Electrophilic Vinylations by Vinyllead Triacetates and Tribenzoates Generated by Tin–Lead Exchange

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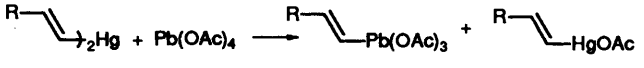
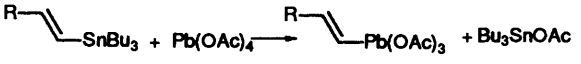
Trimethyl(vinyl)stannanes undergo a rapid tin–lead exchange with lead tetraacetate to give high yields of unstable vinyllead triacetates. Solutions of vinyllead triacetates produced in this way react with soft carbon nucleophiles such as β-dicarbonyl compounds and nitronate salts to give moderate to good yields of *C*-vinylated products. The method is more economical in terms of vinyl group incorporation than previously reported vinylations by vinyllead triacetates. An even faster tin–lead exchange has been observed when trimethyl(vinyl)stannanes are treated with lead tetrabenzoate, and vinylations with this reagent proceeded in significantly higher yields.

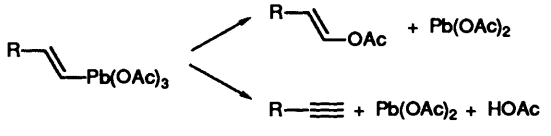
When we introduced vinyllead triacetates as reagents for the vinylation of soft carbon nucleophiles,[1,2] we reported two general methods for their synthesis. One involved the reaction of a divinylmercury compound with lead tetraacetate (Scheme 1), while in the other method a tributyl(vinyl)stannane replaced the mercury derivative (Scheme 2). Because of the instability of vinyllead triacetates, which undergo a relatively fast reductive elimination of lead(II) acetate to yield either an acetylene or an enol acetate[3,4] (Scheme 3), a requirement for their use in



Scheme 1



Scheme 2

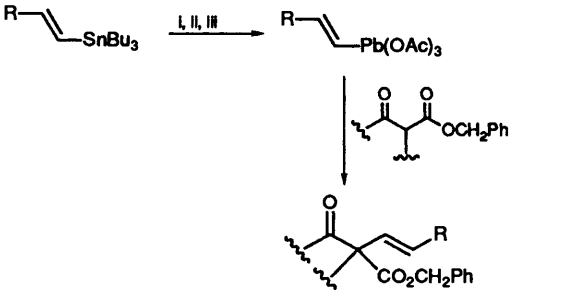


Scheme 3

synthesis is rapid formation. The Hg–Pb exchange of Scheme 1 had the advantage of incorporating a faster metal–metal exchange than in the case of the tin route outlined in Scheme 2, but the method resulted in the wastage of one of the vinyl residues due to the formation of the unreactive vinylmercury acetate. This problem has been addressed by Ikegami and co-workers,[5] and in this paper we present the results of further approaches which increase the efficiency of this method of vinylation.

The Japanese workers, who employed our Hg–Pb exchange method for a vinylation step in a synthesis of the potentially important therapeutic agent, (+)-isocarbacyclin,[6] later reported a Zn–Pb exchange procedure for the vinylation of a series of β-keto benzyl esters[5] outlined in Scheme 4. The latter method was stated to be more economical in terms of vinyl group usage than our procedures; however, as indicated in Scheme 4, 2 equiv. of the vinylstannane were employed. An unexplained feature of the method was the need to use the tributyl(vinyl)-stannane in the preparation of the vinylzinc reagent to obtain satisfactory yields in the vinylation.

During our study of the intermediacy of vinyl cations in some of the decompositions of vinyllead triacetates,[3,4] it emerged that



Scheme 4 *Reagents and conditions:* $RCHCHSnBu_3$ (2.1 equiv.); i, BuLi (2.2 equiv.); ii, $ZnCl_2$ (2.1 equiv.); $Pb(OAc)_4$ (2 equiv.)

the Sn–Pb exchange of trimethyl(vinyl)stannanes was considerably faster than the reaction of the corresponding tributylstannanes, and unlike the variation introduced by Ikegami and co-workers[5] only 1 equiv. of the reagent had to be employed to obtain satisfactory yields in the vinylation of a range of substrates. The method also resulted in a simpler work-up procedure due to the easier removal of trimethyltin acetate from the product. In a study restricted to a small number of examples, it was later found that lead tetrabenzoate was generally more effective than lead tetraacetate in these reactions, resulting in faster metal–metal exchange and higher yields of vinylated β-dicarbonyl compounds.

The general procedure which we initially adopted is outlined for the synthesis of the α-(*E*)-styryl β-keto ester **2** in Scheme 5; trimethyl[(*E*)-styryl]stannane **1** (1.1 mol equiv.) was treated with lead tetraacetate (1.1 mol equiv.) in chloroform for 1 min, the temperature was lowered to 0 °C, and the β-keto ester **3** (1.0 mol equiv.) in chloroform and pyridine (2.2 mol equiv.) was added. After the mixture had been stirred at 0 °C for 30 min and then at room temperature for 3 h, the ester **2** was isolated in 78% yield (entry 1, Table 1).†

The above basic procedure was used to obtain good yields of the (*E*)-styryl derivatives **6**, **8**, **10** and **13**‡ from the dicarbonyl

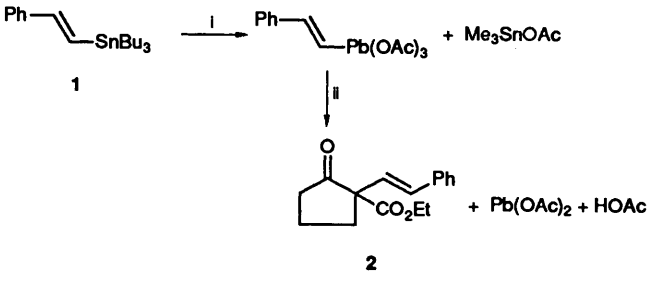
† The lowering of the temperature to 0 °C for the vinylation step was found to give slightly higher yields than those conducted at room temperature (see entry 2, Table 1), presumably due to thermal decomposition of the intermediate vinyllead triacetate resulting from the exothermic nature of the reaction. It proved to be impractical to perform the complete reaction at 0 °C, since the Sn–Pb exchange reaction was found (^{1}H NMR spectroscopy) to be too slow at this temperature.

‡ Nitroolefin **13** decomposed slowly at room temperature with loss of HNO_2 to give cyclohexyl(phenyl)acetylene in almost quantitative yield. This unexpected decomposition, which presumably proceeds through an allene intermediate, would appear to warrant further investigation.

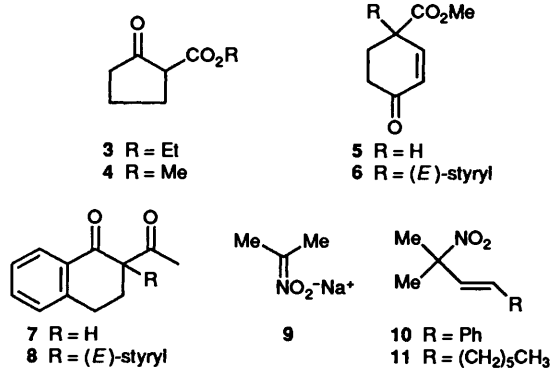
Table 1 Reaction of β-dicarbonyl compounds and sodium nitronates with vinyllead tricarboxylates generated from trimethyl(vinyl)stannanes

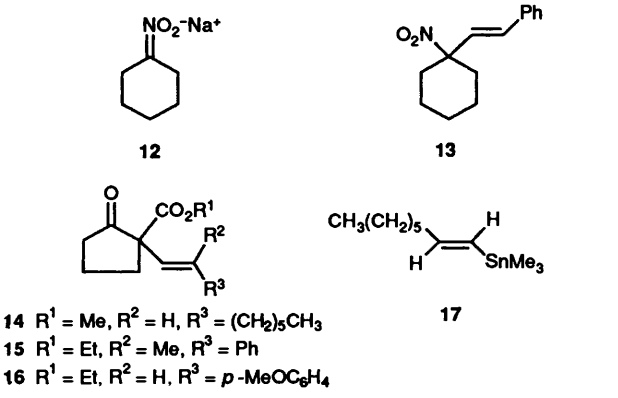
Entry	Substrate	Stannane	$Pb(OCOR)_4$	Conditions[a]	Product	Yield (%)
1	**3**	**1**	LTA	A	**2**	78
2	**3**	**1**	LTA	B	**2**	71
3	**5**	**1**	LTA	A	**6**	66
4	**7**	**1**	LTA	A	**8**	70
5	**9**	**1**	LTA	A	**10**	71
6	**12**	**1**	LTA	C	**13**	71
7	**4**	**17**	LTA	D	**14**	51
8	**9**	**17**	LTA	C	**11**	47
9	**3**	**1**	LTB	B	**2**	84
10	**3**	**19**	LTA	B	**23**	48
11	**3**	**19**	LTB	B	**23**	67
12	**3**	**20**	LTA	B	**15**	53
13	**3**	**20**	LTB	B	**15**	61
14	**3**	**21**	LTA	B	**16**	70
15	**3**	**21**	LTB	B	**16**	84
16	**3**	**22**	LTA	B	**24, 25**	10
17	**3**	**22**	LTB	B	**24, 25**	29

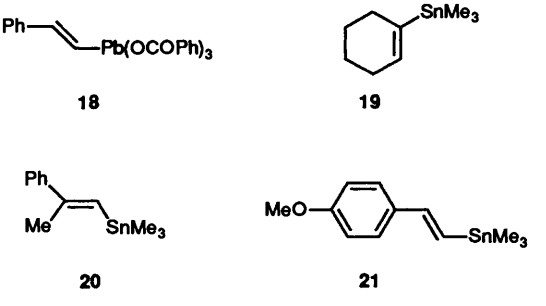
[a] See Experimental section.



Scheme 5 *Reagents and conditions:* i, LTA, $CHCl_3$, room temp., 1.0 min; ii, (3), $CHCl_3$, py, 0 °C



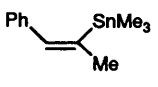




compounds **5** and **7**, and the sodium salts of 2-nitropropane **9** and nitrocyclohexane **12** respectively (entries 3, 4, 5 and 6 respectively, Table 1). Minor modifications required in the case of the nitronate salts were the use of tetrahydrofuran as a cosolvent and the exclusion of pyridine. It is noteworthy that vinylation of the vinylogous β-keto ester **5** occurred exclusively at C-1; this is analogous to the reactions of compound **5** with aryllead triacetates, which produced only C-1 arylated derivatives.[7,8,9]

In vinylations of the keto ester **4** and the sodium salt of 2-nitropropane **9** conducted in the same way as in Scheme 5 with trimethyl[(*E*)-octenyl]stannane **17**, synthetically useful yields of the expected products **14** and **11** were also obtained (entries 7 and 8, Table 1); however, yields were lower than in the corresponding reactions of the styrylstannane **1**.

In an attempt to improve yields in the vinylation reaction, an examination of the reaction of the styrylstannane **1** with lead tetrabenzoate was carried out. It was found that the metal–metal exchange was faster than for the corresponding reaction with lead tetraacetate, and when the keto ester **3** was treated with (*E*)-styryllead tribenzoate **18**, produced when the stannane **1** and lead tetrabenzoate were stirred at room temperature in chloroform for 5 min, an 84% yield of the vinylated compound **2** was obtained (entry 9, Table 1). To examine whether Sn–Pb exchange reactions conducted with lead tetrabenzoate led to improved yields in other cases, vinylations of the keto ester **3** with the vinylstannanes **19**, **20**, **21** and **22** were conducted with both lead tetraacetate and lead tetrabenzoate. Yields were optimised by monitoring the metal–metal exchange reaction by ^1H NMR spectroscopy, and in all cases an effect similar to that found in production of the (*E*)-styryl derivative **2** (entries 2 and 9, Table 1) was observed. Thus, the cyclohexene derivative **23** (entries 10 and 11, Table 1), the (*E*)-β-methylstyryl keto ester **15** (entries 12 and 13, Table 1), the (*E*)-*p*-methoxystyryl derivative **16** (entries 14 and 15, Table 1) and the mixture of (*E*) and (*Z*)-α-methylstyryl keto esters **24** and **25** (entries 16 and 17, Table 1)



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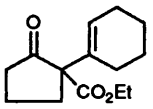

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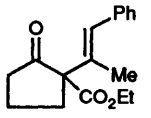

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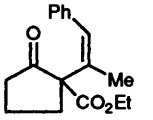

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were obtained in significantly higher yields when lead tetrabenzoate was employed.

Experimental

For general experimental procedures see our earlier paper.[9] *J* Values in Hz. The substrates, ethyl 2-oxocyclopentanecarboxylate **3**, 2-acetyltetralone **7**, 2-nitropropane and nitrocyclohexane were from Aldrich Chemical Co., while methyl 4-oxocyclohex-2-enecarboxylate **5** was prepared as a mixture of double bond isomers as previously reported.[7] Lead tetrabenzoate was prepared from lead tetraacetate and benzoic acid by the method of Hey.[10] Light petroleum refers to the fraction with b.p. 60–80 °C.

Synthesis of Trimethyl(vinyl)stannanes.—The Grignard solution prepared from the vinyl bromide (20 mmol) and magnesium turnings (1.1 mol equiv.) under nitrogen in dry tetrahydrofuran (THF) (25 cm^3) was heated at reflux for 1 h, and then decanted from the excess of magnesium through a cannula. Trimethyltin chloride (1 mol equiv.) in dry THF (15 cm^3) was added dropwise to the stirred solution under nitrogen until it had decolourised. The mixture was stirred at room temperature for a further 16 h, diluted with light petroleum (40 cm^3) and filtered through Celite. The solvent was evaporated from the filtrate and the residue was distilled to yield the trimethyl(vinyl)stannane.

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

(a) *Trimethyl[(E)-styryl]stannane* **1**. 63%, b.p. 115 °C 1.5 mmHg (Kugelrohr) (lit.,[11] 110–114 °C 3.5 mmHg); $\delta_H(CDCl_3)$ 0.25 (9 H, s, ^{119}Sn and ^{117}Sn satellites 56 and 53 Hz respectively, $SnMe_3$), 6.92 (2 H, s, $^2J_{^{119}Sn}$ and $^2J_{^{117}Sn}$ average 75, $^3J_{^{119}Sn}$ and $^3J_{^{117}Sn}$ average 111, 2 × vinyl H), 7.08 – 7.58 (5 H, m, ArH).

(*b*) *Trimethyl[(E)-2-phenylpropenyl]stannane* **20**. 83%, b.p. 130 °C 13 mmHg (lit.,[12] 125 °C 12 mmHg); $\delta_H(CDCl_3)$ 0.19 (9 H, s, ^{119}Sn and ^{117}Sn satellites 55.2 and 52.5 Hz respectively, $SnMe_3$). 2.18 (1 H, br s, Me), 6.22 (1 H, br s, ^{119}Sn and ^{117}Sn satellites 72.1 and 69.4 Hz respectively, vinyl H), 7.09–7.47 (5 H m, ArH). Stereochemistry confirmed by NOE difference spectroscopy; irradiation at δ 2.18 produced no NOE at δ 6.22, but produced a 4% NOE at δ 0.19 and a 3% NOE at δ 7.44; irradiation at δ 6.22 produced no NOE at δ 2.18, but produced a 4% NOE at δ 0.19 and a 9% NOE at δ 7.44. This sample contained 15% of the *Z*-isomer; $\delta_H(CDCl_3)$ −0.19 (9 H, s, ^{119}Sn and ^{117}Sn satellites 54.6 and 52.0 Hz respectively, $SnMe_3$), 2,21 (3 H, d, ^4J 1.50, Me), 5.85 (1 H, q, ^4J 1.50, ^{119}Sn and ^{117}Sn satellites 76.0 and 72.8 Hz respectively, vinyl H), 7.09–7.47 (5 H, m, ArH). Stereochemistry confirmed by NOE difference spectroscopy; irradiation at δ 2.21 production a 2% NOE at δ 5.85, also 7% at δ −0.18 and 4% at δ 7.44; irradiation at δ 5.85 produced a 13% NOE at δ 2.21 and a 25% NOE at δ −0.18.

(c) [(E)-p-*Methoxystyryl*]*trimethylstannane* **21**. 86%, b.p. 120 °C 0.9 mmHg (Kugelrohr) (lit.[13] 104 °C 0.6 mmHg); $\delta_H(CDCl_3)$ 0.10 (9 H, s, ^{119}Sn and ^{117}Sn satellites 55.4 and 53.2 Hz respectively, $SnMe_3$), 3.68 (3 H, s, OMe), 6.60 (1 H, d, ^3J 19.40, vinyl H), 6.74 (1 H, d, ^3J 19.40, vinyl H), 6.75 and 7.25 (4 H, AA'BB', ArH).

(d) *Trimethyl[(Z)-1-phenylprop-1-en-2-yl]stannane* **22**. 82%, b.p. 110 °C 0.4 mmHg (Kugelrohr) (Found: C, 51.7; H, 6.3. $C_{12}H_{18}Sn$ requires C, 51.3; H, 6.5%); λ_{max}(EtOH)/nm 343 (ε 10 329); $\delta_H(CDCl_3)$ 0.03 (9 H, s, ^{119}Sn and ^{117}Sn satellites 54.0 and 52.0 Hz respectively, $SnMe_3$), 2.15 (3 H, d, ^4J 1.75, ^{119}Sn and ^{117}Sn satellites 48 and 46 Hz respectively, Me), 7.18–7.39 (5 H, m, ArH), 7.29 (1 H, m, ^{119}Sn and ^{117}Sn satellite average of 138 Hz). Stereochemistry confirmed by NOE difference spectroscopy; irradiation at δ 2.15 produced an 8% NOE at δ 7.29 and a 6% NOE at δ 0.03, irradiation at δ 7.29 produced a 3% NOE at δ 2.15 and a 4% NOE at δ 0.03, irradiation at δ 0.03 produced a 2% NOE at δ 7.20; $\delta_C(CDCl_3)$ −8.25 (q, ^1J 128.3, ^{119}Sn and ^{117}Sn satellites 343.7 and 327.7 Hz respectively), 27.21 (dq, ^1J 120.5, ^3J 9.8, ^{119}Sn and ^{117}Sn satellite average 49.0 Hz), 126.62 (d, ^1J 161.0), 127.85 (d, ^1J 159.6), 127.98 (d, ^1J 159.6), 141.03 (d, ^1J 148.2, ^{119}Sn and ^{117}Sn satellite average 27.5 Hz), 141.16 (s), 144.34 (s, ^{119}Sn and ^{117}Sn satellites 444.6 and 425.6 Hz respectively).

Trimethyl[(E)oct-1-enyl]stannane **17**.—Butyllithium in hexane (4.6 cm^3, 2.3 mmol) was added dropwise to a stirred solution of (*E*)-1-iodooct-1-ene (2.50 g, 10.5 mmol) in tetrahydrofuran (25 cm^3) at −78 °C under nitrogen, and the mixture was stirred at −78 °C for 1 h. A solution of chlorotrimethylstannane (1.88 g, 9.45 mmol) in tetrahydrofuran (10 cm^3) was added and the mixture was stirred at −78 °C for 1 h, and then at room temperature for 2 h. Light petroleum (100 cm^3) was added, the mixture filtered through Celite and the solvent evaporated off. The residue was distilled to give the *title compound* **17** (1.71 g, 66%) as an oil, b.p. 110 °C 1.5 mmHg (Kugelrohr), which was too moisture sensitive to obtain an elemental analysis; $\delta_H(CDCl_3)$ 0.08 (9 H, s, $SnMe_3$), 0.74 (3 H, t, *J* 7.1, Me), 1.07–1.48 (8 H, m, 4 × CH_2), 2.13 (2 H, m, CH_2), 5.84–5.90 (2 H, m, 2 × vinyl H).

(*Cyclohex-1-enyl*)*trimethylstannane* **19**.—The preparation was carried by the method of Lambert *et al.*[14] to yield an oil (66%), b.p. 60 °C 5 mmHg (lit.[14] 88 °C 12 mmHg); $\delta_H(CDCl_3)$ 0.85 (9 H, s, ^{119}Sn and ^{117}Sn satellites 53.2 and 51.1 Hz respectively, $SnMe_3$), 1.63 (4 H, m, 2 × CH_2), 2.08 (2 H, m, CH_2), 2.18 (2 H, m, CH_2), 5.83 (1 H, m, ^{119}Sn and ^{117}Sn satellites 78.1 and 74.4 Hz respectively, vinyl H).

Synthesis of the α-Vinyl β-Dicarbonyl Compounds and α-Vinyl Nitro Compounds Reported in Table 1.—Method A. The trimethyl(vinyl)stannane (1–5 mmol, 1.1 mol equiv.) in chloroform (2 cm^3) was added to a stirred solution of lead tetraacetate (1.1 mol equiv.) in chloroform (7 cm^3) at room temperature. The solution was stirred at room temperature for 1 min and then added to a solution of the substrate (1.0 mol equiv.) in chloroform (5 cm^3) and pyridine (3.3 mol equiv.) at 0 °C. The mixture was stirred at 0 °C for 30 min and then for 3 h at room temperature. The solution was diluted with chloroform (50 cm^3) and washed in turn with dilute sulfuric acid (1 mol dm^{-3}; 2 × 30 cm^3), aqueous sodium hydrogen carbonate (10%; 30 cm^3), water (40 cm^3) and brine (40 cm^3), and then dried ($MgSO_4$), and evaporated. The residue was then fractionated as indicated.

Method B. A solution of the trimethyl(vinyl)stannane (3–4 mmol, 1.1 mol equiv.) in dry chloroform (5 cm^3) was added to a

stirred solution of the lead(IV) reagent (1.1 mol equiv.) in dry chloroform (10 cm^3) at room temperature. The mixture was stirred at room temperature for the time indicated, and the β-dicarbonyl compound (1.0 mol equiv.) was added. The mixture was stirred at room temperature overnight and then worked up as in method A above.

Method C. As for method A except that the chloroform solution of the vinyl–lead triacetate (1.2 mol equiv.) was added to a solution of the sodium nitronate salt (1.0 mol equiv.) in THF (10 cm_3).

Method D. As for method A except that 1.2 mol equiv. of the stannane was used.

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

(a) *Ethyl* 2-*oxo*-1-[(E)-*styryl*]*cyclopentanecarboxylate* **2**. Obtained by radial chromatography (light petroleum–ethyl acetate, 9:1) as an oil (78%, method A; 71%, method B with LTA; 84% method B and LTB); identical by ^1H NMR and IR spectroscopy with previously prepared material.[2]

(b) *Methyl* 1-[(E)-*styryl*]-4-*oxocyclohex*-2-*enecarboxylate* **6**. Obtained (66%) by method A and fractionation by radial chromatography (light petroleum–ethyl acetate, 22:3) as an oil (Found: M^+, 256.1095. $C_{16}H_{16}O_3$ requires M^+, 256.1099); $\delta_H(CDCl_3)$ 2.23–2.60 (4 H, m, 2 × CH_2), 3.78 (3 H, s, OMe), 6.17 (1 H, d, *J* 10.3, 3-H), 6.33 (1 H, d, *J* 16.3, C*H*=CHPh), 6.48 (1 H, d, *J* 16.3, CH=C*H*Ph), 7.16 (1 H, dd, *J* 10.3, 1.1, 2-H) and 7.14–7.21 (5 H, m, ArH): $\delta_C(CDCl_3)$ 33.6 (C-5 or C-6), 34.4 (C-5 or C-6), 45.3 (C-1), 53.2 (OMe), 126.4 (C-3′ and C-5′), 126.6 (C-2), 127.4 (C-4′), 128.4 (C-2′ and C-6′), 129.0 (vinylic C), 132.3 (vinylic C), 136.6 (C-1′), 147.4 (C-3), 171.6 (*C*O_2Me) and 197.8 (C-4); λ_{max}(EtOH)/nm 251 (ε 15 460); ν_{max}(film)/cm^{-1} 1734 and 1686; *m*/*z* 256 (M, 17%), 198 (M − CO_2CH_2, 46) and 197 (M − CO_2Me, 100).

(c) 2-*Acetyl*-2-[(E)-*styryl*]-3,4-*dihydronaphthalen*-1(2H)-*one* **8**. Obtained (70%) by method A and fractionation by radial chromatography (light petroleum–ethyl acetate, 12:1) as an oil (Found: C, 82.7; H, 6.5. $C_{20}H_{18}O_2$ requires C, 82.7; H, 6.2%); $\delta_H(CDCl_3)$ 2.55 (3 H, s, Me), 2.52–2.64 (1 H, m, 3-H), 2.75–2.82 (1 H, m, 3-H), 2.82–3.18 (2 H, m, 4-H_2), 6.47 (1 H, d, *J* 17.0, C*H*=CHPh), 6.74 (1 H, d, *J* 17.0, CH=C*H*Ph), 7.18–7.52 (8 H, m, ArH) and 8.10 (1 H, d, *J* 7.7, 8-H); $\delta_C(CDCl_3)$ 25.7 (Me), 27.8 (C-3), 30.4 (C-4), 65.9 (C-2), 126.4 (C-3′ and C-5′), 126.7 (C-7), 127.9 (C-4′), 128.0 (C-5 or C-6), 128.5 (C-2′ and C-6′), 128.7 (C-5 or C-6), 129.0 (vinylic C), 131.7 (C-8), 132.7 (vinylic C), 133.9 (C-8a), 136.2 (C-1′), 143.4 (C-4a), 195.8 ($COCH_3$) and 203.8 (C-1); λ_{max}(EtOH)/nm 254.0 (ε 29 580); ν_{max}(film)/cm^{-1} 1712, 1674 and 1599; *m*/*z* 290 (M, 18%) and 248 (M-CH_2CO, 100).

(d) (E)-3-*Methyl*-3-*nitro*-1-*phenylbut*-2-ene **10**. Obtained (71%) by method C and fractionation by HPLC (Whatman Partisil 10 M20) light petroleum–ethyl acetate, 99:1) as an oil (Found: C, 68.8; H, 7.0. $C_{11}H_{13}NO_2$ requires C, 69.1; H, 6.9%); $\delta_H(CDCl_3)$ 1.82 (6 H, s, 2 × Me), 6.51 (1 H, d, *J* 16.2, *H*C=CHPh), 6.66 (1 H, d, *J* 16.2, HC=C*H*Ph) and 7.26–7.46 (5 H, m, ArH); $\delta_C(CDCl_3)$ 26.0 (2 × Me), 87.9 (C-3), 126.8 (C-3′ and C-5′), 128.6 (C-4′), 128.7 (C-2′ and C-6′), 129.2 (HC=CHPh), 131.7 (HC=*C*HPh) and 135.4 (C-1′); λ_{max}-(EtOH)/nm 251 (ε 12 750); ν_{max}(film)/cm^{-1} 1762, 1563 and 1541; *m*/*z* 191 (M, 2%), 145 (M - NO_2, 100), 144 (M − HNO_2, 51) and 130 (145 − Me, 33).

(e) 1-*Nitro*-1-[(E)-*styryl*]*cyclohexane* **13**. Obtained by method C and fractionation by HPLC (Whatman Partisil 10 M20) (light petroleum–ethyl acetate, 99:1) as an oil which decomposed slowly at room temperature with loss of HNO_2 to give cyclohexyl(phenyl)acetylene [15] in >90% yield (Found: M^+ − HNO_2, 184.1235. $C_{14}H_{16}$ requires 184.1252); $\delta_H(CDCl_3)$ 1.33–1.74 (6 H, 3-H_2, 4-H_2 and 5-H_2), 1.89–2.08 (2 H, m, 2-H and 6-H), 2.45–2.60 (2 H, m, 2-H and 6-H), 6.26 (1 H, d, *J* 16.2, *H*C=CHPh), 6.69 (1 H, d, *J* 16.2, HC=C*H*Ph) and 7.23–7.41 (5 H, m, ArH); $\delta_C(CDCl_3)$ 22.5 (C-3 and C-5), 24.7 (C-4), 34.4 (C-2 and C-6), 90.9 (C-1), 126.8 (C-3′ and C-5′), 128.6 (C-4′), 128.7 (C-2′ and C-6′), 129.0 (vinylic C), 133.0 (vinylic C) and 135.4 (C-1′).

(f) *Methyl* 1-[(E)-*oct*-1-*enyl*]-2-*oxocyclopentanecarboxylate* **14**. Obtained (51%) by method D and column chromatography (light petroleum–ethyl acetate, 93:7) as an oil (Found: C, 71.2; H, 9.4. $C_{15}H_{24}O_3$ requires C, 71.4; H, 9.6%); $\delta_H(CDCl_3)$ 0.88 (3 H, t, *J* 6.4, Me), 1.20–1.42 (8 H, m, 4 × CH_2), 1.86–2.23 (5 H, m, 3-H, 4-H_2 and 5-H_2), 2.25–2.42 (2 H, m, allylic CH_2), 2.59 (1 H, m, 3-H), 3.73 (3 H, s, OMe) and 5.51–5.68 (2 H, m, 2 × vinylic H); $\delta_C(CDCl_3)$ 13.7 (C-8′), 19.1 (CH_2), 22.2 (CH_2), 28.3 (CH_2), 28.5 (CH_2), 31.2 (CH_2), 32.2 (CH_2), 33.1 (CH_2), 37.1 (CH_2), 52.3 (OMe), 62.3 (C-1), 125.4 (C-2′), 133.2 (C-1′), 170.8 (*C*O_2Me), 212.4 (C-2); $\nu_{max}(CHCl_3)/cm^{-1}$ 1761 and 1723; *m*/*z* 252 (M, 20%), 224 (M − CO, 22), 193 (M − CO_2Me, 20), 181 (M − C_5H_{11}, 65) 127 (60) and 121 (100).

(g) (E)-2-*Methyl*-2-*nitrodec*-3-*ene* **11**. Obtained (47%) by method C and fractionation by HPLC (Whatman Partisil 10 M20) (light petroleum–ethyl acetate, 49:1) as an oil which slowly decomposed by elimination of HNO_2 (Found: M^+ − NO_2, 153.1641. $C_{11}H_{21}$ requires 153.1643); $\delta_H(CDCl_3)$ 0.88 (3 H, t, *J* 7.2, 10-H_3), 1.23–1.34 (8 H, m, 6-H_2, 7-H_2, 8-H_2 and 9-H_2), 1.69 (6 H, s, 2 × Me), 2.01–2.12 (2 H, m, 5-H_2) and 5.77–5.82 (2 H, m, 3-H and 4-H); $\delta_C(CDCl_3)$ 13.9 (C-10), 18.7 (C-9), 22.5 (C-8), 26.0 (C-7), 28.7 (2 × Me), 28.9 (C-6), 33.2 (C-5), 83.3 (C-2), 130.6 (C-4) and 133.4 (C-3); *m*/*z* 153 (M − NO_2, 10%), 96 (14), 95 (19), 83 (18), 82 (15) and 69 (100).

(h) *Ethyl* 1-(*cyclohex*-1-*enyl*)-2-*oxocyclopentanecarboxylate* [2] **23**. Obtained by method B and radial chromatography (light petroleum–ethyl acetate, 19:1) as an oil, b.p. 100 °C 0.75 mmHg (Kugelrohr); $\delta_H(CDCl_3)$ 1.26 (3 H, t, ^3J 7.20, Me), 1.49–1.76 (4 H, m, 2 × CH_2) 1.76–2.01 (4 H, m, 2 × CH_2), 2.01–2.16 (2 H, m, CH_2), 2.24 (1 H, ddd, ^2J 13.3, ^3J 5.95, ^3J 5.95, 5α-H or 5β-H), 2.31 (2 H, m, CH_2), 2.49 (1 H, ddd, ^2J 13.30, ^3J 8.40, ^3J 6.65, 5α-H or 5β-H), 4.16 and 4.22 (2 H, each dq. each ^2J 12.60 and ^3J 7.20, O*C*H_2CH$_3$) and 5.54 (1 H, m, vinylic H); $\delta_C(CDCl_3)$ 13.96 (Me), 19.13, 21.79, 22.75, 25.36, 25.87, 32.60 and 37.84 (7 × CH_2), 61.30 (O*C*H_2CH$_3$) 67.07 (C-1), 125.42 (*C*H=C), 132.95 (CH=*C*), 170.68 (*C*O_2Et) and 212.90 (C-2); *m*/*z* 236 (M, 3%), 208 (M − CO, 100), 180 (208 − C_2H_4, 93) and 163 (M − CO_2Et, 58); identical by IR with authentic material.[2]

(i) *Ethyl* 2-*oxo*-1-[(E)-2-*phenylprop*-1-*enyl*]*cyclopentanecarboxylate* **15**. Obtained by method B and radial chromatography (light petroleum–ethyl acetate, 19:1) as an oil; $\delta_H(CDCl_3)$ 1.24 (3 H, t, ^3J 7.10, Me), 1.93–2.61 (5 H, m, 2 × CH_2, 5α-H or 5β-H), 2.06 (3 H, d, ^4J 1.36, Me), 2.85 (1 H, m, 5α-H or 5β-H), 4.19 (2 H, q, ^3J 7.10, O*C*H_2CH$_3$), 5.88 (1 H, q, ^4J 1.36, vinylic H) and 7.14–7.45 (5 H, m, ArH), irradiation at δ 2.06 produced no NOE at δ 5.88, a 1% NOE at δ 2.85 and a 3% NOE at δ 7.44, irradiation at δ 5.88 produced no NOE at δ 2.06 and a 10% NOE at δ 7.44; $\delta_C(CDCl_3)$ 13.95 (Me), 17.87 (Me), 19.34, 36.37 and 36.87 (3 × CH_2), 61.56 (O*C*H_2CH$_3$), 61.79 (C-1), 124.96 (aryl C or =CH–), 125.76 (2 × aryl C), 127.19 (aryl C or =CH–), 128.04 (2 × aryl C), 140.90 (aryl C or =*C*Me–), 143.21 (aryl C or =*C*Me–), 170.25 (*C*O_2Et) and 212.46 (C-2); identical by IR with authentic material.[2]

(j) *Ethyl* 1-[2-(E)-p-*methoxystyryl*]-2-*oxocyclopentanecarboxylate* **16**. Obtained by method B and column chromatography (light petroleum–ethyl acetate, 9:1) as an oil, b.p. 250 °C 1.0 mmHg (Kugelrohr); $\delta_H(CDCl_3)$ 1.25 (3 H, t, ^3J 7.20, Me), 1.92–2.45 (5 H, m, 2 × CH_2, 5α-H or 5β-H), 2.71 (1 H, dt, ^2J 13.19, ^3J 7.10, 5α-H or 5β-H), 3.78 (3 H, s, OMe), 4.19 (2 H, q, ^3J, 7.20, O*C*H_2CH$_3$), 6.26 (1 H, d, ^3J 16.43, =CH–), 6.48 (1 H, d, ^3J 16.43, ArC*H*=) 6.85 and 7.32 (4 H, AA′BB′, ArH); $\delta_C(CDCl_3)$ 13.96 (Me), 19.44, 33.35 and 37.37 (3 × CH_2), 55.15 (OMe), 61.67 (O*C*H_2CH$_3$) 62.69 (C-1), 113.86 (2 × Ar*C ortho* to OMe), 123.39 (=*C*H–), 127.65 (2 × Ar*C meta* to OMe),

129.09 (ArC–CH=), 159.37 (ArC–OMe), 170.34 (CO_2Et) and 212.50 (C-2); λ_{max}(EtOH)/nm 268 (17 321); *m/z* 288 (M, 11%), 242 (22), 215 (M − CO_2Et, 24), 187 (215 − CO, 43) and 159 (187 − C_2H_4, 100); identical by IR with authentic material.[2]

(k) *Ethyl 2-oxo-1-[(E)-1-phenylprop-1-en-2-yl]cyclopentanecarboxylate* **24** *and the (Z)-isomer* **25**. Obtained as a 70% (*E*), 30% (*Z*) mixture by method **B** and radial chromatography (light petroleum–ethyl acetate, 49:1) as an oil; $\delta_H(CDCl_3)$ [(*E*)-isomer] 1.27 (3 H, t, ^3J 7.10, Me), 1.82–2.74 (6 H, m, 3 × CH_2), 1.91 (3 H, d, ^4J 1.33, Me), 4.23 (2 H, q, ^3J 7.10, CH_2), 6.37 (1 H, br s, =CH–) and 7.09–7.40 (5 H, m, ArH); [(*Z*)-isomer] *inter alia* 1.88 (3 H, d, ^4J 1.55, Me), 4.24 (2 H, ^3J 7.10, OCH_2CH_3) and 6.62 (1 H, br s, =CH–); $\delta_C(CDCl_3)$ [(*E*)-*isomer*] 14.10 (Me), 29.70 (vinylic Me), 29.37, 33.39 and 38.03 (3 × CH_2), 61.71 (OCH_2CH_3), 66.71 (C-1), 126.83, 128.07, 129.08, (3 × aryl *C*H), 130.58 (=CH–), 135.17 (aryl C), 137.33 (=*C*Me–), 171.50 (CO_2Et) and 214.10 (C-2); identical by IR with authentic material.[2]

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References

1 M. G. Moloney and J. T. Pinhey, *J. Chem. Soc., Chem. Commun.*, 1984, 965.
2 M. G. Moloney and J. T. Pinhey, *J. Chem. Soc., Perkin Trans. 1*, 1988, 2847.
3 M. G. Moloney, J. T. Pinhey and M. J. Stoermer, *J. Chem. Soc., Perkin Trans. 1*, 1990, 2645.
4 J. T. Pinhey and M. J. Stoermer, *J. Chem. Soc., Perkin Trans. 1*, 1991, 2455.
5 S.-I. Hashimoto, Y. Miyazaki, T. Shinoda and S. Ikegami, *Tetrahedron Lett.*, 1989, **30**, 7195.
6 S.-I. Hashimoto, T. Shinoda and S. Ikegami, *J. Chem. Soc., Chem. Commun.*, 1988, 1137.
7 D. J. Ackland and J. T. Pinhey, *J. Chem. Soc., Perkin Trans. 1*, 1987, 2689.
8 D. J. Ackland and J. T. Pinhey, *J. Chem. Soc., Perkin Trans. 1*, 1987, 2695.
9 C. J. Parkinson and J. T. Pinhey, *J. Chem. Soc., Perkin Trans. 1*, 1991, 1053.
10 D. H. Hey, C. J. M. Stirling and G. H. Williams, *J. Chem. Soc.*, 1954, 2747.
11 D. Seyferth, L. G. Vaughan and R. Suzuki, *J. Organomet. Chem.*, 1964, **1**, 437.
12 T. N. Mitchell and W. Reimann, *J. Organomet. Chem.*, 1987, **322**, 141.
13 A. Alvanipour, C. Eaborn and D. R. M. Walton, *J. Organomet. Chem.*, 1980, **201**, 233.
14 J. B. Lambert, G.-T. Wang and D. H. Teranova, *J. Org. Chem.*, 1988, **53**, 5422.
15 S. Elbel, K. Lienert, A. Krebs and H. tom Dieck, *Liebigs Ann. Chem.*, 1981, 1785.

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