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Electrochemical carboxylation of terminal alkynes catalyzed by nickel complexes: unusual regioselectivity

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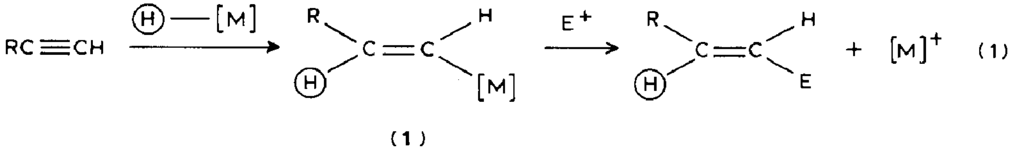
Abstract

The electrochemical reduction of the nickel(II) complex $Ni(bipy)_3(BF_4)_2$ yields an active catalyst for the regioselective functionalization of the 2-position of terminal alkynes with carbon dioxide. A series of α-substituted acrylic acids have been obtained with selectivities of 65–90% and fair overall yields.

Introduction

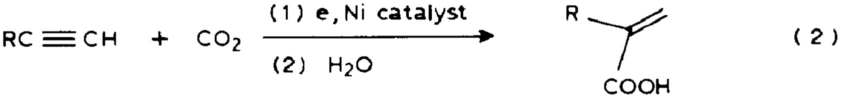
Hydrometallation and carbometallation of alkynes followed by the addition of an electrophilic species constitutes an attractive and efficient route to substituted alkenes [1]. Of particular interest are hydrometallation reactions of terminal alkynes involving alkenyl-aluminum [2], -boron [3] or -zirconium [4] intermediates of type **1**, which allow the preparation of 1,2-disubstituted alkenes in a highly regio- and stereoselective manner (eq. 1).



(1)

The electrophile bonds to the terminal carbon of the former alkyne in an almost 100% *cis* addition.

Here we report a novel electrochemical method involving nickel complexes and carbon dioxide that allows transformation of terminal alkynes into α-substituted acrylic acids of type **2** (eq. 2).



(**2**)

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The reaction is catalyzed by a nickel(0) complex generated "in situ" by electrochemical reduction of a stable nickel(II) catalyst precursor, $Ni(bipy)_3(BF_4)_2$ (bipy = 2,2′-bipyridine). This nickel-mediated carbon dioxide fixation takes place with formation of a carbon–carbon bond between the alkyne units and CO_2, and no alkyne-oxygen bond forming products were observed [5].

Electrochemically generated nickel(0) species have already been used for synthetic applications in dimerizations [6] or in coupling reactions [7], but to our knowledge, no such reactions involving alkyne substrates have previously been reported.

The conventional methods of activating alkynes by nickel(0) complexes [8] involve the use of toxic $Ni(CO)_4$ or the tedious preparation of air-sensitive nickel(0) complexes. The same drawbacks apply to nickel-mediated carbon–carbon bond forming reactions between alkynes and carbon dioxide, which give a variety of reaction products depending on the reaction conditions and the ligands on nickel. Hoberg [9] described a stoichiometrical nickel(0)-TMEDA (or other ligand) mediated preparation of α,β-unsaturated acids; Inoue [10] using phosphine ligands and $Ni(COD)_2$, obtained mixtures of dimers and trimers of the starting alkyne precursor, together with variable quantities of a pyrone derivative; Tsuda [11] prepared bicyclic α-pyrones from diynes under CO_2 pressure, and Walther [12a] optimized the conditions for the nickel(0) catalysed cooligomerization to substituted pyrones. A review of the homogeneous reactions of carbon dioxide with unsaturated substrates has recently appeared [12b].

Results and discussion

Our electrochemical method provides a regioselective way of forming carbon–carbon bonds by simultaneous double activation of terminal alkynes and carbon dioxide under mild conditions ($P(CO_2)$ 1 atm, T 20–80 °C, see Tables 1 and 2) in a catalytic reaction. The reaction is carried out in DMF at constant current densities in an undivided electrolytic cell: the anode is a sacrificial rod of magnesium surrounded by a cathode of carbon fiber. Reactions at the electrode can be written as follows:

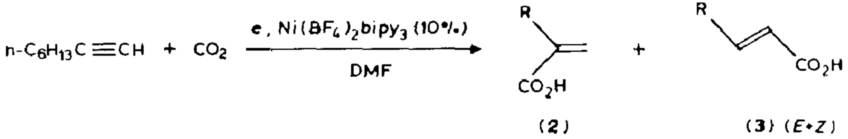
Anode: $Mg \rightarrow Mg^{2+} + 2e$

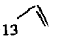
Cathode: $Ni(bipy)_3(BF_4)_2 + 2e \rightarrow Ni^0bipy_2 + bipy + 2BF_4^-$

1-Octyne was used for the optimization of the reaction conditions. Table 1 summarizes some of the main results.

The cationic complex $Ni(bipy)_3(BF_4)_2$ (**4**) is a stable pink solid, easily prepared from $Ni(BF_4)_2 \cdot 6H_2O$ and bipy. As a catalyst, **4** gave slightly better results in terms of yields and selectivity than $NiBr_2(DME)$ (DME = dimethoxyethane) with added bipy (compare entries 2 and 4). On going to acetonitrile, the regioselectivity of the carboxylated adducts **2** and **3** was lowered from 90% to 75% and we observed products derived from solvent attack on the alkyne (entry 1). At 80 °C in DMF the rates were higher with almost no change in selectivity, better yields were obtained, and higher current densities could be imposed. A mixture of DMF/methanol as

Table 1



Entry	Solvent temperature	Catalyst (%)	Supporting electrolyte	Transformed 1-octyne	Products formed [a]	Yield of products (%)	Selectivity **2/3**
1	CH_3CN 20 °C	$NiBr_2DME$ +2 bipy (10%)	n-Bu_4NBF_4	80	**2**+**3**	50	75/25
2	DMF 20 °C	$NiBr_2DME$ +2 bipy (10%)	n-Bu_4NBF_4	70	**2**+**3**	45	89/11
3	DMF+3% MeOH, 20 °C	$NiBr_2DME$ +bipy (10%)	n-Bu_4NBF_4	70	**2**+**3**+ $+C_6H_{13}$ (40%)	70	95/5
4	DMF 20 °C	$Ni(BF_4)_2bipy_3$ (10%)	n-Bu_4NBF_4	70	**2**+**3**	60	90/10
5	DMF, 80 °C	$Ni(BF_4)_2bipy_3$ (10%)	n-Bu_4NBF_4	80	**2**+**3**	85	88/12
6	DMF, 20 °C	$Ni(BF_4)_2bipy_3$ (10%)	KI	70	**2**+**3**	45	91/9

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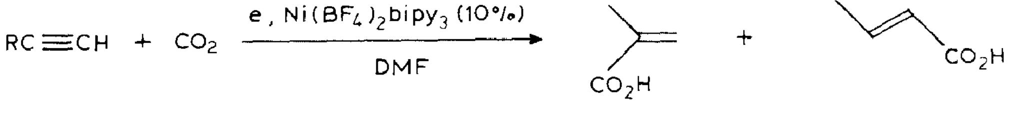
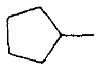
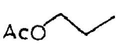
[a] Analysed as acids and isolated as methyl esters; see experimental part. For **3**, *E*/*Z* isomerization takes place under reaction conditions. Anode, Mg; cathode, carbon fiber.

Table 2



(2) (3) (*E*+*Z*)

Entry	R	*T* (°C)	% of transformed alkyne	Products formed	Yield of products [b]	Selectivity **2**/**3**
1	n-C_6H_{13}	20	70	**2**+**3**	60	90/10
2	n-C_3H_7	45	50	**2**+**3**	45	85/15
3	n-$C_{12}H_{25}$	20	80	**2**+**3**	60	88/12
4		50	60	**2**+**3**	50	91/9
5	C_6H_5	20	80	**2**+**3**+$Ph(CH_2)_2CO_2H$ (6%)	35	71/29
6		40	80	**2**+**3**	45	67/35
7		50	80	**2**+**3**+ $CN(CH_2)_3CH{=}CH_2$ (20%)	40	90/10
8		70	60	**2**+**3**+ $AcO(CH_2)_4CO_2H$ (13%)	65	50/50
9		60	10	**2**+**3**	40	65/35
10	$(EtO)_2CH-$	40	70	**2**+**3** [c]	35	70/30

[a] For electrolysis conditions, see Experimental. [b] See Table 1. [c] Analyzed only as methyl esters.

solvent (entry 3) did not give the expected methyl esters but a considerable amount (40%) of reduced alkyne (essentially 1-octene).

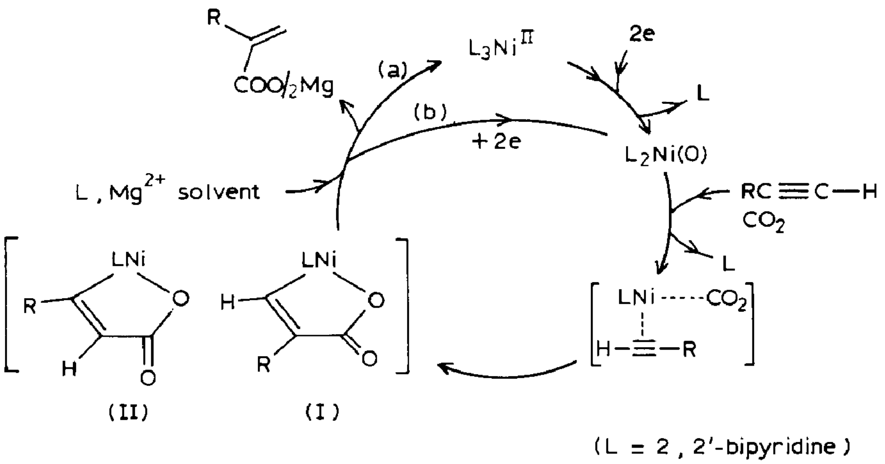
By-products arose essentially from reduction and oligomerization of starting alkynes. Some oligomers but mainly unchanged starting material were obtained in electrolysis carried out in the absence of CO_2, or when dimethylcarbonate or potassium bicarbonate were used instead of carbon dioxide. No significant change was observed on changing the supporting electrolyte from n-Bu_4NBF_4 to KI.

The metal constituting the anode has a determining influence on the reaction. A Mg anode gives selectively carboxylic acid **2**, (for 1-octyne selectivity **2**/**3** 90/10), whereas with a Zn anode selectivity falls to 55/45, and an Al anode does not yield any carboxylated products but gives dimers and trimers of 1-octyne in low yield.

The results for the nickel catalyzed electrocarboxylation for several alkynes are presented in Table 2.

Aliphatic R groups (entries 1–4) gave selectivities in the range of 85–91%; the highest regioselectivity was observed for the more bulky cyclopentyl substituent (entry 4). Phenyl acetylene (entry 5) was also selectively carboxylated at the 2-position, in a 71/29 ratio.

Functionalized alkynes (CN, Cl, OAc, OR, OH) were also carboxylated, although regioselectivities were not as high. 3-Butyn-1-ol (entry 9) was found to react stoichiometrically; the reaction is thought to stop at the stage of nickel alcoholate without Ni/Mg exchange nor Ni^{II} reduction after the first catalytic cycle (see Scheme 1). For functionalized alkynes (entries 6–10, Table 2), the additional

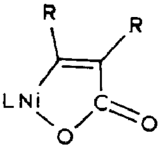


Scheme 1

coordination of the functional groups to the metal center was found to increase the proportion of terminal carboxylated adducts of type **3**.

The results for the carboxylation of disubstituted alkynes will be reported elsewhere.

In our electrochemical approach to in situ generation of nickel(0) species, cyclic voltammetry studies [13] have shown that the starting Ni^{II} complex is reduced in a two-electron single wave at −1.1 V/SCE, and that the electrogenerated Ni^0bipy_2 complexes in DMF are able to coordinate rapidly with terminal alkynes as well as CO_2 to form a hypothetical metallacycle of type **5**:



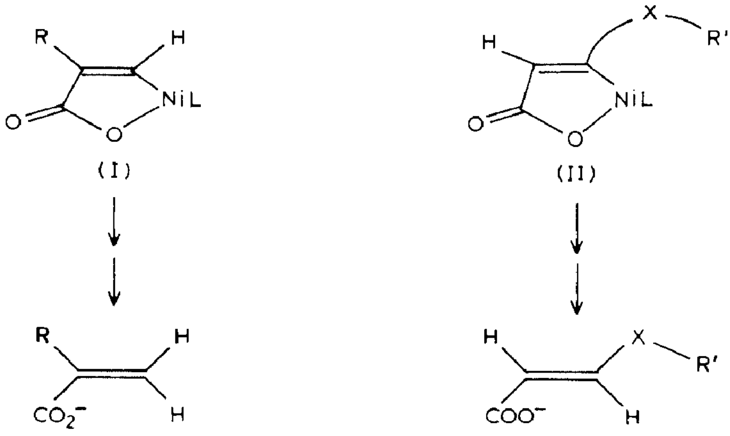
(**5**)

Nickeloxacyclopentenones of type **5** have been isolated and characterized by Hoberg [9b] as intermediate complexes in the carboxylation of symmetrically disubstituted alkynes, but to our knowledge, no examples involving a monosubstituted alkyne has been described.

A proposed catalytic cycle is presented in Scheme 1.

The organometallic nickel(II) species undergoes a fast electrochemical reduction step and the nickel(0) species thus generated undergoes ligand exchange to take up the alkyne and CO_2 and form the isomeric nickel(II) metallocycles I and II (not-isolated). Insertion of carbon dioxide into the metal–carbon bond has been suggested to be the key step in the nickel-catalyzed reactions of carbon dioxide with unsaturated hydrocarbons [14,15]. No nickel-promoted electrochemical reduction of CO_2 [5,16] was observed under our conditions.

The intermediate metallocycles I and II in the presence of Mg^{2+} ions (formed in the anodic oxidation) yield the corresponding magnesium carboxylates, liberating



Scheme 2

the nickel species, which reenters the catalytic cycle, either via a Ni^{II} (path a), Scheme 1) or by direct reduction from these metallocycles to nickel(0) (path b)). The attractiveness of the single-compartment cell, apart from its simplicity, lies in the fact that both anodic and cathodic processes yield essential components for the reaction. It will be appreciated that Scheme 1 presents a simplified version of the actual mechanism for the nickel-catalyzed carboxylation; a more complete scheme would take into account the solvent coordination as well as the nature of the electrodes: change in the sacrificial anodes from Mg, to Al or Zn (as does change in the nature of the cathode) markedly changes the reaction products as well as the regioselectivities.

The selectivities observed for functionalized alkynes (Table 2), can be explained in terms of the behaviour of the isomeric intermediates I and II (Scheme 2). If the substituent R offers no sites for interaction with nickel, the metal occupies the less hindered site of the metallocycle as in I, giving rise to carboxylic acids of type **2**; if R contains additional coordination sites, reaction of the intermediate II, which is even more sterically crowded, becomes competitive, and the reaction is less selective.

The observed regioselectivities of the carboxylated products correspond to those of Reppe's carbonylation reaction [17] of acetylene derivatives, involving use of nickel carbonyl and of carbon monoxide as the carbon source under forcing conditions (high pressure of stoichiometric amounts of $Ni(CO)_4$). The interest in our procedure (eq. 2) lies in the use of carbon dioxide as the source of organic chemicals [5,18] in a catalytic process.

Experimental

Dimethylformamide (DMF) was pre-dried over calcium hydride and freshly distilled from calcium hydride and anhydrous copper sulfate under reduced pressure before the electrolysis. The supporting electrolytes were dried under vacuum (0.1 mmHg) at 50 °C before use. Other reagents were used as supplied.

$Ni(bipy)_3(BF_4)_2$ (**4**) was made by a procedure similar to that used for tris(bipyridine)nickel type complexes [19]. A pink complex separated from an ethanolic solution (200 ml) of $Ni(BF_4)_2 \cdot H_2O$ (10 g, 3×10^{-2} mol) and 2,2′-bipyridine (14.1

g, 9×10^{-2} mol) at room temperature after stirring for 1 h, and was filtered off, washed with diethyl ether, and dried under vacuum (0.1 mmHg) at 70 °C overnight, 20 g of **4** have been isolated (95% yield). IR (Nujol): 3120, 3080, 1608, 1600, 1568, 1490, 1315, 1285, 1250, 1020, 770, 738 cm^{-1}. Elemental analysis. Found: C, 50.38%; H, 3.58%; N, 11.30%; Ni, 7.85. $C_{30}H_{24}B_2F_8N_6Ni$ calcd.: C, 50.41; H, 3.45; N, 11.99; Ni, 8.37%.

General electrolysis procedure:

The two electrode, single-compartment electrochemical cell was similar to that described previously [6]. The anode is cylindrical rod of magnesium (99.8% diameter 1 cm) (or later Zn or Al) surrounded by a carbon fibre cathode (apparent surface 20 cm^2). A DMF (40 ml) solution of **4** (0.3 mmol) containing n-Bu_4NBF_4 (0.5 mmol) was electrolyzed under a carbon dioxide bubbling flow at atmospheric pressure (Alphagaz N45). After passage of 2F/mol of Ni, the alkyne (3 mmol) was slowly added to the solution during 3–4 hours and the electrolysis continued with apparent cathodic current densities of 0.1–0.4 A/dm^2. The disappearance of starting material was monitored by GLC and the reactions stopped when the alkyne consumption was about 80% or the current density had fallen significantly. Faradayic yields were in the range of 50–80%, for reaction times of 8–24 h.

When the electrolysis was stopped, DMF was evaporated under vacuum from one half of the reaction mixture, the residue was dissolved in a dilute aqueous hydrochloric acid and extracted with Et_2O. The organic layer was washed, dried over $MgSO_4$, and evaporated. The acidic products are analyzed by capillary gas chromatography (superox AT 1000, 11 m, He carrier) and by NMR spectroscopy.

The second half of the reaction mixture was esterified directly in DMF by adding anhydrous K_2CO_3 (2 mmol) and methyl iodide (4 mmol) and stirring the mixture at 50 °C for 5 h. The solution was hydrolyzed and extracted with Et_2O, and the organic layer was washed with H_2O, dried over $MgSO_4$, and evaporated. The methyl esters corresponding to acids **2** and **3** were isolated by column chromatography (normal or flash on silica gel) with pentane/Et_2O mixtures as eluent. The products are analyzed by ^1H NMR and IR spectrometry, mass spectroscopy, and GLC.

Conclusion

The electrochemical method describes a mild nickel-mediated hydrocarboxylation method of terminal alkynes with a high selectivity towards products, attached to the 2-position, and is therefore a useful alternative to the synthesis of α-substituted acrylic acids based on the metal-mediated activation of carbon dioxide. The differences in chemical reactivity and selectivity compared with those in the usual hydrometallation procedures is a consequence of the special mechanism operating in our electrochemical carboxylation.

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