



A novel and efficient method for the catalytic direct oxidative carbonylation of 1,2- and 1,3-diols to 5-membered and 6-membered cyclic carbonates

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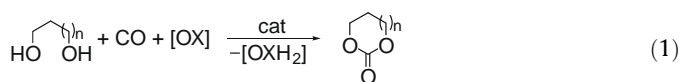
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ABSTRACT

In the presence of a PdI₂-based catalytic system, 1,2-diols undergo an oxidative carbonylation process to afford 5-membered cyclic carbonates in good to excellent yields (84–94%) and with unprecedented catalytic efficiencies for this kind of reaction (up to ca. 190 mol of product per mol of PdI₂). Under similar conditions, 6-membered cyclic carbonates are obtained for the first time through a direct catalytic oxidative carbonylation of 1,3-diols (66–74% yields).

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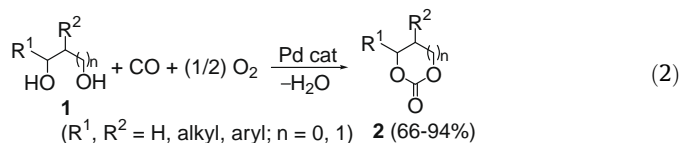
Cyclic carbonates are a very important class of carbonyl compounds, with many important applications in various fields of Science.¹ They are usually prepared either by carboxylation (with CO₂ or its derivatives as carboxylating agents) of suitable substrates (such as diols, epoxides, and olefins) or by indirect carbonylation (with phosgene or its derivatives, including acyclic carbonates, as carbonylating agents) of diols.² Surprisingly, however, the direct, phosgene-free oxidative carbonylation of diols with carbon monoxide (Eq 1, [OX] = oxidizing agent) has so far received limited attention, in spite of the large availability of CO and the attractiveness of the process in view of its high atom economy³ and eco-friendliness.



The stoichiometric oxidative carbonylation of 1,2-diols to give [1,3]dioxolan-2-ones was reported by Tam some years ago to be promoted by PdCl₂ in conjunction with 2 equiv of AcONa.^{4,5} Tam also reported a catalytic version of his reaction [carried out in the presence of 10% of PdCl₂, CuCl₂ as the oxidant (2 equiv with respect to the substrate) and AcONa or Et₃N as the base (2 equiv with respect to the substrate)], which, however, was limited to the conversion of 1-phenyl-1,2-ethanediol into 4-phenyl-[1,3]dioxolan-2-one (with a catalytic turnover of 10) and of 1-(*N*-phenylamino)propane-2,3-diol into a ca. 3:1 mixture of 4-phenylamino-[1,3]dioxolan-2-one and 5-hydroxymethyl-3-phenyloxazolidin-2-one (with a total catalytic turnover of 7.4).^{4,6}

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We have recently reported that PdI₂ in conjunction with an excess of KI is an excellent catalyst for realizing the oxidative carbonylation of β-amino alcohols⁷ and amines⁸ to give 2-oxazolidinones and ureas, respectively. We have now found that the PdI₂-KI system is also a very efficient catalyst for the conversion of 1,2-diols into 5-membered cyclic carbonates, with unprecedented catalytic efficiencies for this kind of reaction (up to ca. 190 mol of product per mol of PdI₂) (Eq 2, *n* = 0). Using the same catalyst, 6-membered cyclic carbonates have been obtained for the first time through the direct catalytic oxidative carbonylation of 1,3-diols (Eq 2, *n* = 1).

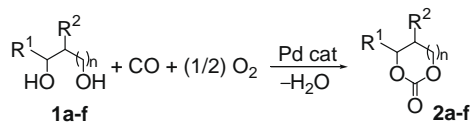


Oxidative carbonylation reaction of 1,2-diols (*n* = 0) was carried out at 100 °C under 20 atm of a 4:1 mixture of CO–air⁹ in *N,N*-dimethylacetamide (DMA) as the solvent (substrate concentration = 0.5 mmol of **1** per mL of DMA), in the presence of 0.5 mol % of PdI₂ in conjunction with 10 equiv of KI. Under these conditions, after 15 h, 1,2-ethanediol **1a** (*n* = 0, R¹ = R² = H) was smoothly converted into [1,3]dioxolan-2-one **2a** in 84% isolated yield (Table 1, entry 1). To the best of our knowledge, this reaction represents the first example of oxidative carbonylation of 1,2-ethanediol to give **2a** with catalytic turnover.^{10–12}

Under similar conditions, other 1,2-diols, bearing an alkyl or a phenyl group substituent, such as butane-1,2-diol **1b** (*n* = 0, R¹ = Et, R² = H) and 1-phenylethane-1,2-diol **1c** (*n* = 0, R¹ = Ph, R² = H), behaved similarly, with formation of the corresponding

Table 1

Synthesis of 5-membered and 6-membered cyclic carbonates **2a–f** by PdI₂/KI-catalyzed oxidative carbonylation 1,2- and 1,3-diols **1a–f**^a



Entry	<i>n</i>	R ¹	R ²	1	1: PdI ₂ molar ratio	Time (h)	Conversion of 1 (%) ^b	2	Yield of 2 (%) ^c
1	0	H	H	1a	200	15	100	2a	84
2	0	Et	H	1b	200	15	100	2b	94
3	0	Ph	H	1c	200	15	100	2c	94
4	1	H	H	1d	200	15	80	2d	42
5	1	H	H	1d	100	15	100	2d	74
6	1	Me	H	1e	100	24	100	2e	66
7	1	H	Me	1f	100	24	100	2f	68

^a All reactions were carried out in DMA (substrate concentration = 0.5 mmol of **1**/mL of DMA, 4 mmol scale based on **1**) at 100 °C under 20 atm of a 4:1 mixture of CO-air in the presence of PdI₂ in conjunction with 10 equiv of KI.

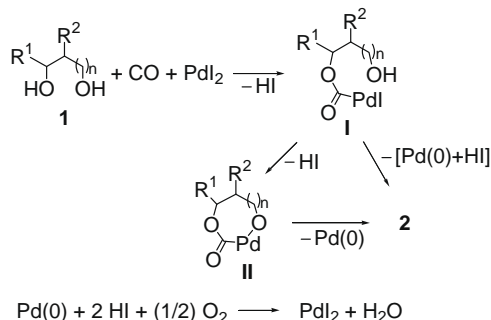
^b Determined by GLC.

^c Isolated yield based on starting **1**.

cyclic carbonates **2b–c** with isolated yields higher than 90% (Table 1, entries 2 and 3).^{11,13}

Our method could also be successfully applied to the first direct catalytic oxidative carbonylation of 1,3-diols, such as 1,3-propanediol **1d** (*n* = 1, R¹ = R² = H), 1,3-butanediol **1e** (*n* = 1, R¹ = Me, R² = H), and 2-methylpropane-1,3-diol **1f** (*n* = 1, R¹ = H, R² = Me) to give the corresponding [1,3]dioxan-2-ones **2d–f** in good yields (Table 1, entries 4–7). As expected in view of their higher conformational mobility, 1,3-diols turned out to be less reactive with respect to 1,2-diols: thus, the reaction of **1d**, carried out under the same conditions as previously employed for 1,2-diols **1a–c** (Table 1, entries 1–3), led to a substrate conversion of 80%, with an isolated yield of [1,3]dioxan-2-one **2d** of 42% (Table 1, entry 4). Better results were however obtained by working with a lower substrate-to-catalyst molar ratio: with 1 mol % of PdI₂, the substrate conversion was quantitative after 15 h, and the yield of **2d** increased to 74% (Table 1, entry 5). Under the same conditions, the reactions of **1e** and **1f** were slightly slower: the substrate conversion reached 100% after 24 h, with isolated yields of the corresponding 6-membered cyclic carbonates **2e** and **2f** of 66% and 68%, respectively (Table 1, entries 6 and 7).^{14–16}

On the basis of what is already known on PdI₂-catalyzed oxidative carbonylation reactions,¹⁷ formation of **2a** may be interpreted as occurring as shown in Scheme 1 (anionic iodide ligands are omitted for clarity). Thus, formation of the alkoxycarbonylpalladium species **I** takes place through the reaction between the alcoholic function of the substrate, CO, and PdI₂, with elimination of



Scheme 1. Mechanism of the PdI₂-catalyzed oxidative carbonylation of diols **1** to give cyclic carbonates **2**. Anionic iodide ligands are omitted for clarity.

HI. Complex **I** may then undergo intramolecular nucleophilic displacement by the second hydroxyl group, with formation of **2a** and elimination of Pd(0) and HI. Alternatively, intermediate **I** may convert into palladacycle derivative **II** with elimination of HI. Reductive elimination eventually leads to the final product and Pd(0). In any case, Pd(0) is then reoxidized to PdI₂ according to the mechanism we demonstrated several years ago,¹⁸ involving initial oxidation of HI by O₂ to give I₂ followed by oxidative addition of the latter to Pd(0).

In conclusion, we have developed the first general method for the catalytic direct oxidative carbonylation of both 1,2- and 1,3-diols, to give the corresponding cyclic carbonates in good to excellent yields (66–94%) and high catalytic efficiencies (up to ca. 190 mol of product per mol of palladium). The present phosgene-free, atom-economical approach for the preparation of cyclic carbonates thus represents a valuable alternative to the currently known methods for their production.

Acknowledgments

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- These conditions (16 atm of CO together with 5 total atm of air, considering that the autoclave was loaded under 1 atm of air) corresponded to 76.2% 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., 3rd ed. In *Kirk-Othmer Encyclopedia of Chemical Technology*; Grayson, M., Eckroth, D., Bushey, G. J., Campbell, L., Klingsberg, A., van Nes, L., Eds.; Wiley-Interscience: New York, 1978; Vol. 4, p 775.
- Under Tam's conditions, no catalytic conversion of **1a** into **2a** was observed: the author reported that 'Attempts to make the reaction with ethylene glycol catalytic in palladium fail probably due to the interaction of ethylene glycol with CuCl₂; no carbonate is formed' (Ref. 4). As regards the oxidative carbonylation of **1a** carried out in the presence of Co(OAc)₂, see note 6.
- Typical carbonylation procedure for the synthesis of 5-membered cyclic carbonates **2a–c**: a 250 mL stainless steel autoclave was charged in the presence of air with PdI₂ (7.0 mg, 1.94 × 10⁻² mmol), KI (32.0 mg, 1.93 × 10⁻¹ mmol) and a solution of **1a–c** (3.88 mmol) in DMA (7.8 mL). The

autoclave was sealed and, while the mixture was stirred, the autoclave was pressurized with CO (16 atm) and air (4 atm). After being stirred at 100 °C for 15 h, the autoclave was cooled, degassed, and opened. The solvent was evaporated under vacuum, and products **2a–c** were purified by column chromatography on silica gel using hexane–acetone from 9:1 to 8:2 as the eluent. The spectroscopic properties of the cyclic carbonates **2a**,¹² **2b**,¹³ and **2c**¹³ thus obtained agreed with those reported in the literature. The yields obtained in each case are reported in Table 1, entries 1–3.

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column chromatography on silica gel using hexane–acetone from 9:1 to 8:2 as the eluent. The spectroscopic properties of the cyclic carbonates **2d**,¹⁵ **2e**,¹⁶ and **2f**¹⁵ thus obtained agreed with those reported in the literature. The yields obtained in each case are reported in Table 1, entries 5–7.

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