Stereoselective Synthesis of β-Lactones containing α-Z-Alkoxycarbonylmethylene Chains by Palladium-catalysed Oxidative Carbonylation of Tertiary α-Hydroxyalkynes

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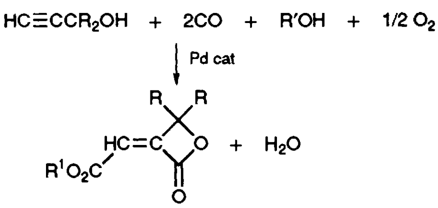
Tertiary α-hydroxyalkynes undergo oxidative carbonylation in alcohols in the presence of catalytic amounts of PdI_2–KI to give β-lactones derived from alkoxycarbonylation at the terminal carbon of the alkyne and *cis*-carbonylation at the internal carbon, followed by carbonyl trapping by the tertiary hydroxy group.

We previously reported a new and efficient method for preparing maleic acids or esters from alkynes, carbon monoxide and alcohols.[1] When this method was applied to tertiary propynyl alcohols we noticed the formation of β-lactones **1** [eqn. (1), R,R′ = alkyl]. Prop-2-yn-1-ol did not however react in this way,[1] and but-1-yn-3-ol gave only a low percentage yield of the corresponding β-lactone, so the formation of β-lactones **1** to a substantial extent appears to be promoted by the presence of the geminal R groups (Ingold–Thorpe effect[2]), which cause ring formation to compete with carbonyl esterification [eqn. (2)].

Although the reaction was carried out in methanol at 80 °C the β-lactone : dicarbonylated products ratio was higher than 3 : 1. In a typical example palladium iodide (2.2 mg, 0.006 mmol), potassium iodide (10.1 mg, 0.061 mmol) and HC≡CC(Me)$_2$OH (1030 mg, 12.2 mmol), dissolved in methanol (56 ml), were placed in a 300 ml autoclave pressurized with CO (15 bar) and air (up to 20 bar of total pressure). The temperature was then raised to 80 °C and the solution was stirred for 6 h. GLC analysis indicated a 54% yield of **1a** (based on dimethylprop-3-yn-1-ol), 12% of **2a**, 2% of the methyl ether of **2b**[3] (from ring opening of **1a** with methanol) and 3% of **3** (cyclic tautomeric form of **2a**).†

Conversion into carbonylated products was 73% and the total yield was 71%. Higher conversions resulted in lower yields. The catalytic efficiency was 1420 mol per mol of palladium. The high **1** : **2** ratio observed in our case means that the acylpalladium complex formed by *cis* carbon monoxide insertion is immediately captured by the hydroxy group, presumably coordinated to palladium as an alkoxy species[1] (Scheme 1).

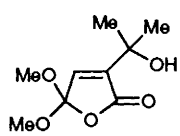


(1)

1a R = R^1 = Me
1b R–R = C_6H_{11}, R^1 = Me
1c R = Me, R^1 = Bu

$$\mathrm{HC{\equiv}CCR_2OH + 2CO + 2R^1OH + 1/2\,O_2 \xrightarrow{\text{Pd cat.}} R^1O_2CCH{=}C(CO_2R^1)CR_2OH + H_2O} \quad (2)$$

2a R = R^1 = Me
2b R = Me, R^1 [C(1)] = H, R^1 [C(4)] = Me



3

The formation of β-lactones from silanes and propynyl alcohols using $Rh_4(CO)_{12}$ as catalyst in the presence of a base was recently reported.[4] This reaction does not involve competition with esterification as in our case and its course on the rhodium(0) catalyst appears to be quite different.[4]

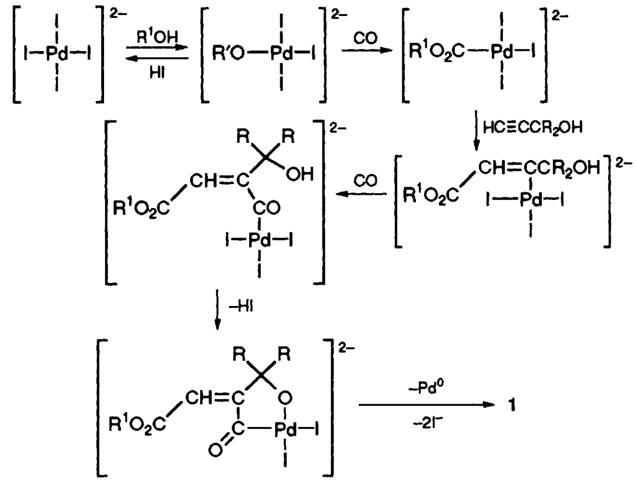
The lactones obtained by the synthesis described above are a new class of compounds of potential interest for many applications.[5] The present method allows their preparation from inexpensive tertiary propynyl alcohols, readily obtainable from acetylene and ketones.[6]

We thank Consiglio Nazionale delle Ricerche, Progetto Finalizzato Chimica Fine e Secondaria, for financial support.

Received, 17th March 1994; Com. 4/01592D

Footnote

† All compounds gave satisfactory elemental analysis. *Selected spectroscopic data*: **1a**, white solid, mp 79–80 °C; IR (KBr, cm^{-1}) 3078vw, 2996vw, 1808s, 1727s, 1690s, 1441w, 1384vw, 1370vw, 1291s, 1229vw, 1205m, 1082w, 1038m, 921w, 885vw, 820w, 786m. ^{1}H NMR (300 MHz, $CDCl_3$), δ 1.67 (s, 6 H, 2 Me), 3.85 (s, 3 H, CO_2Me, 5.92 (s, 1 H, =CH); *m/z* 170 (M$^+$, 1), 155 (32), 141 (5), 126 (30), 125 (46), 113 (100), 111 (68), 95 (12), 83 (43), 82 (32), 73 (21), 67 (90), 65 (21), 59 (65), 53 (65%). **2a**, colourless oil; IR (film, cm^{-1}) 3492m (br), 2983m, 2955m, 1725s, 1649m, 1437s, 1347s, 1260s, 1196s, 1170s, 1046m, 1020m, 970w, 908m, 889w, 823w. ^{1}H NMR (300 MHz, $CDCl_3$), δ 1.46 (s, 6H, 2 Me), 3.73 (s, 3H, CO_2Me), 3.85 (s, 3 H, CO_2Me), 6.11 (s, 1 H, =CH); *m/z* 202 (M$^+$ absent), 187 (15), 171 (7), 159 (9), 155 (100), 153 (20), 143 (6), 139 (6), 127 (55), 114 (13), 113 (59), 111 (11), 85 (9), 83 (6), 82 (7), 69 (6), 59 (32), 53 (10%). **3**, colourless oil; IR (film, cm^{-1}) 3450m (br), 2954s, 2927s, 2850m, 1773s, 1633w, 1463m, 1365m, 1303s, 1195s, 1181s, 1139s, 1080m, 1001s, 937s, 880w, 835w, 791w, 737w. ^{1}H NMR (300 MHz, $CDCl_3$), δ 1.53 (s, 6 H, 2 Me), 3.44 (s, 6 H, 2 OMe), 6.72 (s, 1 H, =CH); *m/z* 202 (M$^+$ absent), 187 (18), 171 (22), 155 (18), 153 (25), 143 (17), 127 (13),



Scheme 1

113 (33), 111 (18), 99 (100), 85 (17), 83 (18), 69 (22), 59 (53), 53 (30%).

References

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