

First Example of Direct Carbon Dioxide Incorporation into 1,3-Diynes: A Highly Regio- and Stereo-selective Nickel-catalysed Electrochemical Reaction

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The electrocatalysis of 2-vinylidene-3-yne carboxylic acids from carbon dioxide and substituted 1,3-diynes is catalysed by a nickel-triamine complex and results in a regio- and stereo-selective addition to one triple bond.

The development of transition-metal catalysed carbon dioxide incorporation into acetylenic hydrocarbons constitutes an attractive topic from a synthetic point of view and because it widens the field of CO₂ activation.^{1,2} In this regard, a few catalytic systems have been reported so far and concern essentially the use of Ni⁰-PR₃ complexes for the synthesis of pyrones³⁻⁵ and the use of electrogenerated Ni⁰-amine systems for the synthesis of unsaturated carboxylic acids.^{6,7}

The carboxylation of non-conjugated α,ω -diynes has also been described.^{5,8} However, to our knowledge, no example concerning direct CO₂ incorporation into conjugated 1,3-diyne systems has yet been reported.

We present here our results on the hydrocarboxylation of substituted 1,3-diynes by electrocatalysis. The electrochemical method utilizing one-compartment cells with a sacrificial magnesium anode has attracted some interest recently because of its simplicity and its synthetic possibilities.⁹

In the hydrocarboxylation reaction of unsaturated hydrocarbons, the electrochemical method enables the use of a catalytic amount of a Ni^{II} precursor (*e.g.* NiBr₂·dme, dme = dimethoxyethane). By the appropriate choice of the ancillary ligand L, the *in situ* reduction of the Ni^{II} yields a Ni⁰-L complex, active for the coupling of CO₂ with the 1,3-diynes, **1** (Scheme 1). The Ni⁰ complex is recycled by further reduction. Electrolyses are carried out in a dimethylformamide (DMF)-Buⁿ₄N⁺BF₄⁻ solution under mild conditions (*T* 20–60 °C, CO₂ pressure of 1–5 atm) at constant current (50 mA). During the experiment, the magnesium anode is oxidized to Mg²⁺.

Table 1 presents the results of the activity of different catalytic systems using tetradeca-6,8-diyne **1a** (R¹ = R² = n-C₅H₁₁) as the model, in order to optimize the experimental conditions.

No reaction occurred in the absence of the nickel complex (entry 1), and the starting diyne was recovered in the absence of CO₂ without any polymerization (entry 2). A remarkable dependence of the reaction product on the ancillary ligand was observed. The Ni(bipy)₃(BF₄)₂ complex (bipy = 2,2'-bipyridine, entry 3), resulted in low CO₂ incorporation favouring the reduction of **1a** into the enyne derivative. Although the bipy ligand was here almost ineffective towards CO₂ fixation, it has been reported to be efficient in the preparation of

nickelacycles from Ni⁰, alkynes and CO₂¹⁰ and in the electrochemical carboxylation of monoalkynes.⁶

Utilizing triphenylphosphine (entry 6) or tricyclohexylphosphine (entry 7) as the ligands, carboxylic acids **2a** and **3a** were obtained with low diyne conversion. Similar results were obtained with the Ni-tmeda system (tmeda = tetramethylethylenediamine, entry 8).

The best results concerning the heterocoupling reaction were obtained with pmdta as the ancillary ligand (pmdta = pentamethyldiethylenetriamine, entries 4 and 5). In a car-

Table 1 Electrochemical hydrocarboxylation of tetradeca-6,8-diyne **1a** (R¹ = R² = n-C₅H₁₁): influence of the catalytic system and the reaction conditions^a

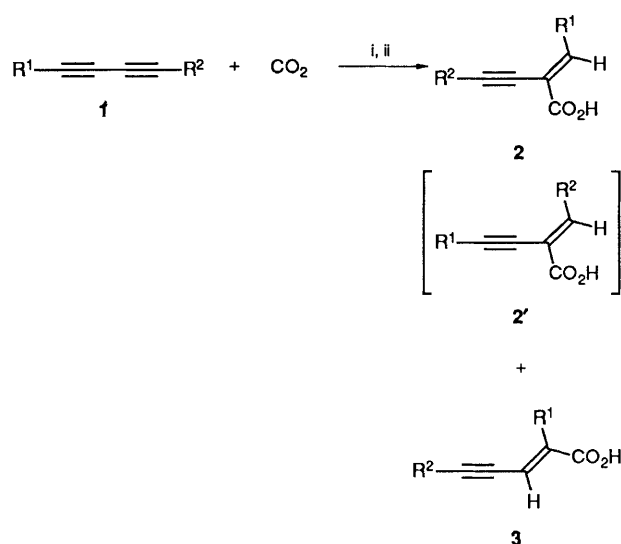
Entry	Complex	Reaction conditions	Isolated products (%)			
			1a	Enyne	Carboxylic acids 2a, 3a ^b	2a:3a
1	none	5 atm 20 °C	>95	—	—	—
2	Ni(bipy) ₃ (BF ₄) ₂	absence of CO ₂ , 20 °C	95	5	—	—
3	Ni(bipy) ₃ (BF ₄) ₂	5 atm, 20 °C	10	50	15	60:40
4	NiBr ₂ ·dme + 2 pmdta	5 atm, 20 °C	15	5	70	70:30
5	NiBr ₂ ·dme + 2 pmdta	1 atm, 65 °C	30	10	50	50:50
6	NiBr ₂ (PPh ₃) ₂ + PPh ₃	5 atm, 20 °C	95	—	5	60:40
7	NiBr ₂ ·dme + 3 P(C ₆ H ₁₁) ₃	5 atm, 20 °C	85	—	10	60:40
8	NiBr ₂ ·dme + 3 tmeda	5 atm, 20 °C	75	5	10	65:35

^a General electrolysis procedure: freshly distilled DMF (40 ml) with added Ni complex (0.3 mmol); **1a** (3 mmol); Buⁿ₄N⁺BF₄⁻ (0.3 mmol); CO₂ bubbling at atm pressure in a glass cell⁹ or at 5 atm in a stainless steel closed cell; 50 mA applied between a Mg anode (cylindrical rod, diameter 1 cm) and a carbon fibre cathode (apparent surface 20 cm²) for 5–7 h. ^b Carboxylic acids are esterified and isolated as methyl esters after column chromatography.⁶ All compounds gave correct spectroscopic data.

Table 2 Ni-pmdta catalysed electrocarboxylation of R¹-≡≡-R^{2a}

Entry	Starting diyne	R ¹	R ²	Reaction conditions ^b	% Conversion	Products ^c (% isolated yield)	Ratio 2:3
1	1a	n-C ₅ H ₁₁	n-C ₅ H ₁₁	5 atm	85	2a (58) + 3a (25)	70:30
2	1b	c-C ₅ H ₉	c-C ₅ H ₉	5 atm	70	2b (86)	97:3
3	1c	Ph	Ph	5 atm	100	2c (40)	100:0
4	1d	<i>p</i> -MeC ₆ H ₄	<i>p</i> -MeC ₆ H ₄	1 atm	100	Monocarboxylic + dicarboxylic acids (15) acids (15)	—
5	1e	MeOCH ₂	MeOCH ₂	5 atm	100	2e (20)	98:2
6	1e	MeOCH ₂	MeOCH ₂	1 atm	75	2e (60)	98:2
7	1f	PhOCH ₂	PhOCH ₂	5 atm	40	2f (88)	98:2
8	1g	Ph	Bu ⁿ	1 atm	95	2g (37) + 3g (16) + 2'g (3)	71:29 ^d
9	1h	MeOCH ₂	Ph	5 atm	90	2h (50) + 2'h (11)	100:0 ^d

^a General electrolysis procedure as in footnote a, Table 1 with NiBr₂·dme (0.3 mmol), pmdta (0.6 mmol), diyne (3 mmol). ^b All reactions carried out at 20 °C. ^c See footnote b, Table 1. Yields correspond to isolated methyl ester/reacted diyne. ^d For isomers **2**, **2'**, the regio-selectivity according to R¹, R² is, for entry 8, **2g**:**2'g**:93:7; for entry 9, **2h**:**2'h**:82:18.



Scheme 1 Reagents and conditions: i, e, Ni^{II} (10%) + L, Mg anode, DMF, Bu₄N⁺ BF₄⁻; ii, H₂O

boxylation carried out at 20 °C at a CO₂ pressure of 5 atm (entry 4), monocarboxylic acids **2a** and **3a** were isolated (as methyl esters) in 70% yield after column chromatography, with a **2a**:**3a** ratio of 70:30. For both regioisomers an exclusive *cis*-addition of CO₂H and H across one of the C≡C units occurred without any isomerization.

The Ni-pmdta system was chosen for the carboxylation of a series of conjugated diynes **1a–h**. The results are gathered in Table 2. The diynes have been prepared according to described procedures.¹¹

For **1b** (R¹ = R² = cyclopentyl, entry 2) carboxylic acid **2b** was formed in excellent yield and 98% regioselectivity. The comparison between entries 1 and 2 (*e.g.*, a much better selectivity for **1b** than for **1a**), accounts for the steric effect of the alkyl substituent.

Diphenylbutadiyne **1c** (entry 3) gave a single isomer **2c**, which was isolated in 40% yield. The *p*-tolyl analogue **1d**, (entry 4) resulted in a 1:1 mixture of mono- and di-carboxylated products. The presence of the *p*-methyl group (compare entries 3 and 4) exerts a strong electronic effect that orientates the mode and selectivity of the reaction towards a bis carbon dioxide incorporation.

When the more polar methoxymethyl or phenoxymethyl groups were used (**1e** and **1f**, entries 5–7) only carboxylic acids **2e** and **2f** respectively were isolated and both reactions were completely stereo- and regio-selective.

Two differently substituted diynes **1g** and **1h** were also examined. In the case of R¹ = Ph, R² = Buⁿ (**1g**, entry 8) three carboxylic acids **2g**, **3g** and **2'g** were isolated. The CO₂ fixation mainly occurred on the phenyl side (93%), the major regioisomer being **2g**. For R¹ = Ph, R² = CH₂OMe (**1h**, entry 9) two isomeric carboxylic acids were formed, both with the carboxy groups in the internal positions of the diyne, *e.g.* isomers **2g**, **2'g**. However, in contrast with entry 8, the CO₂ is preferentially bound to the methoxymethyl site with a **2g**:**2'g** ratio of 82:18. We can therefore conclude that the ability of the substituent as directing group toward CO₂ fixation is alkyl < phenyl < methoxymethyl.

In all the examples studied, except for **1d**, one molecule of CO₂ per diyne unit was incorporated with the net result of an hydrocarboxylation reaction of one of the triple bonds. A preferential and often exclusive CO₂ fixation at the 2 position of the 1,3-diyne occurred (*e.g.* product **2**) with stereodefined *cis*-addition in all cases.

In conclusion, the Ni-pmdta catalysed electrocarboxylation of conjugated diynes enables the regio- and stereo-selective preparation of substituted (*E*)-2-vinylidene-3-yne carboxylic acids in one step under mild conditions.

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