



Research paper

New insights into the alkoxy-carbonylation of propargyl alcohol

A. Scrivanti*, V. Beghetto, M. Bertoldini

Dipartimento di Scienze Molecolari e Nanosistemi, Università Ca' Foscari Venezia, Via Torino 155, I-30172 Mestre, Italy

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ABSTRACT

The challenging carbonylation of propargyl alcohol is effectively catalyzed by Pd(OAc)₂ in combination with diphenyl-(6-methyl-pyridin-2-yl)phosphine and methanesulfonic acid. In dichloroethane at 20–50 °C, the reaction affords with almost complete regioselectivity alkyl 2-(hydroxymethyl)acrylates. Turnover frequency numbers (TOF) of up to 450 h⁻¹ can be achieved working at 50 °C, while a maximum turnover number (TON) of about 730 is obtained at 30 °C. The catalyst longevity is limited because the carbonylation product reacts with the phosphorus atom of the ligand to give a quaternary phosphonium salt. This reaction leads to deactivation of the catalyst and eventually to palladium black formation.

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1. Introduction

The transition-metal catalyzed hydroxy- or alkoxy-carbonylation of alkynes continues to attract considerable attention from academia and industry as confirmed by the numerous reviews available on the subject [1–6].

In particular, earlier studies on the transition-metal catalyzed alkoxy-carbonylation of propargyl alcohol (see Scheme 1) and its derivatives can be traced back to 1950s [7–9], when pioneering experiments were carried out employing Ni(CO)₄ either in stoichiometric or in catalytic fashion [10–15].

The reaction revealed to be very challenging requiring harsh conditions and generally affording complex mixtures from which pure products can be separated only with considerable difficulty.

At the end of the 1960s, Tsuji first employed palladium species, namely PdCl₂ and Pd/C, promoted by hydrochloric acid as the catalysts [16,17]. Under quite severe conditions (T = 100 °C, P(CO) = 100 atm), methoxycarbonylation of propargyl alcohol was found to afford mixtures of 2-methoxymethylacrylate (**Ia**), dimethylitaconate (**II**), and trimethylitaconate (**III**) (Scheme 2).

In terms of control of the chemo- and regioselectivity the best results were obtained by Watanabe and co-workers employing [PtH(SnCl₃)(PPh₃)₂] [18]. In ethanol under quite harsh conditions these authors obtained with almost complete selectivity ethyl 2-(hydroxymethyl)acrylate, albeit with a turnover number of 68.

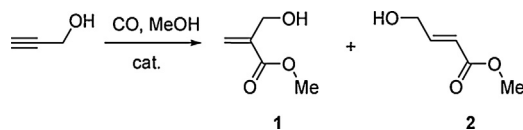
More recently Williams reinvestigated the reaction [19] and suggested that the low reactivity and selectivity obtained are likely due to chelation of the triple bond and the oxygen atom of the propargyl alcohol to the catalyst metal centre.

Summing up it appears that about seventy years after the first attempts, the alkoxy-carbonylation of propargyl alcohol is still an unsolved problem, even if the reaction represents an appealing, atom economical entry to 2-(hydroxymethyl)acrylates (**1** in Scheme 1) which are useful building blocks for the synthesis of natural products [20,21], biologically active compounds [22,23]; and polymers [24–27].

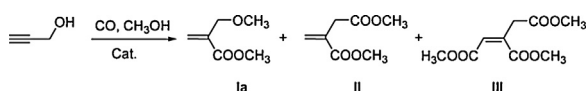
At the beginning of the 1990s E. Drent and co-workers at Shell [28–30] disclosed an alkyne carbonylation catalytic system composed by Pd(OAc)₂, a chelating P-N ligand containing a pyridylphosphine moiety and a strong, non-coordinating acid such as CH₃SO₃H. This catalyst displays outstanding activities being able to furnish TOF as high as 40000 h⁻¹ in methoxycarbonylation of propyne. Even more remarkable are the chemoselectivity and the regioselectivity of this system. As a matter of fact, double carbonylation is never observed and regioselectivity towards methyl methacrylate of up to 99.95% were obtained by Drent and co-workers. These, so far unsurpassed performances, are attributable to the unusual catalytic mechanism which according to experimental [31] and theoretical studies [32,33] entails as the key step the transfer of a proton from the pyridyl nitrogen of phosphine ligand to the terminal carbon atom of the substrate to give a σ-vinyl intermediate. According to these considerations, in particular spurred by the fact that double carbonylation is never observed, we deemed it interesting to investigate the alkoxy-carbonylation of propargyl

* Corresponding author.

E-mail address: scrivant@unive.it (A. Scrivanti).



Scheme 1. Products expected in propargyl alcohol alkoxy carbonylation.



Scheme 2. Esters obtained in propargyl alcohol carbonylation by Tsuji.

alcohol in the presence of Drent's catalyst. In fact, to the best of our knowledge, Drent's catalyst has never been applied to the synthesis of 2-hydroxymethylacrylates, while there are only two papers [28,34], one of which by Drent himself, dealing with its application in intramolecular cyclocarbonylation of alkynols.

2. Experimental

2.1. Materials

All the operations were carried out under argon in Schlenk-type glassware. Propargyl alcohol (Sigma-Aldrich) was distilled before use. Methanol (Sigma-Aldrich) was distilled from magnesium. Amylene stabilized dichloromethane (Sigma-Aldrich) was distilled from CaH_2 , while 1,2-dichloroethane (Sigma-Aldrich) and methanesulfonic acid (Sigma-Aldrich) were used as received. $\text{Pd}(\text{OAc})_2$ was purchased from Engelhard Industries. High purity CO was obtained by SIAD. Diphenyl-(pyrid-2-yl)phosphine and diphenyl-(6-methyl-pyrid-2-yl)phosphine were synthesized according to a literature method [35].

Methyl 2-(hydroxymethyl)acrylate (**1**) [36], methyl 2-(methoxymethyl)acrylate (**1a**) [37], and methyl (E)-4-hydroxybut-2-enoate (**2**) [38] were characterized by recording their GC-MS and NMR spectra which were found in agreement with the literature data.

2.2. Instrumentation

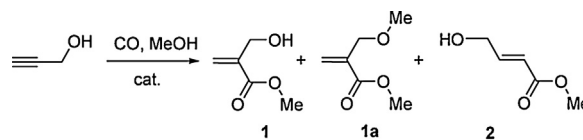
^1H , ^{31}P and ^{13}C NMR spectra were registered in CDCl_3 solutions on a Bruker AVANCE 300 spectrometer operating at 300.11, 121.43 and 75.44 MHz, respectively. GLC analyses were performed on an Agilent 6850 gas chromatograph; GC-MS analyses were performed on a HP 5890 series II gas chromatograph interfaced to a HP 5971 quadrupole mass-detector. ESI-MS analyses were performed using a Finnigan LCQ-Duo ion-trap instrument, operating in positive ion mode (sheath gas N_2 , source voltage 4.0 kV, capillary voltage 21 V, capillary temperature 200 °C).

2.3. Carbonylation experiments

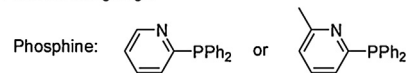
The carbonylation experiments were carried out in a magnetically stirred stainless steel autoclave (total volume about 150 mL) connected to a thermostatic bath (Haake) in order to maintain the reaction temperature constant within ± 1 °C.

As an example, the experimental details for entry 4 of Table 3 are reported: under inert atmosphere, a Schlenk flask containing a small stirring bar was charged with 4.0 mL of 1,2-dichloroethane, 1.0 mL of methanol, 84.0 mg (0.30 mmol) of diphenyl-(6-methyl-pyrid-2-yl)phosphine, 2.2 mg (0.01 mmol) of $\text{Pd}(\text{OAc})_2$, 580 μL (560 mg, 10.0 mmol) of propargyl alcohol, and finally 19 μL (28 mg, 0.30 mmol) of methanesulfonic acid.

The resulting yellow-orange solution was transferred *via canula* into the autoclave. Then the reactor was pressurized with



Cat.: $\text{Pd}(\text{OAc})_2$ / Phosphine/ $\text{CH}_3\text{SO}_3\text{H}$



Scheme 3. General scheme for the methoxycarbonylation of propargyl alcohol.

30 atm of CO and heated at 30 °C. After 2 h the autoclave was cooled at r.t., the residual gas carefully vented off, and the reaction mixture analyzed by GLC.

2.4. Phosponium salts isolation

At the end of a carbonylation experiment, the reaction crude was paper filtered to remove palladium black and then the filtrate was taken to dryness under high vacuum to give a brown oily residue. To this latter 5 mL of diethyl ether were added and the resulting two immiscible phases stirred with a small magnetic bar. After a few minutes, the oily residue tends to become a solid. The supernatant ether phase is carefully decanted and replaced with a fresh aliquot of diethylether. The whole procedure is repeated a few times until a yellow solid is obtained in about 55–65% yield.

(2-(methyl carboxylate)-allyl)(pyridyl-2)-diphenylphosphonium methanesulfonate (**3a**).

^1H NMR (298 K, CDCl_3) δ : 8.84 (d, 1H, $J = 4.0$ Hz, Py), 8.1–7.94 (m, 2H, Py) 7.8–7.4 (overlapping m, 11H, Py and Ph), 6.37 (d, 1H, $J_{\text{H-P}} = 5.0$ Hz, =CHH), 6.16 (d, 1H, $J_{\text{H-P}} = 5.0$ Hz, =CHH), 4.72 (d, 1H, $J_{\text{H-P}} = 15.5$ Hz, P- CH_2), 3.29 (s, 3H, OCH_3), 2.61 (s, 3H, CH_3SO_3).

^{31}P NMR (298 K, CDCl_3) δ : 17.6 (s).

^{13}C NMR (298 K, CDCl_3) δ : 165.5 (d, 1C, $J_{\text{C-P}} = 2.2$ Hz, C=O), 151.7 (d, 1C, $J_{\text{C-P}} = 19.4$ Hz, Py-C2), 144.2 (d, 1C, $J_{\text{C-P}} = 115.9$ Hz, Py-C6), 138.6 (d, 1C, $J_{\text{C-P}} = 10.2$ Hz, Py-C4), 135.2 (d, 1C, $J_{\text{C-P}} = 2.9$ Hz, Ph-*p*), 134.3 (d, 2C, $J_{\text{C-P}} = 9.6$ Hz, Ph-*m*), 133.7 (d, 1C, $J_{\text{C-P}} = 9.7$ Hz, allyl- CH_2), 131.9 (d, 1C, $J_{\text{C-P}} = 24.1$ Hz, Py-C5), 130.2 (d, 2C, $J_{\text{C-P}} = 12.6$ Hz, Ph-*o*), 128.3 ($J_{\text{C-P}} = 3.4$ Hz, Py-C3), 127.8 (d, 1C, $J_{\text{C-P}} = 9.6$ Hz, quaternary allyl-C), 116.9 (d, 1C, $J_{\text{C-P}} = 84.9$ Hz, Ph-*ipso*), 52.3 (s, 1C, OCH_3), 39.4 (s, 1C, CH_3SO_3), 24.9 (d, 1C, $J_{\text{C-P}} = 50.3$ Hz, P- CH_2).

ESI-MS (m/z): 362.11 (100%), calcd. for $\text{C}_{22}\text{H}_{21}\text{NO}_2\text{P}^+$: 362.13.

(2-(methyl carboxylate)-allyl)(6-methyl-pyrid-2-yl)diphenylphosphonium methanesulfonate (**3b**).

^1H NMR (298 K, CDCl_3) δ : 8.1–7.4 (overlapping m, 13H, arom.), 6.47 (d, 1H, $J_{\text{H-P}} = 5.1$ Hz, =CHH), 6.34 (d, 1H, $J_{\text{H-P}} = 5.4$ Hz, =CHH), 4.87 (d, 2H, $J_{\text{H-P}} = 15.6$ Hz, P- CH_2), 3.36 (s, 3H, OCH_3), 2.74 (s, 3H, Py- CH_3), 2.63 (s, 3H, CH_3SO_3).

^{31}P NMR (298 K, CDCl_3) δ : 17.1 (s).

^{13}C NMR (298 K, CDCl_3) δ : 165.3 (d, 1C, $J_{\text{C-P}} = 2.3$ Hz, C=O), 161.5 (d, 1C, $J_{\text{C-P}} = 21.4$ Hz, Py-C2), 142.7 (d, 1C, $J_{\text{C-P}} = 113.7$ Hz, Py-C6), 138.3 (d, 1C, $J_{\text{C-P}} = 10.7$ Hz, Py-C3), 135.1 (d, 1C, $J_{\text{C-P}} = 3.0$ Hz, Ph-*p*) 134.1 (d, 1C, $J_{\text{C-P}} = 9.5$ Hz, allyl- CH_2), 134.0 (d, 2C, $J_{\text{C-P}} = 9.5$ Hz, Ph-*m*), 130.1 (d, 1C, $J_{\text{C-P}} = 12.6$ Hz, Ph-*o*) 128.7 (d, 1C, $J_{\text{C-P}} = 24.0$ Hz), 128.2 (d, 1C, $J_{\text{C-P}} = 3.5$ Hz, Py-C4), 127.9 (d, 1C, $J_{\text{C-P}} = 9.5$ Hz, quaternary allyl-C), 116.6 (d, 1C, $J_{\text{C-P}} = 84.4$ Hz, Ph-*ipso*), 52.2 (s, 1C, OCH_3), 39.2 (s, 1C, CH_3SO_3), 24.3 (s, 1C, Py- CH_3), 24.9 (d, 1C, $J_{\text{C-P}} = 51.7$ Hz, P- CH_2).

ESI-MS (m/z): 376.12 (100%), calcd. for $\text{C}_{23}\text{H}_{23}\text{NO}_2\text{P}^+$: 376.15.

3. Results and discussion

Preliminary carbonylation experiments (see Scheme 3 and Table 1) were carried out under the conditions most usually adopted when using Drent's catalytic system [28–30].

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