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# Neutral vs anionic palladium iodide-catalyzed carbonylation of terminal arylacetylenes

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In memory of Professor Gian Paolo Chiusoli.

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JXFYJPQQHBBLHC-PGMHBOJBSA-N
WYDMAEXBSVRGAF-SSZFMOIBSA-N

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ABSTRACT

The hydroalkoxycarbonylation of terminal arylacetylenes can be carried out in an easy one-step synthesis through the use of $PdI_2$ or $PdI_2$/KI as catalytic systems under non-oxidative conditions, without other ligands and in the absence of added acids. Going from non-polar to polar reaction media, we have noticed a dramatic change in the chemoselectivity of the reaction with prevailing formation of α-, β-unsaturated esters, in the former case, and a mixture of oxidative (maleic esters derivatives) and reductive (mainly unsaturated lactones) carbonylation products in comparable amount, in the latter case. The origin of this behavior can be explained with the different active species at work changing the reaction media: neutral palladium species in non-polar media and ionic palladium species in polar media.



## 1. Introduction

Palladium complexes have been known for a long time to be effective catalysts for many carbonylation reactions of alkene and alkyne derivatives providing new approaches for introducing synthetically versatile carbonyl groups with high efficiency and selectivity [1–3]. These reactions, formally defined as oxidative, reductive, and additive carbonylations, have exhibited different pathways leading to the direct synthesis of a broad variety of acyclic and heterocyclic carbonyl compounds [4–15]. Thus, the hydroalkoxycarbonylation reaction of alkynes leads to the formation of α-, β-unsaturated acids or esters in an easy one-step synthesis (Eq. (1)). The process requires the presence of a catalyst (usually Pd), a phosphine-based ligand, carbon monoxide, water-

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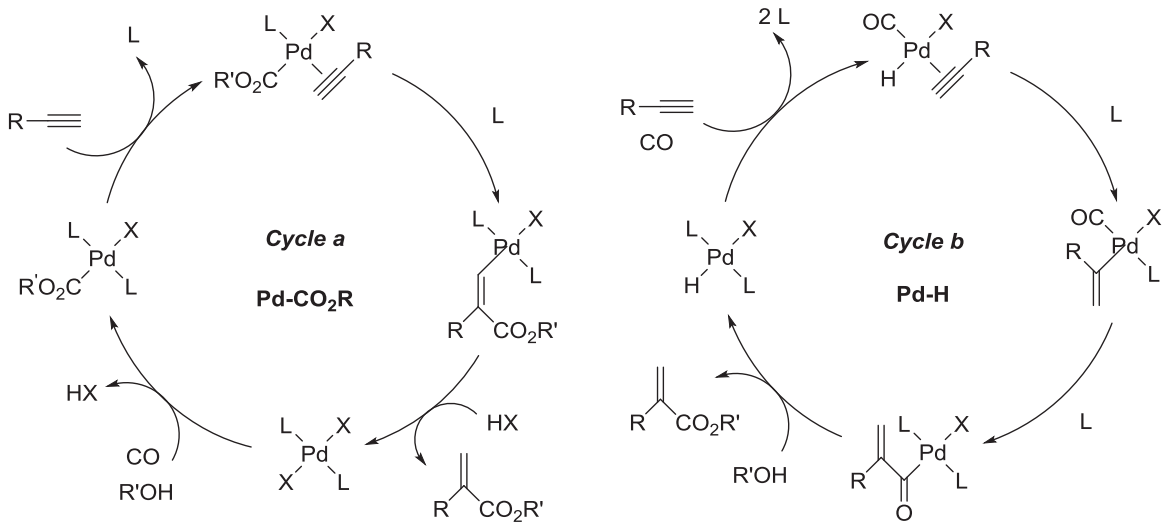
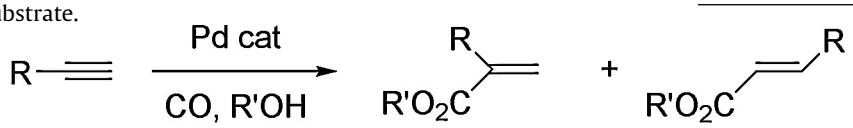



**Scheme 1.** Possible mechanisms for the alkoxycarbonylation of terminal alkynes.

containing solvents or alcohol, and an acidic co-promoter, typically a Bronsted acid [16–21]. The linear/branched product ratio depends on the employed catalytic system, the reaction conditions and the substrate.




(1)

The branched ester is often the preferred one and its derivatives are potential precursors of nonsteroidal anti-inflammatory drugs such as ibuprofen and naproxen [22–24].

In principle, two mechanisms have been proposed for the palladium-catalyzed hydroalkoxycarbonylation of alkynes. One involves the formation of an alkoxycarbonyl–palladium complex $PdCO_2R$ (Scheme 1, cycle a), followed by insertion of the alkyne into the Pd—C bond of the alkoxycarbonyl–metal species and, eventually, protonolysis of the resulting Pd–vinyl intermediate to produce the acrylic ester [25–30].

The other (Scheme 1, cycle b), proceeds through an initial insertion of the alkyne into a Pd—H bond to give a (σ-vinyl) palladium intermediate followed by further CO insertion into the Pd—C bond to afford an acylpalladium complex which, upon alcoholysis, yields the ester, regenerating the hydride [20,31–34].

Experimental evidence for the $PdCO_2R$ path has been provided by some authors under certain conditions [25,28–30]. On the other hand, since most of the carbonylation reactions of alkynes are carried out in the presence of strong proton donors, it is generally agreed that a cationic intermediate is involved. Evidence for the hydrido-like mechanism of acetylene derivatives has been found [31–34], also on the basis of a kinetic study on the hydroalkoxycarbonylation of phenylacetylene [35].

Work in our laboratories has involved the use of $PdI_2$ with an excess of KI as a catalytic system in the reductive or additive carbonylation [36–38] and oxidative alkoxycarbonylation [39–44] reactions of acetylenic derivatives in the absence of any organic ligand. In particular some years ago we reported the $PdI_2$/KI-catalyzed oxidative dicarbonylation reaction of terminal alkynes in the presence of air under mild conditions [45,46]. Dicarbonylated esters, anhydrides or acids were obtained with high catalytic efficiency treating alkynes with carbon monoxide in alcohol or water-containing solvents, respectively, at 25–80 °C. Besides, we reported that oxidative carbonylation of certain alkynes can be carried out catalytically in the absence of added oxidants if it is coupled with a reductive carbonylation reaction at the expense of the same alkyne involved in the oxidative process [47,48]. In this way maleic esters (from oxidative carbonylation) and unsaturated lactones (from reductive carbonylation) are the main products formed under catalytic action of palladium iodide/thiourea [47].

The valuable utility of halides as ancillary ligands being able to fine-tune reactivity and selectivity of a catalyst for a given transformation is well-known [49]. Iodide, in particular, has certain key features that makes it a good promoter of metal catalyzed reactions [50] such as palladium-catalyzed alkoxycarbonylation reactions.

In this work, we have evaluated the catalytic activity of palladium species containing iodide anions in the hydrobutoxycarbonylation of terminal arylacetylenes without other ligands and in the absence of added acids under non-oxidative conditions. The effect of the solvent is also considered and a plausible mechanism is then proposed.

## 2. Experimental

### 2.1. Materials and general methods

All starting acetylenic substrates, alcohols, and solvents were commercial products. Alcohols were distilled and stored under nitrogen over appropriate drying agents. Melting points were determined with an Gallenkamp MPD 350 BM 2.5 apparatus and are uncorrected. GC analyses were performed with a Fisons HRGC Mega 2 Series instrument fitted with a 30 m SE52 capillary column. Merck 60 $F_{254}$ silica gel sheets (0.2 mm thick) were used for TLC analyses. Silica gel 60 (70–230 mesh ASTM) was used for preparative column chromatography. Elemental analyses were carried out with a Carlo Erba Elemental Analyzer Model EA 1108. IR spectra were obtained with a Nicolet 5700 FT-IR spectrophotometer. Mass spectra (*m*/*z*, relative intensity%) were taken with a Hewlett-Packard Mass Selective Detector HP 5973 Series at 70 eV ionizing voltage interfaced with a Hewlett-Packard 6890 Series GC system fitted with a 30 m DB5 capillary column. $^1H$ and $^{13}C$ NMR data were acquired using a Bruker Avance 400 spectrometer in $CDCl_3$ as solvent and with TMS as reference at 25 °C. The absolute configuration of compound **9a** was established by NOESY experiments. Chemical shifts and coupling constants (*J*) are given as δ values (ppm)

and in Hz, respectively. Yields and selectivity for products were determined by $^1$H NMR spectroscopy and GC–FID analyses using the internal standard method.

### 2.2. Preparation of catalysts

#### 2.2.1. Potassium tetraiodopalladate ($K_2PdI_4$)

Into a 50 mL flask, equipped with a condenser an a magnetic stirring bar, $PdI_2$ 360.2 mg (1.0 mmol) and KI 332.0 mg (2.0 mmol) were introduced. Addition of methanol (15 mL) caused the mixture to quickly assume an intense red color. After refluxing for 1 h the mixture was concentrated at reduced pressure, then a black precipitate was recovered by filtration. The product was dried under vacuum giving a quantitative yield.

#### 2.2.2. Supported $PdI_2$ on active carbon ($Pd/C + I_2$)

Into a 50 mL flask, equipped with a condenser and a magnetic stirring bar, 10% Pd/C 106.4 mg (0.1 mmol Pd) and sublimed iodine 25.4 mg (0.2 mmol) were dissolved in methanol (15 mL). The mixture was heated at 60 °C under stirring for 2 h. The cooled mixture was filtered and the solid was dried under vacuum.

### 2.3. Determination of $HCO_2H$ from carbonylation reactions

The method reported by Bocchi et al. [51] was employed with some modifications. The crude reaction mixture was recovered with $CH_2Cl_2$ (25 mL) into a flask of 100 mL containing an excess of $Na_2CO_3$. The suspension was stirred for 24 h at room temperature. Then $CH_2Cl_2$ was eliminated at reduced pressure and benzyl bromide (3.0 mmol) and dry DMF (15 mL) were added. The resulting mixture was allowed to react under stirring at room temperature for 24 h. The organic products were recovered by extraction with ethyl acetate. Removal of DMF was performed by washing with brine. The organic phase, after drying, was subjected to GC–MS analysis, and benzyl formate was quantitatively determined by GC analysis using the internal standard method.

### 2.4. General procedure for carbonylation of acetylenic substrates

The carbonylation reactions were carried out in 45 mL stainless steel high pressure reactors (Parr instruments) fitted with pyrex (containers) vessels. These reactors were heated using oil baths and stirred with magnetic stirrer bars. In a general procedure the calculated amount of Pd catalyst, inorganic salts, additives, and ligands, respectively, if necessary, were introduced into the pyrex vessel. A solution of the substrate and butanol in the solvent of interest was added to the vessel that was placed into the autoclave. The reactor was sealed and flushed four times with carbon monoxide (99.5% Sapio) and pressurized to 10 bar, unless otherwise indicated. The mixture was heated at required temperature for the specified period of time. After cooling to room temperature, the reactor was depressurized and the organic products were separated from the catalyst by careful washing with AcOEt. The solution was washed with brine (3 × 15 mL) and the organic phase dried over magnesium sulfate. The solvent was removed under vacuum and the residue dissolved in a volumetric flask. A portion was analyzed by GC–MS for qualitative detection of the products. Other portions were arranged for quantitative determination by $^1$H NMR spectroscopy and GC–FID analyses using the internal standard method. This procedure allowed recycling of the Pd/C catalyst.

#### 2.4.1. Catalytic hydrobutoxycarbonylation of phenylacetylene in the presence of $PdI_2$

In a typical experiment, $PdI_2$ (9.7 mg, 0.027 mmol), phenylacetylene (0.3 mL, 2.7 mmol), 1-butanol (2.46 mL, 27 mmol), and toluene (4 mL) were charged to the reactor. The autoclave was purged with CO at room temperature, pressurized to 10 bar with CO and heated to 100 °C under stirring for 24 h. After conventional workup the quantitative product determination was carried out by GC–FID analyses and $^1$H NMR spectroscopy.

#### 2.4.2. Catalytic hydrobutoxycarbonylation of phenylacetylene in the presence of 10% Pd/C or $PdI_2$ supported on active carbon

An analogous procedure was used for hydrobutoxycarbonylation of phenylacetylene catalyzed by 10% Pd/C or $PdI_2$ supported on active carbon. For instance, the autoclave (45 mL) was charged with 0.027 mmol of 10% Pd/C treated with $I_2$, 2.7 mmol of phenylacetylene, and 27.0 mmol of 1-butanol in 4.0 mL of toluene. The sealed reactor was flushed four times with CO at room temperature, pressurized with 10 bar of CO and in case with other 2 bar of hydrogen. After reacting at 100 °C for 24 h under stirring, the usual workup was carried out on the reaction mixture. The recovered catalyst was recycled in the next run or submitted again to $I_2$ sorption treatment.

### 2.5. Characterization of products

Identification of known products **3a** [52], **6a** [53], and **8a** [54] was carried out by comparison with literature data. New compounds were characterized by $^1$H, $^{13}$C NMR, MS spectra, IR, and elemental analysis.

*Butyl 2-phenylacrylate* (**2a**): yellow oil; $^1$H NMR ($CDCl_3$): δ 7.46 – 7.35 (5H, m), 6.37 (1H, d, $J$ = 1.3 Hz), 5.90 (1H, d, $J$ = 1.3 Hz), 4.26 (2H, t, $J$ = 6.6 Hz), 1.76 – 1.66 (2H, m), 1.50 – 1.39 (2H, m), 0.97 (3H, t, $J$ = 7.3 Hz);$^{13}$C NMR ($CDCl_3$): δ 166.8, 141.6, 136.8, 128.3, 128.1, 128.0, 126.4, 64.9, 30.6, 19.2, 13.7; MS: *m/z* 204 ($M^+$, 35), 148 (95), 132 (15), 103 (100), 77 (38), 51 (11), 41 (13); IR (NaCl, $cm^{-1}$): ν 3060 (w), 2960 (m), 2934 (m), 1722 (s), 1618 (w), 1599 (w), 1450 (m), 1279 (w), 1195 (m), 1118 (w), 1093 (w), 1074 (w), 1002 (w), 813 (w), 753 (w). Anal. Calcd for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90. Found C, 76.67; H, 7.97.

*Dibutyl 2-phenylmaleate* (**4a**): yellow oil; $^1$H NMR ($CDCl_3$): δ 7.50 – 7.38 (5H, m), 6.30 (1H, s), 4.36 (2H, t, $J$ = 6.7 Hz), 4.18 (2H, t, $J$ = 6.7 Hz), 1.77 – 1.61 (4H, m), 1.47 – 1.34 (4H, m), 0.94 (3H, t, $J$ = 7.3 Hz), 0.93 (3H, t, $J$ = 7.5 Hz); $^{13}$C NMR ($CDCl_3$): δ 168.0, 164.9, 148.7, 133.4, 130.4, 128.9, 126.6, 117.3, 65.7, 64.8, 30.6, 30.0, 19.2, 19.1, 13.7, 13.6; MS: *m/z* 304 ($M^+$, 26), 230 (50), 175 (100), 147 (46), 102 (23), 41 (10); IR (NaCl, $cm^{-1}$): ν 3063 (w), 2952 (m), 2844 (m), 1742 (bs), 1623 (s), 1577 (m), 1498 (m), 1450 (s), 1435 (s), 1359 (s), 1293 (m), 1218 (w), 1159 (m), 1103 (w), 1027 (m), 1004 (m), 888 (m), 835 (m), 774 (s), 754 (m). Anal. Calcd for $C_{18}H_{24}O_4$: C, 71.03; H, 7.95. Found C, 71.32; H, 8.03.

*5,5-Dibutoxy-3-phenylfuran-2(5H)-one* (**5a**): colorless oil; $^1$H NMR ($CDCl_3$): δ 7.87 – 7.84 (2H, m), 7.45 – 7.42 (3H, m), 7.10 (1H, s), 3.45 (2H, t, $J$ = 6.6 Hz), 3.42 (2H, t, $J$ = 6.7 Hz), 1.73 – 1.61 (4H, m), 1.34 – 1.26 (4H, m), 0.97 (3H, t, $J$ = 7.4 Hz), 0.95 (3H, t, $J$ = 7.4 Hz); MS: *m/z* 304 ($M^+$, 9), 230 (14), 175 (100), 148 (62), 147 (78), 102 (60), 57 (19); IR(film, $cm^{-1}$): ν 3088 (w), 2960 (s), 2930 (s), 1773 (s), 1494 (m), 1317 (s), 1135 (s), 1000 (s), 950 (s). Anal. Calcd for $C_{18}H_{24}O_4$: C, 71.03; H, 7.95. Found C, 70.81; H, 7.88.

*Dibutyl 2-phenylsuccinate* (**7a**): colorless oil; $^1$H NMR ($CDCl_3$): δ 7.36–7.23 (5H, m), 4.23–4.01 (5H, m), 3.17 (1H, dd, $J$ = 16.8, 10.2 Hz), 2.63 (1H, dd, $J$ = 16.8, 5.3 Hz), 1.58–1.48 (4H, m), 1.47–1.32 (4H, m), 0.90 (3H, t, $J$ = 7.4 Hz), 0.89 (3H, t, $J$ = 7.5 Hz); $^{13}$C NMR ($CDCl_3$): δ 170.9, 168.5, 137.6, 128.4, 127.5, 127.3, 65.6, 64.6, 46.9, 37.6, 30.3, 30.1, 18.8, 18.7, 13.4, 13.3; MS *m/z*: 306 ($M^+$, 4), 232 (40), 176 (100), 163 (22), 149 (28), 148 (73), 107 (37), 104 (56), 57 (43). Anal. Calcd for $C_{18}H_{26}O_4$: C, 70.56; H, 8.55. Found C, 70.86; H, 8.36.

*Dibutyl 2,5-diphenylhex-2-enedioate* (**9a**): isomer E: colorless oil; $^1$H NMR ($CDCl_3$): δ 7.28 – 7.18 (10H, m), 7.10 (1H, m), 4.24 – 4.13 (4H, m), 3.93 (1H, bs), 2.71 (1H, bd, $J$ = 13.4 Hz), 2.31–2.25 (1H, m), 1.83 – 1.61 (4H, m), 1.36 – 1.29 (4H, m), 0.92 – 0.89 (6H, m);

$^{13}$C NMR ($CDCl_3$): δ 174.4, 168.2, 146.2, 137.2, 134.2, 132.1, 129.2, 128.7, 128.5, 127.8, 127.6, 126.9, 65.3, 64.7, 57.1, 34.1, 30.6, 30.4, 19.1, 13.4, 13.3; MS: *m/z* 408 ($M^+$, 4), 334 (18), 307 (63), 205 (100), 191 (14), 129 (13), 91 (17), 57 (11); IR (NaCl, $cm^{-1}$): ν 2959 (s), 2874 (s), 1733 (s), 1726 (s), 1600 (m), 1494 (m), 1447 (m), 1239 (m), 1161 (m), 752 (m). Isomer Z: colorless oil; $^1$H NMR ($CDCl_3$): δ 7.43 – 7.19 (10H, m), 7.02 (1H, brs), 4.26 – 4.14 (4H, m), 3.94 (1H, bs), 2.96 (1H, m), 2.02–1.95 (1H, m), 1.76 – 1.67 (4H, m), 1.45 – 1.37 (4H, m), 0.97 – 0.90 (6H, m); $^{13}$C NMR ($CDCl_3$): δ 174.6, 166.3, 145.9, 137.0, 134.3, 131.6, 129.0, 128.4, 127.9, 127.7, 127.2, 126.5, 65.8, 64.8, 57.0, 45.4, 34.7, 30.4, 30.2, 19.0, 13.7, 13.6; MS: *m/z* 408 ($M^+$, 2), 334 (8), 307 (41), 205 (100), 191 (10), 129 (12), 91 (18), 57 (15); IR (NaCl, $cm^{-1}$): ν 2960 (s), 2874 (s), 1734 (s), 1625 (m), 1449 (m), 1200 (m), 1172 (m), 773 (m), 699 (m). Anal. Calcd for $C_{26}H_{32}O_4$: C, 76.44; H, 7.90. Found C, 76.65; H, 7.99.

*Butyl 2-p-tolylacrylate* (**2b**): colorless oil; $^1$H NMR ($CDCl_3$): δ 7.38 – 7.35 (2H, m), 7.21 – 7.19 (2H, m), 6.33 (1H, d, *J* = 1.3 Hz), 5.89 (1H, d, *J* = 1.3 Hz), 4.27 (2H, t, *J* = 6.7 Hz), 2.40 (3H, s), 1.76 – 1.69 (2H, m), 1.50 – 1.41 (2H, m), 0.92 (3H, t, *J* = 7.4 Hz); $^{13}$C NMR ($CDCl_3$): δ 166.8, 141.2, 137.7, 133.7, 128.5, 127.9, 125.4, 64.7, 30.4, 20.9, 19.0, 13.5; MS: *m/z* 218 ($M^+$,68), 162 (90), 146 (30), 117 (100), 91 (20), 65 (10), 41 (15); IR (NaCl, $cm^{-1}$): ν 2960 (s), 2932 (s), 2874 (m), 2362 (w), 1732 (s), 1685 (m), 1643 (m), 1513 (w), 1466 (w), 1251 (m), 1202 (w), 1174 (w), 1118 (w), 1060 (w), 1022 (w), 962 (w), 817 (w), 755 (w). Anal. Calcd for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31. Found C, 77.29; H, 8.34.

*Dibutyl 2-p-tolylmaleate* (**4b**): yellow oil; $^1$H NMR ($CDCl_3$): δ 7.41 – 7.38 (2H, m), 7.23 – 7.20 (2H, m), 6.30 (1H, s), 4.38 (2H, t, *J* = 6.7 Hz), 4.20 (2H, t, *J* = 6.7 Hz), 2.39 (3H, s), 1.78 – 1.64 (4H, m), 1.45 – 1.38 (4H, m), 0.95 (3H, t, *J* = 7.4 Hz), 0.94 (3H, t, *J* = 7.4 Hz); $^{13}$C NMR ($CDCl_3$): δ 168.0, 164.9, 148.5, 140.7, 130.3, 129.5, 126.4, 115.9, 65.5, 64.5, 30.4, 30.1, 21.1, 18.9, 18.8, 13.5, 13.4; MS: *m/z* 318 ($M^+$, 29), 244 (40), 189 (78), 162 (100), 145 (17), 115(45), 69 (25), 57 (20), 41 (38); IR (NaCl, $cm^{-1}$): ν 2958 (m), 2924 (s), 2853 (m), 1734 (m), 1700 (s), 1653 (m), 1636 (m), 1607 (m), 1516 (w), 1507 (w), 1458 (w), 1267 (m), 1181 (w), 953 (w), 815 (m). Anal. Calcd for $C_{19}H_{26}O_4$: C, 71.67; H, 8.23. Found C, 71.96; H, 8.15.

*Butyl 2-p-tolylpropanoate* (**6b**): colorless oil; $^1$H NMR ($CDCl_3$): δ 7.37 – 7.34 (2H, m), 7.24 – 7.20 (2H, m), 4.09 (2H, t, *J* = 6.7 Hz), 3.71 (1H, q, *J* = 7.2 Hz), 2.36 (3H, s), 1.62 – 1.55 (2H, m), 1.52 (3H, d, *J* = 7.2 Hz), 1.37 – 1.30 (2H, m), 0.92 (3H, t, *J* = 7.4 Hz); $^{13}$C NMR ($CDCl_3$): δ 174.6, 137.5, 136.4, 129.0, 127.1, 64.3, 45.0, 30.4, 20.9, 18.8, 18.3, 13.4; MS: *m/z* 220 ($M^+$, 20), 164 (6), 120 (17), 119 (100), 117 (8), 91 (12), 57 (6); IR (NaCl, $cm^{-1}$): ν 3058 (w), 2963 (m), 2933 (m), 1720 (s), 1615 (w), 1597 (w), 1451 (m), 1283 (w), 1192 (m), 1093 (w), 1072 (w), 1007 (w), 811 (w), 752 (w). Anal. Calcd for $C_{14}H_{20}O_2$: C, 76.33; H, 9.15. Found C, 76.71; H, 9.24.

*Butyl 2-(4-(pentyloxy) phenyl)acrylate* (**2c**): yellow oil; $^1$H NMR ($CDCl_3$): δ 7.39 – 7.36 (2H, m), 6.93 – 6.88 (2H, m), 6.26 (1H, bs), 5.84 (1H, bs), 4.25 (2H, t, *J* = 7.0 Hz), 3.99 (2H, t, *J* = 6.6 Hz), 1.83 – 1.65 (4H, m), 1.52 – 1.38 (6H, m), 0.97 (3H, t, *J* = 7.3 Hz), 0.95 (3H, t, *J* = 6.8 Hz); $^{13}$C NMR ($CDCl_3$): δ 167.0, 158.9, 140.8, 132.3, 129.2, 124.5, 114.0, 67.8, 64.7, 30.4, 28.7, 27.9, 22.2, 18.8, 13.8, 13.5; MS: *m/z* 290 ($M^+$, 97), 220 (71), 189 (18), 164 (100), 148 (71), 119 (98), 91 (30), 43 (27); IR (NaCl, $cm^{-1}$): ν 2958 (s), 2933 (s), 2873 (s), 1728 (bs), 1698 (w), 1609 (m), 1581 (w), 1573 (w), 1513 (s), 1468 (m), 1381 (w), 1302 (w), 1253 (m), 1175 (w), 1117 (w), 1022 (w), 833 (m). Anal. Calcd for $C_{18}H_{26}O_3$: C, 74.45; H, 9.02. Found C, 74.22; H, 8.94.

*Dibutyl 2-(4-(pentyloxy) phenyl)maleate* (**4c**): yellow oil; $^1$H NMR ($CDCl_3$): δ 7.45 – 7.43 (2H, m), 6.92 – 6.86 (2H, m), 6.24 (1H, s), 4.38 (2H, t, *J* = 6.7 Hz), 4.25 (2H, t, *J* = 6.7 Hz), 4.19 (2H, t, *J* = 6.7 Hz), 1.83 – 1.63 (6H, m), 1.52 – 1.35 (8H, m), 0.97 (3H, t, *J* = 7.4 Hz), 0.95 (3H, t, *J* = 6.9 Hz), 0.94 (3H, t, *J* = 6.9 Hz); $^{13}$C NMR ($CDCl_3$): δ 168.1, 165.1, 160.9, 148.3, 132.3, 128.1, 125.2, 114.6, 67.9, 65.4, 64.4, 30.4, 30.1, 28.7, 28.6, 22.2, 18.9, 18.8, 13.7, 13.5, 13.4; MS: *m/z* 390 ($M^+$, 100), 261 (28), 233 (26), 191 (32), 164 (80), 118 (38), 57 (20), 41 (35); IR (NaCl, $cm^{-1}$): ν 2958 (m), 2924 (s), 2853 (m), 1734 (m), 1718 (m), 1647 (bs), 1521 (w), 1465 (w), 1287 (w), 1251 (w), 1175 (w), 1022 (w), 817 (w); Anal. Calcd for $C_{23}H_{34}O_5$: C, 70.74; H, 8.78. Found C, 71.12; H, 8.73.

*Butyl 2-(4-tert-butylphenyl)acrylate* (**2d**): colorless oil; $^1$H NMR ($CDCl_3$): δ 7.42 – 7.29 (4H, m), 6.34 (1H, d, *J* = 1.2 Hz), 5.91 (1H, d, *J* = 1,2 Hz), 4.27 (2H, t, *J* = 6.7 Hz), 1.78 – 1.70 (2H, m), 1.51 – 1.42 (2H, m), 1.38 (9H, s), 0.98 (3H, t, *J* = 7.4 Hz); $^{13}$C NMR ($CDCl_3$): δ 166.8, 150.9, 141.1, 133.6, 127.7, 125.4, 124.8, 64.7, 34.3, 31.0, 30.5, 19.0, 13.5; MS: *m/z* 260 ($M^+$, 25), 245 (100), 189 (10), 159 (10), 143 (20), 129 (15), 41 (10); IR (NaCl, $cm^{-1}$): ν 3035 (w), 2963 (m), 2903 (w), 2869 (m), 1722 (s), 1616 (m), 1515 (w), 1464 (m), 1395 (w), 1364 (w), 1329 (w), 1312 (w), 1270 (w), 1204 (m), 1184 (m), 1115 (m), 1084 (m), 1018 (w), 945 (w), 840 (m), 812 (w), 755 (w), 738 (w). Anal. Calcd for $C_{17}H_{24}O_2$: C, 78.42; H, 9.29. Found C, 78.61; H, 9.20.

*Dibutyl 2-(4-tert-butylphenyl)maleate* (**4d**): yellow oil; $^1$H NMR ($CDCl_3$): δ 7.47 – 7.39 (4H, m), 6.30 (1H, s), 4.38 (2H, t, *J* = 6.8 Hz), 4.18 (2H, t, *J* = 6.7 Hz), 1.80 – 1.63 (4H, m), 1.47 – 1.40 (4H, m), 1.34 (9H, s), 0.97 (3H, t, *J* = 7.4 Hz), 0.96 (3H, t, *J* = 7.4 Hz); $^{13}$C NMR ($CDCl_3$): δ 167.9, 164.9, 153.8, 148.5, 130.3, 126.3, 125.7, 116.0, 65.5, 64.5, 34.6, 31.0, 30.9, 30.4, 30.2, 18.9, 18.8, 13.4; MS: *m/z* 360 ($M^+$, 18), 345 (100), 289 (16), 231 (10), 143 (12), 57 (16), 41 (14); IR (NaCl, $cm^{-1}$): ν 2961 (s), 2873 (w), 1737 (s), 1721 (s), 1625 (m), 1607 (w), 1516 (w), 1466 (w), 1392 (w), 1366 (w), 1344 (w), 1289 (w), 1269 (w), 1194 (m), 1171 (s), 1112 (s), 1062 (w), 1029 (w), 836 (w). Anal. Calcd for $C_{22}H_{32}O_4$: C, 73.30; H, 8.95. Found C, 73.45; H, 9.03.

*Butyl 2-(biphenyl-4-yl)acrylate* (**2e**): white solid; mp 58 – 59 °C. $^1$H NMR ($CDCl_3$): δ 7.66 – 7.61 (4H, m), 7.58 – 7.55 (2H, m), 7.49 – 7.46 (2H, m), 7.41 – 7.38 (1H, m), 6.41 (1H, d, *J* = 1.0 Hz), 5.99 (1H, d, *J* = 1.0 Hz), 4.29 (2H, t, *J* = 6.6 Hz), 1.79 – 1.66 (2H, m), 1.52 – 1.45 (2H, m), 0.95 (3H, t, *J* = 7.4 Hz); $^{13}$C NMR ($CDCl_3$): δ 166.7, 141.0, 140.8, 140.4, 135.5, 128.6, 128.5, 127.2, 126.9, 126.6, 126.1, 64.8, 30.5, 19.0, 13.5; MS: *m/z* 280 ($M^+$, 95), 224 (70), 208 (30), 179 (100), 152 (22), 89 (15), 41 (10); IR (KBr, $cm^{-1}$): ν 2957 (w), 2871 (w), 1704 (s), 1613 (w), 1486 (w), 1447 (w), 1399 (w), 1330 (m), 1307 (w), 1260 (w), 1200 (s), 1090 (s), 1072 (w), 1008 (w), 964 (m), 914 (w), 840 (m), 771 (m), 739 (m). Anal. Calcd for $C_{19}H_{20}O_2$: C, 81.40; H, 7.19. Found C, 81.62; H, 7.16.

*(E)-Butyl 3-(biphenyl-4-yl)acrylate* (**3e**): colorless oil; $^1$H NMR ($CDCl_3$): δ 7.74 (1H, d, *J* = 16.0 Hz), 7.65 – 7.50 (6H, m), 7.49 – 7.46 (2H, m), 7.42 – 7.38 (1H, m), 6.49 (1H, d, *J* = 16.0 Hz), 4.24 (2H, t, *J* = 6.7 Hz), 1.78 – 1.69 (2H, m), 1.59 – 1.44 (2H, m), 0.99 (3H, t, *J* = 7.4 Hz); $^{13}$C NMR ($CDCl_3$): δ 166.9, 143.8, 147.7, 140.0, 133.2, 128.7, 128.3, 127.6, 127.3, 126.8, 117.9, 64.2, 30.6, 19.0, 13.5; MS: *m/z* 280 ($M^+$, 70), 224 (100), 207 (55), 178 (68), 165 (25), 152 (25), 89 (10); IR (NaCl, $cm^{-1}$): ν 3060 (w), 3031 (w), 2960 (m), 2933 (m), 2872 (m), 1715 (s), 1636 (m), 1605 (w), 1558 (w), 1488 (w), 1449 (w), 1410 (w), 1383 (w), 1325 (m), 1310 (m), 1267 (m), 1172 (s), 1119 (w), 1026 (w), 1007 (w), 984 (m), 834 (m), 767 (m), 738 (m). Anal. Calcd for $C_{19}H_{20}O_2$: C, 81.40; H, 7.19. Found C, 81.08; H, 7.12.

*Dibutyl 2-(biphenyl-4-yl)maleate* (**4e**): yellow solid; mp 141 – 143 °C. $^1$H NMR ($CDCl_3$): δ 7.67 – 7.51 (4H, m), 7.48 – 7.39 (5H, m), 6.38 (1H, s), 4.40 (2H, t, *J* = 6.8 Hz), 4.21 (2H, t, *J* = 6.7 Hz), 1.82 – 1.65 (4H, m), 1.48 – 1.39 (4H, m), 0.98 (6H, t, *J* = 7.2 Hz); $^{13}$C NMR ($CDCl_3$): δ 167.8, 164.8, 145.6, 139.6, 135.6, 128.7, 128.6, 128.0, 127.4, 127.0, 126.9, 116.8, 65.6, 64.6, 30.4, 30.2, 18.9, 18.8, 13.6, 13.5; MS: *m/z* 380 ($M^+$, 95), 324 (15), 280 (10), 267 (10), 251 (40), 224 (80), 207 (12), 178 (100), 165 (10), 152 (18), 69 (27), 57 (23), 41 (45); IR (KBr, $cm^{-1}$): ν 2959 (m), 2929 (m), 2872 (w), 1731 (s), 1681 (s), 1626 (w), 1603 (w), 1483 (w), 1463 (w), 1404 (w), 1358 (w), 1285 (w), 1265 (w), 1172 (m), 1061 (w), 1021 (w), 1007

(w), 840 (m), 765 (m). Anal. Calcd for $C_{24}H_{28}O_4$: C, 75.76; H, 7.42. Found C, 76.07; H, 7.46.

*Dibutyl 2-(biphenyl-4-yl)succinate* (**7e**): yellow oil; $^1$H NMR ($CDCl_3$): δ 7.72 – 7.57 (4H, m), 7.49 – 7.38 (5H, m), 4.09 (4H, m), 4.23 (1H, m), 3.23 (1H, dd, *J* = 16.8, 9.9 Hz), 2.73 (1H, dd, *J* = 16.8, 5.6 Hz), 1.64 – 1.57 (4H, m), 1.37 – 1.27 (4H, m), 1.01 – 0.97 (6H, m); $^{13}$C NMR ($CDCl_3$): δ 169.4, 166.9, 141.0, 136.7, 128.7, 128.5, 127.4, 127.0, 126.8, 126.7, 65.6, 64.6, 46.8, 37.5, 30.4, 30.2, 18.9, 18.8, 13.5, 13.4; MS: *m/z* 382 ($M^+$, 5), 308 (45), 280 (45), 252 (30), 239 (10), 224 (100), 180 (50), 165 (15), 152 (8), 57 (23), 41 (30). Anal. Calcd for $C_{24}H_{30}O_4$: C, 75.36; H, 7.91. Found C, 75.18; H, 7.98.

*Butyl 2-(6-methoxynaphthalen-2-yl)acrylate* (**2f**): yellow oil; $^1$H NMR ($CDCl_3$): δ 7.77 – 7.69 (2H, m), 7.54 – 7.42 (1H, m), 7.28 – 7.14 (3H, m), 6.40 (1H, s), 6.00 (1H, s), 4.28 (2H, t, *J* = 6.6 Hz), 3.95 (3H, s), 1.77 – 1.69 (2H, m), 1.49 – 1.41 (2H, m), 0.97 (3H, t, *J* = 7.4 Hz); $^{13}$C NMR ($CDCl_3$): δ 166.9, 157.8, 141.4, 131.8, 129.6, 129.0, 128.3, 127.1, 126.4, 126.2, 126.0, 125.7, 118.8, 64.8, 55.0, 30.4, 19.0, 13.5; MS: *m/z* 284 ($M^+$, 100), 228 (35), 212 (10), 183 (65), 168 (20), 152 (12), 139 (30), 91 (5), 41 (8); IR (NaCl, $cm^{-1}$): ν 3060 (w), 2959 (s), 2935 (s), 2873 (m), 1724 (s), 1630 (s), 1606 (s), 1504 (m), 1484 (m), 1464 (m), 1414 (w), 1266 (w), 1219 (w), 1195 (w), 1123 (w), 1090 (w), 1033 (m), 931 (w), 893 (w), 853 (m), 810 (m), 761 (w), 737 (w). Anal. Calcd for $C_{18}H_{20}O_3$: C, 76.03; H, 7.09. Found C, 76.34; H, 7.02.

*(E)-butyl 3-(6-methoxynaphthalen-2-yl)acrylate* (**3f**): yellow oil; $^1$H NMR ($CDCl_3$): δ 7.88 – 7.86 (2H, m), 7.82 (1H, d, *J* = 16.0 Hz), 7.78 – 7.64 (4H, m), 6.51 (1H, d, *J* = 16.0 Hz), 4.24 (2H, t, *J* = 6.7 Hz), 3.95 (3H, s), 1.79 – 1.70 (2H, m), 1.49 – 1.42 (2H, m), 0.99 (3H, t, *J* = 7.4 Hz); $^{13}$C NMR ($CDCl_3$): δ 167.0, 158.6, 144.5, 135.4, 129.9, 129.6, 129.4, 128.4, 127.2, 124.0, 119.2, 117.1, 105.7, 64.1, 55.1, 30.6, 19.0, 13.5; MS: *m/z* 284 (M+, 100), 240 (10), 228 (90), 211 (75), 184 (55), 168 (35), 152 (30), 139 (85), 128 (15), 114 (15), 63 (10), 41 (25); IR (NaCl, $cm^{-1}$): ν 2959 (m), 2934 (m), 2873 (w), 1711 (s), 1625 (s), 1602 (m), 1483 (m), 1463 (w), 1416 (w), 1393 (m), 1345 (w), 1262 (s), 1168 (s), 1063 (w), 1031 (m), 982 (w), 851 (m), 807 (w). Anal. Calcd for $C_{18}H_{20}O_3$: C, 76.03; H, 7.09. Found C, 75.79; H, 7.01.

*Dibutyl 2-(6-methoxynaphthalen-2-yl)maleate* (**4f**): yellow oil; $^1$H NMR ($CDCl_3$): δ 7.87 – 7.86 (1H, m), 7.76 – 7.69 (2H, m), 7.60 – 7.58 (1H, m), 7.21 – 7.18 (1H, m), 7.15 – 7.13 (1H, m), 6.43 (1H, s), 4.43 (2H, t, *J* = 6.7 Hz), 4.21 (2H, t, *J* = 6.7 Hz), 3.95 (3H, s), 1.82 – 1.74 (2H, m), 1.72 – 1.67 (2H, m), 1.51 – 1.41 (4H, m), 0.99 (3H, t, *J* = 7.4), 0.98 (3H, t, *J* = 7.4); $^{13}$C NMR ($CDCl_3$): δ 168.1, 165.0, 158.8, 148.7, 135.4, 130.1, 128.2, 128.1, 127.4, 127.1, 123.4, 119.4, 116.0, 105.5, 65.5, 64.5, 55.1, 30.4, 30.2, 18.9, 18.8, 13.5, 13.4; MS: *m/z* 384 ($M^+$, 100), 328 (10), 284 (12), 255 (15), 228 (25), 182 (25), 139 (35), 41 (15); IR (NaCl, $cm^{-1}$): ν 2959 (m), 2934 (m), 2873 (w), 1331 (s), 1716 (s), 1615 (s), 1502 (w), 1484 (m), 1463 (m), 1417 (w), 1394 (m), 1352 (w), 1327 (w), 1261 (s), 1173 (s), 1061 (s), 1030 (m), 853 (m), 806 (w), 747 (w). Anal. Calcd for $C_{23}H_{28}O_5$: C, 71.85; H, 7.34. Found C, 72.06; H, 7.29.

*Butyl 2-(4-fluorophenyl)acrylate* (**2g**): pale yellow oil; $^1$H NMR ($CDCl_3$): δ 7.44 – 7.42 (2H, m), 7.07 – 7.01 (2H, m), 6.36 (1H, d, *J* = 1.1 Hz), 5.88 (1H, d, *J* = 1.1 Hz), 4.25 (2H, t, *J* = 6.7 Hz), 1.74 – 1.67 (2H, m), 1.48 – 1.39 (2H, m), 0.97 (3H, t, *J* = 7.4 Hz); $^{13}$C NMR ($CDCl_3$): δ 166.4, 161.5 (d, *J* = 245 Hz), 140.3, 132.6 (d, *J* = 3.4 Hz), 129.8 (2 C, d, *J* = 8.2 Hz), 126.3, 114.7 (2 C, d, *J* = 21.4 Hz), 64.8, 30.4, 19.0, 13.4; MS: *m/z* 222 (36), 166 (91), 121 (100), 101 (47); IR (film, $cm^{-1}$): ν 2975 (s), 2961 (s), 1735 (s), 1510 (s), 1465 (m), 1383 (m), 1118 (s) 840 (s). Anal. Calcd for $C_{13}H_{15}FO_2$: C, 70.25; H, 6.80. Found C, 70.56; H, 6.83.

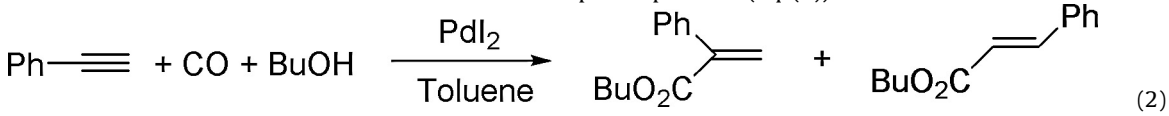
*Dibutyl 2-(4-fluorophenyl)maleate* (**4g**): pale yellow oil; $^1$H NMR ($CDCl_3$): δ 7.51 – 7.48 (2H, m), 7.13 – 7.06 (2H, m), 6.26 (1H, s), 4.37 (2H, t, *J* = 6.8 Hz), 4.20 (2H, t, *J* = 6.7 Hz), 1.78 – 1.57 (4H, m), 1.42 – 1.38 (4H, m), 0.96 (3H, t, *J* = 7.4 Hz), 0.95 (3H, t, *J* = 7.4 Hz); $^{13}$C NMR ($CDCl_3$): δ 167.6, 164.6, 163.5 (d, *J* = 250.0 Hz), 147.3, 129.2, 128.5 (2 C, d, *J* = 8.6 Hz), 117.1, 115.9 (2 C, d, *J* = 21.9 Hz), 65.6, 64.7, 30.4, 30.1, 19.0, 18.9, 13.45, 13.4; MS: *m/z* 322 (9), 248 (31), 193 (100), 166 (97), 120 (46), 57 (17); IR (film, $cm^{-1}$): ν 2977 (s), 2857 (s), 1738 (s), 1725 (s), 1629 (m), 1604 (m), 1383 (m), 1151 (s), 1119 (s). Anal. Calcd for $C_{18}H_{23}FO_4$: C, 67.06; H, 7.19. Found C, 67.24; H, 7.15.

*Butyl 2-(4-fluorophenyl)propionate* (**6g**): pale yellow oil; $^1$H NMR ($CDCl_3$): δ 7.52 – 7.49 (2H, m), 7.11 – 7.03 (2H, m), 4.09 (2H, t, *J* = 6.7 Hz), 3.72 (1H, q, *J* = 7.2 Hz), 1.70 – 1.62 (2H, m), 1.50 (3H, d, *J* = 7.2 Hz), 1.46 – 1.38 (2H, m), 0.95 (3H, t, *J* = 7.4 Hz); $^{13}$C NMR ($CDCl_3$): δ 174 2, 162.3 (d, *J* = 250.3 Hz), 132.6 (d, *J* = 3.4 Hz), 128.7 (2 C, d, *J* = 8.6 Hz), 115.1 (2 C, d, *J* = 21.8 Hz), 64.4, 44.6, 30.0, 18.6, 18.3, 18.2; MS: *m/z* 224 (12), 168 (13), 123 (100), 103 (25), 57 (12); IR (film, $cm^{-1}$): ν 2974 (s), 2868 (s), 1745 (s), 1604 (s), 1511 (s), 1382 (m), 1112 (s), 841 (s). Anal. Calcd for $C_{13}H_{17}FO_2$: C, 69.62; H, 7.64. Found C, 69.82; H, 7.60.

*Dibutyl 2-(4-fluorophenyl)succinate* (**7g**): pale yellow oil; $^1$H NMR ($CDCl_3$): δ 7.24 – 7.13 (2H, m), 7.06 – 7.00 (2H, m), 4.23 (2H, t, *J* = 6.8 Hz), 4.09 (1H, dd, *J* = 9.7, 5.8 Hz), 4.03 (2H, t, *J* = 6.8 Hz), 3.17 (1H, dd, *J* = 16.8, 9.7 Hz), 2.67 (1H, dd, *J* = 16.8, 5.8 Hz), 1.66 – 1.54 (4H, m), 1.38 – 1.26 (4H, m), 0.88 (3H, t, *J* = 7.4 Hz), 0.86 (3H, t, *J* = 7.4 Hz); $^{13}$C NMR ($CDCl_3$): δ 173.3, 171.1, 163.8 (d, *J* = 250.3 Hz), 130.1 (d, *J* = 8.2 Hz), 129.4 (d, *J* = 2.5 Hz), 129.1 (d, *J* = 8.0 Hz), 115.4 (d, *J* = 21.4 Hz), 114.5 (d, *J* = 21.6 Hz), 64.7, 64.4, 46.3, 30.3, 30.2, 30.1, 18.8, 18.7, 13.35, 13.3; MS: *m/z* 324 (2), 251 (14), 250 (39), 194 (100), 181 (18), 166 (91), 128 (33), 122 (58), 57 (52). IR (film, $cm^{-1}$): ν 2976 (s), 2870 (s), 1743 (s), 1741 (s), 1602 (s), 1380 (m), 1110 (s). Anal. Calcd for $C_{18}H_{25}FO_4$: C, 66.65; H, 7.77. Found C, 66.78; H, 7.81.

## 3. Results and discussion

We initially tested the activity of $PdI_2$ as catalytic precursor in the hydroalkoxycarbonylation of phenylacetylene **1a** with 1-butanol and CO in toluene, without any oxidant. The α-, β-unsaturated butyl esters of 2-phenylpropenoic acid **2a** (butyl atropate) and 3-phenylpropenoic acid **3a** (butyl cinnamate) were the expected products (Eq. (2)).

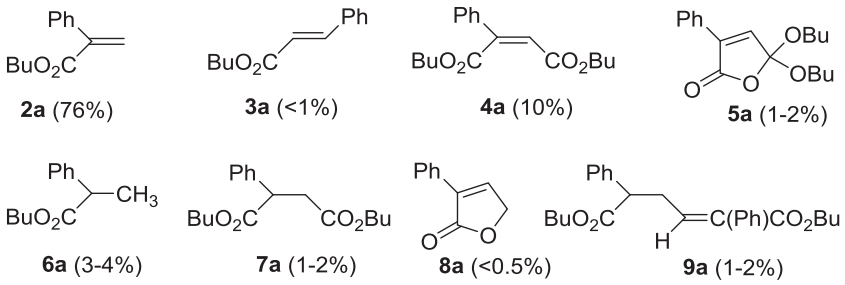



(2)

### 3.1. Reaction conditions

In a typical procedure, **1a** (2.7 mmol) was caused to react with CO (10 bar) and 1-butanol (27 mmol) in the presence of $PdI_2$ (0.027 mmol) in toluene (4 mL) under stirring at 100 °C for 8 h. Under these conditions 76% yield of butyl atropate **2a** was obtained with total conversion of **1a**. Beside compound **2a**, its regioisomer **3a** and other carbonylation products were also formed. Yields and identified product structures are shown in Scheme 2. While dibutyl phenylmaleate **4a** and its cyclic isomer **5a** derive from an oxidative dicarbonylation process, 3-phenylfuran-2(5*H*)-one **8a** is a reductive carbonylation product. Small amounts of carbonylation compounds **6a** and **7a** and two isomers of **9a**, formally resulting from two molecules of butyl atropate, were also detected in the reaction mixture.

The molar ratio of products **2a**:**3a** was 98–99:2–1, while the average selectivity to **2a** amounted at 78–80% under the reported conditions. The tenfold molar excess of 1-butanol with respect to phenylacetylene proved to be appropriate; in fact, using an excess




**Scheme 2.** Products obtained from the $PdI_2$-catalyzed hydrobutoxycarbonylation of **1a** in toluene.

of only four moles of alcohol in mixture with toluene, a drop of the yield of **2a** to 62% was observed. The use of methanol instead of 1-butanol in toluene depressed the atropate yield to 24%, while MeOH as the sole reaction solvent caused a rapid deactivation of the catalyst by palladium black precipitation. The best results were obtained carrying out the reaction at 80–100 °C. Higher temperature negatively affected the conversion of **1a** and the selectivity to **2a**, leading to a more rapid catalyst deactivation (Fig. S1, Supporting information section). The yield of **2a** was also influenced by the CO pressure, being the value of 10 bar the best one under these reaction conditions (Fig. S2, Supporting information section). We also found a clear dependence of the conversion of **1a** and the yield of **2a** on the $PdI_2$ concentration (Fig. S3, Supporting information section). Increasing the volume of toluene in the reaction mixture, keeping fixed amounts of reagents and molar ratios, yield of **2a** was reduced because of a lower conversion of phenylacetylene. Toluene added in 4 mL volume proved to be optimal under the previously determined reaction conditions. As a result, for most experiments, temperature, CO pressure and amount of toluene were maintained at 100 °C, 10 bar, and 4 mL, respectively. Finally, different molar ratios **1a**/$PdI_2$ have been tested (Table S1, Supporting information section). On the base of these results, 1% of $PdI_2$ was used in most of the reactions reported in the present study. Turnover numbers higher than 100 could be obtained by using lower catalyst loading, with a simultaneous decrement of the conversion.

### 3.2. Yield of *2a* vs reaction time

The progress of the yield of **2a** vs the reaction time under the previously determined reaction conditions is reported in Table 1 and Fig. 1. Yield of **2a** and TOF attain to considerable values after 15 min only. The high initial reaction rate allows the 92% of the total amount of **2a** to be formed. In the residual time the yield of **2a** increases more slowly achieving a plateau (75–76%). It was noticed that a similar trend was followed for the formation of double carbonylation products **4a** and **5a**, reaching high concentrations after just a few minutes. This observation supports the fact that products **4a** and **5a** are formed by independent processes and are not the result of consecutive reactions.

**Table 1**
Effect of reaction time on the yield of 2a.

| Time (h) | Yield (%) **2a** | TOF[a] |
|---|---|---|
| 0 | 0 | – |
| 0.25 | 63 | 252 |
| 0.5 | 67 | 134 |
| 1 | 70 | 70 |
| 2 | 73 | 36 |
| 4 | 75 | 19 |
| 8 | 76 | 10 |

Reaction conditions: **1a** (2.7 mmol), 1-butanol (2.5 mL, 27 mmol), CO (10 bar), $PdI_2$ (0.027 mmol), toluene (4 mL), 100 °C.
[a] TOF (turnover frequency) = mol product/molPd × h.

### 3.3. Effect of water addition

Reported experimental evidences [31–34] suggest that the catalytic cycle of hydroalkoxycarbonylation of alkyl- and arylacetylenes can start through the in situ formation of a palladium hydride species. Under our acid-free conditions, we verified that $PdI_2$ complexes did not oxidize *n*-butanol to butyraldehyde or its corresponding acetals, ruling out the possibility that a palladium hydride derivative is formed through this way. Therefore, water remains the most obvious reagent able to form a palladium hydride (I–Pd–H) complex under CO pressure [36–38,45,55–57]. Considering the amount of $PdI_2$ used (0.027 mmol), in principle, only 0.5 μL of water, probably the residual moisture of the solvents, would be enough for the hydride formation. An examination of the effect of the amount of water on the reaction course showed a reduction of the yield of **2a** (Fig. 2), mainly due to the partial conversion of **1a**. Moreover in the presence of an excess of water, a reduction of the selectivity of **2a** was observed, due to the concomitant increase of products **4a**, **5a** (up to 15% with 50 μL of $H_2O$) and the formation of not negligible amounts of furanone **8a** (5% with 50 μL of $H_2O$) which is supposed to be generated by the presence of a Pd–H species (see Section 3.7).

The presence of a Pd–H species under water gas shift (WGS) reaction conditions was previously reported by us [58]. $^1$H NMR analysis in dioxane $d_8$ showed the presence of a broad signal at −4.3 ppm attributable to Pd–H species. Hydride-forming palladium catalysts have been reported to give formic acid or its derivatives in the presence of $CO_2$, generated by decarboxylation of a $PdCO_2H$ complex as shown in Scheme 3. The formation of formic acid was experimentally verified under our reaction conditions by transformation in its benzyl ester [51].

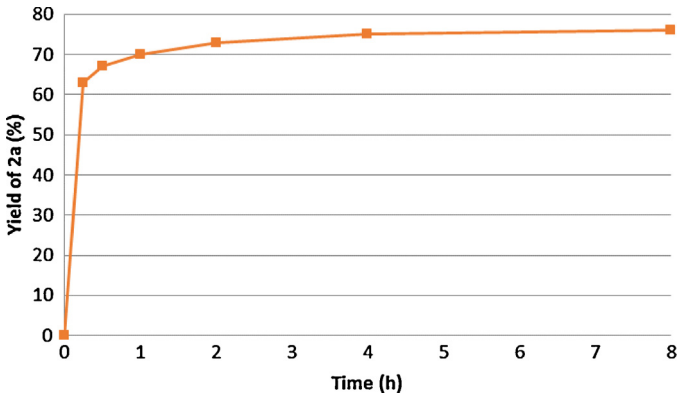



**Fig. 1.** Yeilds of **2a** vs reaction time.

**Table 2**
Activities of various palladium catalysts in the hydrobutoxycarbonylation of **1a** in toluene.

| Run | Catalyst precursor | Time | Conv. (%) | Product yields (%) | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | (h) | **1a** | **2a** | **3a** | **4a** | **5a** | **6a** | **7a** | **8a** |
| 1 | $PdI_2$ | 8 | 99 | 76 | <1 | 10 | 2 | 4 | 1 | – |
| 2 | $K_2PdI_4$ | 8 | 92 | 72 | <1 | 10 | 1 | 5 | 1 | 1 |
| 3 | $PdI_2$ + 10KI | 8 | 90 | 72 | <1 | 9 | 1 | 5 | 1 | – |
| 4 | Pd(10%)/C + $I_2$ | 8 | 76 | 51 | – | 11 | 2 | 5 | 2 | – |
| 5 | Recycling from 4 | 8 | – | – | – | – | – | – | – | – |
| 6 | Recycling from 4 + $I_2$ | 8 | 58 | 32 | 2 | 11 | 2 | 5 | 2 | 1 |
| 7[a] | Pd(10%)/C + $I_2$ | 8 | 77 | 57 | – | 9 | 1 | 5 | 1 | – |
| 8[b] | Pd(10%)/C + $I_2$ | 8 | 77 | 65 | – | 4 | 1 | 3 | 1 | – |
| 9 | $PdI_2$ + 5$Bu_4NI$ | 24 | 75 | – | – | 25 | 9 | – | 5 | 33 |
| 10[a] | $PdI_2$ + 5$Bu_4NI$ | 24 | 77 | – | – | 25 | 7 | – | 2 | 31 |
| 11 | $PdI_2$ + 3.5tu | 24 | 15 | 7 | – | 5 | – | – | – | 2 |
| 12 | $Pd(OAc)_2$ | 24 | 3 | 1 | – | – | – | – | – | – |
| 13 | $PdCl_2$ | 24 | 5 | 2 | <1 | 1 | – | – | – | – |
| 14 | $Pd(PPh_3)_2Cl_2$ | 24 | 79 | 34 | 30 | 8 | 2 | 3 | – | – |
| 15[c] | $PdI_2$ + 2$PPh_3$ | 24 | 63 | 10 | 37 | 6 | 1 | – | 1 | 4 |

Reaction conditions: **1a** (2.7 mmol), 1-butanol (2.5 mL, 27 mmol), CO (10 bar), Pd–cat (0.027 mmol), toluene (4 mL), 100 °C.
[a] Cyclohexane (4.0 mL) was used as cosolvent in place of toluene.
[b] 3 bar of $H_2$ were added.
[c] 5% of **9a** was also formed.

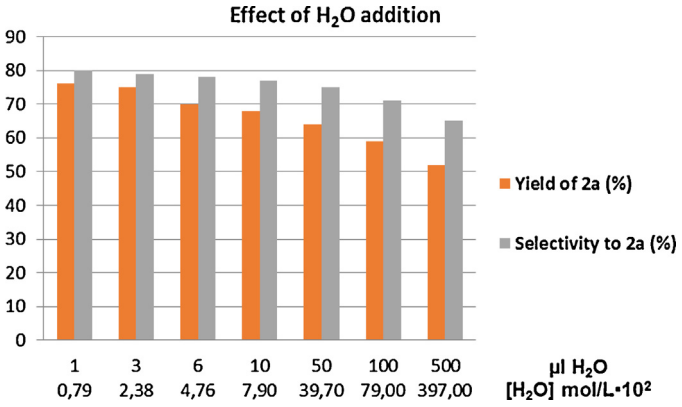
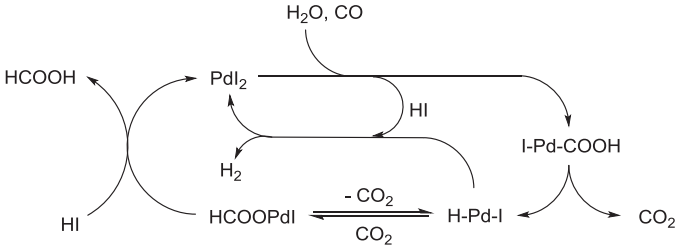



**Fig. 2.** Effect of $H_2O$ addition.




**Scheme 3.** Possible pathways in the presence of $PdI_2$, CO, and $H_2O$.

### 3.4. Activities of various palladium catalysts

Various palladium precursors were tested in the hydrobutoxycarbonylation of phenylacetylene and the results are shown in Table 2. All the carbonylation reactions were carried out according to the usual procedure.

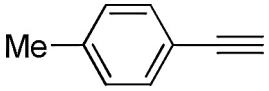
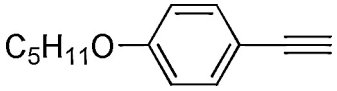
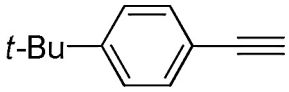
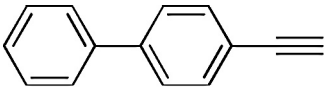
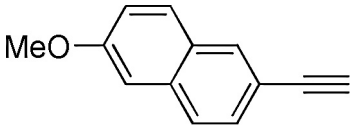
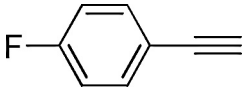
Comparable catalytic activities were obtained using $PdI_2$, $K_2PdI_4$, and $PdI_2$ + 10KI in toluene (runs 1–3, Table 2). Runs 4–8 were carried out in the presence of a catalyst precursor obtained by mixing iodine with 10% Pd/C (see Section 2 for details). After ascertaining the ineffectiveness of 10% Pd/C even with addition of an excess of KI, the reaction carried out in the presence of Pd/C + $I_2$ catalytic system gave a good yield in **2a** (run 4, Table 2). Recovering Pd/C by filtration and recycling it for another reaction under the same conditions, no conversion of **1a** was observed (run 5, Table 2). If the residual solid was subjected to further iodine treatment and caused to react again, the expected products were formed in lower yield (run 6, Table 2). Again the recovered catalyst was inactive for carbonylation. These experiments indicate that the carbonylation can apparently occur in homogeneous phase (Fig. S4, Supporting information section), iodine being able to partially transfer palladium into the solution, allowing, under CO atmosphere, the formation of a $PdI_2$–carbonyl complex. It is noteworthy that the carbonylation of phenylacetylene catalyzed by the Pd/C + $I_2$ system, is positively affected by the presence of molecular hydrogen (run 8, Table 2). A similar hydrogen effect has been previously found with a phosphine-free $PdCl_2$-based catalyst in the hydrocarboalkoxylation of olefins [59] and in the Pd(II)-dppb catalyzed hydroesterification of terminal alkynes with syngas [60]. The beneficial effect of hydrogen can probably be attributed to the possibility to stabilize a I–Pd–H intermediate. The use of $PdI_2$ + 5$Bu_4NI$ as catalyst precursor led to a complete suppression of butyl atropate and cinnamate either in toluene or in cyclohexane giving oxidative dicarbalkoxylation derivatives **4a** and **5a** and hydrogenated/reductive carbonylation products **6a**–**8a** in almost equimolecular amount (runs 9 and 10, Table 2). It is likely that tetrabutylammonium iodide provided for transferring $PdI_2$ in toluene or cyclohexane mixture as a $PdI_4^{2-}$ anion. A palladium anionic species would be then responsible for this dramatic shift of selectivity. We have reported that reactions, in which oxidative carbonylation is combined with a reduction process, took place in methanol using $PdI_2$ and tiourea as ligand [47,48]. The same catalytic system was not effective in less polar media (run 11, Table 2). $Pd(OAc)_2$ and $PdCl_2$ were practically inactive for this reaction (runs 12 and 13, Table 2) endorsing the usefulness of iodide anion as ligand. The addition of phosphine ligands to $PdI_2$ or $PdCl_2$ affected the regioselectivity of the reaction leading to a remarkable increase in the yield of butyl cinnamate **3a** (runs 14 and 15, Table 2).

### 3.5. Hydrobutoxycarbonylation of various terminal acetylenes

The reactivity of substituted phenylacetylene derivatives was then verified under optimized reaction conditions. The results are reported in Table 3.

The results show that the reactions work quite nicely. In some cases it is noticed a loss of regioselectivity (runs 2, 4, and 5, Table 3), whereas substrates containing methyl, *t*-butyl, or fluoro groups

**Table 3**
$PdI_2$-catalyzed butoxycarbonylation of arylacetylenes in toluene.

| Run | Starting reagent **1** | | Conv. (%) | Product yields (%) | | | |
|---|---|---|---|---|---|---|---|
| | | | **1** | **2** | **3** | **4** | **6**+**7**[a] |
| 1 |  | 1b | 80 | 60 | – | 7 | 6 |
| 2 |  | 1c | 99 | 71 | 14 | 2 | 2 |
| 3 |  | 1d | 83 | 63 | - | 9 | 6 |
| 4 |  | 1e | 81 | 33 | 25 | 9 | 8 |
| 5 |  | 1f | 78 | 43 | 7 | 12 | 8 |
| 6 |  | 1g | 72 | 48 | – | 10 | 10 |

Reaction conditions: **1** (2.7 mmol), 1-butanol (2.5 mL, 27 mmol), CO (10 bar), $PdI_2$ (0.027 mmol), toluene (4 mL), 100 °C, 24 h.
[a] **6**:**7** molar ratio is about 4:1.

maintain high regioselectivity towards the branched esters (runs 1, 3, and 6, Table 3).

### 3.6. Influence of the reaction media

Having defined the suitable reaction conditions and studied the influence of different parameters and additives on the hydrobutoxycarbonylation of phenylacetylene in toluene/*n*-butanol mixture, we then investigated the influence of various reaction media consisting of mixtures of *n*-butanol and a cosolvent in the presence of $PdI_2$ = A, or $PdI_2$ + 10KI = B as catalyst precursors (Table 4). The conversion of phenyacetylene after 8 h of reaction in media containing high polarity cosolvents such as DMA and DMF, was quite limited in comparison with mixtures containing apolar or low polarity cosolvents where high conversions were attained in the first hours of reaction. Thus an extension of the reaction time to 24 h became necessary to reach comparable conversions under usual reaction conditions. In Table 4 solvent permittivity ($\epsilon$) is also reported and runs are arranged in order of decreasing yield of **2a** with $PdI_2$-catalyst(A).

Data in Table 4 emphasize that catalyst precursors A and B promote the formation of **2a** as the main product in reaction media for which the polarity of butanol is reduced by the addition of an apolar aprotic solvent. Indeed, it may be noticed that the yield of **2a** achieves the highest value in cyclohexane, toluene or anisole as cosolvents (runs 1–3, Table 4). On the other hand the addition of a polar aprotic solvent to *n*-butanol led to a significant reduction of the yield of **2a** together with a considerable slowing down of the reaction rate (runs 4, 5, and 7–11, Table 4) [61]. More important, a different distribution of products was observed changing from apolar to polar cosolvents. In apolar or in low polarity media, products of oxidative dicarbonylation **4a** and **5a** were always present achieving the highest yield in anisole mixture (18%) along with 5–7% of hydrogenated products **6a** and **7a** (runs 1–3, Table 4). Moreover the formation of furanone **8a** was completely suppressed with both the catalytic systems employed (runs 1–3, Table 4). In mixtures containing the most polar solvents, along with remarkable amounts of **4a** and **5a**, the reductive carbonylation product **8a** was also present, which, in conjunction with hydrogenated products **6a** and **7a**, almost quantitatively balanced the formation of the oxidative dicarbonylation products **4a** and **5a** (runs 4, 5, and 7–11, Table 4). Solvents such as MeCN and PhCN gave the highest yields of oxidative and reductive carbonylation compounds (runs 9, 10, and 12, Table 4), likely due to their highest solvation power towards palladium ionic species that probably are at work under these conditions. This change in the chemoselectivity of the process resulted more marked with an excess of iodide anions (catalyst B = $PdI_2$ + 10KI). The carbonylation product **9a**, mainly formed in mixtures containing amide solvents such as DMA, NMP, and DMF (runs 7, 8, and 11 Table 4), is present as a mixture of E/Z isomers (molar ratio ranges from 1:2 to 3:1), and could come formally from a palladium-mediated dimerization of **2a** (Scheme 4). Longer alcohols, such as hexanol, led to comparable results when MeCN was used as cosolvent (run 12, Table 4) [62]. Small amounts of butyl formate were found in the reactions carried out in the presence of $PdI_2$ or $PdI_2$ + 10KI with most solvent employed.

### 3.7. Proposed reaction pathways

Mainly two factors play a fundamental role in this carbonylation process: the nature of the palladium catalyst precursor containing iodide anions and the reaction media. Both of these have a noticeable effect on the chemoselectivity as well as on the rate of the reaction.

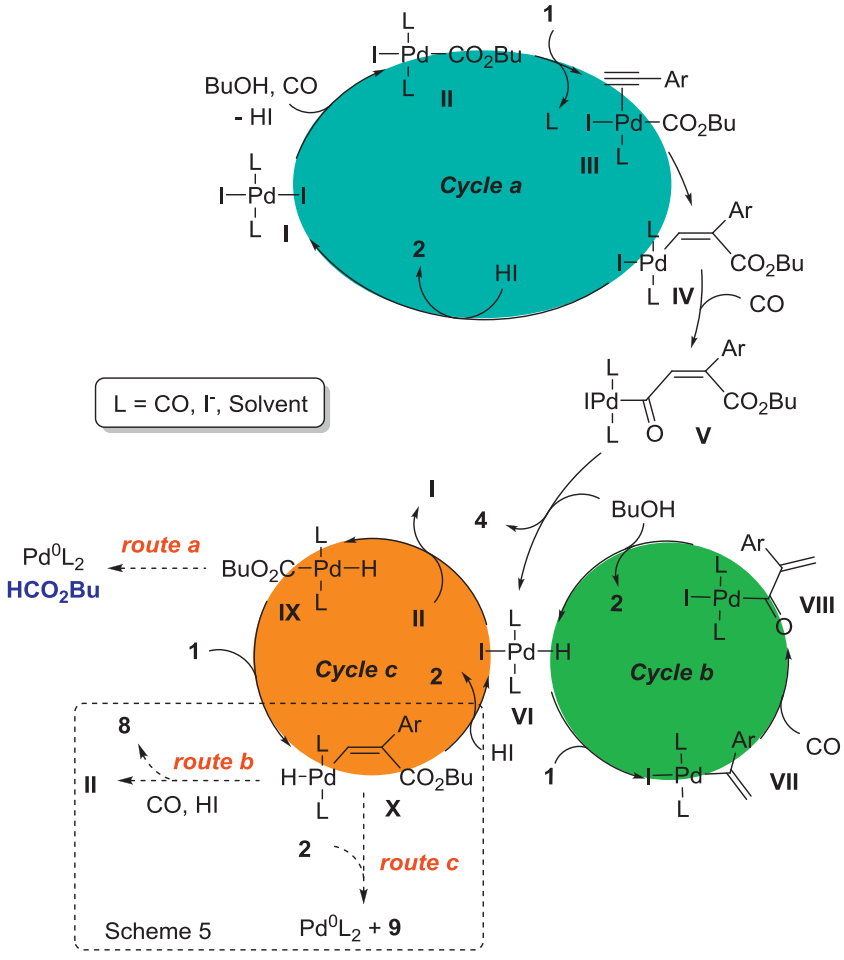
To understand the course of this carbonylation reaction, the following points should taken into account.

1) Remarkable changes in chemoselectivity on going from aprotic apolar to polar reaction media were observed.
2) A reduction of the selectivity to **2a**, and the concomitant formation of **4a**, **5a**, and **8a** were observed when an excess of water was used.

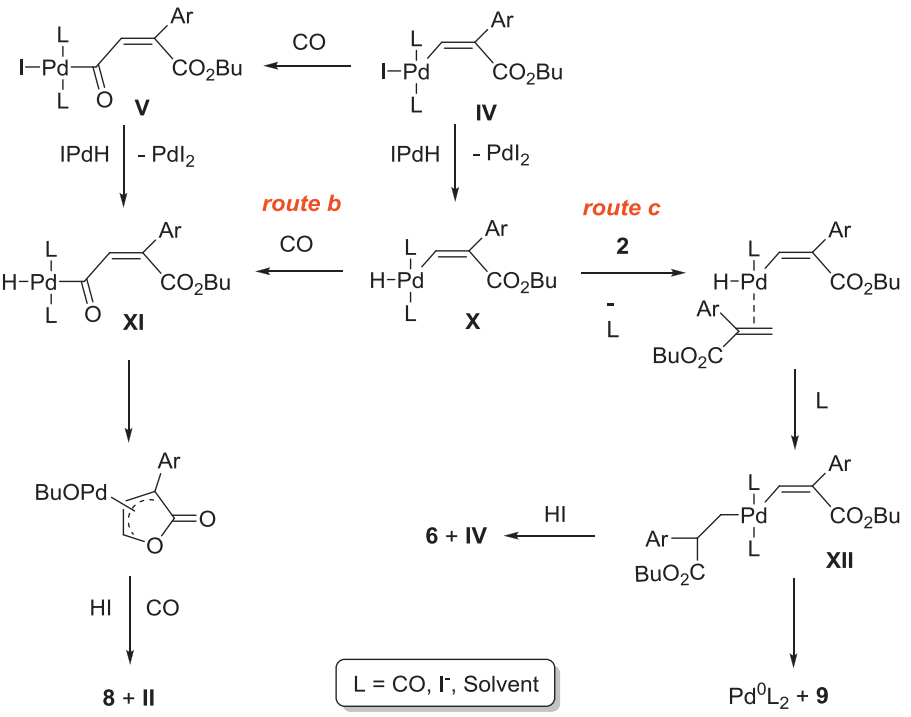
3) The formation of double carbonylation products **4** and **5** points out that the hydrobutoxycarbonylation process can start via Pd–COOBu.
4) The addition of $Bu_4NI$ to the reaction mixture (toluene/butanol) led to the exclusive formation of oxidative dicarbalkoxylation derivatives **4a** and **5a** and hydrogenated/reductive carbonylation products **6a**–**8a** in almost equimolecular amount.
5) Butyl formate and formic acid were detected in the reaction mixture.
6) Addition of hydrogen gas had a beneficial effect on the reaction carried out in butanol–toluene medium (run 8, Table 3), supporting the occurrence of the hydride mechanism.

Because of a considerable difference in the solvation power of the reaction media and a marked coordination strength of the iodide ligand, palladium intermediates likely undergo modifications inducing dramatic changes in the chemoselectivity of the reaction. Although a clear correlation between solvent permittivity ($\epsilon$) and the behavior of the catalytic systems does not exist, we suggest, according to the above considerations, an explanation of the reaction course leading to regioisomer **2** and the other isolated products (Schemes 4 and 5).

Since we start from a palladium(II) precursor, complex **I**, according to a well-established mechanism [39–44,47,48], adds BuOH and CO in sequence leading to IPd–$CO_2$Bu(**II**) (cycle a, Scheme 4). The intermediate **II** inserts **1** generating **IV**, which, upon protonolysis by HI, leads to product **2** with regeneration of $L_2PdI_2$ **I**. The I–Pd–vinyl complex **IV** can also insert another molecule of CO with formation of **V**, which can undergo butanolysis providing **4** and the I–Pd–H species **VI**. The latter can independently produce **2** following the well-known palladium-hydride pathway (cycle b, Scheme 4) [31–34]. Thus, simultaneous reaction routes to product **2** seem possible, the relative importance of these two ways being probably influenced by the amount of $H_2O$ in the reaction mixture (Scheme 3). I–Pd–H species **VI** through a hydride-exchange [31,63,64] with IPd–$CO_2$Bu(**II**) could form the H–Pd–$CO_2$Bu intermediate **IX**, responsible for the butylformate detection. Insertion of a molecule of **1** on **IX** leads to intermediate **X** (cycle c, Scheme 4), which in its turn can follow several pathways: (1) reaction with HI producing **2** and H–Pd–I; (2) coordination and insertion of another molecule of CO leading to **XI**, which, after rearrangement and protonolysis by HI, provides **8** and **II** (route b, Scheme 5); and (3) insertion of a molecule of **2** forming **XII** (route c, Scheme 5), which, after HI addition, releases product **6** and intermediate **IV**, or, alternatively, delivers compound **9** and Pd(0) by a reduction elimination step. In this last case we cannot exclude a palladium-mediated umpolung coupling [65]. Palladium hydrides as reducing species are reported in the literature [31]. Their intermediacy in reductive carbonylation of benzyl alcohols was proposed by Cavinato and Toniolo [66] and their reactions with allyl ether or ester were described [67]. It would appear that Pd–H species, that could justify the formation of compounds **6**, **8** [58], and **9**, are involved in these carbonylation processes as shown in Schemes 4 and 5. Intermediates **X** and **XI** could be generated through a metathetical exchange from the corresponding **IV** and **V** complexes and the H–Pd–I species **VI** (Scheme 5) [31,63,64]. For the formation of




**Scheme 4.** Proposed reaction pathways for the $PdI_2$-catalyzed hydrobutoxycarbonylation of arylacetilenes.




**Scheme 5.** Possible formation pathways for product 6, 8, and 9.

derivatives **4** and **8**, we can postulate an alternative mechanism which involves a hydride transfer between two acyl chains within the same complex likely formed by disproportionation [48]. This reaction, also named "symmetrization", readily occurs in many cases as reported in the literature [68,69]. Palladium (0) species can be reconverted to HPdI by the intermediacy of HI and butanol [70].

In low polarity media, dissociation and stabilization of ionic complexes are reduced, so that neutral intermediates would appear to be involved. Compound **2**, which is the main product under these conditions, can be mostly formed through $PdCO_2R$ intermediate according to the pathways mentioned in the introduction (Scheme 1, cycle a). The formation of the double carbonylation product **4**, gives rise, in the absence of corresponding reductive carbonylation product **8**, to a Pd–H species (Scheme 4) and it needs its reconversion to $PdI_2$ under our non-oxidative conditions, likely through the intervention of $CO_2$ on Pd(hydride) intermediate (Scheme 3). In fact, the interaction of I–Pd–H with $CO_2$ leads to the formation of a palladium-formate intermediate through

**Table 4**
Hydrobutoxycarbonylation of phenylacetylene in different solvent/*n*-butanol mixture.

| Run | Solvent | Catalyst | Time | Conv. (%) | Product yields (%) | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | ($\epsilon$) | | (h) | **1a** | **2a** | **4a**+**5a**[a] | **6a**+**7a**[b] | **8** | **9** |
| 1 | Cyclohexane | A | 8 | 98 | 76 | 10 | 6 | – | 2 |
| | (2.0) | B | 8 | 92 | 73 | 10 | 6 | – | – |
| 2 | Toluene | A | 8 | 99 | 76 | 12 | 7 | – | 1 |
| | (2.38) | B | 8 | 91 | 72 | 10 | 6 | – | – |
| 3 | Anisole | A | 8 | 95 | 69 | 18 | 7 | – | 1 |
| | (4.4) | B | 8 | 87 | 60 | 18 | 5 | – | – |
| 4 | AcOEt | A | 8 | 91 | 66 | 13 | 6 | 3 | 1 |
| | (6.02) | B | 8 | 82 | 46 | 17 | 6 | 9 | 1 |
| 5 | DME | A | 8 | 79 | 59 | 12 | 4 | 3 | – |
| | (7.23) | B | 8 | 67 | 22 | 22 | 3 | 17 | – |
| 6 | 1-Butanol | A | 8 | 76 | 57 | 9 | 4 | 1 | 2 |
| | (17.51) | B | 8 | 66 | 53 | 5 | 3 | 2 | – |
| 7 | DMA | A | 24 | 76 | 57 | 5 | 2 | 1 | 9 |
| | (37.78) | B | 24 | 72 | 48 | 10 | 2 | 9 | 2 |
| 8 | NMP | A | 24 | 88 | 52 | 2 | – | – | 25 |
| | (32.2) | B | 24 | 71 | 36 | 8 | 2 | 7 | 12 |
| 9 | MeCN | A | 24 | 50 | 33 | 9 | 2 | 5 | – |
| | (37.5) | B | 24 | 56 | – | 26 | 1 | 27 | – |
| 10 | PhCN | A | 24 | 33 | 19 | 7 | 2 | 3 | – |
| | (26) | B | 24 | 61 | – | 30 | 2 | 27 | – |
| 11 | DMF | A | 24 | 17 | 9 | 6 | – | – | – |
| | (38.71) | B | 24 | 33 | 16 | 5 | – | 4 | 6 |
| 12 | MeCN/1-Hexanol | B | 24 | 62 | 3 | 28 | – | 29 | – |

Reaction conditions: **1a** (2.7 mmol), alcohol (27 mmol), CO (10 bar), Pd–cat (0.027 mmol), solvent (4 mL), 100 °C. In all experiments yields of **3a** range from 0 to 1.0%.
[a] 4a:5a molar ratio is about 5:1.
[b] 6a:7a molar ratio is about 4:1.

**Table 5**
Hydrobutoxycarbonylation of 1a with a palladium (0) species.

| Run | **1a**/KI | Solvent | **1a**/$Pd_2(dba)_3$ | Time (h) | Conv. (%) | Product yields (%) | | |
|---|---|---|---|---|---|---|---|---|
| | | | | | | **2a** | **4a** + **5a** | **8a** |
| 1 | 10 | MeCN | 1.5 | 6 | 24 | – | Trace | 19 |
| 2 | 10 | MeCN | 100 | 16 | 50 | 8 | 18 | 18 |
| 3 | – | Toluene | 100 | 24 | 54 | 45 | 4 | Trace |

Reaction condition: **1a** (2.7 mmol), *n*-butanol (27 mmol), BuI (5.4 mmol), CO (10 bar), $Pd_2(dba)_3$ solvent (4 mL), 100 °C.

insertion into the Pd—H bond [71–73]. As shown in Scheme 3 the I–Pd–$O_2$CH species can be an intermediate able to regenerate $PdI_2$ with elimination of $HCO_2H$. Then the $CO_2$ could reduce the Pd–H concentration restoring $PdI_2$, which is responsible for the $IPdCO_2Me$ formation.

Moving from an apolar to a polar solvent, the palladium hydride reactivity may be altered, and the previously suggested interaction between palladium hydride and arylacetylene becames less effective. This may be due to the saturation of coordination sites in Pd(II) intermediates in the presence of highly polar solvents and iodide anions. The intermediate palladium complexes shift towards ionic species which induce different reaction pathways, leading to, oxidative, additive and reductive dicarbonylation products (**4–8**). In particular, in polar media the oxidative carbonylation products (**4**, **5**) are always balanced by those of reduction (**6**–**8**) even at low conversion values, and this can be explained with the combination of cycles a and c (route b, Scheme 4), that involve intermediates **II–VI**, **IX**, **X**. Moreover carbonylation of phenylacetylene carried out in toluene– or cyclohexane–butanol mixture in the presence of $PdI_2$ and 5 equiv of $Bu_4NI$ yielded exclusively oxidative **4** and **5** and reductive carbonylation products, **6**–**8** (runs 4 and 5, Table 2). In this case, even in apolar media the catalyst system is likely formed by $PdI_4^{2-}$ and $NBu_4^+$ bulky ions.

In order to gain further insight into the role played by Pd–H species in this reaction, an alternative approach was considered: the hydrobutoxycarbonylation of **1a** was carried out in MeCN, using $Pd_2(dba)_3$ as catalytic precursor in molar ratio with **1a** close to a stoichiometric value (**1a**/$Pd_2(dba)_3$ = 1.5), in presence of BuI (2 equiv), giving selectively furanone **8a** (run 1, Table 5). In this case it is supposed that the oxidative addition of BuI to Pd(0) and a subsequent β-hydride elimination step, provide a Pd–H species which is responsible for the furanone formation. Performing the reaction catalytically, (**1a**/$Pd_2(dba)_3$ = 100), products **8a** and **4a** + **5a** were obtained in the same molar amounts, along with **2a** (run 2, Table 5), according to the previously reported results (run 9, Table 4). The same reaction in toluene with a catalytic amount of $Pd_2(dba)_3$ (1 mol%) led to phenyl atropate **2a** exclusively (45% after 24 h, run 3, Table 5), confirming that, on the basis of the previous considerations, Pd–H species can be an active catalyst in the hydrobutoxycarbonylation of arylacetylenes.

In general, palladium catalyzed hydroesterification of arylacetylenes apparently may proceed through either Pd–$CO_2R$ (Scheme 1, cycle a) or Pd–H (Scheme 1, cycle b) species. Depending on the reaction conditions (KI excess, $Bu_4NI$, solvent), the coordinated ligands can significantly change the properties of the complexes involved, going from neutral to anionic species, and thus directing the overall process towards different pathways. Pathways depicted in Schemes 3–5 appear to be consistent with the experimental results. However, further work is needed to identify unequivocally the palladium intermediate complexes involved.

In conclusion, we have shown that a very simple catalytic system, consisting of pure $PdI_2$ or in conjunction with an excess of KI, is able to catalyze the hydrobutoxycarbonylation of arylacetylenes to branched esters with good catalytic efficiency. The best results in terms of α-, β-unsaturated esters were obtained carrying out the reaction in non-polar solvents such as cyclohexane or toluene. Addition of aprotic polar solvents such as MeCN or PhCN to butanol suppresses the atropate formation leading to a mixture of oxidative and reductive carbonylation products in comparable amount. The same result can be obtained by the addition of $NBu_4I$ to the reaction when a non-polar solvent is employed. Experimental evidences support the proposed reaction pathways.

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## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.molcata.2014.11.028.

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