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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 electrosynthesis 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 CO_2 activation.[1,2] In this regard, a few catalytic systems have been reported so far and concern essentially the use of Ni^0–PR_3 complexes for the synthesis of pyrones[3–5] and the use of electrogenerated Ni^0–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 CO_2 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 electrosynthesis. 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.* $NiBr_2$·dme, dme = dimethoxyethane). By the appropriate choice of the ancillary ligand L, the *in situ* reduction of the Ni^{II} yields a Ni^0–L complex, active for the coupling of CO_2 with the 1,3-diynes, **1** (Scheme 1). The Ni^0 complex is recycled by further reduction. Electrolyses are carried out in a dimethylformamide (DMF)–$Bu^n_4N^+BF_4^-$ solution under mild conditions (*T* 20–60 °C, CO_2 pressure of 1–5 atm) at constant current (50 mA). During the experiment, the magnesium anode is oxidized to Mg^{2+}.

Table 1 presents the results of the activity of different catalytic systems using tetradeca-6,8-diyne **1a** (R^1 = R^2 = n-C_5H_{11}) 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 CO_2 without any polymerization (entry 2). A remarkable dependence of the reaction product on the ancillary ligand was observed. The $Ni(bipy)_3(BF_4)_2$ complex (bipy = 2,2′-bipyridine, entry 3), resulted in low CO_2 incorporation favouring the reduction of **1a** into the enyne derivative. Although the bipy ligand was here almost ineffective towards CO_2 fixation, it has been reported to be efficient in the preparation of nickelacycles from Ni^0, alkynes and CO_2[10] 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** ($R^1 = R^2$ = n-C_5H_{11}): influence of the catalytic system and the reaction conditions[a]

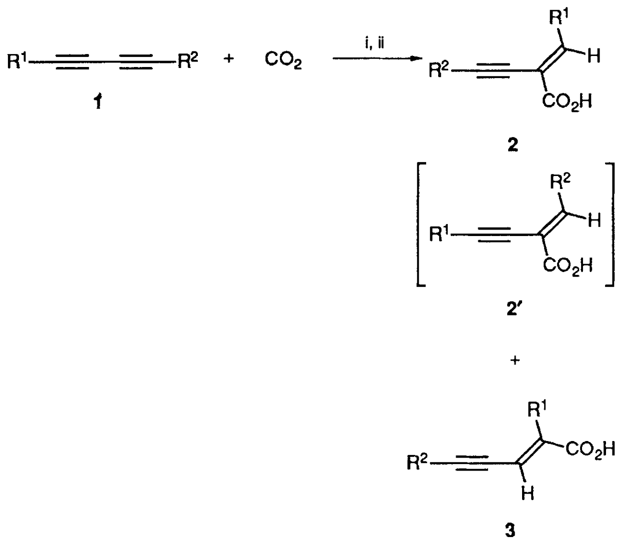
			Isolated products (%)			
Entry	Complex	Reaction conditions	**1a**	Enyne	Carboxylic acids **2a, 3a**[b]	**2a**:**3a**
1	none	5 atm 20 °C	>95	—	—	
2	$Ni(bipy)_3(BF_4)_2$	absence of CO_2, 20 °C	95	5	—	
3	$Ni(bipy)_3(BF_4)_2$	5 atm, 20 °C	10	50	15	60:40
4	$NiBr_2$·dme + 2 pmdta	5 atm, 20 °C	15	5	70	70:30
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 $P(C_6H_{11})_3$	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); $Bu^n_4N^+BF_4^-$ (0.3 mmol); CO_2 bubbling at atm pressure in a glass cell[9] 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 cm^2) 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 $R^1{-}{\equiv}{-}{\equiv}{-}R^2$[a]

Entry	Starting diyne	R^1	R^2	Reaction conditions[b]	% Conversion	Products[c] (% isolated yield)	Ratio **2**:**3**
1	**1a**	n–C_5H_{11}	n–C_5H_{11}	5 atm	85	**2a** (58) + **3a** (25)	70:30
2	**1b**	c-C_5H_9	c-C_5H_9	5 atm	70	**2b** (86)	97:3
3	**1c**	Ph	Ph	5 atm	100	**2c** (40)	100:0
4	**1d**	*p*-MeC_6H_4	*p*-MeC_6H_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 $NiBr_2$·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 R^1, R^2 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, $Bu^n_4N^+BF_4^-$; ii, H_2O

boxylation carried out at 20 °C at a CO_2 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 CO_2H 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** ($R^1 = R^2$ = 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 R^1 = Ph, $R^2 = Bu^n$ (**1g**, entry 8) three carboxylic acids **2g**, **3g** and **2′g** were isolated. The CO_2 fixation mainly occurred on the phenyl side (93%), the major regioisomer being **2g**. For R^1 = Ph, $R^2 = CH_2OMe$ (**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 CO_2 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 CO_2 fixation is alkyl < phenyl < methoxymethyl.

In all the examples studied, except for **1d**, one molecule of CO_2 per diyne unit was incorporated with the net result of an hydrocarboxylation reaction of one of the triple bonds. A preferential and often exclusive CO_2 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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