*Tetrahedron* Vol. 44, No. 2, pp. 481 to 490, 1988
Printed in Great Britain.

0040-4020/88 $3.00+.00


# THE PALLADIUM-TRIBUTYLAMMONIUM FORMATE REAGENT IN THE STEREOSELECTIVE HYDROGENATION, AND STEREO- AND REGIOSELECTIVE HYDROARYLATION OF ALKYL 4-HYDROXY-2-ALKYNOATES: A ROUTE TO SUBSTITUTED BUTENOLIDES

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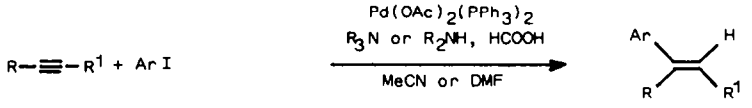
(*Received in UK 22 October* 1987)

Abstract - The reaction of aryl iodides with alkyl 4-hydroxy-2-alkynoates in the presence of formic acid, tri-n-butylamine and a palladium(II) catalyst provides a convenient route to functionalized substituted butenolides through a one pot hydroarylation/cyclization reaction. In the presence of formic acid, tri-n-butylamine and a palladium(II) catalyst, alkyl 4-hydroxy-2-alkynoates undergo a one pot hydrogenation/cyclization reaction to the butenolide ring. By increasing the excess of formic acid, direct formation of saturated γ-lactones can be observed. Reactions occur with high stereoselectivity and, in the case of the hydroarylation, with good regioselectivity.

## INTRODUCTION

The reaction of aryl iodides with acetylenic systems (diarylacetylenes[1a], arylethynylcarbinols[1b], aryl and alkylethynylsilanes[1c]) in the presence of a palladium catalyst, formic acid, and a secondary or tertiary amine, results in the formation of substituted olefinic derivatives.




R = $R^1$ = Ar

R = Ar; $R^1$ = —C(OH)

R = Ar, alkyl; $R^1$ = $Me_3Si$

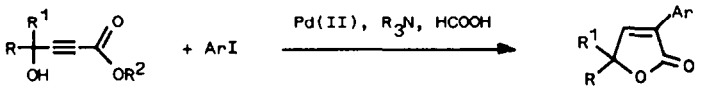
Scheme 1

This hydroarylation reaction, which can tolerate various common functional groups, occurs with high stereoselectivity and, depending on the nature of the substituents on the sp carbon atoms, with good regioselectivity. In practice, this reaction allows the alkynes to be the precursors of substituted alkenes with defined regio- and stereochemistry.

Since the syn stereochemistry of addition[2] pushes the substituent R and $R^1$ on the same side of the carbon-carbon double bond, we speculated that in the presence of suitable functionalities

intramolecular cyclization could follow the addition step. Therefore, the reaction could provide new access to a variety of substituted cyclic derivatives.

Consequently on the basis of this hypothesis as well as the regioselectivity observed in the reaction of arylethynyl, dialkylcarbinols[1b] we tried applying this hydroarylation/cyclization procedure to the synthesis of the substituted butenolides (3), by reacting aryl iodides (2) with alkyl 4-hydroxy-2-alkynoates (1).




(1) (2) (3)

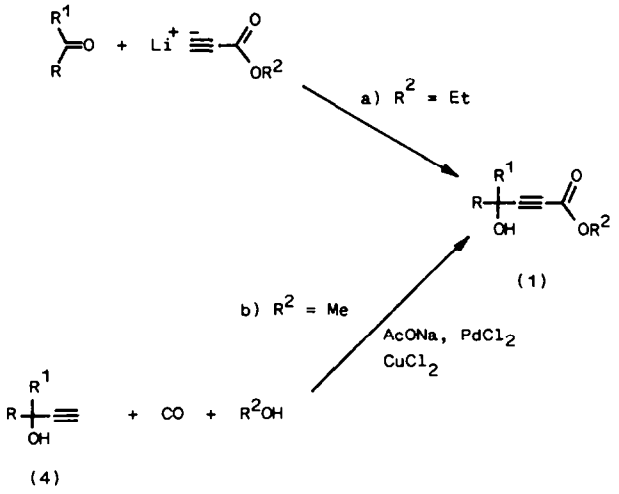
Scheme 2

Moreover there is a continual interest in synthetic methods[3] for the preparation of butenolide derivatives as the butenolide moiety is present in numerous biologically active natural products and may be useful as a synthon for the construction of complex structures.

The results of this study are reported hereafter.

## RESULTS AND DISCUSSION

The starting alkyl 4-hydroxy-2-alkynoates (1) were prepared either by treating aldehydes and ketones with lithium ethylpropinoate according to Midland[5] (Scheme 3, a) (Table 1) or by treating ethynylcarbinols (4) with carbon monoxide in methanol using catalytic amounts of $PdCl_2$ and an excess of $CuCl_2$ in the presence of sodium acetate according to Tsuji[6](Scheme 3, b) (Table 2).



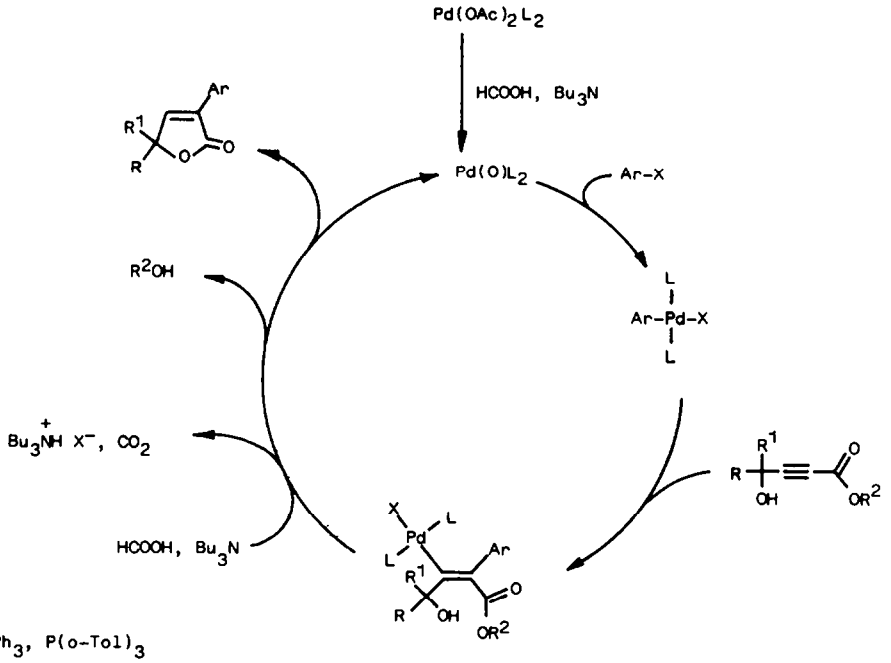

(1) (4)

Scheme 3

Usually, the extention of the above conditions for palladium-catalysed carbonylation of terminal alkynes to ethynylcarbinols gave the best results with crowded systems (Table 2, entries i,l,m,o)[7]. Otherwise, the reaction of the corresponding carbonyl compounds with lithium ethylpropinoate gave ethyl 4-hydroxy-2-alkynoates in better yields.

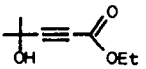
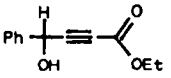
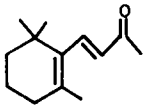
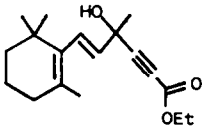
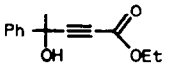
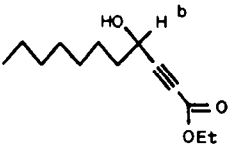
The reaction of alkyl 4-hydroxy-2-alkynoates with a variety of aryl iodides in the presence

of $Pd(OAc)_2L_2$(L = $PPh_3$, $P(o\text{-}Tol)_3$) (5 mol %), formic acid, and tri-n-butylamine gave the desired butenolides (3) in good to high yields (Table 3) most likely according to the scheme illustrated below:



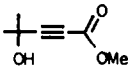
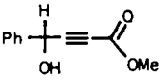
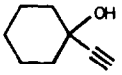
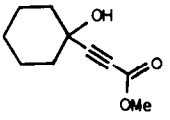
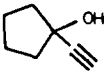
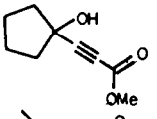
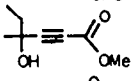
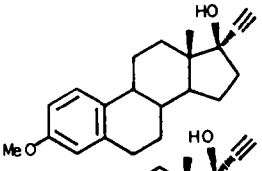
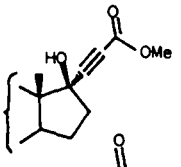
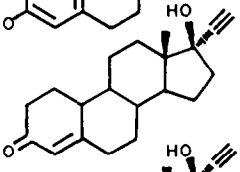
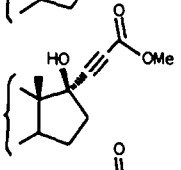
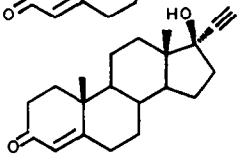
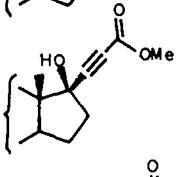
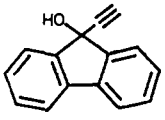
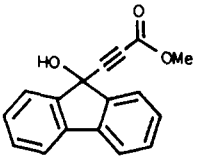
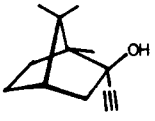
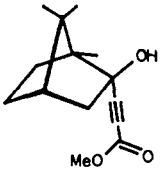

Scheme 4

Table 1 - Ethyl 4-Hydroxy-2-alkynoates Prepared from Lithium Ethylpropinoate and Ketones or Aldehydes.[a]

| Entry | Ketone or aldehyde | Ethyl 4-hydroxy-2-alkynoate (1) |
|---|---|---|
| a |  |  |
| b |  |  |
| c |  |  |
| d |  |  |
| e |  |  |

a) All of these compounds were prepared according to reference 5 in comparable yields. b) Isolated in 66% yield.

Table 2 - Methyl 4-Hydroxy-2-alkynoates Prepared Through Palladium-Catalysed Carbonylation of Ethynylcarbinols[a]

| Entry | Ethynylcarbinol (4) | Methyl 4-hydroxy-2-alkynoate (1) | (% yield)[b] |
|---|---|---|---|
| a' |  |  | 30 |
| b' |  |  | 21 |
| f |  |  | 30 |
| g |  |  | 26 |
| h |  |  | 38 |
| i |  |  | 75 |
| l |  |  | 84 |
| m |  |  | 88 |
| n |  |  | 55 |
| o |  |  | 65 |

a) All of these compounds were prepared according to reference 6. b) Yields refer to single non-optimized runs, are calculated on the starting ethynyl carbinols and are for pure, isolated products.

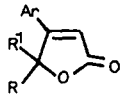
Table 3 - Palladium-Catalysed Hydroarylation of Alkyl 4-Hydroxy-2-alkynoates (1)[a]

| Entry | Alkyl 4-hydroxy--2-alkynoate (1) | Aryl iodide (2) | Phosphine | Reaction time (hr) | Butenolide (3) (% yield)[b] | Butenolide (5) (% yield)[b] |
|---|---|---|---|---|---|---|
| a | 1a' | 4-MeO-$C_6H_4$-I | $PPh_3$ | 6 | 60 | - |
| b | " | 4-HO-$C_6H_4$-I | " | 6 | 61 | - |
| c | " | 3-$HOCH_2$-$C_6H_4$-I | " | 6 | 50 | - |
| d | 1a | Ph-I | $P(o\text{-}Tol)_3$ | 8 | 49 | 9 |
| e | 1d | 4-MeO-$C_6H_4$-I | " | 7 | 66 | 15 |
| f | " | " | $PPh_3$ | 7 | 57 | 14 |
| g | 1h | 3-Me-$C_6H_4$-I | $P(o\text{-}Tol)_3$ | 7 | 59 | 9 |
| h | 1i | 4-MeO-$C_6H_4$-I | " | 6 | 93 | - |
| i | " | 2-MeO-$C_6H_4$-I | " | 9 | 67 | - |
| l | " | 3-F-$C_6H_4$-I | " | 6 | 84 | - |
| m | 1c | 4-Cl-$C_6H_4$-I | " | 6 | 41 | - |
| n | " | Ph-I | " | 6 | 57 | 4 |
| o | 1f | 4-MeO-$C_6H_4$-I | " | 7 | 58 | 11 |
| p | 1g | PhI | " | 8 | 46 | 11 |
| q | 1l | 4-Cl-$C_6H_4$-I | " | 8 | 57 | - |
| r | " | 4-F-$C_6H_4$-I | " | 8 | 41 | - |
| s | 1e | 4-MeO-$C_6H_4$-I | " | 12 | 32 | 31 |

a) Reactions were carried out at 60°C with a molar ratio (1):(2):HCOOH:n-$Bu_3N$:Pd(OAc)$L_2$ = 1:2.4:2.6:3.4:0.05. b) Yields refer to single non-optimized runs, are calculated on the starting alkyl 4-hydroxy-2-alkynoates, and are for pure, isolated products.

Cyclization to the butenolide ring occurs under hydroarylation conditions.

The regioselectivity of the reaction is good and appears to be determined mainly by steric and coordinating factors[1b] favouring the formation of the C-Pd bond on the carbon near the hydroxy group. Accordingly, the isomeric butenolides (5) were usually isolated in low yield.




(5)

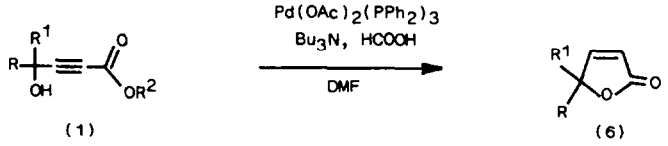
The structure of butenolides (3) and (5) was assigned on the grounds of $^1$H-NMR analysis. Vinylic protons of (3) are downfield from vinylic protons of (5). As an example, in compounds (3e) and (5e), $\delta$ values ($CDCl_3$) of vinylic protons are 7.64 and 6.40, respectively ( $\delta$ values for a variety of related 4-aryl-butenolides have been reported[3e] to be in the 6.23-6.40 range).

The use of catalysts containing phosphines with different steric demands could cause some change in the regiochemical course of the reaction (Table 3, entries e and f). Even the yield of the reaction seems to be affected by the steric hinderance of the ligand. These points, however, have not been investigated.

As expected, when an alkyl 4-hydroxy-2-alkynoate containing a less hindered secondary alcoholic group was reacted under usual conditions, a lack of regiochemistry was observed. For example, the reaction of (1e) with 4-methoxyphenyl iodide produced the corresponding isomeric

butenolides (3) and (5) in yields of 32 and 31 % respectively (Table 3, entry s).

We also attempted the reaction of alkyl 4-hydroxy-2-alkynoates with formic acid and tri-n-butylamine in the presence of the palladium catalyst. Under these conditions, a variety of alkyl 4-hydroxy-2-alkynoates containing tertiary and secondary hydroxy groups underwent a one-pot hydrogenation/cyclization to butenolides (6) in good to high yield (Table 4).




(1) (6)

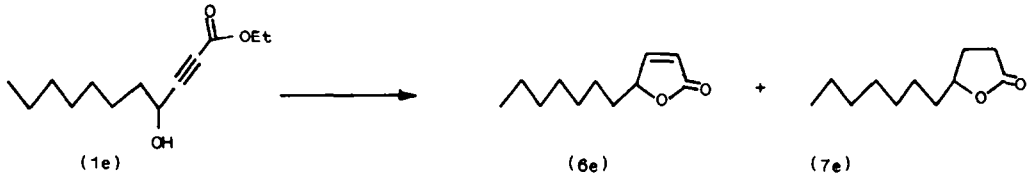
Scheme 5

Table 4 - Palladium-Catalysed Hydrogenation of Alkyl 4-Hydroxy-2-alkynoates[a]

| Entry | Alkyl 4-hydroxy-2-alkynoate (1) | Reaction time (hr) | Butenolide (6) (% yield)[b] |
|---|---|---|---|
| a | 1i | 6 | 73 |
| b | 1l | 8 | 78 |
| c | 1o | 6 | 81 |
| d | 1n | 5 | 75 |
| e | 1e | 7 | 69[c] |
| f | 1m | 6 | 85 |

a) Reactions were carried out at 60°C by using $Pd(OAc)_2(PPh_3)_2$ as the catalyst with a molar ratio (1):HCOOH:n-$Bu_3N$:$Pd(OAc)_2(PPh_3)_2$ = 1:2.6:3.4:0.02, unless otherwise specified. b) Yields refer to single non-optimized runs, are calculated on the starting alkyl 4-hydroxy-2-alkynoates, and are for pure isolated products. c) Carried out with an excess of about 50% of HCOOH.

With (1e), an alkyl 4-hydroxy-2-alkynoate containing a secondary hydroxy group, the outcome of the reaction depended on the amount of formic acid while formation of the corresponding butenolide and saturated γ-lactone can be observed. Thus, while under usual conditions, (1e) was converted into an 85/15 mixture of (6e) and (7e) (65% total yield), when formic acid was reduced to about 50% excess it was possible to isolate (6e) in 69% yield and an increase of formic acid to about 300% excess gave (7e) in 64% yield.



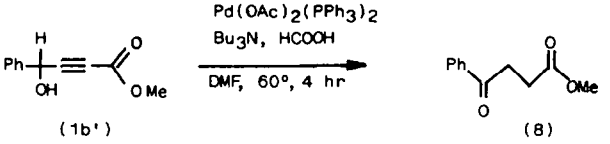
(1e) (6e) (7e)

Scheme 6

No attempts were made (prolonging the reaction times, increasing the temperature and/or excess

of formic acid etc.) to ascert whether the palladium-tributylammonium formate reagent could be used for the one pot preparation of saturated γ-lactones from more hindered alkyl 4-hydroxy-2--alkynoates.

Finally, it is worth reporting that the reaction of (1b') under usual hydrogenation conditions, instead of the expected cyclic derivative produced the γ-keto ester (8) in 65% yield.




(1b') (8)

Scheme 7

## CONCLUSIONS

More and more, palladium-catalysed hydroarylation of acetylenic systems is emerging as a versatile and convenient reaction for the synthesis of a variety of functionalized derivatives. The results reported here show that this reaction may be successfully applied to the preparation of the derivatized butenolide ring. Furthermore, the one-pot hydrogenation/cyclization of alkyl 4-hydroxy--2-alkynoates to butenolides in the presence of the palladium-tributylammonium formate reducing system appears to be a useful alternative to established procedures using molecular hydrogen/Lindlar catalyst followed by acid catalysed cyclization[8]. Even the formation of γ-lactones may be of synthetic value and the formation of γ-keto esters would seem to disclose an efficient and practical route to precursors of a variety of heterocyclic compounds.

Studies along this line are in progress.

## EXPERIMENTAL

M.ps are uncorrected and were determined with a Büchi 510 apparatus. All starting materials, catalysts, solvents, and amines are commercially available ande were used without further purification. Reactions were carried out on a 1.0-5.0 mmol scale. The products were purified by flash chromatography on silica gel 40-63 μ (Merck) eluting with n-hexane/AcOEt mixtures.

$^1$H-NMR spectra were recorded with a Varian EM390 Spectrometer (TMS internal standard). IR spectra were recorded with a Perkin-Elmer 683 Spectrometer. MS spectra were recorded with a Hewlett-Packard HP 5980A Spectrometer equipped with a Data System 5934A.

All of the isolated products gave satisfactory microanalyses.

General procedure of hydroarylation of alkyl 4-hydroxy-2-alkynoates.

This is exemplified by the reaction of (1i) with 4-methoxyphenyl iodide. Compound (1i) (0.38 g, 1.04 mmol), $Pd(OAc)_2$ (0.024 g, 0.052 mmol), and tri-o-tolilphosphine (0.062 g, 0.1 mmol) were added to a stirred solution of 4-methoxyphenyl iodide (0.584 g, 2.5 mmol) and tributylamine (0.84 ml, 3.54 mmol) in DMF (2 ml). The mixture was gently purged with nitrogen, and formic acid (0.1 ml, 2.74 mmol) was added all at once. The mixture was stirred at 60 °C under a nitrogen atmosphere for 7 hr. AcOEt and water were added, and the organic layer was separated, washed with water, dried ($Na_2SO_4$)and concentrated at reduced pressure. The residue was purified by flash chromatography. Elution with a 90/10 n-hexane/AcOEt mixture gave compound (3h) (0.428 g, 93% yield).

General procedure of hydrogenation of alkyl 4-hydroxy-2-alkynoates.

This is exemplified by the hydrogenation of (1i). Tributylamine (0.86 ml, 3.7 mmol) and $Pd(OAc)_2(PPh_3)_2$ (0.017 g, 0.022 mmol) were added to a stirred solution of (1i) (0.4g,1.1 mmol) in DMF ( 2 ml) . The mixture was purged with nitrogen, and formic acid (0.11 ml, 2.9 mmol) was added all at once. The mixture was stirred at 60 °C under a nitrogen atmosphere for 6 hr, AcOEt and 0.1 N HCl were added, and the organic layer was separated, washed with water, dried ($Na_2SO_4$), and concentrated at reduced pressure. The residue was purified by flash chromatography. Elution with an 85/15 n-hexane/AcOEt mixture gave (6a) (0.27 g, 73% yield).

Hydrogenation of ethyl 4-hydroxy-2-undecynoate (1e).

a) Usual conditions: tributylamine (1.5 ml, 6.32 mmol) and $Pd(OAc)_2(PPh_3)_2$ (0.028 g, 0.036 mmol) were added to a stirred solution of (1e)(0.42 g, 1.86 mmol) in DMF (2 ml). The mixture was purged

Table 5 - Characterization of Compounds (1)

| Compound | M.p. (°C) | I.R. ν ($cm^{-1}$) | $^1$H-NMR δ (ppm)[a] | MS m/e |
|---|---|---|---|---|
| 1e | oil | 3420, 2250, 1720[b] | 4.41 (m,1H), 4.26 (q, J = 7.5 Hz, 2H), 3.07 (m, $D_2O$ exchange, 1H), 2.0-1.1 (m, 12H), 1.29 (t, J =7.5 Hz, 3H), 0.87 (t, 3H) | 127 |
| 1i | 130-131 | 3450, 2230, 1740 1620[c] | 7.34-6.60 (m, 3H), 3.79 (s, 3H), 3.78 (s, 3H), 0.89 (s, 3H) | 368 |
| 1l | 175-180 (dec) | 3340, 2230, 1715[c] | 5.88 (bs, 1H), 3.79 (s, 3H), 0.92 (s, 3H) | 356 |
| 1m | 183-185 | 3350, 2220, 1710[c] | 5.79 (bs, 1H), 3.78 (s, 3H), 1.19 (s, 3H), 0.90 (s, 3H) | 370 |
| 1n | oil | 3440, 2250, 1715[b] | 7.90-7.23 (m, 8H), 3.72 (s, 3H), 2.80 (bs, $D_2O$ exchange), 1H) | 264 |
| 1o | oil | 3500, 2250, 1720[b] | 3.79 (s, 3H), 2.24 (s, $D_2O$ exchange, 1H), 1.04 (s, 3H), 0.96 (s, 3H), 0.86 (s, 3H) | 95 |

a) $CDCl_3$. b) Liquid film. c) KBr.

with nitrogen and formic acid (0.18 ml, 4.9 mmol) was added all at once. The mixture was stirred at 60 °C under a nitrogen atmosphere for 7 hr, AcOEt and 0.1 N HCl were added, and the organic layer was separated, washed with water, dried ($Na_2SO_4$), and concentrated at reduced pressure. The residue was purified by flash chromatography. Elution with a 95/5 n-hexane/AcOEt mixture gave compounds (6e) (0.188 g, 55% yield) (Table 7) and (7e) (0.035 g, 10% yield): mp oil; IR (liquid film) 1780 $cm^{-1}$; $^1$H-NMR ($CDCl_3$) δ : 4.52 (m, 1H), 2.68-1.08 (m, 16H), 0.88 (t, 3H); MS(m/e) 85.

b) 50% Excess of formic acid: tributylamine (0.83 ml, 3.5 mmol) and $Pd(OAc)_2(PPh_3)_2$ (0.026 g, 0.035 mmol) were added to a stirred solution of (1e) (0.4 g, 1.75 mmol) in DMF (2 ml). The mixture was purged with nitrogen and formic acid (0.1 ml, 2.71 mmol) was added all at once. The mixture was stirred at 60 °C under a nitrogen atmosphere for 7 hr. After the usual work-up, compound (6e) (0.220 g, 69% yield) was isolated by flash chromatography.

c) 300% Excess of formic acid: tributylamine (2.82 ml, 12 mmol) and $Pd(OAc)_2(PPh_3)_2$ (0.036 g, 0.048 mmol) were added to a stirred solution of (1e) (0.54 g, 2.38 mmol) in DMF (2 ml). The mixture was purged with nitrogen, and formic acid (0.35 ml, 9.3 mmol) was added all at once. The mixture was stirred at 60 °C under a nitrogen atmosphere for 7 hr. After the usual work-up, compound (7e) (0.23 g, 64% yield) was isolated by flash chromatography.

Hydrogenation of methyl 4-phenyl-4-hydroxy-2-butynoate (1b').

Tributylamine (1.38 ml, 5.8 mmol) and $Pd(OAc)_2(PPh_3)_2$ (0.025 g, 0.034 mmol) were added to a stirred solution of (1b') (0.32 g, 1.7 mmol) in DMF (2 ml). The mixture was purged with nitrogen and formic acid (0.17 ml, 4.5 mmol) was added all at once. The mixture was stirred at 60 °C under a nitrogen atmosphere for 4 hr, AcOEt and 0.1 N HCl were added, and the organic layer was separated, washed with water, dried ($Na_2SO_4$), and concentrated at reduced pressure. The residue was purified by flash chromatography. Elution with a 90/10 n-hexane / AcOEt mixture gave methyl 4-phenyl-4-oxo-butanoate (8) (0.21 g, 65% yield): mp oil; IR (liquid film) 1740, 1690, 1600, 750, 695 $cm^{-1}$; $^1$H-NMR ($CDCl_3$)δ: 8.16-7.96 (m, 2H), 7.69-7.32 (m, 3H), 3.70 (s, 3H), 3.32 (t, J = 6 Hz, 2H), 2.76 (t, J = 6 Hz, 2H); MS (m/e), 192, 105, 77.

Aknowledgments - Research was supported by a grant from "Ministero della Pubblica Istruzione" (Italian Ministry of Education) (Italy).

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Table 6 - Characterization of Compounds (3)

| Compound | M.p. (°C) | I.R. $\nu$(cm$^{-1}$) | $^1$H-NMR $\delta$ (ppm)[a] | MS m/e |
|---|---|---|---|---|
| 3a | 63-65 | 1750, 1610, 830[b] | 7.82 (AA' part of an AA'BB' system, 2H), 7.39 (s,1H), 6.92 (BB' part of an AA'BB' system, 2H), 3.80 (s,3H), 1.50 (s, 6H) | 218, 147 |
| 3b | 163-165 | 3260, 1725, 1615, 835[b] | 7.77 (AA' part of an AA'BB' system, 2H), 7.38 (s,1H), 6.89 (BB' part of an AA'BB' system, 2H) 5.67 (bs, $D_2O$ exchange, 1H), 1.53 (s, 6H) | 204, 133 |
| 3c | 53-56 | 3450, 1745, 795, 695[b] | 7.90-7.63 (m,2H), 7.53 (s,1H),7.47-7.27 (m,2H), 4.68 (s,2H), 2.50 (bs, $D_2O$ exchange, 1H), 1.50 (s, 6H) | 218, 147 |
| 3d | 69-70 | 1730, 780, 680[b] | 8.03-7.80 (m,2H), 7.55 (s,1H),7.52-7.33 (m, 3H), 1.52 (s, 6H) | 188, 173, 145, 117 |
| 3e | 70-71 | 1750, 1600, 830 770, 700[c] | 7.88 (AA' part of an AA'BB' system, 2H), 7.64 (s,1H), 7.57-6.90 (m,5H), 6.92 (BB' part of an AA'BB' system, 2H), 3.80 (s, 3H), 1.83 (s, 3H) | 280, 265, 237, 209 |
| 3g | oil | 1750, 1610, 800 700[c] | 7.85-7.62 (m,2H), 7.49 (s,1H),7.42-7.15 (m,2H), 2.37 (s, 3H), 1.86 (m, 2H), 1.48 (s, 3H), 0.92 (t, J = 7.5 Hz, 3H) | 216, 187 |
| 3h | 86-89 | 1750, 1610, 840[d] | 7.90 (AA' part of an AA'BB' system, 2H), 7.57 (s,1H), 7.33-6.62 (m,5H), 3.84 (s, 3H), 3.78 (s,3H), 1.10 (s, 3H) | 444, 227 |
| 3i | 175-176 | 1750, 1610, 760[d] | 8.22 (dd, J =2.0 Hz, J =7.5 Hz,1H), 7.99 (s,1H), 7.53-6.60 (m,6H), 3.90 (s, 3H), 3.77 (s, 3H), 1.09 (s, 3H) | 444, 227 |
| 3l | 250(dec) | 1750, 1610, 800 690[d] | 7.86-6.62 (m,8H), 3.80 (s,3H), 1.12 (s, 3H) | 432, 227 |
| 3m | 99-101 | 1745, 1600, 830[d] | 7.89 (AA' part of an AA'BB' system, 2H), 7.58 (s,1H), 7.42 (BB' part of an AA'BB' system, 2H), 6.28 (bd,J = 16.5 Hz,1H), 5.51 (d,J=16.5 Hz,1H), 1.98 (m,2H), 1.67 (s,3H), 1.63 (s, 3H), 1.80-1.33 (m, 4H), 0.96 (s,3H) | 358, 356, 343, 341, 259, 257 |
| 3n | 46-48 | 1755, 1600, 750, 700[c] | 8.03-7.83 (m,2H), 7.57 (s,1H),7.53-7.37 (m,3H), 6.28 (bd, J = 16.5 Hz, 1H), 5.52 (d, J = 16.5 Hz, 1H),1.99 (m, 2H), 1.67 (s, 3H), 1.63 (s,3H), 1.80-1.33 (m, 4H), 0.96 (s, 3H) | 322, 289 223 |
| 3o | 120-121 | 1750, 1610, 840[c] | 7.89 (AA' part of an AA'BB' system, 2H), 7.50 (s,1H), 6.95 (BB' part of an AA'BB' system, 2H), 3.84 (s,3H), 2.00-1.40 (m, 10H) | 258, 215 |
| 3p | 67-68 | 1740, 1615, 770, 690[d] | 8.07-7.80 (m,2H), 7.52 (s,1H),7.60-7.27 (m, 3H), 2.20-1.73 (m, 8H) | 214, 185 |
| 3q | 210-211 | 1750, 840[d] | 7.88 (AA' part of an AA'BB' system, 2H), 7.98 (s,1H), 7.41 (BB' part of an AA'BB' system,2H), 5.88 (s, 1H), 1.14 (s, 3H) | 438, 436 |
| 3r | 175-177 | 1750, 1670, 850[d] | 8.03-7.80 (m,2H), 7.60 (s,1H),7.27-7.00 (m, 2H), 5.88 (s,1H), 1.13 (s, 3H) | 420, 215 |
| 3s | 50-52 | 1740, 1610, 830[d] | 7.91 (AA' part of an AA'BB' system, 2H), 7.49 (d, J = 2.2 Hz, 1H), 6.98 (BB' part of an AA'BB' system, 2H), 5.03 (m,1H), 3.83 (s,3H), 1.97-1.10 (m, 12H), 0.88 (t, 3H) | 288, 189, 133 |

a) $CDCl_3$. b) Nujol. c) Liquid film. d) KBr.

Table 7 - Characterization of Compounds (6)

| Compound | M.p. (°C) | I.R. $\nu$ ($cm^{-1}$) | $^1$H-NMR $\delta$ (ppm)[a] | MS m/e |
|---|---|---|---|---|
| 6a | 174-175 | 1760[b] | 7.57 (d, J = 6Hz, 1H), 7.33-6.60 (m, 3H), 6.00 (d, J = 6 Hz, 1H) 3.79 (s, 3H), 1.07 (s, 3H) | 338, 227 |
| 6b | 138-140 | 1760, 1670[b] | 7.47 (d, J = 6 Hz, 1H), 5.97 (d, J = 6 Hz, 1H), 5.20 (s, 1H), 1.09 (s, 3H) | 326, 215 |
| 6c | 95-96 | 1740[b] | 7.50 (d, J = 6 Hz, 1H), 6.07 (d, J = 6 Hz, 1H), 2.50-2.20 (m, 1H), 2.03-1.10 (m, 6H), 1.13 (s, 3H), 0.91 (s, 3H), 0.72 (s, 3H) | 206, 110, 95 |
| 6d | 127-128 | 1760, 1600[b] | 7.85-7.22 (m, 9H), 6.43 (d, J = 6 Hz, 1H) | 234 |
| 6e | oil | 1760[c] | 7.55 (dd,J = 6 Hz,J =1.5 Hz, 1H), 6.12 (dd,J = 6 Hz,J =1.5 Hz, 1H), 5.08 (m, 1H), 1.90-1.03 (m, 12H), 0.87 (t, 3H) | 182, 97, 84 |
| 6f | 144-145 | 1770, 1670[b] | 7.53 (d, J = 6 Hz, 1H), 5.99 (d, J = 6 Hz, 1H), 5.79 (s, 1H), 1.20 (s, 3H), 1.07(s, 3H) | 340, 229 |

a) $CDCl_3$. b) KBr. c) Liquid film.


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