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Catalytic and selective synthesis of lactones and bis-lactones by palladium acetate/1,4-bis(diphenylphosphino)butane system under syngas conditions

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Dedicated to Professor Renato Ugo who made a great contribution to catalysis and organometallic chemistry. We have learned a great deal from him

Abstract

The combination of palladium acetate and 1,4-bis(diphenylphosphino)butane (dppb) proved once again to form an effective catalytic system for the selective cyclocarbonylation of 2-allyl phenols and other bis-2-allyl phenol systems such as steroids and other important compounds. The reactions afforded new important five-, six- and seven-membered ring lactones and bis-lactones. The seven-membered ring lactones were predominant in most reactions.

Keywords: Carbonylation; Cyclocarbonylation; Lactones; Palladium acetate; 2-Allyl phenols

1. Introduction

Lactones and lactams containing both saturated and unsaturated five, and larger rings, are of interest because of their use in building up biologically active compounds which exhibit pharmacologically activity (fungicidal, anti-tumoral and anti-inflammatory) [1–5] and because of their ability to undergo ring opening, such compounds can be used for the synthesis of polyesters [6,7].

In the past decade, various routes to lactones based on cyclocarbonylation reaction have been described in the literature and the palladium-based catalysts were among the most efficient for such processes. Recent examples include cyclocarbonylation of allylic and homoallylic alcohols [8–14], alkynes and acetylenic alcohols [15–32]. The preparation of lactones compounds can also be achieved by direct insertion of carbon monoxide into four-membered cyclic ether [33,34] or by the use of phase transfer catalysis for lactonisation of numerous unsaturated alcohols [35]. The cyclocarbonylation reactions catalysed by palladium complexes, with few exceptions [21,23,36], exhibited preference for five- or six-membered ring lactones.

The six- or seven-membered rings lactones were not easy to prepare selectively and catalytically. An intriguing goal of industrial and academic researches is to obtain lactones selectively and with high yields. Recently, the cyclocarbonylation of 2-allyl phenols,

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in the presence of $Pd(OAc)_2$/1,4-bis(diphenylphosphino)butane (dppb) as catalytic system, giving five-, six- or seven-membered rings lactones with high yields and relatively good selectivity were reported [37].

We have explored further our research in the area of catalytic cyclocarbonylation. We now wish to report the successful application of the general catalytic system, $Pd(OAc)_2$/dppb, in the selective cyclocarbonylation reactions for the preparation of new substituted lactones and bis-lactones.

2. Experimental

2.1. Materials and measurements

Most chemicals were used as obtained from commercial sources. $Pd(OAc)_2$ and dppb are commercially available while allylphenols derivatives were prepared according to literature procedures [38]. Toluene was dried and distilled from sodium under nitrogen.

Melting points were taken on an electro thermal apparatus. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AC-200 at room temperature and chemical shifts are reported relative to Me_4Si. IR and MS spectra were performed, respectively, on FT-IR Jasco or IR Perkin-Elmer 683, and Hewlett-Packard GC/Mass MSD 5971 instruments. The molecular weights were determined using an LC mass spectrometer 1100 Series (Agilent) equipped with an atmospheric pressure chemical ionisation (APCI) interface.

2.2. General procedure for the cyclocarbonylation reactions

Palladium acetate (0.01 mmol), and dppb (0.04 mmol) were dissolved in 5 ml of dry toluene and the allyl phenol derivative (1 mmol) was added. The autoclave was purged three times with CO and pressurised with CO and H_2. The reaction mixture was heated with stirring for 24 h at 100 °C (oil bath temperature). The reaction mixture was cooled to room temperature, the solution was concentrated and the residue was extracted with ether. The lactones were purified by chromatography using petroleum ether and diethylether as eluant.

2.3. Selected spectroscopic data

2.3.1. Compound **3a**

mp 143–146 °C. IR (nujol) 3079, 2927, 2858, 2344, 1766, 1600, 1587, 1567, 1485, 1453, 1428, 1345, 1310, 1283, 1243, 1218, 1197 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ: 7.76 (d, J = 8.3 Hz, 1H), 7.30–7.13 (m, 3H), 7.03–6.97 (m, 2H), 2.86 (t, J = 7.1 Hz, 2H), 2.56 (t, J = 7.1 Hz, 2H), 2.25 (quintuplet, J = 7.1 Hz, 2H) ppm. ^{13}C NMR ($CDCl_3$) δ: 187.0, 162.6, 152.7, 146.0, 143.5, 135.5, 135.3, 122.7, 122.1, 121.7, 121.4, 120.1, 117.1, 109.4, 30.9, 28.4, 26.1 ppm. MS m/z (%): 304 (M^+, 83), 276 (40), 259 (38), 77 (12), 55 (100), 43 (8).

2.3.2. Compound **4a**

FT-IR (KBr) 2920, 2850, 2781, 1770, 1490, 1461, 1428, 1332, 1247, 1200, 1178, 1126, 1100, 1040, 963 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ: 7.70 (s, br, 1H), 7.23–7.12 (m, 2H), 5.00 (d, J = 9.5 Hz, 1H), 4.94 (s, 1H), 4.29 (d, J = 9.5 Hz, 1H), 2.91–2.95 (m, 5H), 2.38–2.33 (m, 2H), 2.20–2.03 (m, 2H) ppm. ^{13}C NMR ($CDCl_3$) δ: 171.29, 156.12, 153.80, 153.12, 152.99, 151.79, 147.31, 146.53, 146.39, 146.31, 146.22, 146.13, 145.96, 145.79, 145.56, 145.50, 145.41, 145.37, 145.31, 145.24, 145.17, 144.72, 144.57, 144.43, 144.32, 143.21, 143.03, 142.74, 142.62, 142.22, 142.18, 142.06, 142.04, 141.92, 141.81, 141.74, 141.70, 141.50, 140.23, 140.20, 139.84, 139.20, 136.68, 134.94, 129.02, 128.21, 125.28, 82.72, 69.99, 68.91, 40.03, 31.15, 29.69, 28.38, 26.73 ppm. LC–MS (APCI interface) calculated M: 899 amu; observed ($M - H^+$): 900 ($M + 1$) amu.

2.3.3. Compound **5a**

Sticky solid at room temperature. FT-IR (neat) 2953, 2922, 2852, 1769, 1694, 1605, 1584, 1484, 1455, 1377, 1341, 1240, 1202, 1126, 1092, 1041, 961, 873, 837, 808, 754, 718 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ: 9.98 (s, 1H), 7.83 (dd, J = 2.0 Hz, J = 8.0 Hz, 1H), 7.78 (d, J = 2 Hz, 1H), 7.26 (d, J = 8.0 Hz, 1H), 2.93 (t, J = 7.2 Hz, 2H), 2.52 (t, J = 7.2 Hz, 2H), 2.25 (quintuplet, J = 7.2 Hz, 2H) ppm. ^{13}C NMR ($CDCl_3$) δ: 190.7, 170.0, 156.3, 134.1, 131.1, 130.9, 130.8, 120.2, 31.2, 28.3, 26.3 ppm. MS m/z (%): 190 (M^+, 26), 162 (64), 161 (13), 145 (6), 135 (41), 115 (6), 105 (7), 91 (8), 77 (19), 63 (7), 55 (100).

*2.3.4. Compound **6a***

Oil. IR ($CHCl_3$) 3084, 3019, 2985, 2941, 2871, 1764, 1587, 1491, 1451, 1426, 1221, 1204, 1156, 1133, 1111, 1045, 1025 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 7.00 (dd, $J = 1.0$ Hz, $J = 7.9$ Hz, 1H), 6.82–6.74 (m, 2H), 6.14–5.95 (m, 1H), 5.48–5.26 (m, 2H), 4.55–4.50 (m, 2H), 2.78 (t, $J = 7.0$ Hz, 2H), 2.48 (t, $J = 7.0$ Hz, 2H), 2.17 (quintuplet, $J = 7.0$ Hz, 2H) ppm. ^{13}C NMR ($CDCl_3$) δ: 171.8, 155.8, 145.2, 132.7, 130.8, 119.6, 117.4, 115.6, 113.0, 68.8, 30.7, 28.1, 26.0 ppm. MS *m/z* (%): 218 (M^+, 100), 177 (54), 163 (10), 149 (84), 133 (19), 121 (12), 107 (13), 105 (26), 103 (11), 91 (15), 77 (25), 55 (39), 41 (27).

*2.3.5. Compound **6b***

mp 63–65 °C. IR ($CHCl_3$) 3020, 2922, 1759, 1592, 1494, 1452, 1432, 1207, 1160, 1089, 1028 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 6.96 (d, $J = 8.8$ Hz, 1H), 6.78 (d, $J = 8.8$ Hz, 1H), 6.73 (s, 1H), 6.06–5.97 (m, 1H), 5.46–5.27 (m, 2H), 4.53–4.49 (m, 2H), 2.96–2.70 (m, 3H), 1.36 (d, $J = 5$ Hz, 3H) ppm. ^{13}C NMR ($CDCl_3$) δ: 171.8, 155.0, 145.8, 133.0, 123.8, 117.8, 117.3, 114.0, 69.3, 34.1, 31.9, 15.4 ppm. MS *m/z* (%): 218 (M^+, 51), 177 (38), 149 (100), 149 (84), 121 (8), 107 (12), 103 (6), 91 (10), 77 (14), 65 (5), 55 (4), 41 (7).

*2.3.6. Compound **7a***

mp 102–104 °C. IR ($CHCl_3$) 3330, 3020, 2960, 2928, 1730, 1190, 865, 810, 720 cm^{-1}. ^1H NMR ($CDCl_3$) 6.86–6.64 (m, 3H), 2.87–2.71 (m, 1H), 2.57–2.47 (m, 2H), 2.37–2.21 (m, 1H), 2.16–2.00 (m, 1H), 0.99 (d, $J = 6.2$ Hz, 3 H) ppm. ^{13}C NMR ($CDCl_3$) δ: 172.7, 153.6, 144.9, 130.0, 119.9, 116.9, 114.4, 38.4, 36.0, 33.5, 20.4 ppm. MS *m/z* (%): 192 (M^+, 68), 123 (17), 107 (4), 91 (4), 77 (7), 69 (100), 55 (5), 41 (7).

*2.3.7. Compound **8a***

Oil. IR (neat) 3380, 1755, 1595, 1190, 1145, 870, 810, 780 cm^{-1}. ^1H NMR ($CDCl_3$) 6.95 (d, $J = 8.2$ Hz, 1H), 6.78–6.69 (m, 2H), 3.19–3.10 (m, 1H), 2.49–2.31 (m, 3H), 1.69–1.54 (m, 1H), 1.32 (d, $J = 6.8$ Hz, 3 H) ppm. ^{13}C NMR ($CDCl_3$) δ: 173.3, 154.0, 144.8, 134.9, 119.9, 113.9, 112.7, 34.7, 31.2, 31.1, 17.2 ppm. MS *m/z* (%): 192 (M^+, 38), 147 (14), 138 (10), 137 (100), 109 (8), 91 (7), 77 (5), 55 (5).

*2.3.8. Compound **9a***

mp 142–144 °C. IR (neat) 3590, 1755, 1605, 1510, 1390, 1135, 1090 cm^{-1}. ^1H NMR ($CDCl_3$) 8.02 (d, $J = 8.3$ Hz, 1H), 7.72 (d, $J = 8.3$ Hz, 1H), 7.40–7.26 (m, 2H), 6.84 (d, $J = 7.4$ Hz, 1H), 5.50 (s, broad, 1H), 3.17–3.08 (m, 1H), 2.80–2.53 (m, 3H), 2.20–2.11 (m, 1H), 1.13 (d, $J = 6.4$ Hz, 3H) ppm. ^{13}C NMR ($CDCl_3$) δ: 171.9, 151.7, 146.3, 126.9, 126.8, 126.7, 125.1, 124.9, 119.5, 113.8, 109.0, 38.9, 36.3, 35.0, 20.6 ppm. MS *m/z* (%): 242 (M^+, 63), 197 (10), 174 (15), 173 (100), 145 (11), 127 (11), 115 (19), 69 (27).

*2.3.9. Compound **10a***

mp 50 °C with decomposition. IR (neat) 3358, 3069, 1735, 1602, 1516, 1389, 1242, 1155, 1042, 803, 758 cm^{-1}. ^1H NMR ($CDCl_3$) 8.09 (d, $J = 8.7$ Hz, 1H), 7.76 (d, $J = 8.7$ Hz, 1H), 7.44–7.32 (m, 2H), 6.84 (d, $J = 7.4$ Hz, 1H), 5.47 (s, broad, 1H), 3.50–3.41 (m, 1H), 2.56–2.09 (m, 3H), 1.86–1.72 (m, 1H), 1.48 (d, $J = 6.8$ Hz, 3 H) ppm. ^{13}C NMR ($CDCl_3$) δ: 172.1, 151.4, 146.2, 129.5, 126.8, 126.7, 124.5, 122.0, 119.7, 114.2, 108.9, 35.8, 31.6, 31.5, 17.6 ppm. MS *m/z* (%): 242 (M^+, 60), 207 (4), 197 (10), 188 (16), 187 (100), 186 (5), 141 (8), 128 (7), 127 (5), 115 (7), 43 (6).

*2.3.10. Compound **11a** (or **11b**)*

mp decomposition >200 °C. IR ($CHCl_3$): 3010, 2960, 2920, 1750, 1490, 1408, 1352 1200, 1115 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 6.79 (s, 2H), 3.27–3.20 (m, 2H), 2.51–2.33 (m, 6H), 1.98–1.51 (m, 2H), 1.36 (d, $J = 6.8$ Hz, 6 H) ppm. ^{13}C NMR ($CDCl_3$) δ: 171.4, 148.9, 133.4, 116.9, 34.6, 31.2, 31.1, 17.3 ppm. MS *m/z* (%): 274 (M^+, 42), 220 (14), 219 (100), 191 (3), 165 (3), 164 (4), 163 (5), 91 (2), 55 (3).

*2.3.11. Compound **11b** (or **11a**)*

mp 153–154 °C. IR ($CHCl_3$) 3020, 2960, 2860, 1765, 1493, 1410, 1355, 1310, 1250, 1163, 1115 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 6.79 (s, 2H), 3.25–3.08 (m, 2H), 2.50–2.28 (m, 6H), 1.79–1.58 (m, 2H), 1.33 (d, $J = 6.7$ Hz, 6 H) ppm. ^{13}C NMR ($CDCl_3$) δ: 171.2, 148.8, 133.4, 116.9, 34.6, 31.14, 31.12, 17.3 ppm. MS *m/z* (%): 274 (M^+, 34), 220 (15), 219 (100), 191 (4), 165 (4), 164 (5), 163 (6), 91 (4), 55 (5).

*2.3.12. Compound **12a***

GC–MS analyses have evidenced the presence of only one of the two possible isomers.

mp 222 °C (decomposition). IR ($CHCl_3$) 3020, 2960, 2930, 1758, 1495, 1420, 1350, 1245, 1185, 1130, 870, 810 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 6.93 (s, 2H), 2.99–2.88 (m, 2H), 2.64–2.40 (m, 6H), 2.22–2.06 (m, 2H), 1.33 (d, $J = 6.1$ Hz, 6 H) ppm. ^{13}C NMR ($CDCl_3$) δ: 170.2, 148.6, 129.1, 120.7, 38.4, 35.8, 33.5, 20.4 ppm. MS *m*/*z* (%): 274 (M^+, 36), 205 (10), 91 (3), 69 (100), 41 (7).

2.3.13. Compound ***13a***

GC–MS analyses have evidenced the presence of two isomers unfortunately not isolable by column chromatography.

IR ($CHCl_3$) of the mixture: 3020, 2960, 1760, 1460, 1345, 1280, 1180, 1140, 1120, 1025 cm^{-1}. ^1H NMR ($CDCl_3$) of the mixture; δ: 7.03 (s, aromatic protons); 3.00–2.09 (m, aliphatic protons) 1.15 (d, $J = 6.0$ Hz, CH_3) and 1.11 (d, $J = 5.7$ Hz, CH_3) ppm. ^{13}C NMR ($CDCl_3$) of the mixture; δ: 170.04, 169.98, 149.38, 149.36, 128.78, 128.60, 118.66, 118.64, 38.14, 38.09, 33.46, 33.20, 31.78, 31.60, 26.0, 20.43, 20.37 ppm. GC–MS of the isomer number 1: *m*/*z* (%): 274 (M^+, 38), 206 (10), 91 (4), 69 (100), 41 (7). GC–MS of the isomer number 2: *m*/*z* (%): 274 (M^+, 35), 206 (10), 91 (4), 69 (100), 41 (7).

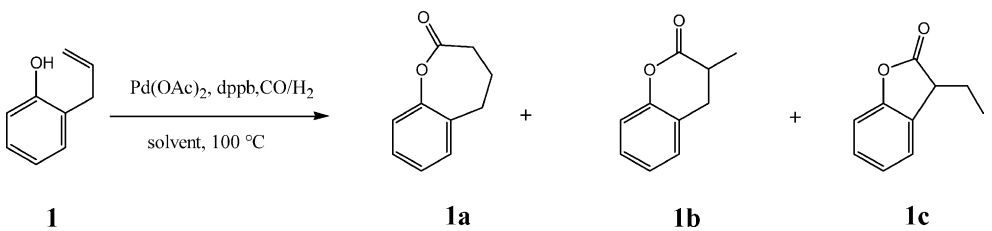
3. Results and discussion

As mentioned earlier, we have previously explored the cyclocarbonylation reaction of 2-allylphenol in the presence of the homogeneous catalytic system $Pd(OAc)_2$/dppb, in toluene, under CO/H_2 mixture to produce easily the seven-membered ring lactone **1a** as the major product. When the same reaction was conducted in dichloromethane, a mixture of lactones **1a**, **1b** and **1c** was obtained [37] (Scheme 1).

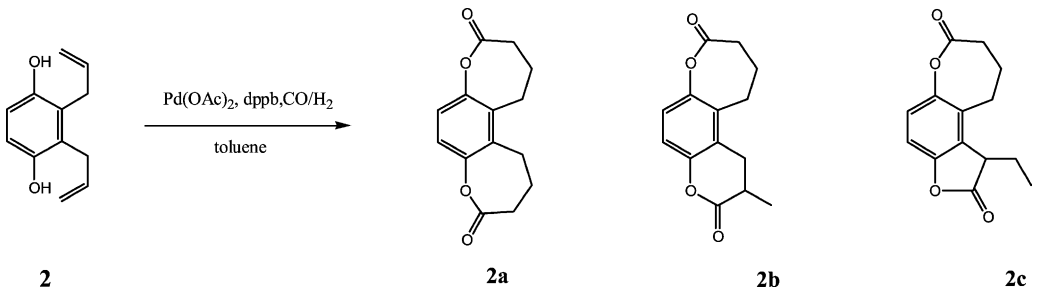
As continuation of our research in this area, we have explored the cyclocarbonylation of steroids and we have found a novel method for the preparation of steroid–lactone molecules [39].

Recently, we have applied the same homogeneous catalytic system formed of $Pd(OAc)_2$ and dppb to bis-allylphenols affording the bis-lactones as the products of the double carbonylation reactions (Scheme 2) [40]. The regioselectivity of the reaction depends strongly on the experimental conditions; the bis-cyclocarbonylation reaction can be addressed to prepare bis-lactones with two different ring sizes (7–6, 7–5, 6–6) [40].

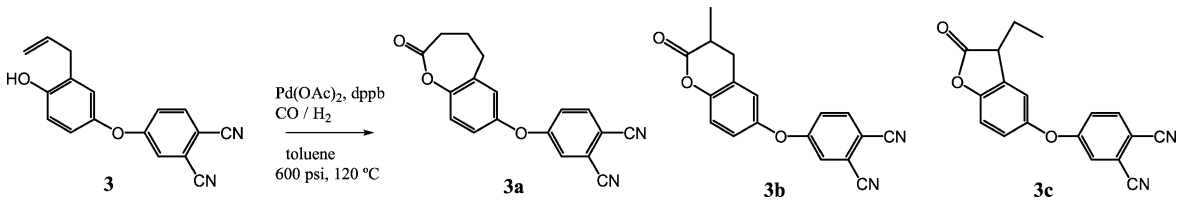
The objective of the present study is to validate this general catalytic system formed of $Pd(OAc)_2$ and



Scheme 1.



Scheme 2.



Scheme 3.

dppb. We would like also to assess its catalytic activity for cyclocarbonylation of other substrates containing other functionalities (cyano, formyl, fullerene group, etc.) for the preparation of lactones that can be used as building blocks for new compounds.

For instance, the dicyano lactone derivative **3a** has been easily prepared by cyclocarbonylation reaction of 4-phenoxy (3′-allyl-4′-hydroxy phthalonitrile) **3** according the Scheme 3.

The treatment of **3** (1.0 mmol) with (0.01 mmol of $Pd(OAc)_2$ and dppb (0.04 mmol) in toluene under 1/5 mixture of carbon monoxide and hydrogen (total pressure: 600 psi) at 100 °C for 24 h resulted in 90% conversion (Table 1, entry 1) with a good selectivity toward the seven-membered ring lactone **3a**. Trace amounts of six- and five-membered ring lactones (**3b** and **3c**) were also detected and identified by GC–MS (a complete characterisation of them was not possible because of the small amount obtained).

The use of CH_2Cl_2 in place of toluene resulted in a similar conversion and the seven-membered ring lactone was also formed as the major product of the reaction (Table 1, entry 2). Nearly complete conversion of **3a** was achieved using 1/1 ratio of CO/H_2 in toluene or CH_2Cl_2 as a solvent. The use of excess of hydrogen versus carbon monoxide ($CO/H_2 = 100/500$ psi) or a lower total pressure (200 psi) led to the decrease in the catalytic activity of the catalyst and the conversions dropped to 45 and 35%, respectively (Table 1, entries 4 and 5). However, the selectivity toward the seven-membered ring lactone was always maintained high (85–86%). In addition, no reaction was observed in the absence of H_2 (600 psi of CO).

When 2-allyl-6 fulleropyrrolidine-phenol **4** was used as a reactant and dppb/$Pd(OAc)_2$ ratio was 2, the reaction resulted in 98% conversion with a good selectivity for the seven-membered ring lactone **4a** (Scheme 4). Small amounts of six- and five-membered ring lactones (10%) were also found and detected in LC–MS spectra; however, the complete characterisation of these minor products was not possible because of the small amount obtained.

Other 2-allyl phenols and 2-allyl naphthols were also considered in the cyclocarbonylation reaction catalysed by the system $Pd(OAc)_2$/dppb/CO/H_2/toluene at 100 °C for 24 h. The results are summarised in Table 2. The total isolated yields of the lactones were very high (77–95%) and the selectivities toward the seven-membered ring lactones were excellent (90–99%). The reaction could tolerate various

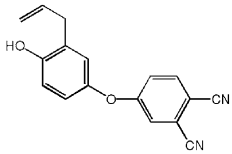
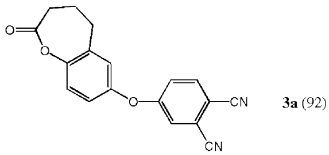
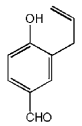
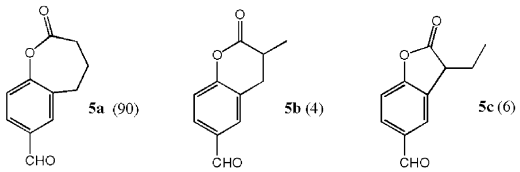
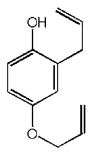
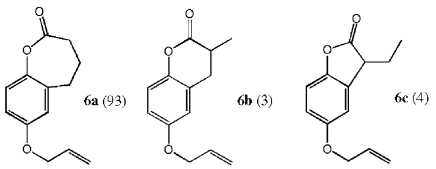
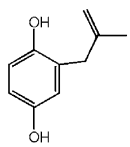
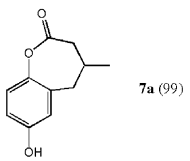
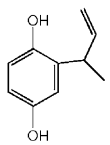
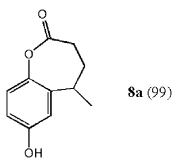
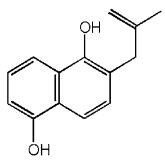
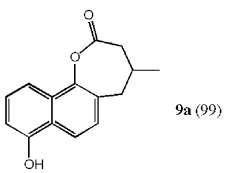
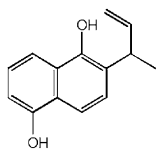
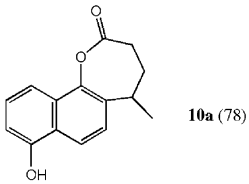
Table 1
Cyclocarbonylation reactions of **3**

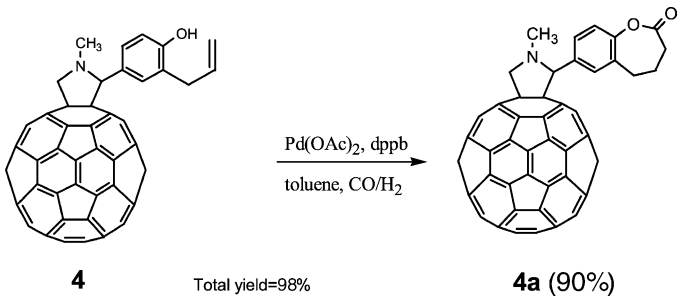
Entry	Solvent	P_{CO} (psi)	P_{H_2} (psi)	Conversion (%)	Product distribution (%)		
					3a	**3b**	**3c**
1	Toluene	500	100	90	88	6	6
2	CH_2Cl_2	500	100	89	86	7	7
3	Toluene	300	300	95	90	3	7
4	CH_2Cl_2	300	300	90	89	5	6
5	Toluene	100	500	45	86	5	9
6	Toluene	100	100	35	85	5	10

Reaction conditions: substrate **3** (1.0 mmol); $Pd(OAc)_2$ (0.01 mmol); dppb (0.04 mmol); solvent (5 ml); 100 °C; 24 h.

functionalities on the benzene ring such as formyl (Table 2, entry 2), allyl ether (Table 2, entry 3), substituted napthyl group (Table 2, entries 6 and 7) and other important functionalities (Table 2, entries 1, 4 and 5). The reaction of cyclocarbonylation seems to have more general scope and can be applied to various substrates with different functional groups producing new series of lactones that can

Table 2
Cyclocarbonylation of 2-allyl phenols (and 2-allyl naphthols) derivatives by $Pd(OAc)_2$/dppb/CO/H_2/toluene at 100 °C for 24 h

Entry	Substrates	Selectivity of lactones (%)	Isolated yields (%)
1	 **3**	 **3a** (92)	81
2	 **5**	 **5a** (90) **5b** (4) **5c** (6)	88
3	 **6**	 **6a** (93) **6b** (3) **6c** (4)	92
4	 **7**	 **7a** (99)	90
5	 **8**	 **8a** (99)	95
6	 **9**	 **9a** (99)	81
7	 **10**	 **10a** (78)	77



Scheme 4.

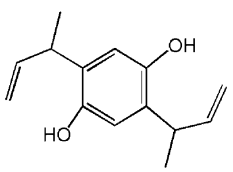
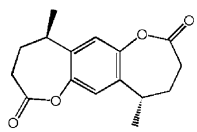
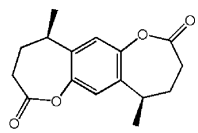
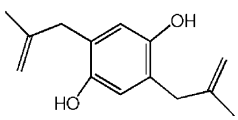
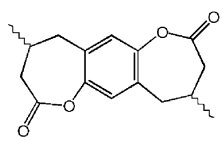
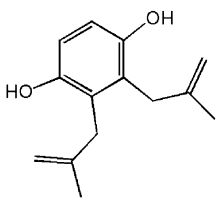
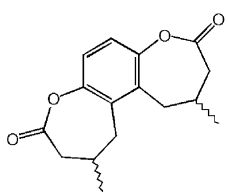
have a potential application in organic synthetic chemistry.

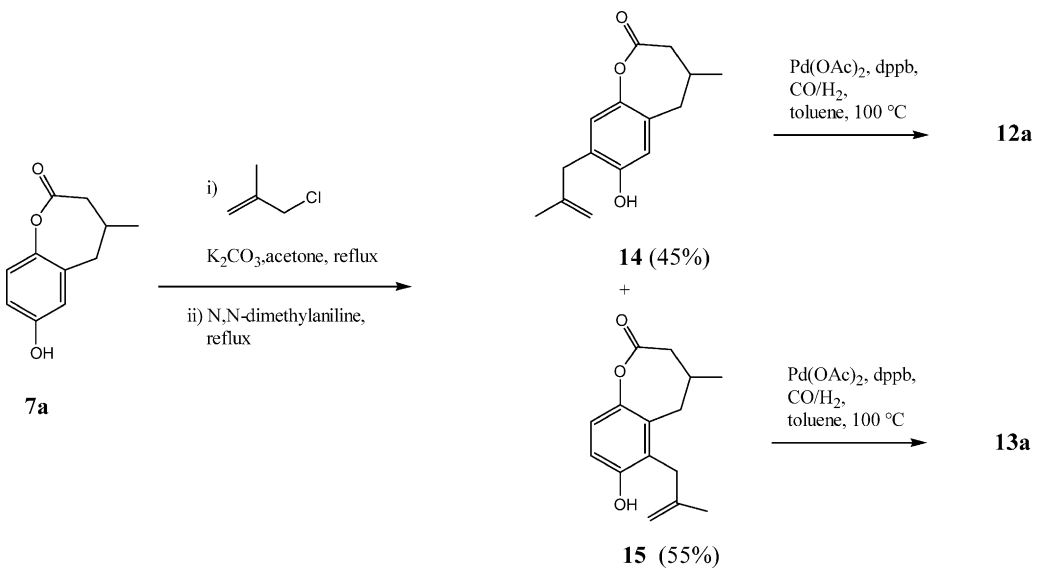
Interestingly, the carbonylation of the bis-2-allyl phenols was successfully achieved by the same catalytic system including $Pd(OAc)_2$/dppb/toluene/CO/H_2 at 100 °C for 24 h (Table 3, entries 1, 2 and 3). The isolated yields were excellent (90–93%) and the regioselectivity was in favour of the seven–seven-membered ring lactones (95–97%).

Although the two isomers **11a** and **11b** were isolated as pure compounds by column chromatography and characterized by GC–MS, ^{1}H NMR and ^{13}C NMR analyses, they are at the moment under investigation for the attribution of the exact formulation.

Products **12a** and **13a** could also be obtained by cyclocarbonylation of **14** and **15**, easily prepared via the allylation and the subsequent Claisen rearrangement **7a** (Scheme 5).

Table 3
Cyclocarbonylation of bis-allylphenol by $Pd(OAc)_2$/dppb/CO/H_2/toluene

Entry	Substrate	Selectivity of bis-lactones (%)	Isolated yields (%)
1	 **11**	 **11a** (50%)  **11b** (50%)	90
2	 **12**	 **12a** (95)	92
3	 **13**	 **13a** (97) mixture of two isomers	93



Scheme 5.

4. Conclusion

The catalytic system formed of palladium acetate and dppb catalysed successfully the cyclocarbonylation of variously substituted allylphenol derivatives to produce selectively seven-membered ring lactones in excellent yields. We have examined various representative examples of cyclocarbonylation reactions including fullerene and phthalonitrile derivatives which can be added to the important lists of new organic materials.

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