Stereoselective synthesis of (*Z*)-α-(alkoxycarbonyl)methylene β- and γ-lactones by palladium-catalysed oxidative carbonylation of alkynols

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(*Z*)-α-(Alkoxycarbonyl)methylene β- and γ-lactones can be obtained in fair to excellent yields and with high catalytic efficiencies by PdI_2/KI-catalysed oxidative dialkoxycarbonylation of propynyl alcohols (α,α-dialkyl substituted, or α-monoalkyl substituted with a sufficiently bulky alkyl group) and but-3-yn-1-ols, respectively. Reactions are carried out in alcoholic media under mild conditions (70–80 °C and 20 atm of a 3 : 1 mixture of carbon monoxide and air). Reaction pathways are discussed.

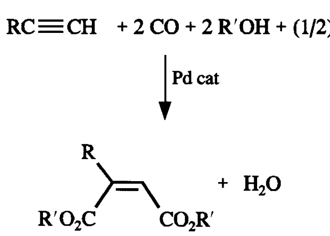
Introduction

Transition metal-catalysed carbonylation of alkynols is an attractive route to α-methylene lactone derivatives. The α-methylene lactone unit occurs in some natural products, which show a wide spectrum of physiological activity.[1] A palladium-catalysed synthesis of α-methylene γ-lactones was achieved by additive monocarbonylation of but-3-yn-1-ols.[2] More recently, palladium-catalysed oxidative monocarbonylation of but-3-yn-1-ols to α-methoxymethylene γ-lactone derivatives was also reported, while catalytic oxidative dicarbonylation to α-(methoxycarbonyl)methylene γ-lactones was obtained only in the case of 4-(trimethylsilyl)but-3-yn-1-ols.[3] β-Lactones were not formed by analogous carbonylations of propynyl alcohols, however.[4] α-(Triorganosilyl)methylene β-lactones were obtained by rhodium-catalysed silylcarbonylation of alkynols.[5]

We now report the synthesis of (*Z*)-α-(alkoxycarbonyl)-methylene β- and γ-lactones by palladium-catalysed oxidative dicarbonylation of propynyl alcohols (α-alkyl substituted) and but-3-yn-1-ols, respectively. A preliminary account, limited to α,α-disubstituted propynyl alcohols, was published recently.[6]

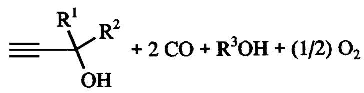
Results and discussion

Earlier we described a new and efficient method for the oxidative carbonylation of alk-1-ynes to maleic diesters.[7] The reactions were carried out in alcoholic media at 25–60 °C and 20 atm of a CO–air mixture (3 : 1) in the presence of catalytic amounts of PdI_2 + 10 KI [eqn. (1)].



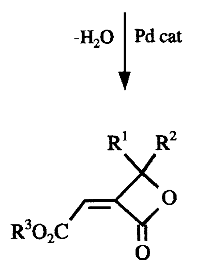
(1)

If the method is applied to substituted propynyl alcohols (α,α-dialkyl substituted, or α-monoalkyl substituted with a sufficiently bulky alkyl group), β-lactone derivatives with (*Z*)-α-(alkoxycarbonyl)methylene chains are formed as the main products, according to eqn. (2). The stereoselectivity observed



1

a $R^1 = R^2 =$ Me
b $R^1 =$ Et, $R^2 =$ Me
c R^1-$R^2 = (CH_2)_5$
d $R^1 =$ H, $R^2 = CHEt_2$



(2)

2

a $R^1 = R^2 = R^3 =$ Me
b $R^1 =$ Et, $R^2 = R^3 =$ Me
c R^1–$R^2 = (CH_2)_5$, $R^3 =$ Me
d $R^1 =$ H, $R^2 = CHEt_2$, $R^3 =$ Me
e $R^1 = R^2 =$ Me, $R^3 =$ Bu

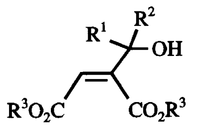
is in agreement with the *syn* character of the carbon monoxide insertion reaction.[8,9]

The main by-products are maleic diesters **3**, acetylenic esters **4** (corresponding to oxidative monocarbonylation) and products **5** derived from ring opening of **2** by alcohol attack at C-4. The latter reaction is characteristic of the β-lactone unit.[1d] It has been ascertained that the isolated β-lactones **2** are slowly converted into **5** when heated in alcoholic media at 80 °C. For example, **2a** was partly converted into **5a** (7%) when treated with methanol at 80 °C for 6 h. Small amounts of products **6** (cyclic tautomeric form[7] of **3**), **7**, **8** and **9** were detected in the reaction mixtures deriving from **1a** and **1c**. Compound **7** originates from etherification of the alcoholic function of **3** (a reaction which also occurs with simple propynyl alcohol),[7] while **8** corresponds to ring opening of **2** by attack at C-4 by the reaction with water. Formation of **9** implies a β-hydroxy elimination from the

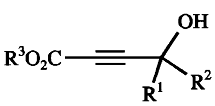
Table 1 Reactions of α-substituted propynyl alcohols with CO–air (3 : 1) and MeOH at 80 °C, initial pressure 20 atm at 20 °C, PdI_2–KI molar ratio 1 : 10, substrate conc./mol dm^{-3} (in MeOH): 0.22

Run	Substrate	Substrat- Substrate : catalyst	*t*/h	Conv'n (%)[a]	Yield of **2** (%)[a]	Total yield (%)[a]	Product : catalyst
1	**1a**	500	3	95	80	95[b]	475
2	**1a**	2000	6	73	54	71[c]	1420
3[d]	**1a**	2000	15	53	45	53[e]	1060
4	**1b**	100	5	90	76	86[f]	86
5	**1b**	1000	6	70	56	70[g]	700
6	**1c**	100	5	80	57	78[h]	78
7	**1c**	1000	8	64	41	62[i]	620
8	**1d**	500	4	84	52	81[j]	405
9	**1d**	2000	6	72	31	68[k]	1360

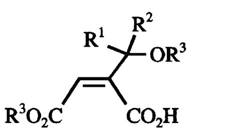
[a] Based on starting propynyl alcohol, by GLC. [b] Including **3a** (10%), **5a** (1%), **6a** (3%) and **7a** (1%). [c] Including **3a** (12%), **5a** (2%) and **6a** (3%). [d] Reaction carried out at 60 °C. [e] Including **3a** (6%) and **6a** (2%). [f] Including **3b** (6%), **4b** (1%) and **5b** (3%). [g] Including **3b** (6%), **4b** (3%) and **5b** (5%). [h] Including **3c** (4%), **4c** (4%), **5c** (2%), **8c** (8%) and **9c** (3%). [i] including **3c** (6%), **4c** (3%), **5c** (4%), **8c** (6%) and **9c** (2%). [j] Including **3d** (26%) and **4d** (3%). [k] Including **3d** (33%) and **4d** (4%).



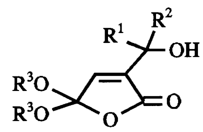
3a - e



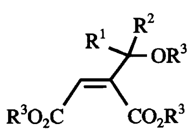
4b - d



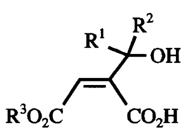
5a - c



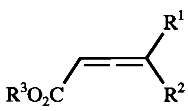
6a, e



7a, e



8c



9c

a $R^1 = R^2 = R^3 = Me$
b $R^1 = Et, R^2 = R^3 = Me$
c R^1-$R^2 = (CH_2)_5, R^3 = Me$
d $R^1 = H, R^2 = CHEt_2, R^3 = Me$
e $R^1 = R^2 = Me, R^3 = Bu$

initially formed (alkoxycarbonyl)vinylpalladium complex resulting from alkoxycarbonylation of **1**.

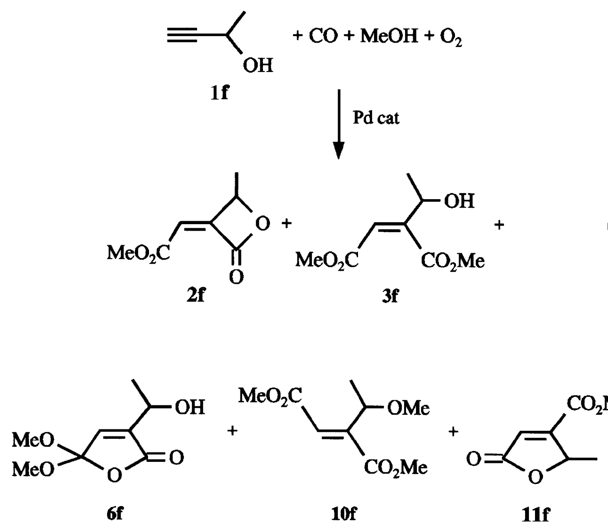
Table 1 reports the results obtained with different substituted propynyl alcohols at 80 °C in methanol as the solvent, using substrate : catalyst ratios of 100–2000. The reaction took place even at 60 °C, although the reaction rate was decreased, as shown by comparison between run 2 and run 3.

Reactions can also be effected using higher alcohols as the solvent. Under conditions similar to those of run 1, but using a substrate/Pd molar ratio = 100, the reaction of **1a** in butan-1-ol proceeded more slowly, giving 75% conversion in 5 h, with 44% yield of **2e**, 22% of **3e**, 2% of **6e** and 3% of **7e**.

Although the reactions were carried out in alcohols at 80 °C, selectivities for β-lactones **2** were rather good, ranging from 43 to 85%. Reaction times longer than those reported resulted in lower selectivities for **2**, although the total yields were higher.

Substrate reactivity tends to be lower when steric hindrance exerted by alkyl substituents increases. For example, in the case of **1a**, 1420 mol of carbonylated products per mol of palladium used could be obtained after 6 h (run 2), while 700 and 620 mol of products per mol of catalyst were obtained using **1b** (run 5) and **1c** (run 7) after 6 and 8 h, respectively.

The presence of alkyl substituents α to the triple bond is essential in order to achieve good selectivities for β-lactones. Product distribution deriving from unsubstituted propynyl alcohol is similar to that of simple alkyl- or aryl-acetylenes, the corresponding maleic diester and its cyclic isomer being the main products of the reaction with no formation of the β-lactone derivative.[7] On the other hand, yields of β-lactones deriving from α-monoalkylsubstituted propynyl alcohols are very low if the alkyl group is not sterically demanding. Thus, but-3-yn-2-ol **1f**, when allowed to react in methanol for 2 h under the usual conditions (substrate : catalyst = 2000), yielded only 2% of the corresponding β-lactone **2f** at 80% conversion. Maleic diester **3f** (50%), its cyclic tautomer **6f** (9%), the fumaric derivative **10f** (12%) and γ-lactone **11f** (6%) accounted for the converted substrate [eqn. (3)].



(3)

Product **10f** derives from etherification of the alcoholic function of **3f** with double bond isomerization, while the presence of small amounts of **11f** implies *Z* to *E* isomerization of a carbonylated species which must occur within a palladium-bonded intermediate, since *Z* to *E* isomerization of the maleic derivatives does not readily occur under our conditions.[7]

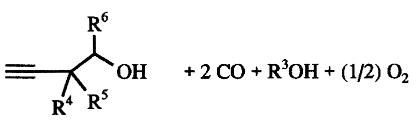
γ-Lactones with (*Z*)-α-(alkoxycarbonyl)methylene chains were obtained by PdI_2/KI-catalysed oxidative dialkoxycarbonylation of but-3-yn-1-ols **12** [eqn. (4)].

Table 2 reports the results obtained with different butynols using methanol as the solvent, with a substrate : catalyst molar ratio of 500. Reactions were carried out at 70 rather than 80 °C

Table 2 Reactions of but-3-yn-1-ols with CO–air (3 : 1) and MeOH at 70 °C, initial pressure 20 atm at 20 °C, PdI_2–KI molar ratio 1 : 10, substrate–Pd molar ratio 1 : 500, substrate conc./mol dm^{-3} (in MeOH): 0.22

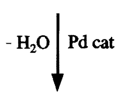
Run	Substrate	*t*/h	Conv'n (%)[a]	Yield of **13** (%)[a]	Total yield (%)[a]	Product : catalyst
10	**12g**	12	99	86	99[b]	495
11	**12h**	12	98	94	98[c]	490
12[d]	**12i**	24	92	73	92[e]	460
13	**12j**	15	100	93[f]	93[f]	465
14	**12k**	15	100	28	94[g]	470

[a] Based on starting but-3-yn-1-ol, by GLC (unless otherwise noted). [b] Including **14g** (13%). [c] Including **14h** (4%). [d] Reaction carried out at 80 °C. [e] Including **15i** (19%). [f] Isolated yield. [g] Including **14k** (62%) and **16k** (4%).

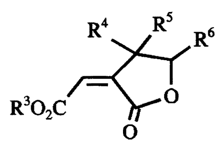


12

g $R^4 = R^5 = R^6 = H$
h $R^4 = R^5 = H, R^6 = Me$
i $R^4 = R^5 = Me, R^6 = H$
j $R^4 = H, R^5–R^6 = (CH_2)_3$ (*cis*)
k $R^4 = H, R^5–R^6 = (CH_2)_3$ (*trans*)

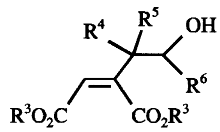


(4)

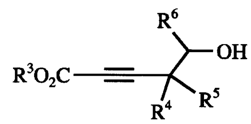


13

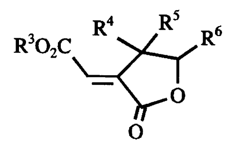
g $R^4 = R^5 = R^6 = H, R^3 = Me$
h $R^4 = R^5 = H, R^3 = R^6 = Me$
i $R^3 = R^4 = R^5 = Me, R^6 = H$
j $R^4 = H, R^5–R^6 = (CH_2)_3$ (*cis*), $R^3 = Me$
k $R^4 = H, R^5–R^6 = (CH_2)_3$ (*trans*), $R^3 = Me$



14g, h, k



15i



16k

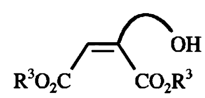
g $R^4 = R^5 = R^6 = H, R^3 = Me$
h $R^4 = R^5 = H, R^3 = R^6 = Me$
i $R^3 = R^4 = R^5 = Me, R^6 = H$
k $R^4 = H, R^5–R^6 = (CH_2)_3$ (*trans*), $R^3 = Me$

in order to maximize the selectivity in γ-lactones **13**, except for less reactive substrates such as 2,2-dimethylbut-3-yn-1-ol (**12i**, run 12).

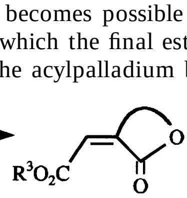
In contrast to the propynyl alcohols, substitution α to the triple bond of but-3-yn-1-ols is not necessary in order to direct the carbonylation process towards ring closure to give γ-lactones selectively. But-3-yn-1-ol **12g**, pent-4-yn-2-ol **12h** and *cis*-2-ethynylcyclopentan-1-ol **12j** were, in fact, converted into their corresponding γ-lactones **13g**, **13h** and **13j** in excellent yields (runs 10, 11 and 13, respectively). Maleic diesters **14g** and **14h** were formed as by-products in the reactions of compounds **12g** and **12h**. Where there was dialkyl substitution α to the triple bond as in **12i**, the reaction was slower, and the product yield of the γ-lactone **13i** lower, with the acetylenic ester **15i** being obtained as a by-product (run 12). When cyclization is disfavoured by molecular geometry, as in the case of *trans*-2-ethynylcyclopentan-1-ol **12k**, product distribution changes in favour of maleate, the γ-lactone being obtained as a by-product (run 14).

According to what has been previously reported,[7,8,10] the carbonylation process should be initiated by *syn* addition of an alkoxycarbonylpalladium species to the triple bond followed by carbon monoxide insertion to give an acylpalladium intermediate (Scheme 1; anionic iodide ligands are omitted for simplicity). The acylpalladium intermediate can be formed (a) starting from the alcoholic solvent R^3OH;[7,10] in this case, two different directions of attack on the triple bond are possible (path *a* and *b*, respectively); (b) starting from the alcoholic function of the substrate[8] (path *c*).

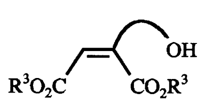
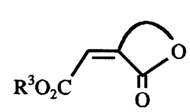
In the case of intermediate **I**, intramolecular attack by the hydroxy group on the acylpalladium moiety would readily explain lactone formation, while intermolecular attack by R^3OH would account for the maleic diester formation (Scheme 2). On the other hand, the acylpalladium moiety of the regioisomeric intermediate **II** can only undergo intermolecular attack by R^3OH to give the maleic diester [eqn. (5)], the intra-

II + R^3OH ⟶  + $[Pd^0 + HI]$ (5)

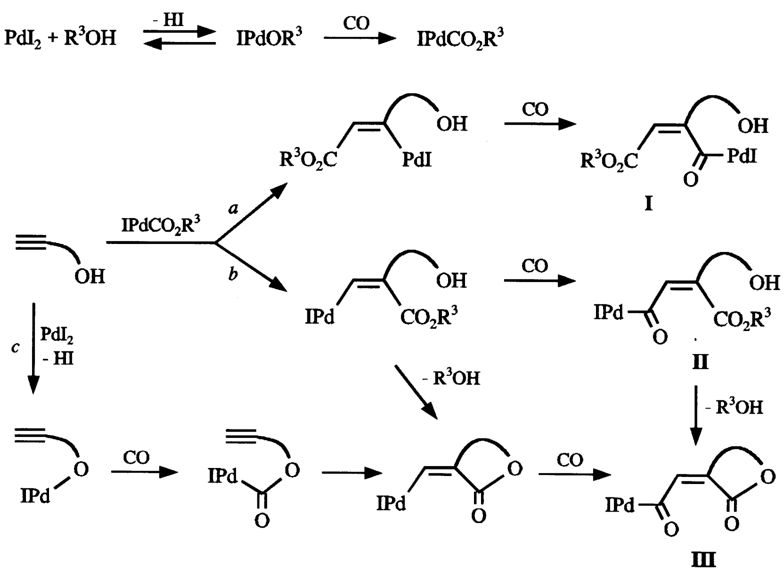
molecular attack by the hydroxy group being impossible for geometric reasons. Lactone formation, however, is compatible with path *b* as well, since in this case an intramolecular ester exchange reaction becomes possible with formation of intermediate **III**, from which the final ester lactone is obtained by R^3OH attack on the acylpalladium bond [eqn. (6)]. Also, the

III + R^3OH ⟶  + $[Pd^0 + HI]$ (6)

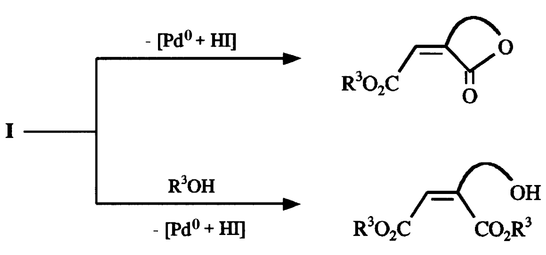
maleic diester could lactonize according to eqn. (7). As

 ⟶  + R^3OH (7)

depicted in Scheme 1, intermediate **III** can be formed directly by path *c*, without passing through path *b*.



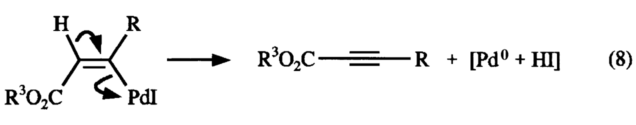
Scheme 1



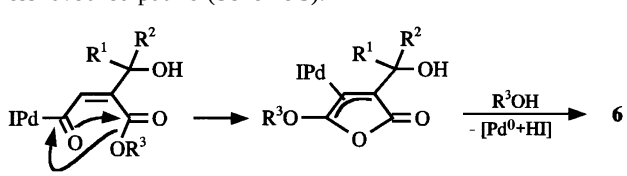
Scheme 2

Which of these pathways is the main reaction route appears to be dependent on the nature of the starting alkynol.

In respect of propynyl alcohols, although path *c* would readily explain β-lactone formation, it does not explain the experimental result that β-lactones are formed as the main products only when α,α-dialkyl substitution (or monoalkyl substitution, with the alkyl group sufficiently bulky) is present on the triple bond. On the other hand, the isolated maleic diesters **3** are not converted into the corresponding β-lactones **2** under the reaction conditions, which means that an intramolecular ester exchange reaction is not at work. Consequently, β-lactones are not formed by path *b*, which is the route normally followed under our conditions by arylacetylenes and alkylacetylenes with no substituents α to the triple bond (including propynyl alcohol).[7] Therefore, experimental results strongly suggest path *a* as the main reaction route. This is also supported by the formation of by-products **4**, which necessarily derive from path *a* [eqn. (8), R = CR^1R^2OH].



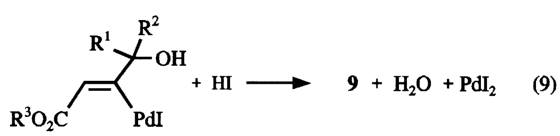
The small amounts (2–3%) of products **6** are formed by the less favoured path *b* (Scheme 3).[7]



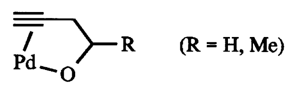
Scheme 3

Inversion of the regiochemistry of insertion of the triple bond into the Pd–CO_2R^3 bond when the triple bond is α.α-dialkyl substituted or α-monoalkyl substituted with a bulky alkyl group is clearly caused by the steric effect exerted by the alkyl groups α to the triple bond, which favours the bonding between the alkoxycarbonyl group and the less congested terminal carbon. A similar effect was observed by Nogi and Tsuji in the $PdCl_2$-catalysed carbonylation of prop-2-yn-1-ol and 2-methylbut-3-yn-2-ol in methanol as the solvent.[4a] In the presence of geminal alkyl groups, as in **1a–c**, ring formation at the acylpalladium intermediate level is favoured in respect to carbonyl esterification by the gem-dialkyl effect.[11] This allows formation of β-lactones to a substantial extent even in the presence of an alcohol as the solvent. The lower β-lactone : maleate ratio obtained in the case of **1d** is reasonable, since the *gem*-dialkyl effect is not at work when only one alkyl group α to the triple bond is present, and therefore the intermolecular attack by R^3OH becomes more competitive in respect to the intramolecular attack by the hydroxy group.

Alkyl substitution α to the triple bond slows down the carbon monoxide insertion into the palladium–vinyl bond, so the vinylpalladium intermediate can undergo side reactions such as β-hydrogen elimination and/or HI-promoted allenic rearrangement. This explains the formation of by-products **4** [eqn. (8), R = CR^1R^2OH] and **9c** [eqn. (9), R^1–R^2 = $(CH_2)_5$, R^3 = Me].



In the case of butynols **12g** and **12h**, path *a* should not be at work, since there are no substituents α to the triple bond and, therefore, the initial addition of the alkoxycarbonyl group occurs on the internal carbon of the triple bond ultimately leading to maleic diesters **14g** and **14h** (path *b*). To ascertain whether the latter could be converted into γ-lactones **13g** and **13h** we followed their behaviour under the reaction conditions without noticing lactonization. Thus, γ-lactones **13g** and **13h** must be formed by path *c*. This pathway could be favoured in respect to path *b*, even in an alcoholic solvent, due to the formation of a particularly stable five-membered chelate alkoxypalladium complex **IV**.[3]



IV

On the other hand, the small amounts of maleic diesters **14g** and **14h** must be formed by path *b*, since the isolated γ-lactones **13g** and **13h** are not converted into **14g** and **14h** under the described reaction conditions.

Path *a* is at work when the butynol is α,α-dialkyl substituted, as in **12i**, as suggested by the formation as a by-product of the acetylenic ester **15i** [eqn. (8), R = CMe_2CH_2OH]. Both path *c* and path *a* may account for γ-lactone formation in this case.

In conclusion, α-substituted propynyl alcohols and but-3-yn-1-ols can efficiently undergo, under mild conditions, oxidative dialkoxycarbonylation to (*Z*)-α-(alkoxycarbonyl)methylene β- or γ-lactones respectively with good selectivity and high catalytic efficiency, in the presence of a catalytic system based on the PdI_4^{2-} anion.

Experimental

Mps were determined on a Reichert Thermovar melting point apparatus and are uncorrected. Elemental analyses were carried out with a Carlo Erba Elemental Analyser Mod. 1106. IR Spectra were recorded on a Perkin-Elmer Paragon 1000 PC FT-IR spectrometer. Mass spectra were obtained using an HP 5972A spectrometer at 70 eV ionizing voltage. ^{1}H NMR Spectra were taken on a Bruker AC300 spectrometer and run on $CDCl_3$ solutions with Me_4Si as internal standard. Chemical shifts and coupling constants (*J*) are given as δ values (ppm) and in Hz, respectively.

The reaction mixtures were analysed by TLC (SiO_2 or Al_2O_3) or by GLC using capillary columns with polymethylsilicone + 5% phenylsilicone (HP-5) or TPA-modified polyethyleneglycol (HP-FFAP) as the stationary phase. Quantitative determination of the products was carried out by GLC using the internal standard method. Products were separated by conventional extraction techniques, followed by chromatographic procedures on silica or allumina with suitable eluents. Merck silica gel 60 (60–230 mesh) and neutral allumina 90 (70–230 mesh) were used for column chromatography. Analytical TLC plates and silica gel 60F254 for PTLC were purchased from Merck.

Preparation of alkynols

Acetylenic alcohols 2-methylbut-3-yn-2-ol **1a**, 3-methylpent-1-yn-3-ol **1b**, 1-ethynylcyclohexanol **1c**, but-3-yn-2-ol **1f**, but-3-yn-1-ol **12g** and pent-4-yn-2-ol **12h** are commercial products (Aldrich, Fluka). 2,2-Dimethylbut-3-yn-1-ol **12i**[12] *cis*-2-ethynylcyclopentanol **12j**[2a] and *trans*-2-ethynylcyclopentanol **12k**[2a] were prepared according to literature procedures.

4-Ethylhex-1-yn-3-ol 1d

This alkynol, prepared by ethynylation[13] of 2-ethylbutanal, which is commercially available, was a colourless liquid, bp 72–73 °C/15 mmHg (Found: C, 76.3; H, 11.0. $C_8H_{14}O$ requires C, 76.2; H 11.1%); ν_{max}(film)/cm^{-1} 3380m br, 3309s, 2963s, 2934s, 2877s, 2113w, 1462m, 1381m, 1330w, 1277w, 1247w, 1129w, 1024m and 890w; δ_H 0.93 (3 H, t, *J* 7.25, Me), 0.94 (3 H, t, *J* 7.32, Me), 1.30–1.68 (5 H, m, CH_2CHCH_2), 2.45 (1 H, d, *J* 2.24, C≡CH) and 4.42 (1 H, dd, *J* 2.24 and 4.37, C*H*OH); *m/z* 126 (M^+, absent), 125 (<0.5%), 111 (4), 98 (6), 97 (16), 93 (8), 84 (27), 83 (22), 79 (8), 77 (12), 71 (41), 70 (39), 69 (20), 67 (8), 65 (4), 57 (16), 56 (51), 55 (100) and 53 (22).

General procedure for catalytic oxidative carbonylation of alkynols

The carbonylations were carried out in a 300 cm^3 stainless steel autoclave (Parr) with magnetic stirring. In a typical experiment the autoclave was charged in the presence of air with PdI_2, KI (10 mol per mol of palladium) and the appropriate alkynol dissolved in MeOH or BuOH. The autoclave was pressurized with CO (15 atm) and air (up to 20 atm of total pressure) and heated and stirred for the required time. Care must be taken to fill the autoclave to levels that allow the presence of a sufficient amount of oxygen necessary for the reoxidation cycle. Reaction times, temperature, substrate concentration and substrate to catalyst ratios used are indicated in Tables 1 and 2.

Separation of products

Compounds **2a**, **3a** + **6a** and **5a** were eluted in this order by chromatography through a SiO_2 column, using a concentration gradient of hexane–ethyl acetate from 90 : 10 to 0 : 100. Products **3a** and **6a** were subsequently separated by column chromatography (SiO_2) using a mixture of light petroleum (bp 40–70 °C)–acetone (95 : 5) as eluent. Pure compound **7a** was obtained from an experiment similar to run 2 but carried out for 15 h. Chromatographic separation was effected on the crude reaction mixture on a SiO_2 column (hexane–ethyl acetate from 90 : 10 to 0 : 100; order of elution: **7a**, **2a**, **3a** + **6a**, **5a**). Products **7e**, **2e**, **6e** (in a mixture with **2e**), **3e** and **5e** were eluted in this order by chromatography through a SiO_2 column, using a concentration gradient of hexane–acetone from 98 : 2 to 0 : 100. Product **6e** was subsequently separated from **2e** by PTLC (SiO_2) using hexane–acetone (90 : 10) as eluent. Products **4b**, **2b**, **3b** and **5b**; **9c**, **4c**, **2c**, **3c**, **5c** and **8c**; **4d**, **2d** and **3d**; **10f**, **11f**, **2f**, **3f** and **6f** (in a mixture with **3f**) were eluted in the order as above using a concentration gradient of hexane–ethyl acetate from 90 : 10 to 0 : 100. Product **6f** was identified by mass, IR and ^{1}H NMR spectroscopy directly in the mixture with **3f**.

Compounds **13g** and **14g** were eluted in this order by chromatography through a SiO_2 column, using a concentration gradient of chloroform–acetone from 100 : 0 to 98 : 2. Products **13h** and **14h** were separated in a similar way. Product **13j** was purified through a SiO_2 column, using chloroform as eluent. Products **16k**, **13k** and **14k** and **15i** and **13i** were eluted in the order as above using chloroform as eluent.

Characterization of products

Identification of known products **7a**[4a] and **9c**[14] was carried out by comparison with literature data. New compounds were identified by elemental analysis and IR, ^{1}H NMR and MS data.

4,4-Dimethyl-3-[(*Z*)-(methoxycarbonyl)methylene]-1-oxacyclobutan-2-one 2a. White solid, mp 79–80 °C (Found: C, 56.7; H, 6.0. $C_8H_{10}O_4$ requires C, 56.5; H, 5.9%); ν_{max}(KBr)/cm^{-1} 3078vw, 2996vw, 1808s, 1727s, 1690s, 1441w, 1384vw, 1370vw, 1291s, 1229vw, 1205m, 1082w, 1038m, 921w, 885vw, 820w and 786m; δ_H 1.67 (6 H, s, 2 Me), 3.85 (3 H, s, CO_2Me) and 5.92 (1 H, s, =CH); *m/z* 170 (M^+, <0.5%), 155 (28), 141 (3), 126 (51), 125 (61), 113 (100), 112 (21), 111 (92), 98 (7), 95 (13), 85 (13), 83 (39), 82 (31), 73 (16), 69 (15), 67 (98), 65 (21), 59 (66) and 53 (80).

4-Ethyl-3-[(*Z*)-(methoxycarbonyl)methylene]-4-methyl-1-oxacyclobutan-2-one 2b. White solid, mp 34–35 °C (Found: C, 58.6; H, 6.6, $C_9H_{12}O_4$ requires C, 58.7; H, 6.5%); ν_{max}(film)/cm^{-1} 2978m, 2955m, 2885w, 1817s, 1733s, 1694m, 1461m, 1437m, 1382w, 1338s, 1287s, 1162s, 1081s, 1018m, 901w, 882w, 823m and 785m; δ_H 1.04 (3 H, t, *J* 7.48, Me), 1.64 (3 H, s, Me), 1.95 (2 H, q, *J* 7.48, CH_2), 3.84 (3 H, s, CO_2Me) and 5.97 (1 H, s, =CH); *m/z* 184 (M^+, <0.5%), 169 (2), 156 (9), 155 (100), 141 (2), 125 (65), 113 (99), 97 (7), 85 (5), 82 (11), 81 (28), 79 (16), 77 (5), 69 (6), 59 (18), 57 (16) and 53 (36).

3-[(*Z*)-(Methoxycarbonyl)methylene]-1-oxaspiro[3,5]nonan-2-one 2c. White solid, mp 71–72 °C (Found: C, 63.0; H, 6.6. $C_{11}H_{14}O_4$ requires C, 62.9; H, 6.7%); ν_{max}(KBr)/cm^{-1} 2940m, 2861w, 1807s, 1725s, 1690m, 1447m, 1294m, 1170w, 1033m, 903m and 790m; δ_H 1.37–2.07 (10 H, m, 5 CH_2), 3.85 (3 H, s, CO_2Me) and 6.00 (1 H, s, =CH); *m/z* 210 (M^+, 1%), 195 (1), 178 (13) 168 (18), 165 (9), 155 (22), 154 (58), 151 (50), 150 (42), 140 (27), 137 (23), 126 (22), 123 (53), 122 (33), 113 (29), 107 (19), 105 (25), 99 (20), 95 (37), 94 (23), 91 (31), 82 (34), 81 (28), 80 (22), 79 (47), 77 (24), 69 (39), 67 (35), 65 (19), 59 (39), 55 (100) and 53 (79).

3-[(*Z*)-Methoxycarbonyl)methylene]-4-(pentan-3-yl)-1-oxacyclobutan-2-one 2d. Colourless oil (Found: C, 62.5; H, 7.6. $C_{11}H_{16}O_4$ requires C, 62.3; H, 7.5%); ν_{max}(film)/cm^{-1} 2965m, 2940w, 2879w, 1825s, 1734s, 1695w, 1461w, 1437w, 1337m, 1287m, 1213m, 1118m, 1069m and 870m; δ_H 0.95 (3 H, t, *J* 7.48, Me), 0.96 (3 H, t, *J* 7.48, Me), 1.35–1.59 (4 H, m, 2 CH_2), 1.68–1.80 (1 H, m, C*H*Et$_2$), 3.85 (3 H, s, CO_2Me), 4.94 (1 H, dd, *J* 6.76 and 1.64, CHOC=O) and 6.04 (1 H, d, *J* 1.64, =CH); *m/z* 212 (M^+, <0.5%), 183 (2), 153 (2), 142 (52), 141 (10), 110 (100), 95 (2), 82 (9), 71 (11), 69 (5), 59 (13), 55 (12) and 53 (16).

3-[(*Z*)-(Butoxycarbonyl)methylene]-4,4-dimethyl-1-oxacyclobutan-2-one 2e. Colourless oil (Found: C, 62.4; H, 7.4. $C_{11}H_{16}O_4$ requires C, 62.3; H, 7.5%); ν_{max}(film)/cm^{-1} 2963m, 2935m, 2875w, 1821s, 1730s, 1693m, 1461w, 1387w, 1374w, 1331m, 1274s, 1173s, 1066s, 1026m, 1015m, 908w, 819w, 793m and 719w; δ_H 0.95 (3 H, t, *J* 7.36, Me), 1.35–1.52 (2 H, m, CH_2), 1.58–1.75 (2 H, m, CH_2), 1.67 (6 H, s, 2 Me), 4.23 (2 H, t, *J* 6.69, CH_2OC=O) and 5.93 (1 H, s, =CH); *m/z* 212 (M^+, absent), 197 (<0.5%), 157 (6), 155 (3), 141 (19), 140 (25), 139 (100), 126 (2), 113 (8), 112 (53), 111 (80), 99 (8), 97 (13), 83 (51), 69 (10), 67 (34), 59 (14), 57 (52), 56 (21), 55 (19) and 53 (24).

3-[(*Z*)-(Methoxycarbonyl)methylene]-4-methyl-1-oxacyclobutan-2-one 2f. Colourless oil (Found: C, 53.6; H, 5.2. $C_7H_8O_4$ requires C, 53.8; H, 5.1%); ν_{max}(film)/cm^{-1} 2956w, 2918w, 1822s, 1733s, 1696w, 1438m, 1337m, 1291m, 1260m, 1218m, 1135m, 1111m, 1077m, 1019m, 909s, 831w and 732s; δ_H 1.63 (3 H, d, *J* 6.33, Me), 3.85 (3 H, s, CO_2Me), 5.13 (1 H, qd, *J* 6.33 and 1.62, CHOC=O) and 6.00 (1 H, d, *J* 1.62, =CH); *m/z* 156 (M^+, 60%), 141 (1), 128 (6), 125 (29), 124 (100), 113 (28), 97 (33), 96 (11), 85 (14), 82 (42), 69 (11), 59 (18), 55 (41), 54 (12) and 53 (19).

Dimethyl (*Z*)-2-(1-hydroxy-1-methylethyl)but-2-enedioate 3a. Colourless oil (Found: C, 53.5; H, 7.0. $C_9H_{14}O_5$ requires C, 53.5; H, 6.9%); ν_{max}(film)/cm^{-1} 3492m br, 2983m, 2955m, 1725s, 1649m, 1437s, 1347s, 1260s, 1196s, 1170s, 1046m, 1020m, 970w, 908m, 889w and 823w; δ_H 1.46 (6 H, s, 2 Me), 3.73 (3 H, s, CO_2Me), 3.85 (3 H, s, CO_2Me) and 6.11 (1 H, s, =CH); *m/z* 202 (M^+, absent), 187 (14%) 171 (6), 159 (7), 155 (100), 153 (16), 143 (3), 139 (5), 127 (53), 114 (13), 113 (65), 111 (11), 99 (5), 85 (12), 83 (6), 82 (8), 69 (8), 59 (41) and 53 (15).

Dimethyl (*Z*)-2-(1-hydroxy-1-methylpropyl)but-2-enedioate 3b. Colourless oil (Found: C, 55.5; H, 7.4. $C_{10}H_{16}O_5$ requires C, 55.6; H, 7.4%); ν_{max}(film)/cm^{-1} 3509m br, 2978m, 2954m, 2884w, 1728s, 1647m, 1456m, 1437m, 1348m, 1259s, 1202s, 1168s, 1063w, 1036m, 1014m, 928w, 910w, 887w and 736w; δ_H 0.93 (3 H, t, *J* 7.43, Me), 1.42 (3 H, s, Me), 1.65–1.78 (2 H, m, CH_2), 3.74 (3 H, s, CO_2Me), 3.85 (3 H, s, CO_2Me) and 6.08 (1 H, s, =CH); *m/z* 216 (M^+, absent), 201 (1%), 187 (10), 169 (10), 167 (7), 156 (9), 155 (100), 141 (15), 127 (6), 125 (6), 124 (4), 114 (5), 113 (47), 97 (2), 85 (6), 82 (5), 73 (7), 69 (5), 59 (9), 57 (11), 55 (8) and 53 (11).

Dimethyl (*Z*)-2-(1-hydroxycyclohexyl)but-2-enedioate 3c. White solid, mp 59–60 °C (Found: C, 59.4; H, 7.4. $C_{12}H_{18}O_5$ requires C, 59.5; H, 7.4%); ν_{max}(KBr)/cm^{-1} 3496m br, 2937m, 2860w, 1727s, 1645w, 1436m, 1346m, 1258s, 1200m, 1166s, 989w and 882w; δ_H 1.09–1.86 (10 H, m, 5 CH_2), 3.73 (3 H, s, CO_2Me), 3.85 (3 H, s, CO_2Me) and 6.12 (1 H, s, =CH); *m/z* 242 (M^+, absent), 211 (9%), 210 (54), 193 (21), 183 (37), 182 (48), 178 (55), 167 (40), 155 (25), 154 (93), 151 (62), 150 (56), 140 (51), 139 (19), 136 (19), 126 (24), 123 (41), 122 (30), 113 (31), 105 (21), 98 (21), 95 (32), 94 (21), 82 (29), 81 (49), 79 (21), 69 (38), 68 (25), 67 (22), 59 (46), 55 (100) and 53 (57).

Dimethyl (*Z*)-2-(2-ethyl-1-hydroxybutyl)but-2-enedioate 3d. Colourless oil (Found: C, 58.9; H, 8.1. $C_{12}H_{20}O_5$ requires C, 59.0; H, 8.2%); ν_{max}(film)/cm^{-1} 3510m br, 2961s, 2935m, 2877m, 1728s, 1651m, 1461m, 1437m, 1347m, 1265s, 1201s, 1169s, 1086w, 1052w, 1019m and 974w; δ_H 0.88 (3 H, t, *J* 7.35, Me), 0.91 (3 H, t, *J* 7.27, Me), 1.17–1.66 (5 H, m, CH_2CHCH_2), 3.74 (3 H, s, CO_2Me), 3.83 (3 H, s, CO_2Me), 4.49 (1 H, dd, *J* 3.84 and 1.67, C*H*OH) and 6.13 (1 H, d, *J* 1.67, =CH); *m/z* 244 (M^+, absent), 213 (1%), 174 (4), 173 (4), 143 (9), 142 (100), 141 (21), 140 (14), 113 (7), 110 (50), 99 (6), 82 (7), 71 (8), 69 (4), 59 (9), 55 (10) and 53 (8).

Dibutyl (*Z*)-2-(1-hydroxy-1-methylethyl)but-2-enedioate 3e. Colourless oil (Found: C, 62.8; H, 9.2. $C_{15}H_{26}O_5$ requires C, 62.9; H, 9.1%); ν_{max}(film)/cm^{-1} 3496m br, 2961s, 2935m, 2874w, 1720s, 1646m, 1465m, 1391m, 1339m, 1253s, 1173s, 1062m, 1042w, 962w, 890w and 735m; δ_H 0.93 (3 H, t, *J* 7.30, Me), 0.95 (3 H, t, *J* 7.31, Me), 1.33–1.53 (4 H, m, 2 CH_2), 1.47 (6 H, s, 2 Me), 1.53–1.76 (4 H, m, 2 CH_2), 4.12 (2 H, t, *J* 6.70, CH_2OC=O), 4.25 (2 H, t, *J* 6.67, CH_2OC=O) and 6.10 (1 H, s =CH); *m/z* 286 (M^+, absent), 271 (8%), 243 (1), 229 (5), 213 (7), 197 (10), 169 (6), 157 (13), 141 (100), 139 (49), 124 (5), 113 (55), 111 (26), 99 (14), 83 (15), 69 (7), 59 (22), 57 (57) and 55 (10).

Dimethyl (*Z*)-2-(1-hydroxyethyl)but-2-enedioate 3f. Colourless oil (Found: C, 51.1; H, 6.5. $C_8H_{12}O_5$ requires C, 51.1; H, 6.4%); ν_{max}(film)/cm^{-1} 3441m br, 2983w, 2956m, 1726s, 1654m, 1438m, 1358m, 1270s, 1203s, 1172s, 1080m, 1007w, 925w and 890w; δ_H 1.39 (3 H, d, *J* 6.57, Me), 3.75 (3 H, s, CO_2Me), 3.85 (3 H, s, CO_2Me), 4.59 (1 H, qd, *J* 6.57 and 1.50, C*H*OH) and 6.12 (1 H, d, *J* 1.50, =CH); *m/z* 188 (M^+, absent), 173 (19%), 157 (17), 145 (22), 141 (78), 129 (12), 124 (19), 114 (19), 113 (100), 97 (32), 85 (24), 82 (19), 69 (19), 59 (40), 55 (22) and 53 (40).

Methyl 4-hydroxy-4-methylhex-2-ynoate 4b. Colourless oil (Found: C, 61.5; H, 7.8. $C_8H_{12}O_3$ requires C, 61.5; H, 7.7%); ν_{max}(film)/cm^{-1} 3421m br, 2977m, 2941m, 2884w, 2236m, 1718s, 1457m, 1437m, 1373w, 1256s, 1164m, 1137w, 1035m, 994w, 926m and 753m; δ_H 1.06 (3 H, t, *J* 7.46, Me), 1.53 (3 H, s, Me), 1.70–1.81 (2 H, m, CH_2) and 3.79 (3 H, s, CO_2Me); *m/z* 156 (M^+, absent), 155 (<0.5%), 141 (12), 128 (7), 127 (100), 125 (9), 113 (8), 109 (12), 96 (11), 95 (61), 85 (24), 81 (8), 71 (6), 69 (9), 59 (4), 57 (8), 55 (7) and 53 (84).

Methyl 3-(1-hydroxycyclohexyl)prop-2-ynoate 4c. White solid, mp 39–40 °C (Found: C, 66.0; H, 7.7. $C_{10}H_{14}O_3$ requires C, 65.9; H, 7.7%); ν_{max}(film)/cm^{-1} 3265m br, 2937m, 2861w, 2237m, 1713s, 1451m, 1435m, 1285m, 1242s, 1074m, 1042m, 944w and 753w; δ_H 1.20–2.03 (10 H, m, 5 CH_2) and 3.78 (3 H, s, CO_2Me); *m/z* 182 (M^+, <0.5%), 167 (2), 151 (27), 150 (46), 139 (44), 135 (18), 126 (30), 122 (57), 121 (49), 111 (57), 108 (26), 107 (96), 98 (38), 95 (77), 94 (59), 82 (24), 81 (41), 80 (34), 79 (76), 77 (22), 69 (36), 67 (37), 66 (32), 59 (17), 55 (87) and 53 (100).

Methyl 5-ethyl-4-hydroxyhept-2-ynoate 4d. Colourless oil (Found: C, 65.1; H, 8.8. $C_{10}H_{16}O_3$ requires C, 65.2; H, 8.7%); ν_{max}(film)/cm^{-1} 3426m br, 2963s, 2935s, 2878m, 2235m, 1720s, 1461m, 1436m, 1383w, 1255s, 1132w, 1053m, 1025m, 968w, 907w and 753m; δ_H 0.93 (3 H, t *J* 7.32, Me), 0.94 (3 H, t, *J* 7.32, Me), 1.30–1.68 (5 H, m, CH_2CHCH_2), 3.79 (3 H, s, CO_2Me) and 4.54 (1 H, d, *J* 4.47, C*H*OH); *m/z* 184 (M^+, absent) 166 (<0.5%), 153 (4), 124 (1), 115 (6), 114 (100), 110 (2), 99 (5), 85 (3), 82 (14), 81 (7), 71 (6), 68 (5), 67 (4), 59 (3), 55 (12) and 53 (15).

4-Methyl hydrogen (*Z*)-2-(1-methoxy-1-methylethyl)but-2-enedioate 5a. Colourless oil (Found: C, 53.4; H, 7.0. $C_9H_{14}O_5$ requires C, 53.5, H, 6.9%); ν_{max}(film)/cm^{-1} 3600–2800m br, 2983m, 2950m, 1725s, 1642m, 1435m, 1380m, 1330m, 1173s and 1069m; δ_H 1.42 (6 H, s, 2 Me), 3.23 (3 H, s, OMe), 3.83 (3 H, s, CO_2Me) and 6.02 (1 H, s, =CH); *m/z* 202 (M^+, absent), 155 (78%), 140 (8), 112 (8), 111 (7), 100 (4), 83 (100), 73 (10), 67 (11), 59 (7) and 53 (10).

4-Methyl hydrogen (*Z*)-2-(1-methoxy-1-methylpropyl)but-2-enedioate 5b. Colourless oil (Found: C, 55.5; H, 7.3. $C_{10}H_{16}O_5$ requires C, 55.6; H, 7.4%); ν_{max}(film)/cm^{-1} 3600–2800m br, 2926s, 1732s, 1646m, 1462m, 1438m, 1379m, 1329m, 1260m, 1176s, 1079m and 899w; δ_H 0.88 (3 H, t, *J* 7.43, Me), 1.39 (3 H, s, Me), 1.77 (2 H, q, *J* 7.43, CH_2), 3.22 (3 H, s, OMe), 3.77 (3 H, s, CO_2Me) and 6.00 (1 H, s, =CH); *m/z* 216 (M^+, absent), 184 (<0.5%), 169 (4), 156 (7), 155 (66), 141 (9), 140 (6), 125 (6), 112 (6), 97 (13), 83 (100), 81 (6), 79 (5), 69 (3), 67 (3), 65 (3), 59 (3) and 53 (17).

4-Methyl hydrogen (*Z*)-2-(1-methoxycyclohexyl)but-2-enedioate 5c. Colourless oil (Found: C, 59.6; H, 7.3. $C_{12}H_{18}O_5$ requires C, 59.5; H, 7.4%); ν_{max}(film)/cm^{-1} 3600–2800m br, 2940s, 1732s, 1645m, 1437m, 1324m, 1198s and 1072m; δ_H 1.15–

2.07 (10 H, m, 5 CH_2), 3.19 (3 H, s, OMe), 3.76 (3 H, s, CO_2Me) and 6.00 (1 H, s, =CH); *m/z* 242 (M^+, absent), 210 (4%), 195 (3), 180 (36), 167 (100), 166 (91), 154 (28), 153 (54), 152 (40), 151 (45), 139 (54), 137 (39), 135 (13), 123 (29), 121 (15), 110 (28), 109 (58), 105 (31), 95 (82), 91 (26), 82 (30), 81 (27), 79 (35), 77 (33), 69 (24), 67 (20), 65 (24), 59 (4), 55 (31) and 53 (51).

5,5-Dimethoxy-3-(1-hydroxy-1-methylethyl)-1-oxacyclopent-3-en-2-one 6a. Colourless oil (Found: C, 53.6; H, 6.8. $C_9H_{14}O_5$ requires C, 53.5; H, 6.9%); ν_{max}(film)/cm^{-1} 3450m br, 2954s, 2927s, 2850m, 1773s, 1633w, 1463m, 1365m, 1303s, 1195s, 1181s, 1139s, 1080m, 1001s, 937s, 880w, 835w, 791w and 737w; δ_H 1.53 (6 H, s, 2 Me), 3.44 (6 H, s, 2 OMe) and 6.72 (1 H, s, =CH); *m/z* 202 (M^+, absent), 187 (17%), 171 (21), 159 (3), 155 (17), 153 (28), 143 (11), 139 (11), 127 (12), 113 (36), 111 (16), 99 (100), 85 (15), 83 (15), 69 (20), 59 (53) and 53 (18).

5,5-Dibutoxy-3-(1-hydroxy-1-methylethyl)-1-oxacyclopent-3-en-2-one 6e. Colourless oil (Found: C, 62.7; H, 9.0. $C_{15}H_{26}O_5$ requires C, 62.9; H, 9.1%); ν_{max}(film)/cm^{-1} 3521m br, 2961s, 2935m, 2875w, 1771s, 1462m, 1287s, 1173s and 733m; δ_H 0.92 (6 H, t, *J* 7.36, 2 Me), 1.30–1.50 (4 H, m, 2 CH_2), 1.50–1.77 (4 H, m, 2 CH_2), 1.53 (6 H, s, 2 Me), 3.54–3.75 (4 H, m, 2 CH_2OC=O) and 6.72 (1 H, s, =CH); *m/z* 286 (M^+, absent), 271 (3%), 229 (1), 213 (32), 183 (5), 157 (46), 141 (28), 139 (100), 127 (22), 124 (7), 113 (25), 111 (36), 99 (8), 95 (8), 83 (16), 59 (17), 57 (39) and 55 (12).

5,5-Dimethoxy-3-(1-hydroxyethyl)-1-oxacyclopent-3-en-2-one 6f. This compound was obtained as a 3 : 7 mixture with **3f**. Signals reported here refer to **6f** only; ν_{max}(film)/cm^{-1} 1776s; δ_H 1.46 (3 H, d, *J* 6.60, Me), 3.44 (6 H, s, 2 OMe), 4.67 (1 H, qd, *J* 6.60 and 1.60, C*H*OH) and 6.86 (1 H, d, *J* 1.60, =CH); *m/z* 188 (M^+, absent), 173 (5%), 157 (41), 141 (8), 129 (16), 115 (10), 113 (11), 110 (6), 99 (100), 97 (30), 91 (4), 85 (10), 82 (7), 71 (10), 69 (21), 59 (29), 55 (25) and 53 (28).

Dibutyl (*Z*)-2-(1-butoxy-1-methylethyl)but-2-enedioate 7e. Colourless oil (Found: C, 66.8; H, 10.0. $C_{19}H_{34}O_5$ requires C, 66.7; H, 9.9%); ν_{max}(film)/cm^{-1} 2959s, 2934m, 2873m, 1731s, 1645w, 1465m, 1383m, 1338m, 1249m, 1171s, 1071m, 1037w and 735m; δ_H 0.91 (3 H, t, *J* 7.20, Me), 0.93 (3 H, t, *J* 7.23, Me), 0.95 (3 H, t, *J* 7.21, Me), 1.30–1.75 (12 H, m, 3 CH_2CH_2), 1.41 (6 H, s, 2 Me), 3.34 (2 H, t, *J* 6.78, CH_2O), 4.12 (2 H, t *J* 6.70, CH_2OC=O), 4.24 (2 H, t, *J* 6.78, CH_2OC=O) and 5.97 (1 H, s, =CH); *m/z* 342 (M^+, absent), 327 (3%), 271 (2), 253 (2), 241 (2), 218 (8), 197 (12), 196 (22), 195 (10), 185 (3), 156 (6), 141 (70), 140 (100), 139 (49), 129 (3), 115 (15), 113 (8), 112 (22), 111 (25), 83 (14), 67 (7), 59 (49), 57 (39) and 55 (10).

4-Methyl hydrogen (*Z*)-2-(1-hydroxycyclohexyl)but-2-enedioate 8c. Colourless oil (Found: C, 58.0; H, 7.1. $C_{11}H_{16}O_5$ requires C, 57.9; H, 7.0%); ν_{max}(film)/cm^{-1} 3600–2800m, br, 2940s, 1732s, 1607m, 1437m, 1260s and 1172s; δ_H 1.15–2.07 (10 H, m, 5 CH_2), 3.76 (3 H, s, CO_2Me) and 5.77 (1 H, s, =CH); *m/z* 228 (M^+, absent), 178 (77%), 150 (64), 149 (24), 135 (11), 132 (47), 131 (21), 122 (33), 105 (100), 104 (37), 103 (24), 94 (19), 91 (67), 79 (45), 78 (57), 77 (40), 65 (21), 63 (23) and 53 (14).

Dimethyl (*E*)-2-(1-methoxyethyl)but-2-enedioate 10f. Colourless oil (Found: C, 53.4; H, 6.9. $C_9H_{14}O_5$ requires C, 53.5; H, 6.9%); ν_{max}(film)/cm^{-1} 2986w, 2954m, 1725s, 1651w, 1436m, 1364w, 1258s, 1216s, 1119m, 1010m, 898w and 867w; δ_H 1.49 (3 H, d, *J* 6.60, Me), 3.27 (3 H, s, OMe), 3.78 (3 H, s, CO_2Me), 3.82 (3 H, s, CO_2Me), 4.81 (1 H, qd, *J* 6.60 and 0.60, C*H*OMe) and 6.63 (1 H, d, *J* 0.60, =CH); *m/z* 202 (M^+, absent), 187 (12%), 171 (29), 170 (100), 159 (7), 155 (13), 142 (19), 139 (25), 127 (15), 123 (5), 113 (21), 112 (36), 111 (19), 97 (11), 83 (74), 75 (43), 69 (12), 59 (69) and 53 (32).

4-(Methoxycarbonyl)-5-methyl-1-oxacyclopent-3-en-2-one 11f. Colourless oil (Found: C, 53.7; H, 5.2. $C_7H_8O_4$ requires C, 53.8; H, 5.1%); ν_{max}(film)/cm^{-1} 2992w, 2958m, 1774s, 1730s, 1635w, 1439m, 1358m, 1300m, 1233s, 1163m, 1060m, 960m and 766m; δ_H 1.59 (3 H, dd, *J* 6.75 and 0.24, Me), 3.91 (3 H, s, CO_2Me), 5.29 (1 H, qd, *J* 6.75 and 1.94, CHOC=O) and 6.67 (1 H, dq, *J* 1.94 and 0.24, =CH); *m/z* 156 (M^+, 3%), 141 (23), 127 (6), 125 (23), 124 (11), 114 (100), 113 (49), 99 (6), 97 (7), 85 (12), 82 (17), 69 (9), 59 (25) and 53 (66).

3-[(*Z*)-Methoxycarbonyl)methylene]-1-oxacyclopentan-2-one 13g. Colourless oil (Found: C, 53.7; H, 5.2. $C_7H_8O_4$ requires C, 53.8; H, 5.1%); ν_{max}(film)/cm^{-1} 2995m, 2955m, 2927w, 1763s, 1735s, 1677m, 1435m, 1377m, 1335m, 1259s, 1183s, 1102m, 1009s, 959w and 898m; δ_H 3.06 (2 H, td, *J* 7.17 and 2.64, CH_2C=), 3.83 (3 H, s, CO_2Me), 4.42 (2 H, t, *J* 7.17, CH_2OC=O) and 6.38 (1 H, t, *J* 2.64, =CH); *m/z* 156 (M^+, 2%), 127 (33), 125 (100), 124 (99), 112 (44), 99 (24), 97 (62), 96 (54), 82 (35), 81 (19), 69 (84), 68 (20), 59 (94), 55 (12) and 53 (55).

3-[(*Z*)-(Methoxycarbonyl)methylene]-5-methyl-1-oxacyclopentan-2-one 13h. Colourless oil (Found: C, 56.4; H, 6.0. $C_8H_{10}O_4$ requires C, 56.5; H, 5.9%); ν_{max}(film)/cm^{-1} 2981m, 2954m, 1761s, 1735s, 1677m, 1435m, 1387w, 1343m, 1261s, 1185s, 1108w, 1083m, 1040w, 1011m and 947w; δ_H 1.45 (3 H, d, *J* 6.29, Me), 2.62 (1 H, distorted ddd, *J* 17.26, 6.31 and 2.84, C*H*H), 3.15 (1 H, distorted ddd, *J* 17.26, 7.25 and 2.34, CH*H*), 3.83 (3 H, s, CO_2Me), 4.64–4.77 (1 H, m, CHOC=O) and 6.31–6.35 (1 H, m, =CH); *m/z* 170 (M^+, <0.5%), 155 (5), 139 (34), 138 (28), 127 (47), 123 (12), 110 (100), 99 (33), 95 (15), 83 (13), 69 (21), 67 (23), 59 (37) and 53 (10).

4,4-Dimethyl-3-[(*Z*)-methoxycarbonyl)methylene]-1-oxacyclopentan-2-one 13i. Colourless oil (Found: C, 58.6; H, 6.4. $C_9H_{12}O_4$ requires C, 58.7; H, 6.5%); ν_{max}(film)/cm^{-1} 2967m, 1760s, 1735s, 1669m, 1614w, 1463m, 1435m, 1367m, 1327m, 1267m, 1224m, 1141m, 1053m, 1012m, 902w and 790w; δ_H 1.31 (6 H, s, 2 Me), 3.84 (3 H, s, CO_2Me), 4.08 (2 H, s, CH_2) and 6.21 (1 H, s, =CH); *m/z* 184 (M^+, 6%), 169 (3), 154 (50), 153 (82), 152 (14), 140 (40), 139 (20), 127 (24), 126 (92), 125 (100), 124 (18), 111 (57), 97 (39), 96 (21), 95 (21), 94 (16), 83 (16), 81 (43), 79 (28), 67 (78), 66 (24), 65 (25), 59 (41), 55 (17) and 53 (66).

4-[(*Z*)-Methoxycarbonyl)methylene]-*cis*-2-oxabicyclo[3.3.0]-octan-3-one 13j. White solid, mp 45–46 °C (Found: C, 61.2; H, 6.1. $C_{10}H_{12}O_4$ requires C, 61.2; H, 6.1%); ν_{max}(KBr)/cm^{-1} 2977m, 2961m, 1753s, 1723s, 1669m, 1431m, 1369m, 1329m, 1264m, 1199m, 1185m, 1148m 1096m, 1034m, 1013m, 913w, 772w and 650w; δ_H 1.52–1.85 (4 H, m, ring), 1.92–2.15 (2 H, m, ring), 3.41–3.51 (1 H, m, 5-H), 3.84 (3 H, s, CO_2Me), 4.98–5.06 (1 H, m, 1-H) and 6.33 (1 H, d, *J* 2.25, =CH); *m/z* 196 (M^+, 15%), 165 (81), 164 (27), 152 (37), 140 (100), 139 (42), 137 (65), 136 (74), 124 (18), 119 (17), 112 (15), 111 (25), 109 (44), 108 (70), 107 (33), 95 (31), 93 (25), 91 (47), 81 (53), 80 (49), 79 (80), 77 (36), 74 (14), 67 (36), 59 (50) and 53 (41).

4-[(*Z*)-(Methoxycarbonyl)methylene]-*trans*-2-oxabicyclo-[3.3.0]octan-3-one 13k. White solid, mp 83–84 °C (Found: C, 61.2; H, 6.2. $C_{10}H_{12}O_4$ requires C, 61.2; H, 6.1%); ν_{max}(KBr)/cm^{-1} 2991w, 2959w, 1767s, 1730s, 1679m, 1435m, 1306m, 1259s, 1175m, 1136m, 1115m, 1055w, 1006m, 939w, 910w and 882w; δ_H 1.43–1.80 (2 H, m, ring), 1.87–2.27 (4 H, m, ring), 2.69 (1 H, tdd, *J* 11.61, 6.25 and 3.14, 5-H), 3.78–3.90 (1 H, m, 1-H), 3.82 (3 H, s, CO_2Me) and 6.10 (1 H, d, *J* 3.14, =CH); *m/z* 196 (M^+, 6%), 165 (19), 164 (17), 150 (15), 140 (32), 137 (17), 136 (100), 112 (40), 109 (16), 108 (21), 91 (19), 81 (29), 79 (23), 77 (14), 65 (10), 59 (18) and 53 (28).

Dimethyl (*Z*)-2-(2-hydroxyethyl)but-2-enedioate 14g. Colourless oil (Found: C, 51.0; H, 6.5. $C_8H_{12}O_5$ requires C, 51.1; H, 6.4%); ν_{max}(film)/cm^{-1} 3435m br, 2955m, 2888w, 1737s, 1650m, 1437m, 1371m, 1275s, 1205s, 1172s, 1123w, 1045m, 974w and 756w; δ_H 2.59 (2 H, td, *J* 6.12 and 1.23, CH_2), 3.73 (3 H, s, CO_2Me), 3.79 (2 H, t, *J* 6.12, CH_2OH), 3.84 (3 H, s, CO_2Me) and 5.97 (1 H, t, *J* 1.23, =CH); *m/z* 188 (M^+, absent), 157 (14%), 126 (100), 125 (32), 99 (14), 98 (43), 69 (34), 68 (39), 67 (19), 59 (40) and 53 (15).

Dimethyl (*Z*)-2-(2-hydroxypropyl)but-2-enedioate 14h. Colourless oil (Found: C, 53.4; H, 6.8. $C_9H_{14}O_5$ requires C, 53.5; H, 6.9%); ν_{max}(film)/cm^{-1} 3443m br, 2995m, 1725s, 1649m, 1437m, 1373m, 1273s, 1202s, 1172s, 1129m, 1082w, 1015w, 972w, 943w and 843w; δ_H 1.25 (3 H, d, *J* 6.21, Me), 2.43 (1 H, distorted ddd, *J* 14.07, 8.41 and 1.05, C*H*H), 2.53 (1 H, distorted ddd, J 14.07, 4.12 and 1.39, CHH), 3.74 (3 H, s, CO_2Me), 3.85 (3 H, s, CO_2Me), 3.93–4.11 (1 H, m, CHOH) and 5.92–5.96 (1 H, m, =CH); m/z 202 (M^+, absent), 187 (<0.5%), 171 (3), 158 (5), 139 (12), 127 (20), 126 (100), 99 (11), 98 (39), 69 (20), 68 (30), 67 (15), 59 (26) and 53 (6).

Dimethyl (*Z*)-2-[*trans*-(2-hydroxycyclopentyl)]but-2-enedioate 14k. Colourless oil (Found: C, 58.1; H, 7.0. $C_{11}H_{16}O_5$ requires C, 57.9; H, 7.0%); ν_{max}(film)/cm^{-1} 3439m, br, 2954s, 2877w, 1718s, 1644m, 1437m, 1378m, 1271s, 1201s, 1171s, 1019m, 975w, 873w and 756m; δ_H 1.53–1.87 (4 H, m, ring), 1.90–2.10 (2 H, m, ring), 2.56-2.73 (1 H, m, CHC=), 3.72 (3 H, s, CO_2Me), 3.84 (3 H, s, CO_2Me), 4.10–4.21 (1 H, m, CHOH) and 5.90 (1 H, d, J 1.22, =CH); m/z 228 (M^+, absent), 197 (12%), 196 (24), 168 (22), 164 (16), 152 (48), 140 (100), 139 (41), 137 (79), 136 (50), 124 (23), 112 (18), 111 (28), 109 (61), 108 (36), 107 (16), 96 (16), 93 (13), 91 (18), 81 (53), 80 (28), 79 (49), 67 (20), 59 (74), 55 (22) and 53 (28).

Methyl 4,4-dimethyl-5-hydroxypent-2-ynoate 15i. Colourless oil (Found: C, 61.3; H, 7.8. $C_8H_{12}O_3$ requires C, 61.5; H, 7.7%); ν_{max}(film)/cm^{-1} 3443m br, 2972m, 2874w, 2235m, 1717s, 1436m, 1295m, 1261s, 1061m, 1028m and 754w; δ_H 1.27 (6 H, s, 2 Me), 3.50 (2 H, s, CH_2) and 3.77 (3 H, s, CO_2Me); m/z 156 (M^+, absent), 155 (<0.5%), 126 (100), 125 (63), 111 (44), 95 (21), 94 (97), 93 (18), 83 (25), 82 (20), 79 (42), 67 (74), 66 (25), 65 (23), 59 (16) and 53 (26).

4-[(*E*)(Methoxycarbonyl)methylene]-*trans*-2-oxabicyclo-[3.3.0]octan-3-one 16k. Colourless oil (Found: C, 61.0; H, 6.2. $C_{10}H_{12}O_4$ requires C, 61.2; H, 6.1%); ν_{max}(film)/cm^{-1} 2957w, 2922m, 1781s, 1730s, 1437m, 1343w, 1265s, 1209m, 1175m, 1125m, 1052m, 1015m and 739s; δ_H 1.55–1.85 (2 H, m, ring), 1.90–2.06 (1 H, m, ring), 2.10–2.24 (2 H, m, ring), 2.25–2.45 (1 H, m, ring), 2.72–2.85 (1 H, m, 5-H), 3.76–3.93 (1 H, m, 1-H), 3.79 (3 H, s, CO_2Me) and 6.68 (1 H, d, J 3.52, =CH); m/z 196 (M^+, <0.5%), 165 (32), 164 (12), 152 (53), 140 (54), 139 (28), 137 (48), 136 (100), 124 (27), 120 (17), 113 (23), 112 (20), 111 (37), 109 (58), 108 (46), 107 (24), 97 (11), 96 (21), 91 (30), 81 (62), 80 (35), 79 (65), 77 (33), 67 (22), 65 (33), 59 (72), 55 (28) and 53 (46).

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Paper 6/03892A
Received 4*th June* 1996
Accepted 9*th September* 1996