



Synthetic Communications An International Journal for Rapid Communication of Synthetic Organic Chemistry

ISSN: 0039-7911 (Print) 1532-2432 (Online) Journal homepage: http://www.tandfonline.com/loi/lsyc20

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To cite this article: I. Chiarotto & I. Carelli (2002) PALLADIUM-CATALYZED ELECTROCHEMICAL CARBONYLATION OF ALKYNES UNDER VERY MILD CONDITIONS, Synthetic Communications, 32:6, 881-886, DOI: 10.1081/SCC-120002698

To link to this article: http://dx.doi.org/10.1081/SCC-120002698



Published online: 16 Aug 2006.



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PALLADIUM-CATALYZED ELECTROCHEMICAL CARBONYLATION OF ALKYNES UNDER VERY MILD CONDITIONS

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ABSTRACT

Terminal alkynes were carbonylated under very mild conditions to yield acetylenecarboxylates under atmospheric pressure of carbon monoxide at room temperature using palladium(II) catalyst in combination with its anodic recycling at a graphite electrodes.

Palladium(II)-catalyzed carbonylation of terminal alkynes in methanol gives methyl acetylenecarboxylates. These reactions are carried out using $PdCl_2$ as catalyst and stoichiometric amounts of $CuCl_2$ as reoxidant.¹ However, from a synthetic and environmental point of view, it is important to develop a halogen-free and copper-free reoxidant system. Recently, Sakurai et al. reported a new oxidation system,

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Pd(OAc)₂ /chlorohydroquinone/ molybdovanadophosphate (NPMoV), to render the reaction catalytic in palladium(II).² However, a high pressure of carbon monoxide and dioxygen are still required. The electrochemical reoxidation of Pd(0) in the carbonylation of acetylenic compounds has also been reported, but none of these methods occur without reducing the triple bonds and acetylenecarboxylates are not produces.^{3,4}

In this study, we wish to report a new procedure for the electrochemical synthesis of methyl acetylenecarboxylates from alkynes, under mild conditions, using a palladium complex as catalyst, carbon monoxide (p CO=1 atm) and methanol at room temperature. The process is outlined in the following reaction (Equation 1).

$$R \xrightarrow{Pd cat} R \xrightarrow{Pd cat} CO_2CH_3 + 2H^+ + 2e^-$$
(1)
(1) (1) (2) (2)

The reaction proceeds under atmospheric pressure of carbon monoxide at 25°C in a CH₃CN/CH₃OH solvent in the presence of bases (NaOAc or NEt₃) using a catalytic amount of a palladium(II) complex regenerated by oxidation of an intermediate Pd(0) complex at the anode. The results for the electrolyses using various palladium complexes are summarized in Table 1. Accordingly, phenylacetylene **1a** was recovered in 90% yield when it was reacted in CH₃CN/CH₃OH (7:3) solution containing *n*-Bu₄NBF₄ (0.2 mol dm⁻³) in the presence of 10 mol% of Pd(OAc)₂(PPh₃)₂, and two equivalents of base, under one atmosphere of carbon monoxide, without

Table 1. Carbonylation of Phenylacetylene (1a) to Methyl Acetylenecarboxylate (2a) in the Presence of Palladium(II) Complexes

Catalyst	Recovered 1a (%)	Yield $2a$ $(\%)^a$	Current Efficiency (%) ^b	
$Pd(PPh_3)_2(OAc)_2$	23	56 (73)	93	
Pd(PPh ₃) ₂ Cl ₂	20	57 (71)	95	
PdCl ₂	48	22 (42)	85	
$Pd(PPh_3)_4$	22	45 (58)	77	

^aYields are relative to the initial **1a** and determinated by GC analyses. Yields in parentheses are relative to the disappearance of **1a**. ^bCurrent efficiency was calculated in comparison with theoretic coulomb (2F/mol).

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any electrochemical oxidation; methyl phenylacetylenecarboxylate **2a** was obtained in only 8% yield.

The Pd(OAc)₂(PPh₃)₂/electrode system is an efficient catalyst, as good as the PdCl₂(PPh₃)₂/electrode system. It is of interest that PdCl₂(PPh₃)₂ and Pd(OAc)₂(PPh₃)₂ gave higher yields of methyl phenylacetylenecarboxylates than PdCl₂ (Table 1). The PPh₃ ligand stabilizes the intermediate Pd(0) complex. Pd(OAc)₂(PPh₃)₂ may generate a Pd(0) complex in a slow reaction;⁵ however, this latter will be oxidized at the anode back to Pd(OAc)₂(PPh₃)₂. The electrochemical reoxidation of Pd(0) under atmospheric pressure of CO appears to be an interesting alternative to the PdCl₂/CuCl₂ or Pd(II)/HQ-Cl/NPMoV procedures working under high pressure of carbon monoxide and dioxygen.

As proposed by Heck, for the carbonylation of olefins and acetylenes, the electrocarbonylation of terminal alkynes is considered to proceed via a similar mechanism (Scheme 1).⁶



Because of the *syn* addition of $L_2(OAc)PdCOOR'$ on the alkyne, the formation of HPd(OAc)(PPh₃)₂ by a β -hydride *syn* elimination is impossible. The presence of the base is essential as a proton trapper by elimination of the H⁺ from the β position.⁷

Table 2 shows the results for the carbonylation of various terminal alkynes by using $Pd(OAc)_2(PPh_3)_2$ as catalyst and NaOAc or NEt₃ as

Table 2. Carbonylation of Various Terminal Alkynes 1 to Methyl Acetylenecarboxylate 2^{a}

No	Alkyne 1	Product 2	Alkyne 1(%) ^b	Yield 2(%) ^{b, c}
1	Ph 1a	Ph-=COOCH ₃ 2a	23	56
2	()	Соосн ₃ 2b	20	56
3		OH $2c$ $COOCH_3$	35	53
4	1d	2d COOCH ₃	18	56
5 ^d 6 ^d	1a 1b	2a 2b	10 5	70 87

^a The electrolyses of phenylacetylene (1a), 1-ethynylcyclohexene (1b), 1-ethynyl-1cyclohexanol (1c), 1-hexyne (1d), (1 mmol), were carried out in 0.03 dm⁻³ of CH₃CN/CH₃OH (7:3) solvent, containing *n*-Bu₄NBF₄ 0.2 mol dm⁻³, Pd(OAc)₂(PPh₃)₂ (0.1 mmol) and NaOAc (2 mmol) under CO (1 atm) at +0.4 V vs SCE at 25°C. Each reaction was stopped after 8-10 hours.^b Yields of 1a-d and 2a-d were determined by GC analysis. ^c Yields relative to the initial 1a-d.^d Triethylamine (2 mmol) was used instead of NaOAc.

bases. It seems that the use of NEt_3 as a base is in favour of a more efficient catalytic cycle (compare Entries 1–5 and 2–6, Table 2).⁵ When NEt_3 was used as base, the reaction occurs in shorter times suggesting that the Pd(II) catalyst is more efficiently recycled in the presence of NEt_3 than with NaOAc.

The reaction is considered to proceed by the elimination of H^+ in the β position in complex [A], induced by the base (Scheme 1).⁷ NEt₃ is probably more efficient than AcO⁻ in this reaction. The Pd(0) is then generated in

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higher concentrations from complex [A] in the presence of NEt₃ and can be reoxidized to Pd(II) at the anode. Moreover, when acetate was used as base, acetic acid is formed from complex [A] concomitantly with the Pd(0) complex. We have reported that Pd(0) undergoes oxidative addition with acetic acid to form a cationic palladium(II) hydride (Equation 2).⁸

$$Pd(PPh_3)_2 + Ac OH \implies HPd^+(PPh_3)_2 + Ac O^{-1}$$
(2)

Under such conditions the Pd(0) complex generated from [A] (Scheme 1) would be partially stored under the form of HPd(II) L_2^+ , a reaction which is in competition with its reoxidation at the anode.

We are presently using the electrochemical oxidation of Pd(0) complexes at the anode in other catalytic carbonylation reactions. This method is promising as an efficient and mild system to reoxidize Pd(0) to Pd(II) in reactions catalyzed by palladium. We will report those results shortly.

EXPERIMENTAL

General

A potentiostat AMEL model 552 equipped with an integrator was used in controlled potential electrolysis. GC measurements were carried out on a Supelco SPB-5 $30 \text{ m} \times 0.25 \text{ mm}$ capillary column using a Hewlett Packard 5890 gaschromatography instrument.

Alkynes **1a-d**, palladium complexes and all other reagents are commercially available and were used as received.

Electrolysis of alkynes with palladium complexes. General procedure. The electrolysis was carried out on solution of alkyne (1 mmol) in 0.03 dm^{-3} of CH₃CN/CH₃OH (7:3) containing *n*-Bu₄NBF₄ (0.2 mol dm⁻³) as supporting electrolyte, in the presence of palladium catalyst, (0.1 mmol) and NaOAc or NEt₃ (2 mmol) under one atmosphere of CO at + 0.4 V vs SCE at 25°C. A graphite electrode, of apparent area 3 cm², was used as the working electrode. The counter-electrode was a Pt wire and the reference was a saturated calomel electrode (SCE). At the end of the electrolyses, yields were calculated by GC analysis of crude reaction mixtures by comparison with authentic samples of standards.

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ACKNOWLEDGMENTS

This work has been supported by the Consiglio Nazionale Delle Ricerche (CNR, Italy), the Ministero dell'Università e della Ricerca Scientifica e Technologica (MURST, Italy). We want to thank Dr. Anny Jutand for helpful discussions and Mr. Marco Di Pilato for his technical contribution.

REFERENCES

- 1. Tsuji, J.; Takahashi, M.; Takahashi, T. Tetrahedron Lett. 1980, 21, 849-850.
- 2. Sakurai, Y.; Sakaguchi, S.; Ishii, Y. Tetrahedron Lett. **1999**, 40, 1701–1704.
- 3. Alper, H.; Despeyroux, B.; Woell, J.B. Tetrahedron Lett. **1983**, *24*, 5691–5694.
- Hartstok, F.W.; McMahon, L.B.; Tell, I.P. Tetrahedron Lett. 1993, 34, 8067–8070; Hartstok, F.W.; Wayner, D.D.M. Tetrahedron Lett. 1994, 35, 8137–8140.
- 5. Amatore, C.; Jutand, A.; M'Barki, M.A. Organometallics **1992**, *11*, 3009–3013.
- 6. Heck, R.F. J. Am. Chem. Soc. 1972, 94, 2712–2719.
- 7. Negishi, E. Acc. Chem. Res. 1982, 15, 340-348.
- Amatore, C.; Jutand, A.; Meyer, G.; Carelli, I.; Chiarotto, I. Eur. J. Inorg. Chem. 2000, 8, 1855–1859.

Received in the Netherlands March 23, 2001