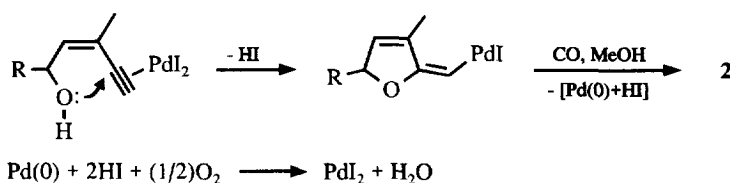


ml) was pressurized with air (10 atm) and CO (up to 100 atm of total pressure). The temperature was then raised to 70°C and the solution was stirred for 15 h. GLC analysis indicated a 82% yield of **2a** (based on starting **1a**) and 8% of 2,3-dimethylfuran **3a** at total substrate conversion. After the usual work-up, **2a** was isolated by column chromatography (SiO₂, pentane-AcOEt from 95 : 5 to 90 : 10 as eluent) (1.12 g, 73%).³

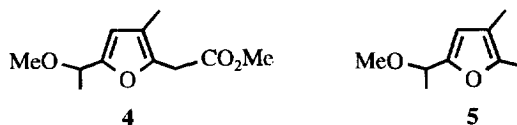
Analogously to what has been proposed for the Pd(II)-catalysed intramolecular alkoxy-alkoxycarbonylation of γ - or δ -hydroxyalkenes to give tetrahydrofuran- or tetrahydropyran-2-acetic esters,^{4,5} the formation of furans **2** can be viewed as occurring through *anti-exo-dig* intramolecular nucleophilic attack of the hydroxy group on the triple bond coordinated to palladium⁶ followed by alkoxy-carbonylation and aromatization (Scheme 1; anionic iodide ligands are omitted for simplicity).



Scheme 1

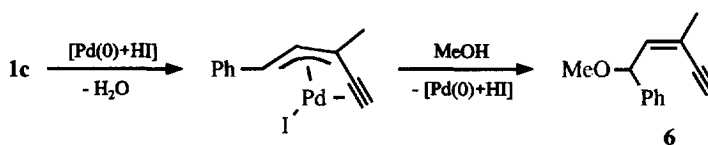
Both a high carbon monoxide partial pressure and an excess of KI are important in order to direct the catalytic process towards the carbonylative pathway. This is likely to be due to the need for stabilizing the vinylpalladium intermediate against protonation. In fact, by reducing the total pressure at 20 atm, after 15 h the yields of **2a** and **3a** were 50% and 14%, respectively. When the reaction was carried out at 100 atm (CO : air = 9:1) using only 10 mol of KI^{1,7} per mol of PdI₂, the **2a** : **3a** ratio obtained was about 3 with a total yield of 68%. In the latter case, a higher substrate conversion rate was observed (97% conversion after 4 h using a substrate : Pd ratio = 2000), probably due to the diminished competition between the iodide ligands and the substrate for coordination to palladium.

In the case of enynols **1** substituted with an alkyl group the reaction gave less satisfactory results owing to the formation of by-products deriving from an unusual methoxylation at the α carbon of the alkyl group. For example, the carbonylation of **1b** under the usual conditions afforded **2b** (36%), **3b** (4%) and the corresponding methoxy derivatives **4** (20%) and **5** (9%).



The occurrence of these by-products could be strongly curtailed by further increasing the KI : PdI₂ molar ratio. In fact, when the reaction of **1b** was carried out using a KI : PdI₂ molar ratio = 300 rather than 50, after 20 h GLC yields of **2b** and **3b** were 64% and 9%, respectively, with compound **4** (4%) and **5** (3%) being formed only in little amounts. Column chromatography [SiO₂, light petroleum (bp 40-60)-diethyl ether = 99 : 1 as eluent] afforded pure **2b** (55%).

With secondary enynols substituted with an aryl group, such as **1c**, an undesired side reaction was the etherification of the alcoholic function^{7b,8} with formation of **6**. This is probably due to the formation of a particularly stable π -allyl intermediate, in which the allyl system is conjugated to the phenyl substituent. This intermediate readily undergoes methanol attack to give **6** (Scheme 2).



Scheme 2

This side reaction was easily minimized by working at lower temperature,^{7b} even though the reaction rate was decreased. Thus, by reacting **1c** under the usual conditions but at 50 °C and using Pd : KI : substrate molar ratios = 1 : 100 : 200, after 52 h **2c** was obtained in 67 % GLC yield. Products **3c** (4 %) and **6** (9 %) were also detected in the reaction mixture. Pure **2c** (58%) was recovered by column chromatography (SiO₂, hexane-AcOEt from 95 : 5 to 90 : 10 as eluent).

The fact that an oxidative cyclization-monocarbonylation can be obtained with high selectivity, in spite of the multifunctional character of the substrates, is noteworthy in view of the ability of the PdI₂/KI system to selectively catalyse the oxidative dialkoxycarbonylation in the case of simple alk-1-ynes,^{7b} propynyl alcohols^{1,7} and 3-yn-1-ols.^{1b} Furthermore, no protonolysis or substitutive carbonylation of the allyl moiety^{7a,8} was observed.

This is the first example of synthesis of furan-2-acetic derivatives *via* direct carbonylation of nonfuranoid substrates. Furan-2-acetic acid was obtained by Co(CO)₄⁻-catalysed carbonylation of furfuryl chloride.⁹ A recently developed method for the synthesis of furan-2-acetic esters starting from (*Z*)-2-en-4-yn-1-ols, not involving organometallic catalysis, required a sequence of 2 or more steps [2 steps for (*Z*)-3-methylpent-2-en-4-yn-1-ol, 3 steps for enynols bearing an alkyl substituent α to the hydroxyl group; no examples were reported with secondary enynols substituted with an aryl group].¹⁰

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3. All new compounds were fully characterised by IR and ^1H NMR spectroscopies, mass spectrometry, and elemental analysis. Spectroscopic and MS data of selected products: **2a**, colourless oil; IR (film): ν/cm^{-1} 2954 (m), 2929 (w), 1743 (s), 1509 (m), 1436 (m), 1339 (m), 1274 (m), 1215 (m), 1167 (s), 1089 (m), 1007 (m), 892 (m) and 739 (m); ^1H NMR (300 MHz, CDCl_3): δ/ppm 1.99 (s, 3 H, Me), 3.62 (s, 2 H, CH_2), 3.71 (s, 3 H, CO_2Me), 6.21 (d, 1 H, $^3J = 1.73$ Hz, 4-H) and 7.27 (d, 1 H, $^3J = 1.73$ Hz, 5-H); MS (EI, 70 eV): m/z 154 (M^+ , 23), 96 (6), 95 (100), 67 (8), 66 (5), 65 (9) and 59 (3). **2b**, colourless oil; IR (film): ν/cm^{-1} 2973 (m), 2953 (m), 1745 (s), 1575 (m), 1436 (m), 1376 (m), 1336 (m), 1274 (m), 1232 (m), 1167 (s), 1102 (m), 1010 (m), 946 (w) and 806 (m); ^1H NMR (300 MHz, CDCl_3): δ/ppm 1.19 (t, 3 H, $^3J = 7.56$ Hz, CH_3CH_2), 1.94 (s, 3 H, Me), 2.58 (q, 2 H, $^3J = 7.56$ Hz, CH_3CH_2), 3.58 (s, 2 H, $\text{CH}_2\text{CO}_2\text{Me}$), 3.71 (s, 3 H, CO_2Me) and 5.81 (s, 1 H, 4-H); MS (EI, 70 eV): m/z 182 (M^+ , 17), 125 (3), 124 (9), 123 (100), 108 (7), 93 (3), 79 (5), 77 (5), 65 (5), 59 (4) and 53 (4). **2c**, pale yellow oil; IR (film): ν/cm^{-1} 2951 (m), 2926 (w), 1742 (s), 1633 (w), 1603 (m), 1553 (w), 1485 (m), 1448 (m), 1435 (m), 1338 (m), 1265 (m), 1218 (m), 1167 (s), 1098 (m), 1055 (w), 1008 (w), 933 (w), 811 (w), 761 (s) and 693 (m); ^1H NMR (300 MHz, CDCl_3): δ/ppm 2.03 (s, 3 H, Me), 3.68 (s, 2 H, CH_2), 3.72 (s, 3 H, CO_2Me), 6.49 (s, 1 H, 4-H), 7.18-7.26 (m, 1 H, 4'-H), 7.30-7.39 (m, 2 H, 3'-H) and 7.57-7.65 (m, 2 H, 2'-H); MS (EI, 70 eV): m/z 230 (M^+ , 31), 172 (12), 171 (100), 141 (4), 128 (13), 115 (3), 105 (3), 77 (8), 59 (2) and 51 (3). **4**, colourless oil; IR (film): ν/cm^{-1} 2954 (w), 2927 (m), 1742 (s), 1437 (m), 1375 (w), 1266 (s), 1202 (w), 1168 (m), 1097 (m), 1005 (w), 910 (m) and 740 (s); ^1H NMR (300 MHz, CDCl_3): δ/ppm 1.47 (d, 3 H, $^3J = 6.62$ Hz, CH_3CH), 1.97 (s, 3 H, Me), 3.28 (s, 3 H, OMe), 3.62 (s, 2 H, CH_2), 3.71 (s, 3 H, CO_2Me), 4.29 (q, 1 H, $^3J = 6.62$ Hz, CH_3CH) and 6.10 (s, 1 H, 4-H); MS (EI, 70 eV): m/z 212 (M^+ , 31), 197 (100), 181 (87), 165 (6), 153 (30), 139 (42), 138 (12), 125 (12), 123 (22), 122 (28), 121 (25), 107 (15), 95 (13), 93 (16), 91 (9), 79 (11), 77 (21), 65 (10), 59 (24) and 55 (10).
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5. In spite of the formal analogy, only little amounts ($\leq 5\%$) of **2** are formed by applying Semmelhack's procedure to enynols **1**. For example, starting from **1a**, methyl 3-methylfuran-2-acetate **2a** (4%) and 2,3-dimethylfuran **3a** (48%) were formed along with an unidentified heavy residue.
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