hg satellites gave $J_{1,Hg}$ 227 Hz, 1-H).

Preparation of Tributyl[(E)-*styryl*]*stannane* (**36**).—Compound (**36**) was prepared from β-bromostyrene as previously reported.^{36} The material obtained (56% yield) contained *ca.* 20% of the (Z)-isomer, and showed δ(CDCl$_3$) 0.60—1.90 (27 H, m), 6.19 (0.2 H, d, J 14 Hz, *cis* vinyl H), 6.87 (1.6 H, s, 2 × *trans*

vinyl H), 7.62 (0.2 H, d, J 14 Hz, *cis* vinyl H), and 7.10—7.50 (5 H, m, ArH).

Tributyl(*cyclopent*-1-*enyl*)*stannane* (**37**).—The preparation was carried out according to the method of Paquette *et al.*^{37} from the toluene-*p*-sulphonylhydrazone of cyclopentanone.^{38} The crude material was purified by passage through a column of alumina in light petroleum, followed by preparative gas chromatography (5% Apieson L on Chromosorb G at 200 °C), to give the *title compound* (**37**) as a liquid (20% yield), b.p. 115—125 °C at 0.6 mmHg (Found: C, 56.8; H, 10.2. $C_{17}H_{34}Sn$ requires C, 57.2; H, 9.6%); δ_H(CDCl$_3$) 0.83—1.02, 1.10—1.94 (29 H, m, 3 × C$_4$H$_9$ and 1 × CH$_2$), 2.18—2.58 (4 H, m, 2 × CH$_2$), and 5.87 (1 H, m, 2-H); δ_C(CDCl$_3$) 9.3 (Me), 13.8 (CH$_2$), 23.5 (CH$_2$), 27.4 (CH$_2$), 29.3 (CH$_2$), 34.4 (CH$_2$), 39.5 (CH$_2$), 130.9 (=CSn), and 140.8 (=CH).

Preparation of the α-*Vinyl* β-*Dicarbonyl Compounds Reported in Table* 1.—Lead tetra-acetate (1—2 mol equiv.) was added to a solution of the mercury compound (0.05—0.25 mmol) in chloroform, and the mixture was stirred at room temperature for 1—15 min. A solution of the keto ester (**5**) (1.0 mol equiv.) in chloroform (sufficient to give a reactant concentration of 0.12—0.25M) containing pyridine (0—50 mol equiv.) was added, and the mixture was stirred overnight at room temperature, diluted with chloroform, washed successively with hydrochloric acid (3M) and water, dried (Na$_2$SO$_4$), and evaporated. The residue was dissolved in ether, the solution was washed successively with aq. sodium hydroxide (3M) and water, and the solvent was evaporated off. The product was purified for analysis by chromatography, followed in some cases by h.p.l.c. (Water Associates μ-Porasil column).

The following compounds were prepared according to the above general method.

(a) *Ethyl* 2-*oxo*-1-[(E)-*styryl*]*cyclopentanecarboxylate* (**6**) (65%) was obtained as an oil after p.l.c. (light petroleum–ethyl acetate, 9:1) (Found: C, 74.2; H, 6.8%; M^+, 258.1254. $C_{16}H_{18}O_3$ requires C, 74.4; H, 7.0%; M, 258.1256); λ_{max} (dioxane) 255 nm (ε 5 200); ν_{max} (film) 1 740 and 1 720 cm^{-1}; δ(CDCl$_3$) 1.22 (3 H, t, J 7.0 Hz, Me), 1.91—2.93 (6 H, m, 3 × CH$_2$), 4.21 (2 H, q, J 7.0 Hz, CH$_2$), 6.36 (1 H, d, J 16.0 Hz, vinyl H), 6.55 (1 H, d, J 16.0 Hz, vinyl H), and 7.18—7.50 (5 H, m, ArH).

(b) *Ethyl* 1-[(E)-*p*-*methoxystyryl*]-2-*oxocyclopentanecarboxylate* (**14**) (52%) was obtained as an oil after p.l.c. (CHCl$_3$) and h.p.l.c. (ethyl acetate–light petroleum, 8:92) (Found: C, 71.0; H, 6.9%; M^+, 288.1377. $C_{17}H_{20}O_4$ requires C, 70.8; H, 7.0%; M, 288.1361); λ_{max} (EtOH) 273 nm (ε 8 700); ν_{max} (film) 1 750 and 1 710 cm^{-1}; δ(CDCl$_3$) 1.26 (3 H, t, J 7.1 Hz, Me), 1.82—2.87 (6 H, m, 3 × CH$_2$), 3.80 (3 H, s, OMe), 4.20 (2 H, q, J 7.1 Hz, CH$_2$), 6.25 (1 H, d, J 16.2 Hz, vinyl H), 6.45 (1 H, d, J 16.2 Hz, vinyl H), and 6.85 and 7.32 (4 H, AA'BB', *m*-H and *o*-H respectively).

(c) *Ethyl* 1-(2,2-*diphenylvinyl*)-2-*oxocyclopentanecarboxylate* (**15**) (59%) was obtained as an oil after p.l.c. (CHCl$_3$) and h.p.l.c. (ethyl acetate–light petroleum, 3:97) (Found: C, 79.0; H, 6.8. $C_{22}H_{22}O_3$ requires C, 79.0; H, 6.6%); λ_{max} (cyclohexane) 235 and 260 nm (ε 11 300 and 11 700); ν_{max} (film) 1 740 and 1 710 cm^{-1}; δ(CDCl$_3$) 1.20 (3 H, t, J 7.0 Hz, Me), 1.48—2.66 (6 H, m, 3 × CH$_2$), 4.02 (2 H, q, J 7.0 Hz, CH$_2$), 6.40 (1 H, s, vinyl H), and 6.98—7.44 (10 H, m, ArH).

(d) *Ethyl* 1-(2-*methylprop*-1-*enyl*)-2-*oxocyclopentanecarboxylate* (**16**) (46%) was obtained as an oil after column chromatography (chloroform–light petroleum, 1:1) and h.p.l.c. (ethyl acetate–light petroleum, 2.5:97.5) (Found: C, 68.2; H, 8.6. $C_{12}H_{18}O_3$ requires C, 68.5; H, 9.2%); ν_{max} (film) 1 760 and 1 720 cm^{-1}; δ(CDCl$_3$) 1.24 (3 H, t, J 7.2 Hz, Me), 1.64 (3 H, d, J 1.3 Hz, Me), 1.76 (3 H, d, J 1.45 Hz, Me), 1.85—2.94 (6 H, m, 3 × CH$_2$), 4.18 (2 H, q, J 7.2 Hz, CH$_2$), and 5.29 (1 H, m, vinyl H).

(e) *Ethyl 2-Oxo-1-[(E)-2-phenylprop-1-enyl]cyclopentane-carboxylate* (**17**) (51%) was obtained as an oil after p.l.c. (CHCl$_3$) and h.p.l.c. (ethyl acetate–light petroleum, 3:97) (Found: C, 74.8; H, 7.7%; M^+, 272.1405. C$_{17}$H$_{20}$O$_3$ requires C, 75.0; H, 7.4%; M, 272.1412); $\lambda_{max.}$(cyclohexane) 248 nm (ε 11 800); $\nu_{max.}$(film) 1 750 and 1 720 cm^{-1}; δ(CDCl$_3$) 1.25 (3 H, t, J 7.0 Hz, Me), 2.05 (3 H, d, J 1.4 Hz, Me), 2.00—2.93 (6 H, m, 3 × CH$_2$), 4.20 (2 H, d, J 7.0 Hz, CH$_2$), 5.85 (1 H, q, J 1.4 Hz, vinyl H), and 7.21—7.41 (5 H, m, ArH). Irradiation at δ 2.05 gave a 2.1% n.O.e. at δ 7.40 but no n.O.e. was observed at δ 5.85.

(f) *Ethyl 1-(cyclopent-1-enyl)-2-oxocyclopentanecarboxylate* (**18**) (65%) was obtained as an oil after column chromatography (chloroform–light petroleum, 1:1) and h.p.l.c. (ethyl acetate–light petroleum, 5:95) (Found: C, 69.1; H, 8.0%; M^+, 222.1255. C$_{13}$H$_{18}$O$_3$ requires C, 70.2; H, 8.2%; M, 222.1256); $\nu_{max.}$(film) 1 760 and 1 720 cm^{-1}; δ(CDCl$_3$) 1.27 (3 H, t, J 7.0 Hz, Me), 1.77—2.73 (12 H, m, 6 × CH$_2$), 4.20 (2 H, q, J 7.0 Hz, CH$_2$), and 5.61 (1 H, m, vinyl H).

(g) *Ethyl 1-(cyclohex-1-enyl)-2-oxocyclopentanecarboxylate* (**19**) (80%) was obtained as an oil after column chromatography (chloroform–light petroleum, 1:1) and h.p.l.c. (ethyl acetate–light petroleum, 5:95) (Found: C, 71.3; H, 8.4. C$_{14}$H$_{20}$O$_3$ requires C, 71.2; H, 8.4%); $\nu_{max.}$ 1 760 and 1 740 cm^{-1}; δ(CDCl$_3$) 1.26 (3 H, t, J 7.2 Hz, Me), 1.38—2.68 (14 H, m, 7 × CH$_2$), 4.20 (2 H, q, J 7.2 Hz, CH$_2$), and 5.55 (1 H, m, vinyl H).

(h) Ethyl 2-oxo-1-[(*E*)-1-phenylprop-1-en-2-yl]cyclopent-anecarboxylate (**20**) (11%) was obtained as an oil after p.l.c. (chloroform) (Found: M − CO, 244.1458. C$_{17}$H$_{20}$O$_3$ requires M − CO, 244.1463); δ(CDCl$_3$) 1.27 (3 H, t, J 7.0 Hz, Me), 1.79—2.83 (6 H, m, 3 × CH$_2$), 1.90 (3 H, d, J 1.2 Hz, Me), 4.23 (2 H, q, J 7.0 Hz, CH$_2$), 6.38 (1 H, m, vinyl H), and 7.29 (5 H, m, ArH). Irradiation at δ 6.38 gave a 4.1% n.O.e. at δ 7.29 and a 5.2% n.O.e. at δ 2.30, but no n.O.e. at δ 1.90; m/z 272 (M, 3%), 244 (M − CO, 55), and 171 (244 − CO$_2$Et, 100).

Isolation of the α-Vinyl β-Dicarbonyl Compounds Reported in Table 2.—To the dicarbonyl compound (0.7 mmol) and the mercury compound (**1**) (1—2 mol equiv.) in dimethyl sulphoxide (5 ml) was added lead tetra-acetate (1.9—4.1 mol equiv.) in a mixture of dimethyl sulphoxide (3 ml) and acetic acid (0.1 ml), and the solution was stirred at room temperature over-night. The mixture was diluted with chloroform, washed successively with water and dilute hydrochloric acid, dried (Na$_2$SO$_4$), and the solvent was evaporated off. The yield of the product was determined by ^{1}H n.m.r. spectroscopy, and each product was isolated as indicated below.

(a) *Ethyl 2-oxo-1-[(E)-styryl]cyclohexanecarboxylate* (**28**) was obtained by p.l.c. (ethyl acetate–light petroleum, 1:9) and h.p.l.c. (ethyl acetate–light petroleum, 5:95) as an oil (Found: C, 74.3; H, 7.9%; M^+, 272.1414. C$_{17}$H$_{20}$O$_3$ requires C, 75.0; H, 7.4%; M, 272.1412); $\lambda_{max.}$(hexane) 255 nm (ε 5 600); $\nu_{max.}$(film) 1 730 cm^{-1}; δ(CDCl$_3$) 1.25 (3 H, t, J 7.3 Hz, Me), 1.54—2.90 (8 H, m, 4 × CH$_2$), 4.24 (2 H, q, J 7.3 Hz, CH$_2$) 6.45 (1 H, d, J 16.0 Hz, vinyl H), 6.69 (1 H, d, J 16.0 Hz, vinyl H), and 7.18—7.50 (5 H, m, ArH).

(b) *Ethyl (E)-2-acetyl-2-methyl-4-phenylbut-3-enoate* (**30**) was obtained by p.l.c. (ethyl acetate–light petroleum, 1:9) as an oil (Found: C, 72.9; H, 7.4. C$_{15}$H$_{18}$O$_3$ requires C, 73.2, H, 7.4%); $\lambda_{max.}$(hexane) 254 nm (ε 7 000); $\nu_{max.}$(film) 1 720 cm^{-1}; δ(CDCl$_3$) 1.30 (3 H, t, J 7.2 Hz, Me), 1.60 (3 H, s, 2-Me), 2.22 (3 H, s, MeCO), 4.27 (2 H, q, J 7.2 Hz, CH$_2$), 6.45 (1 H, d, J 16.0 Hz, vinyl H), 6.72 (1 H, d, J 16.0 Hz, vinyl H), and 7.22—7.52 (5 H, m, ArH); m/z 246 (M, 0.8%) and 204 (M − CH$_2$CO, 100).

(c) *2-Methyl-2-[(E)-styryl]cyclohexane-1,3-dione* (**32**) was obtained by p.l.c. (ethyl acetate–light petroleum, 1:9) as an oil (Found: M^+, 228.1155. C$_{15}$H$_{16}$O$_2$ requires M, 228.1149); δ(CDCl$_3$) 1.42 (3 H, s, Me), 1.66—3.12 (6 H, m, 3 × CH$_2$), 6.17 (1 H, d, J 16.0 Hz, vinyl H), 6.33 (1 H, d, J 16.0 Hz, vinyl H), and

7.30 (5 H, m, ArH); m/z 228 (M^+, 100%), 172 (M − C$_3$H$_4$O, 91), 157 (172 − CH$_3$, 56) 129 (M − C$_5$H$_7$O$_2$, 63).

(d) *5-Ethyl-5-[(E)-styryl]barbituric acid* (**34**) was obtained by column chromatography (acetone–light petroleum, 1:5) as crystals, m.p. 169—172 °C (from chloroform) (Found: C, 64.7; H, 5.4; N, 11.0. C$_{14}$H$_{14}$N$_2$O$_3$ requires C, 65.1; H, 5.5; N, 10.9%); $\lambda_{max.}$(EtOH) 258 nm (ε 16 900); $\nu_{max.}$(Nujol) 3 180, 3 070, and 1 720 cm^{-1}; δ(CDCl$_3$) 0.94 (3 H, t, Me), 2.31 (2 H, q, CH$_2$), 6.20 (1 H, d, J 16.0 Hz, vinyl H), 6.64 (1 H, d, J 16.0 Hz, vinyl H), 7.20—7.42 (5 H, m, ArH), and 8.90 (2 H, s, exch. with D$_2$O, 2 × NH); m/z 258 (M, 69%) and 229 (M − CHO, 100).

Cyclopent-1-enyl-lead Triacetate (**21b**).—A solution of lead tetra-acetate (541 mg, 1.2 mmol) in dry chloroform (0.5 ml) was added to a solution of tributyl(cyclopent-1-enyl)stannane (**37**) (342 mg, 1.05 mmol) in dry chloroform (0.5 ml) and the mixture was stirred at room temperature for 5 h, then filtered; dry, cold light petroleum (10 ml) was added, and the mixture was cooled to 0 °C. The title compound (**21b**) precipitated as a brown solid (100 mg, 21%) and was collected by filtration under dry argon, δ_H(CDCl$_3$) 1.80—3.00 (6 H, m, 3 × CH$_2$), 2.10 (9 H, s, 3 × Me), and 6.39 (1 H, m, vinyl H); δ_C(CDCl$_3$) 20.6 (q, Me), 22.5 (t, CH$_2$), 31.0 (t, CH$_2$), 35.9 (t, CH$_2$), 133.4 (s, CPb), 141.5 (d, =CH), and 179.3 (s, CO).

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