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Cyclocarbonylation reactions of allylphenols and allylnaphthols catalyzed by Pd/C–1,4-bis(diphenylphosphine)butane[†]

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Palladium/activated carbon (Pd/C) in the presence of 1,4-bis(diphenylphosphino)butane is an efficient heterogeneous catalyst for cyclocarbonylation reactions of 2-allyl phenols affording five-, six-, and seven-membered ring lactones. Various examples of cyclocarbonylation are reported and the regioselectivity is compared with the homogeneous system. Both commercial Pd/C and Pd/C prepared from activated carbons obtained from vegetable and polymeric wastes are investigated. Copyright © 2002 John Wiley & Sons, Ltd.

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INTRODUCTION

Transition-metal-catalyzed cyclocarbonylation reactions represent an attractive strategy for the synthesis of cyclic compounds, which are often difficult to prepare through other synthetic methodologies. A number of examples of carbonylation reactions of unsatured alcohols and amines for the formation of lactones and lactams, which have found applications in pharmacological and commercial field, are reported in the literature.[1,2]

In 1996, one of us described the regioselective cyclocarbonylation of 2-allylphenol derivatives, using palladium acetate [$Pd(OAc)_2$] and 1,4-bis(diphenylphosphino)butane (dppb) as a homogeneous catalytic system, for the synthesis of five-, six- or seven-membered ring lactones, and it was found that the selectivity of the process was dependent on the solvent and CO/H_2 ratio.[3] More recently, the previously mentioned catalytic system has been validated for the synthesis of a large variety of molecules, such as bis-lactones and estrone derivatives.[4,5]

To our knowledge, very few examples of heterogeneous catalysis are reported in the literature for this class of reaction. For an example, palladium–montmorillonite clay was demonstrated as an effective catalyst for the cyclocarbonylation reactions of 2-allylphenols, affording seven-membered ring lactones as the principal products.[6] The obvious advantages associated with the use of heterogeneous catalysis (easy separation and re-use of the catalysts) prompted us to investigate the possibility of using palladium/activated carbon (Pd/C) as a catalytic heterogeneous system for the cyclocarbonylation reactions.

In this context, we report our results concerning some examples of heterogeneous cyclocarbonylation reactions using as catalyst both Pd/C commercial and two different Pd/C samples prepared using activated carbon supports (home-prepared) obtained from almond shells and polymeric discard materials (as renewable organic sources).

RESULTS AND DISCUSSION

Previously, we demonstrated that the cyclocarbonylation reactions of 2-allylphenol (**1**) using the homogeneous catalytic system $Pd(OAc)_2$–dppb, toluene as the solvent, and a 1/1 mixture of CO/H_2 produced the seven-membered ring lactone as the major product (entry 1, Table 1); when the reaction was conducted using a 1/5 mixture of CO/H_2 and

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Table 1. Cyclocarbonylation reactions[a] of 2-allylphenol (**1**)

Entry	Catalyst	Solvent	P_{CO} (psi)	P_{H_2} (psi)	Conversion (%)	Product distribution		
						1a	**1b**	**1c**
1[b]	$Pd(OAc)_2$	Toluene	300	300	96	2	3	95
2[b]	$Pd(OAc)_2$	CH_2Cl_2	100	500	98	76	18	6
3[b]	$Pd(OAc)_2$	CH_2Cl_2	500	100	80	14	70	16
4	Pd/C	Toluene	300	300	70	25	30	45
5	Pd/C	CH_2Cl_2	100	500	95	85	15	–
6	$Pd/C_{(V)}$	Toluene	300	300	90	31	26	43
7	$Pd/C_{(P)}$	Toluene	300	300	85	20	25	55
8	$Pd/C_{(V)}$	CH_2Cl_2	500	100	90	10	20	70
9	$Pd/C_{(V)}$	CH_2Cl_2	100	500	70	74	22	4
10	$Pd/C_{(P)}$	CH_2Cl_2	100	500	90	73	24	3

[a] Reaction conditions: substrate (1.0 mmol), catalyst Pd/C (0.01 mmol palladium); dppb (0.04 mmol); solvent (5 ml); temperature (120 °C); reaction time (24 h).

[b] Data from Ref. 3.

dichloromethane, the five-membered ring lactone was obtained as the principal product of the reaction and only minor amounts of six- and seven-membered rings lactones were formed (entry 2, Table 1). In the case of a major amount of carbon monoxide (5/1 mixture of CO/H_2), the six-membered ring lactone was obtained as the principal product (entry 3, Table 1).

In this work we have used both Pd/C commercial (purchased from Sigma–Aldrich cy) and two different Pd/C systems, where activated carbon, used as support, was prepared by us from vegetal and polymeric discards and labeled respectively $Pd/C_{(V)}$ and $Pd/C_{(P)}$.

The first reaction investigated was the cyclocarbonylation of 2-allylphenol (**1**) (Scheme 1) using commercial Pd/C (5 wt% of palladium) and dppb as the catalytic system for the production of the lactones **1a**–**c**.

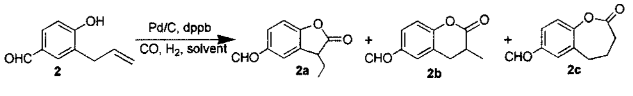
Treatment of **1** in toluene with a 1/1 mixture of carbon monoxide and hydrogen with a catalytic amount of commercial Pd/C (5 wt% of palladium) and dppb at 120 °C and for 24 h resulted in a 70% conversion to the formation of a five-, six-, and seven-ring lactones mixture with a moderate regioselectivity for the seven-membered ring (Table 1, entry 4). In contrast, a 95% conversion resulted when using dichloromethane and a 1/5 mixture of CO/H_2, and the five-membered ring lactone was the major product in this case. Nearly complete conversion was observed when using $Pd/C_{(V)}$ (1 wt% of palladium; 90% conversion) and $Pd/C_{(P)}$ (1 wt% of palladium; 85% conversion) (Table 1, entries 6 and 7) in place of commercial Pd/C in toluene and 1/1 CO/H_2, and the regioselectivity found was similar to that observed using the commercial Pd/C in the same reaction conditions.

A conversion ranging from 70 to 90% was found using dichloromethane as the solvent and a 1/5 mixture of CO/H_2; in this case, the five-membered ring lactone was the major product (entries 9 and 10, Table 1).

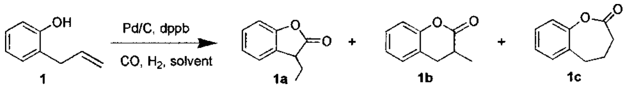
The conclusion from the results obtained is that by using a 5/1 mixture of CO/H_2 and dichloromethane as the solvent, the seven-membered ring lactone was formed with good regioselectivity in the presence of $Pd/C_{(V)}$ (entry 8, Table 1); when using a 1/5 mixture of CO/H_2 and dichloromethane, in the presence of $Pd/C_{(V)}$ or $Pd/C_{(P)}$ as catalyst, the formation of the five-membered ring lactone is promoted (Table 1, entries 9 and 10). That is, the selectivity of the heterogeneous system is almost comparable to the homogeneous one, and in some cases it is better.

The cyclocarbonylation reactions of other substrates, such as 2-allyl-4-hydroxybenzaldehyde (**2**) and 1-allyl-naphthalen-2-ol (**3**), were also investigated (Schemes 2 and 3), and the selectivity observed was comparable to that observed for 2-allylphenol (**1**).

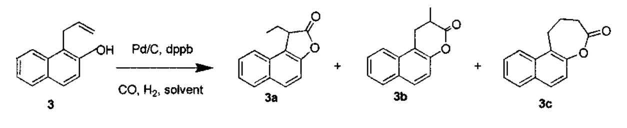
As shown in Table 2, in the case of the cyclocarbonylation



Scheme 2.



Scheme 1.



Scheme 3.

Table 2. Cyclocarbonylation reactions[a] of 3-allyl-4-allylphenol (**2**) and 1-allyl-naphthalen-2-ol (**3**)

							Product distribution (%)		
Entry	Substrate	Catalyst	Solvent	P_{CO} (psi)	P_{H_2} (psi)	Conversion (%)	**2a**	**2b**	**2c**
1	**2**	$Pd(OAc)_2$	Toluene	300	300	>95	4	8	90
2	**2**	$Pd(OAc)_2$	CH_2Cl_2	100	500	95	42	46	12
3	**2**	$Pd/C_{(V)}$	Toluene	300	300	>95	30	39	31
4	**2**	$Pd/C_{(V)}$	CH_2Cl_2	100	500	>95	43	46	11
5	**2**	$Pd/C_{(V)}$	CH_2Cl_2	500	100	>95	14	53	33
6	**2**	$Pd/C_{(V)}$	THF	500	100	n.r.	–	–	–
7	**2**	$Pd/C_{(V)}$	DME	500	100	n.r.	–	–	–
8	**3**	$Pd(OAc)_2$	Toluene	300	300	84	–	10	90
9	**3**	$Pd(OAc)_2$	CH_2Cl_2	100	500	70	9	58	33
10	**3**	$Pd/C_{(V)}$	CH_2Cl_2	500	100	>95	10	20	70
11	**3**	$Pd/C_{(V)}$	CH_2Cl_2	100	500	90	70	23	7
12	**3**	$Pd/C_{(P)}$	CH_2Cl_2	100	500	90	70	24	6
13	**3**	Pd/C	CH_2Cl_2	100	500	70	5	67	28

[a] Reaction conditions: substrate (1.0 mmol), catalyst Pd/C (0.01 mmol palladium); dppb (0.04 mmol); solvent (5 ml); temperature (120 °C); reaction time (24 h).

of **2** and **3** in toluene with a 1/1 mixture of CO/H_2 using the homogeneous catalytic system $Pd(OAc)_2$–dppb, a good selectivity to the seven-membered ring lactone is observed (entries 1 and 8, Table 2); the selectivity decreases when using dichloromethane as the solvent and a 1/5 mixture of CO/H_2 (entries 2 and 9, Table 2).

A higher conversion, but with minor selectivity, was observed in the case of compound **2** (entries 3–5, Table 2).

Finally, in the case of the cyclocarbonylation reaction of **3**, it is possible to observe that a better regioselective conversion to the five-membered ring lactone was obtained using $Pd/C_{(V)}$ and $Pd/C_{(P)}$ as catalytic heterogeneous systems, CH_2Cl_2 as the solvent, and a 1/5 mixture of CO/H_2 (entries 11 and 12, Table 2); in some cases the selectivity observed was better than with the homogeneous system. No appreciable cyclocarbonylation reaction was observed in the case of tetrahydrofuran (THF) or dimethoxyethane (DME) as the solvent in the reaction (entries 6 and 7, Table 2).

Although the study of the pathway of these reactions was not the main aim of this work, we report a hypothesis to justify the selectivity observed in these reactions for the formation of the seven-membered ring lactone. As the first step, we suppose there is an oxidative addition to palladium(0) (generated onto the surface of the solid carbon phase on exposure to carbon monoxide and hydrogen) of the O—H bond of the phenolic substrates and, successively, the coordination of the double bond to palladium having dppb coordinated in a monodentate fashion. Intramolecular hydropalladation, coordination of CO, its insertion, and its successive reductive elimination produces the seven-membered ring lactone. Five- and six-membered ring lactones are formed by the competitive insertion of carbon monoxide on the intermediate η^3 generated in the isomerization of the double bond of the allyl phenol.

CONCLUSION

We can conclude that both commercial Pd/C and palladium samples supported on activated carbons obtained from vegetable wastes, in the presence of dppb, catalyze the cyclocarbonylation reactions of 2-allylphenol, the 3-allyl-4-hydroxy-benzaldehyde, and the 1-allyl-naphthalen-2-ol, affording the lactones.

The regioselectivity obtained in the cyclocarbonylation reactions using Pd/C as a heterogeneous catalytic system is, in some cases, different than in the homogeneous system and depends on the reaction conditions (CO/H_2 ratio and solvent).

Relative to the substrate **3**, the regioselectivity observed in the case of the Pd/C catalyst prepared from vegetable discards (Table 2, entries 11 and 12) was appreciably different from the homogeneous system (Table 2, entry 2), and in any case also different from the commercial Pd/C (Table 2, entry 13).

The heterogeneous systems produce evident advantages associated with easy separation and re-use of the catalysts (some experiments were repeated, recycling five or more times the Pd/C catalyst, and an analogous conversion and selectivity of within 5% of experimental error was observed).

EXPERIMENTAL

Materials and measurements

Most chemicals were used as obtained from commercial sources. $Pd(OAc)_2$ and dppb are commercially available (Aldrich). 2-Allylphenol (**1**), 2-allyl benzaldehyde, 2-allyl-4-hydroxybenzaldehyde (**2**), and 1-allyl-naphthalen-2-ol (**3**) were prepared according to literature procedures.[7,8]

Toluene was dried and distilled from sodium under nitrogen. Dichloromethane was distilled from P_2O_5 under nitrogen.

Melting points were obtained on an electrothermal apparatus ^1H and ^{13}C NMR spectra were recorded on a Bruker AC-200 or on a Bruker 400 Avance spectrometer at room temperature and chemical shifts are reported relative to Me_4Si. IR and mass spectrometry (MS) were performed, respectively, on Perkin–Elmer 683, or FT-IR Jasco, and Hewlett-Packard GC/Mass MSD 5971 instruments.

$Pd/C_{(V)}$ and $Pd/C_{(P)}$ catalysts were prepared by wet impregnation of the activated carbons, used as supports, with an acidified solution of $PdCl_2$ (Enghelard) having an appropriate concentration of palladium. The palladium content of both samples was 1% by weight.

Activated carbons, used as supports for $Pd/C_{(V)}$ and $Pd/C_{(P)}$ catalysts, were prepared by carbonization in an inert atmosphere (nitrogen) and subsequent activation with air of the waste materials (almond shells and polymeric discards). The surface areas of the carbons obtained were respectively 511 $m^2\ g^{-1}$ for the $C_{(V)}$ sample and 488 $m^2\ g^{-1}$ for the $C_{(P)}$ sample.

General procedure for the cyclocarbonylation reactions

Pd/C (0.01 mmol Pd) and dppb (0.04 mmol) were suspended in 5 ml of dry toluene and the allyl phenol derivative (1 mmol) was added. The autoclave was purged three times with carbon monoxide and successively pressurized with carbon monoxide and hydrogen. The reaction mixture was heated at 120 °C (oil bath temperature) with stirring for 24 h. The reaction mixture was cooled to room temperature, filtered, and the solvent evaporated under vacuum; the residue was extracted with ether. The lactones were separated, purified by chromatography (SiO_2) using petroleum ether and diethyl ether as eluant, and characterized.

Lactones

The following lactones are known compounds and have spectral data in accord with the literature data: **1a, 1b, 1c, 3a, 3b** and **3c**.[3]

Characterization data for new lactones

*3-Ethyl-2-oxo-2,3-dihydro-benzofuran-5-carbaldehyde (*2a*)*

Oil; FT-IR: 2960, 2918, 2848, 2738 2360, 2340, 1812, 1684, 1241, 1043 cm^{-1}.

^1H NMR ($CDCl_3$) δ (ppm): 9.96 (s, 1H), 7.88 (d, $J = 8.4$ Hz, 1H), 6.85 (s, 1H), 7.27 (d, $J = 8.4$ Hz, 1H), 3.79 (t, $J = 6.0$ Hz, 1H), 2.12 (dq, $J = 6$ Hz, $J = 7.4$ Hz, 2H), 0.99 (t, $J = 7.4$ Hz, 3H).

^{13}C NMR ($CDCl_3$) δ (ppm): 190.7, 176.0, 158.3, 133.0, 132.8, 128.4, 124.7, 111.2, 44.1, 24.2, 10.1.

MS, *m/z* (%): 190 (61), 162 (34), 161 (100), 147 (8), 133 (28), 119 (8), 115 (10), 105 (13), 91 (12), 77 (15), 63 (5), 51 (8).

*3-Methyl-2-oxo-chroman-6-carbaldehyde (*2b*)*

Mp. 80–83 °C; FT-IR: 2979, 2917, 2848, 1771, 1696, 1684, 1245, 1136, 1121 cm^{-1}.

^1H NMR ($CDCl_3$) δ (ppm): 9.92 (s, 1H), 7.77 (d, $J = 8.2$ Hz, 1H), 7.73 (s, 1H), 7.16 (d, $J = 8.2$ Hz, 1H), 3.10 (dd, $J = 5.3$ Hz, $J = 15.0$ Hz, 1H), 3.97–2.73 (m, 2H), 1.38 (d, $J = 6.5$ Hz, 3H).

^{13}C NMR ($CDCl_3$) δ (ppm): 190.6, 170.3, 156.2, 132.7, 130.7, 129.4, 123.7, 117.4, 33.8, 31.2, 15.2.

MS, *m/z* (%): 190 (66), 162 (37), 161 (100), 147 (6), 133 (25), 115 (10), 105 (12), 91 (12), 77 (14), 63 (6), 51 (8).

*2-Oxo-2,3,4,5-tetrahydro-benzo[*b*]oxepine-7-carbaldehyde (*2c*)*

Sticky solid at room temperature; FT-IR: 2953, 2922, 2852, 1769, 1694, 1605, 1584, 1484, 1455, 1377, 1341, 1240, 1202, 1126, 1092, 1041, 961, 873, 837, 808, 754, 718 cm^{-1}.

^1H NMR ($CDCl_3$) δ (ppm): 9.98 (s, 1H), 7.83 (dd, $J = 2$ Hz, $J = 8$ Hz, 1H), 7.78 (d, $J = 2$ Hz, 1H), 7.26 (d, $J = 8$ Hz, 1H), 2.93 (t, $J = 7.2$ Hz, 2H), 2.52 (t, $J = 7.2$ Hz, 2H), 2.25 (quint., $J = 7.2$ Hz, 2H).

^{13}C NMR ($CDCl_3$) δ (ppm): 190.7, 170.0, 156.3, 134.1, 131.1, 130.9, 130.8, 120.2, 31.2, 28.3, 26.3.

MS, *m/z* (%): 190 (26), 162 (64), 161 (13), 145 (6), 135 (41), 115 (6), 105 (7), 91 (8), 77 (19), 63 (7), 55 (100).

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