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Palladium-catalyzed oxidative heterocyclodehydration-alkoxycarbonylation of 3-yne-1,2-diols: a novel and expedient approach to furan-3-carboxylic esters

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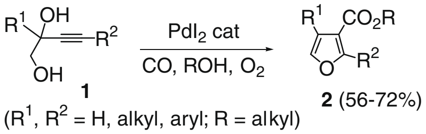
ABSTRACT

A novel and convenient approach to furan-3-carboxylic esters **2** is presented, based on palladium-catalyzed direct oxidative carbonylation of readily available 3-yne-1,2-diols **1**. The process, corresponding to a sequential combination between a 5-*endo-dig* heterocyclodehydration step and an oxidative alkoxycarbonylation stage, is catalyzed by PdI_2 in conjunction with an excess of KI under relatively mild conditions (100 °C in ROH under 40 atm of a 4:1 mixture of CO-air).

Furans are a very important class of heterocyclic derivatives. The furan motif is present in many important naturally occurring and biologically active compounds,[1] and furan derivatives find extensive application in many applicative fields.[2] The possibility to construct functionalized furans in a regioselective way by heterocyclization of suitable acyclic precursors has accordingly attracted an increasing attention,[3] and several methods have been developed to date for the synthesis of substituted furans by annulation processes, mainly based on metal catalysis.[4] However, to the best of our knowledge, no direct synthesis of furan-3-carboxylic esters **2** by carbonylation of acyclic precursors has been reported so far.[5] In this Letter, we report a novel, convenient and atom-economical[6] method for the preparation of this important class of heterocyclic derivatives,[7] based on direct oxidative carbonylation of readily available 3-yne-1,2-diols **1**[8] (Eq. (1)).



(1)

The process, corresponding to a sequential combination between a 5-*endo-dig* heterocyclodehydration step and an oxidative alkoxycarbonylation stage, is catalyzed by a very simple catalytic system, consisting of PdI_2 in conjunction with an excess of KI and oxygen as the oxidant, and takes place at 100 °C in an alcohol as the solvent, under 40 atm of a 4:1 mixture of CO-air[9].

Our first experiments were carried out using 2-methyloct-3-yne-1,2-diol **1a** (R^1 = Me, R^2 = Bu), which was let to react at 80 °C in MeOH (**1a** concentration = 0.25 mmol per mL of MeOH) under 20 atm of a 4:1 mixture of CO-air, in the presence of PdI_2 (1 mol %) and KI (10 mol %). After 2 h, the GC–MS analysis of the reaction crude showed a substrate conversion of ca. 70% and the formation of two products, whose MS spectra were compatible with the furan-3-carboxilic ester derivatives **2a** and **3a**, respectively (Table 1, entry 1).

Product **2a** (28% GLC yield) was easily isolated by column chromatography, and its structure fully confirmed by spectroscopic techniques, while every attempt to isolate pure **3a** (13% GLC yield) failed. However, an indirect proof of the validity of the proposed structure was given by the results obtained from the reaction carried out at 100 °C rather than 80 °C: in fact, product **3a** partly converted into the methyl ester **2a** (Table 1, entry 2), which is in agreement with methanolysis of **3a** with formation of **2a** and **1a**. Clearly, a higher selectivity toward **2a** was to be expected working at lower substrate concentration. The result shown in entry 3 (Table 1) confirmed that this was indeed the case: with an **1a** concentration of 0.05 mmol per mL of MeOH, the GLC yield of **2a** and **3a** turned out to be 60% and 2%, respectively. A still higher **2a**/**3a** ratio was obtained with a lower **1a** concentration, but the total yield obtained was less satisfactory (Table 1, entry 4). On the other hand, the use of a lower amount of KI (5 mol per mol of PdI_2, Table 1, entry 5) led to better results with respect to the initial reaction, carried out with a KI/PdI_2 molar ratio of 10 (Table 1, entry 1). A further decrease of the KI/PdI_2 ratio was, however, detrimental (Table 1, entry 6). Finally, an increase of the total pressure to 40 atm caused a significant increase of the total yield (81%, entry 7).

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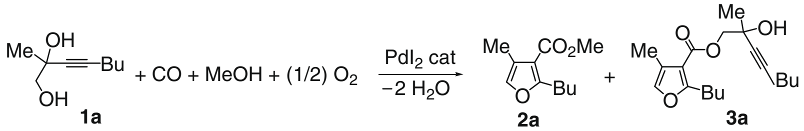
Table 1
Reactions of 2-methyloct-3-yne-1,2-diol **1a** with CO, O_2, and MeOH in the presence of the PdI_2-KI catalytic system[a]



Entry	PdI_2:KI:**1a** molar ratio	*T* (°C)	Concentration of **1a**[c]	Yield of **2a**[d] (%)	Yield of **3a**[d] (%)	Total yield[d] (%)
1[b]	1:10:100	80	0.25	28	13	41
2	1:10:100	100	0.25	55	9	64
3	1:10:100	80	0.05	60	2	62
4	1:10:100	80	0.02	45	1	46
5	1:5:100	80	0.25	52	15	67
6	1:2:100	80	0.25	37	9	46
7[e]	1:10:100	80	0.25	49	32	81

[a] Unless otherwise noted, all reactions were carried out in MeOH for 2 h under 20 atm (at 25 °C) of a 4:1 mixture of CO-air. Unless otherwise noted, substrate conversion was quantitative in all cases.

[b] Substrate conversion was 70%, by GLC.

[c] mmol of **1a** per mL of MeOH.

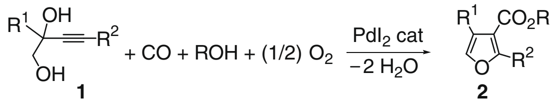
[d] Based on starting **1a**, by GLC.

[e] The reaction was carried out under 40 atm (at 25 °C) of a 4:1 mixture of CO-air.

Based on these results, the next experiment was carried out at 100 °C under 40 atm of a 4:1 mixture of CO-air with a substrate concentration of 0.05 mmol per mL of MeOH, in the presence of PdI_2 + 5 KI. Under these optimized conditions, the reaction selectively led to the methyl furan-3-carboxylate **2a** with a GLC yield of 76% and an isolated yield of 69% (Table 2, entry 1). Other differently substituted 3-yne-1,2-diols **1b–e** behaved similarly, to give the corresponding furan-3-carboxylates selectively with yields ranging from 56% to 72% (Table 2, entries 2–5). The reaction also worked well using EtOH rather than MeOH as the solvent and nucleophile, as shown by the result obtained in Table 2, entry 6.[10,11]

On the basis of the existing knowledge on PdI_2-catalyzed carbonylative annulation reactions,[12,13] we can propose the mechanism shown in Scheme 1 for the formation of **2** from **1**. Thus, a 5-*endo-dig* cyclization may occur by intramolecular nucleophilic attack of the hydroxyl group at C-1 on the triple bond coordinated to the metal center, followed by alkoxycarbonylation of the resulting vinylpalladium intermediate and dehydration or vice versa, with formation of **2**, Pd(0) and HI. The latter is then reoxidized to PdI_2 by the action of iodine, formed in its turn by oxidation of HI by oxygen.[12–14]

Table 2
Synthesis of furan-3-carboxylic esters **2** by PdI_2-catalyzed oxidative carbonylative heterocyclization of 3-yne-1,2-diols **1**[a]

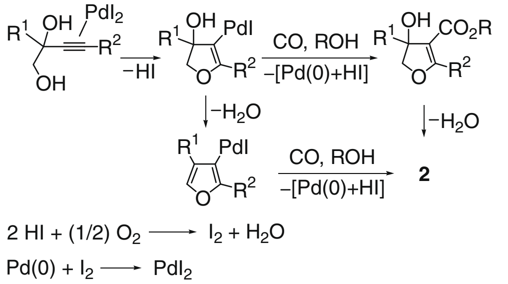


Entry	**1**	R^1	R^2	R	**2**	Yield of **2**[b] (%)
1	**1a**	Me	Bu	Me	**2a**	69[c]
2	**1b**	Me	Ph	Me	**2b**	60
3	**1c**	Ph	Bu	Me	**2c**	61
4	**1d**	Ph	Ph	Me	**2d**	56
5	**1e**	H	Bu	Me	**2e**	72
6	**1a**	Me	Bu	Et	**2a′**	66

[a] All reactions were carried out in ROH (substrate concentration = 0.05 mmol per mol of ROH, 1–2 mmol scale based on **1**) at 100 °C for 2 h under 40 atm (at 25 °C) of a 4:1 mixture of CO-air, in the presence of PdI_2 (1 mol %) in conjunction with KI (KI/PdI_2 molar ratio = 5). Substrate conversion was quantitative in all cases.

[b] Isolated yield based on starting **1**.

[c] The GLC yield was 76%.



Scheme 1. Plausible reaction pathways leading to furan-3-carboxylic esters **2**. Anionic iodide ligands are omitted for clarity.

In conclusion, we have reported the first example of a direct synthesis of an important class of heterocyclic derivatives, such as furan-3-carboxylic esters, by a one-step carbonylative heterocyclization approach. The method is based on the use of readily available substrates (3-yne-1,2-diols, CO, and O_2) and a very simple catalytic system (PdI_2-KI), and is characterized by good product yields and high atom economy.

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8. Substrates **1** were easily prepared by alkynylation of the appropriate α-hydroxy aldehyde or α-hydroxy ketone using an excess of $R^3C{\equiv}CLi$ or $R^3C{\equiv}CMgBr$.
9. These conditions (32 atm of CO together with 9 total atm of air, considering that the autoclave was loaded under 1 atm of air) corresponded to 78.0% of CO in air and were outside the explosion limits for CO in air (ca. 16–70% at 18–20 °C and atmospheric pressure, 14.8–71.4% at 100 °C and atmospheric pressure. At higher total pressure, the range of flammability decreases: for example, at 20 atm and 20 °C the limits are ca. 19% and 60%. See: Bartish, C. M.; Drissel, G. M. In: *Kirk-Othmer Encyclopedia of Chemical Technology*; Grayson, M., Eckroth, D., Bushey, G. J., L. Campbell, L., Klingsberg, A., van Nes, L., Eds., 3rd ed.; Wiley-Interscience: New York, 1978; Vol. 4, p 775.
10. Typical procedure for the oxidative carbonylative annulation of 3-yne-1,2-diols **1** to furan-3-carboxylic esters **2**: A 250 mL stainless steel autoclave was charged in the presence of air with PdI$_2$ (5.0 mg, 1.39×10^{-2} mmol), KI (11.5 mg, 6.93×10^{-2} mmol), and a solution of **1** (1.39 mmol) in ROH (R = Me or Et, 28 mL). The autoclave was sealed and, while the mixture was stirred, the autoclave was pressurized with CO (32 atm) and air (up to 40 atm). After being stirred at 100 °C for 2 h, the autoclave was cooled, degassed, and opened. The solvent was evaporated, and the products were purified by column chromatography on silica gel (eluent: 9:1 hexane–acetone for **2a** and **2b**; 95:5 hexane–AcOEt for **2c** and **2d**; 6:4 hexane–acetone for **2e**; 98:2 hexane–AcOEt for **2a′**) to give pure furans **2**, which were fully characterized by spectroscopic techniques and elemental analysis.[11]
11. *Characterization data for products*: For **2a**: Yellow oil. IR (film): $\nu = 1739, 1442, 1256, 763$ cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 7.04$ (s, br, 1H), 3.82 (s, 3H), 2.98–2.90 (m, 2H), 2.13 (s, br, 3H), 1.69–1.57 (m, 2H), 1.42–1.28 (m, 2H), 0.92 (t, $J = 7.3$, 3H) ppm; ^{13}C NMR (75 MHz, CDCl$_3$): $\delta = 165.2$, 164.3, 137.9, 121.2, 113.2, 50.8, 30.2, 27.9, 22.4, 13.7, 9.9 ppm; GC–MS (EI, 70 eV): $m/z = 196$ (M$^+$, 25), 154 (32), 153 (100), 139 (32), 135 (44), 123 (47); Anal. Calcd for C$_{11}$H$_{16}$O$_3$ (196.24): C, 67.32; H, 8.22. Found: C, 67.23; H, 8.24. For **2b**: Yellow oil. IR (film): $\nu = 1728, 1448, 1225, 758$ cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 7.79$–7.74 (m, 1 H), 7.45–7.36 (m, 4 H), 7.24 (q, $J = 0.9$, 1H), 3.80 (s, 3H), 2.20 (d, $J = 0.9$, 3H) ppm; ^{13}C NMR (75 MHz, CDCl$_3$): $\delta = 164.9$, 158.0, 139.2, 129.4, 129.1, 128.4, 128.1, 128.0, 122.6, 51.2, 10.0 ppm; GC–MS (EI, 70 eV): $m/z = 216$ (M$^+$, 82), 185 (100), 128 (53), 127 (33); Anal. Calcd for C$_{13}$H$_{12}$O$_3$ (216.23): C, 72.21; H, 5.59. Found: C, 72.30; H, 5.60. For **2c**: Colorless oil. IR (film): $\nu = 1718, 1438, 1391, 1292, 1121, 758$ cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 7.38$–7.29 (m, 5H), 7.27 (s, 1H), 3.70 (s, 3H), 3.04–2.96 (m, 2H), 1.76–1.64 (m, 2H), 1.47–1.33 (m, 2H), 0.95 (t, $J = 7.3$, 3H) ppm; ^{13}C NMR (75 MHz, CDCl$_3$): $\delta = 164.6$, 164.2, 138.4, 132.2, 129.2, 127.9, 127.3, 112.3, 51.0, 30.2, 27.9, 22.4, 13.8 ppm; GC–MS (EI, 70 eV): $m/z = 258$ (M$^+$, 41), 215 (39), 197 (100), 183 (54), 128 (34), 127 (49); Anal. Calcd for C$_{16}$H$_{18}$O$_3$ (258.31): C, 74.39; H, 7.02. Found: C, 74.19; H, 7.03. For **2d**: Yellow solid, mp = 27–28 °C. IR (KBr): $\nu = 1717, 1540, 1482, 1385, 1266, 1152, 924, 768$ cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 7.83$–7.77 (m, 2H), 7.50 (s, 1H), 7.47–7.30 (m, 8H), 3.68 (s, 3H) ppm; ^{13}C NMR (75 MHz, CDCl$_3$): $\delta = 165.1$, 156.6, 139.2, 131.7, 130.1, 129.2, 128.6, 128.33, 128.26, 127.7, 127.6, 113.7, 51.6 ppm; GC–MS (EI, 70 eV): $m/z = 278$ (M$^+$, 100), 247 (92), 191 (42), 189 (55), 105 (42); Anal. Calcd for C$_{18}$H$_{14}$O$_3$ (278.30): C, 77.68; H, 5.07. Found: C, 77.60; H, 5.07. For **2e**: Colorless oil. IR (film): $\nu = 1720, 1605, 1442, 1307, 1201, 1039, 736$ cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 7.24$ (d, $J = 2.0$, 1H), 6.63 (d, $J = 2.0$, 1H), 3.82 (s, 3H), 3.00 (t, $J = 7.7$, 2H), 1.72–1.59 (m, 2 H), 1.42–1.29 (m, 2H), 0.93 (t, $J = 7.3$, 3H) ppm; ^{13}C NMR (75 MHz, CDCl$_3$): $\delta = 164.5$, 163.5, 140.4, 113.0, 110.7, 51.2, 30.1, 27.3, 22.3, 13.7 ppm; GC–MS (EI, 70 eV): $m/z = 182$ (M$^+$, 56), 153 (42), 140 (96), 139 (87), 125 (47), 121 (74), 109 (100); Anal. Calcd for C$_{10}$H$_{14}$O$_3$ (182.22): C, 65.91; H, 7.74. Found: C, 65.79; H, 7.72. For **2a′**: Colorless oil. IR (film): $\nu = 1722, 1267, 1073$ cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 7.04$ (q, $J = 1.3$, 1H), 4.29 (q, $J = 7.2$, 2H), 2.98–2.91 (m, 2H), 2.14 (d, $J = 1.3$, 3H), 1.69–1.58 (m, 2H), 1.42–1.26 (m, 2H), 1.35 (t, $J = 7.2$, 3H), 0.92 (t, $J = 7.5$, 3H) ppm; ^{13}C NMR (75 MHz, CDCl$_3$): $\delta = 164.8$, 164.1, 137.8, 121.2, 113.2, 59.8, 30.3, 28.0, 22.4, 14.4, 13.8, 10.0 ppm; GC–MS (EI, 70 eV): $m/z = 210$ (M$^+$, 29), 139 (100); Anal. Calcd for C$_{12}$H$_{18}$O$_3$ (210.27): C, 68.54; H, 8.63. Found: C, 68.53; H, 8.64.
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