ChemComm

Palladium-catalysed formation of maleic anhydrides from CO, CO_2 and alk-1-ynes

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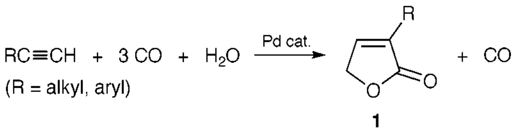
Received (in Liverpool, UK) 8th April 1999, Accepted 20th May 1999

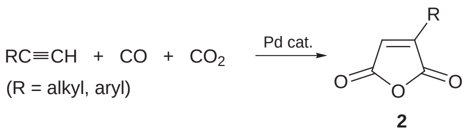
Carbon dioxide causes palladium-catalysed synthesis of unsaturated γ-lactones from alk-1-ynes and CO to shift towards maleic anhydrides.

We recently showed that working in dioxane–water at 80 °C under a 10 atm pressure of CO in the presence of PdI_2 and 10 equiv. of KI leads to catalytic reductive carbonylation of alk-1-ynes with formation of furan-2(5*H*)-ones (Scheme 1).[1] Oxidation of CO to CO_2 accounts for the stoichiometry of the process.



Scheme 1

We now find that in the presence of added CO_2 another catalytic reaction takes place, consisting of the formation of maleic anhydrides according to Scheme 2.



Scheme 2

Table 1 reports the results obtained with and without additional CO_2 pressure. By working under the same reaction conditions which selectively lead to furanones but under an additional 40 atm pressure of CO_2, the product distribution was clearly altered in favour of maleic anhydrides, although the overall reaction rate was decreased.

Both the presence of small amounts of water and the nature of Pd^{II} counterion were essential to the process, only traces of products being obtained under anhydrous conditions or using $PdCl_2$ and 10 equiv. of KCl as catalyst. Decomposition to Pd metal occurred only to a limited extent. In any case, Pd metal was not a catalytically active species for the present reaction, as shown by control experiments.

Table 1 Reactions of alk-1-ynes (100 equiv.) with CO (10 atm), CO_2 and H_2O (200 equiv.) in dry dioxane in the presence of PdI_2 (1 equiv.) and KI (10 equiv.), substrate conc.: 0.5 mmol ml^{-1} dioxane, T = 80 °C

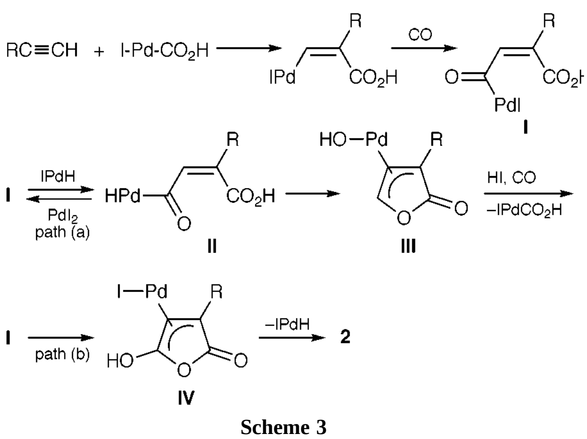
Substrate	$P(CO_2)$/ atm	t/h	Yield (%)[a] 1	2
BuC≡CH	—	15	77[b]	7
BuC≡CH	40	64	32[c]	47
PhC≡CH	—	15	67	traces
PhC≡CH	40	24	30	34

[a] Based on starting alk-1-yne, by GLC. [b] 4-Butyl-2(5*H*)-furan-2-one (8%) was also detected in the reaction mixture. [c] 4-Butyl-2(4*H*)-furan-2-one (10%) was also present in the reaction mixture.

The effect of CO_2 can be rationalised in the following way (Scheme 3; anionic iodide ligands are omitted for simplicity). An I-Pd-CO_2H species,[2] stabilised by iodide ligands, is first generated from PdI_2, CO and H_2O and then inserts the alkyne and CO to give intermediate **I**. At this point two pathways are possible. Formation of furanones requries the intervention of a palladium hydride species,[3] which must derive from decarboxylation[4] of I-Pd-CO_2H, as shown in Scheme 3. Hydride exchange on complex **I** by H-Pd-I[5] followed by reductive cyclization of intermediate **II** leads to allylpalladium complex **III**, whose protonolysis affords **1** with regeneration of the catalytically active species [path (*a*)]. On the other hand, anhydrides can be formed *via* tautomerization of acylpalladium intermediate **I**[6] followed by elimination of Pd^0 and HI or I-Pd-H [path (*b*)]. This reaction is stoichiometric and reoxidation is needed to start a new cycle.[6,7] However, in the presence of an excess of CO_2 I-Pd-H can be reconverted into a catalytically active form. In fact, CO_2 may insert into the palladium hydride bond[8] with formation of either a I-Pd-CO_2H species (which can directly start a new cycle) or a Pd-O(CO)H species, whose protonolysis by HI would afford PdI_2. In both cases no reoxidation is needed and the anhydride cycle can go on. Moreover, in the presence of added CO_2, the decarboxylation equilibrium is shifted to the left and the anhydride cycle becomes competitive with the reduction pathway leading to furanones.

In summary, we have shown that under our conditions CO_2 strongly influences the distribution of products. In the presence of an excess of added CO_2 the resulting concentration of palladium hydride species is reduced in favour of Pd-CO_2H and/or Pd-O(CO)H species, thus minimising furanone formation and allowing the anhydride cycle to run.

The reaction reported here is the first example in which CO and CO_2 are used together for the catalytic formation of unsaturated cyclic anhydrides. The stoichiometric formation of an anhydride from a metallacyclic complex, CO and CO_2 in two steps was described some years ago.[9] In the recently reported



Scheme 3

oxidative cyclization–alkoxycarbonylation of propynylamines carried out in the presence of CO_2, the role of CO_2 in the catalytic cycle was very different (*in situ* generation of a propynyl carbamate, which then underwent cyclization and alkoxycarbonylation).[10]

The authors gratefully acknowledge the Ministero dell'Università e della Ricerca Scientifica e Tecnologica (MURST) for financial support (Progetto d'Interesse Nazionale PIN 9803026360).

Notes and references

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2 This I-Pd-CO_2H species should form analogously to alkoxycarbonylpalladium halides but could not be isolated. Similar hydroxycarbonyl complexes are known with other metals, however; for representative examples, see Y.-X. He and D. Sutton, *J. Organomet. Chem.*, 1997, **538**, 49 and references cited therein.

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Communication 9/02814E