Journal of Organometallic Chemistry, 364 (1989) C33–C36
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands
JOM 9808PC

Preliminary communication

Nickel-catalyzed reductive electrocarboxylation of disubstituted alkynes

Elisabet Duñach, Sylvie Dérien and Jacques Périchon

Laboratoire d'Electrochimie, Catalyse et Synthèse Organique (L.E.C.S.O.) C.N.R.S., U.M. 28, 2, rue Henri-Dunant 94320, Thiais (France)

(Received January 4th, 1989)

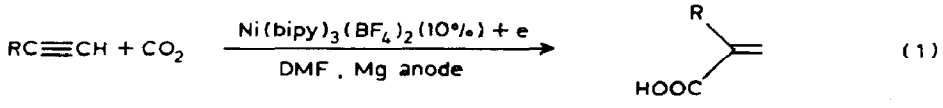
Abstract

Electrochemically reduced $Ni(bipy)_3(BF_4)_2$ catalyzes the reaction of carbon dioxide with disubstituted alkynes to yield mono- and di-carboxylated derivatives. The reaction is performed under mild conditions in an undivided cell fitted with a sacrificial magnesium anode.

The direct conversion of carbon dioxide into carbon containing chemicals is a particularly important process [1]. Activation of CO_2 by transition metal complexes is a very active research field, and despite the interest in the development of CO_2 chemistry, there are only a few homogeneous and catalytical reactions which lead to the incorporation of carbon dioxide into an organic product [2].

In the case of alkyne substrates, Ni^0 complexes have shown to be active catalysts for carbon dioxide fixation and a variety of reaction products (carboxylic acids, pyrones, alkyne oligomers, etc.) can be obtained, depending on the reaction conditions and the nature of the ancillary ligands [2,3]. Thus, α-pyrones are isolated from alkynes [4] (or diynes [5]) under high CO_2 pressure with $Ni(COD)_2/PR_3$ as the catalytic system, but α,β-unsaturated acids are formed stoichiometrically with $Ni(COD)_2$/TMEDA (or other ligands) [6].

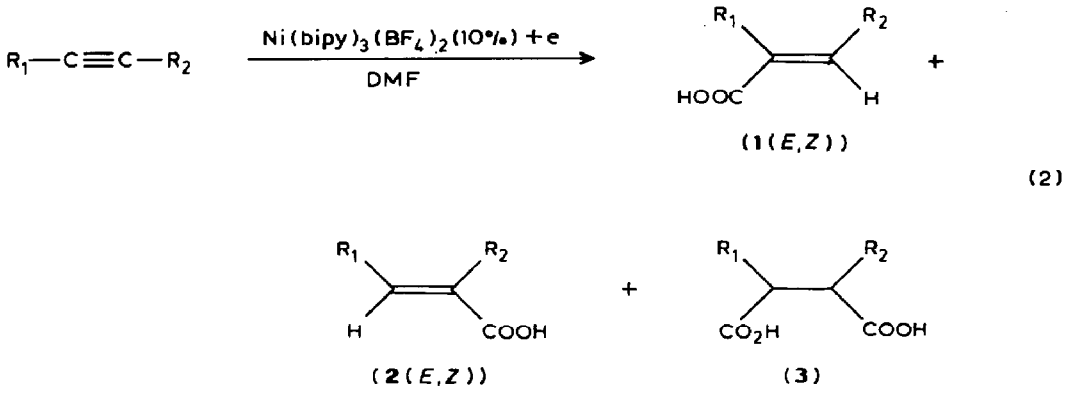
We recently described the carboxylation of terminal alkynes catalyzed by electrogenerated Ni^0 complexes [7] to yield selectively α-substituted acrylic acids (eq. 1).



(1)

We present here our results of a study of the electrocarboxylation of disubstituted alkynes (eq. 2). The reaction is catalyzed by a low valent nickel complex generated in situ by electrochemical reduction of a stable Ni^{II} catalyst precursor,

0022-328X/89/$03.50



$Ni(bipy)_3(BF_4)_2$(bipy = 2,2′-bipyridine). The carboxylation is carried out in DMF at constant current density in an undivided electrolytic cell: the anode is a sacrificial rod of magnesium surrounded by a cathode of carbon fiber.

The reactions at the electrodes can be represented as follows:

Anode: $Mg \rightarrow Mg^{2+} + 2e$

Cathode: $Ni(bipy)_3(BF_4)_2 + 2e \rightarrow Ni^0 bipy_2 + bipy + 2BF_4^-$

As shown by cyclic voltammetry studies [8], the Ni^{II} complex is reduced in a two electron single wave (−1.1 V SCE), and the electrogenerated $Ni^0 bipy_2$ complex in DMF coordinates the alkyne as well as CO_2. After carbon–carbon bond formation, magnesium carboxylates are formed, the nickel species being recycled [7]. The presence of the catalyst allows more selective nickel-mediated carboxylation than the direct electrochemical (non-catalyzed) carboxylation of activated acetylenes [9].

The results of the electrocarboxylation of several alkynes are summarized in Table 1.

Selective monocarboxylation of 4-octyne (entry 1) afforded the corresponding α,β-unsaturated acid **1** ($R^1 = R^2 = n\text{-}C_3H_7$) in 85% yield as a 88/12 mixture of *cis*/*trans* isomers. No CO_2 incorporation took place in the absence of the catalyst.

Diphenylacetylene (entry 2) was carboxylated at 80 °C to give a 1/2 mixture of unsaturated and saturated monocarboxylic acids. Less than 5% of carboxylation occurred at room temperature, and at a higher CO_2 pressure ($P(CO_2)$ 5 atm, T 20 °C) a 7/3 mixture of **1** and **3** was formed. *cis*- and *trans*-stilbene were obtained as a by-products in all cases. The bulky bis(trimethylsilyl)acetylene (entry 3) reacted slowly with CO_2 to yield a 8/2 mixture of mono- and di-carboxylated compounds. Again, an increase in the CO_2 pressure to 5 atm did not significantly enhance the selectivity or the reaction rate.

To our knowledge, no example of a reaction of CO_2 with unsymmetrically disubstituted alkynes has been reported, and little is known about the factors controlling orientation in carboxylation reactions with such substrates. Under the electrochemical conditions phenylpropyne (entry 4) reacted selectively with one molar equivalent of CO_2. A **1/2** regioselectivity of 62/38 was found, with α-methylcinnamic acid as the major isomer. The direction of CO_2 fixation into phenylpropyne contrasts with that in the carboxylation of phenylacetylene, in which atropic

Table 1

Nickel-catalyzed electrochemical carboxylation of disubstituted alkynes.

$$R^1C{\equiv}CR^2 + CO_2 \xrightarrow[DMF]{e,\ catalyst\ (10\%)} \mathbf{1} + \mathbf{2} + \mathbf{3}$$

Entry	R^1	R^2	T(°C)	Converted alkyne	Reaction products [a] (%)	
					Monocarboxylic acids (**1,2**)	Dicarboxylic acids (**3**)
1	n-C_3H_7	n-C_3H_7	20	78%	85	8
2	Ph	Ph	80	85%	64 [b]	6
3	$(CH_3)_3Si$	$(CH_3)_3Si$	80	40%	30 [c]	8
4	CH_3	Ph	20	85%	65 [d]	7
5	Ph	CO_2Et	5	70%	20	55
6	CH_3	CO_2Et	5	90%	20	30
7	CH_3	$(CH_2)_2OCOCH_3$	50	30%	45 [d]	–

[a] General procedure: one compartment cell; DMF, 40 ml; $Ni(bipy)_3(BF_4)_2$, 0.6 mmol; alkyne, 6 mmol; n-Bu_4NBF_4, 0.3 mmol; CO_2 bubbling at atmospheric pressure; 50 mA applied between a Mg anode and a carbon fiber cathode for 15 h. Carboxylic acids were esterified and analyzed as methyl esters after column chromatography. Yields are expressed in terms of the yielded isolated products relative to the amount of alkyne that has reacted. [b] 1/2 mixture of **1** and its saturated analog, 25% stillbene was formed. [c] Mixture of isomers. [d] Selectivity **1/2**: entry 4: 62/38; entry 7: 53/47.

acid was formed selectively [7] (eq. 1), suggesting that steric effects can be a predominant factor in determining orientation.

Electrocarboxylation of 3-pentynyl acetate at $P(CO_2)$ 1 atm (entry 7) afforded a 53/47 mixture of regioisomers **1** and **2**. An identical **1/2** ratio was observed at $P(CO_2)$ 5 atm. This is in agreement with the presence of two similar sterically and electronically demanding groups, with no additional coordination of the acetate group to the nickel center that would favour carboxylation on the methyl side, e.g. isomer **1**.

Electron-deficient alkynes such as ethyl phenylpropiolate (entry 5) or ethyl-2-butynoate (entry 6), underwent dicarboxylation more rapidly, together with reduction and carboxylative oligomerization of the starting alkynes. For both substrates, regioisomer **1** was predominant among the monocarboxylic acids formed.

We conclude that disubstituted alkynes can be selectively carboxylated under mild conditions ($P(CO_2)$ 1 atm) with $Ni(bipy)_3(BF_4)_2$ as the catalyst by a very simple one-compartment cell electrolysis procedure. The carboxylation occurs more slowly than that of terminal acetylenes [7], particularly when two bulky substituents are present (e.g. TMS, Ph). The selectivity of mono-relative to di-carboxylation strongly depends on the nature of the alkyne, with non-conjugated or phenyl substituent, α,β-unsaturated carboxylic acids are formed selectively, and with more electron deficient substrates (e.g. conjugated esters) 1,2-dicarboxylation the rate is higher.

It is difficult to assess the relative importance of electronic and steric effects in the direction of CO_2 incorporation in unsymmetrically substituted alkynes. It seems likely that steric factors play an important role in determining the orientation. The observed regioselectivities correlate with the triple bond polarization (according to ^{13}C chemical shifts of acetylenic carbons [10]), the CO_2 bonding preferentially to the carbon centre with the lowest charge density.

References

1 S. Inoue, N. Yamazaki, Organic and Bio-Organic Chemistry of Carbon Dioxide, Tokyo, 1982.
2 For recent reviews see: (a) P. Braunstein, D. Matt, D. Nobel, Chem. Rev., 88 (1988) 747 and refs. therein; (b) D. Walther, Coord. Chem. Rev., 79 (1987) 735 and refs. therein.
3 E. Labbé, E. Duñach, J. Périchon, J. Organomet. Chem., 353 (1988) C51.
4 D. Walther, H. Schönberg, E. Dinjus, J. Organomet. Chem., 334 (1987) 377.
5 T. Tsuda, S. Morikawa, R. Sumiya, T. Saegusa, J. Org. Chem., 53 (1988) 3140.
6 H. Hoberg, D. Schaefer, G. Burkhart, C.J. Krüger, M.J. Romao, J. Organomet. Chem., 266 (1984) 203.
7 E. Duñach, J. Périchon, J. Organomet. Chem., 352 (1988) 239.
8 E. Labbé, E. Duñach, S. Sibille, J. Périchon, to be published.
9 (a) S. Wawzonet, D. Wearring, J. Am. Chem. Soc., 81 (1959) 2067. (b) E. Lamy, L. Nadjo, J.M. Savéant, N.J. Chem., 3 (1979) 21 and refs therein.
10 (a) H. Meier, E. Estavridon, C. Storek, Angew. Chem. Int. Ed. Engl., 25 (1986) 809. (b) F. Camps, J. Coll, J.M. Moretó, J. Torras, J. Org. Chem., in press.