Journal of Organometallic Chemistry, 424 (1992) 213–224
Elsevier Sequoia S.A., Lausanne
JOM 22277

New C–C bond formation through the nickel-catalysed electrochemical coupling of 1,3-enynes and carbon dioxide

Sylvie Dérien [a], Jean-Claude Clinet [b], Elisabet Duñach [a] and Jacques Périchon [a]

[a] *Laboratoire d'Electrochimie, Catalyse et Synthèse Organique, UMR 28, C N R S, 2, rue Henri-Dunant, 94320 Thiais (France)*
[b] *Laboratoire de Coordination Organique, C.N.R S, UA 255, ICMO, Bât 420, Université Paris-Sud, 91405 Orsay Cedex (France)*

(Received June 7, 1991)

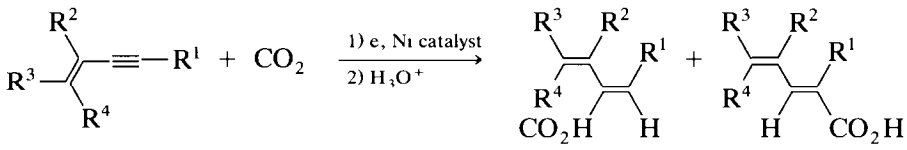
Abstract

A series of 1,3-enynes has been carboxylated in a nickel-catalysed electrochemical reaction carried out in a single-compartment cell fitted with a consumable magnesium anode. When 2,2′-bipyridine (bipy) or pentamethyldiethylene triamine (PMDTA) are added as the ancillary ligands, an overall hydrocarboxylation of the triple bond occurs through stereoselective *cis*-addition.

Introduction

Simultaneous activation of CO_2 and unsaturated hydrocarbons by transition-metal complexes represents an interesting possibility for forming new carbon–carbon bonds, allowing use of CO_2 as the raw material for the synthesis of fine chemicals [1–3].

The incorporation of CO_2 into isolated C–C triple bonds can be brought about by using Ni^0 complexes [4–7]. Among conjugated systems, the carboxylation of 1,3-dienes has been thoroughly investigated for catalysis by Pd, Ni and Rh complexes [1,8]. However, there has, to our knowledge, been no report dealing with the direct carbon dioxide incorporation into conjugated enynes, **1** (Scheme 1). The reactivity of such conjugated systems towards CO_2 presents interesting questions; e.g., will CO_2 be incorporated at the double or the triple bond, and how will the conjugation and the substrate substitution affect the new carbon–carbon bond formation? There is already a useful range of reactions of conjugated enynes in the presence of organometallic reagents: their hydrogenation by homogeneous Pd^{2+} complexes takes place at the triple bond [9], whereas with Ru complexes 1,2-addition to the double bond predominates [10]. Furthermore, the addition of copper reagents to these systems leads to different regiochemistries depending on the enyne structure [11].



1 **2** **3**

	R^1	R^2	R^3	R^4
1a	H	$(CH_2)_4$		H
1b	CH_3	$(CH_2)_4$		H
1c	n-C_3H_7	$(CH_2)_4$		H
1d	n-C_4H_9	CH_3	H	H
1e	n-C_6H_{13}	H	H	H
1f	n-C_5H_{11}	H	H	n-C_5H_{11}
1g	n-C_5H_{11}	H	n-C_5H_{11}	H

Scheme 1

We present here our results on the direct, nickel-catalysed electrochemical incorporation of CO_2 into 1,3-enynes **1** leading to the preparation of stereodefined diene carboxylic acids of type **2** and **3** as depicted in Scheme 1.

Results and discussion

General considerations

The synthesis of doubly-unsaturated carboxylic acids such as the dienes **2** or **3** from hydrocarbons **1** by conventional methods generally requires a multistep procedure [12]. In our method the preparation of regioisomers **2** and **3** is performed in one step under mild conditions. The electrochemical method involves use of a catalytic amount of a Ni^{II} complex (0.1 equiv. with respect to the enyne), either $NiBr_2$-dme (dme = 1,2-dimethoxyethane) associated with the ancillary ligand PMDTA (PMDTA = pentamethyldiethylene triamine) or $Ni(bipy)_3(BF_4)_2$ (bipy = 2,2′-bipyridine). The carboxylations are carried out at 1–5 atm of CO_2 in DMF at constant intensity, in a single-compartment electrolysis cell fitted with a magnesium anode. We have previously used this method successfully in the conversion of monoalkynes to substituted acrylic acids [7,13].

The results of the carboxylation of a series of enynes **1a**–**1g** are presented in Tables 1–3. Electrolysis was stopped after consumption of 2.5–4 F per mol of enyne. The 1,3-enynes were chosen in order to examine the effect of various substitution patterns on reactivity, and were prepared by literature methods [14].

Terminal and internal enyne derivatives **1a** and **1f** were used as model compounds in an examination of the influence of the reaction conditions and of the ancillary ligand on the CO_2 incorporation. A significant influence of the ligand in the electrocarboxylation of alkynes was previously pointed out [7c].

Table 1 summarizes some of the results. It will be seen that whereas PMDTA and bipy were efficient ligands in bringing about the carboxylation, triphenylphosphine (entries 5,6,12) was not. With both PMDTA and bipy, the main products

Table 1

Influence of the catalytic system and the reaction conditions on the electrochemical carboxylation of 1,3-enynes

$$1 + CO_2 \xrightarrow{e,\ catalyst} 2 + 3$$

Entry	Enyne	Catalytic system	$P(CO_2)$ [a] (atm)	Recovered **1**	Monocarboxylic acids **2**, **3**
1	**1a**	$NiBr_2$dme + 2 PMDTA	1	25	70
2	**1a**	$NiBr_2$dme + 2 PMDTA	5	20	80
3	**1a**	$Ni(bipy)_3(BF_4)_2$	1	50	5
4	**1a**	$Ni(bipy)_3(BF_4)_2$	5	10	68
5	**1a**	$NiBr_2$dme + 3 PPh_3	1	95	–
6	**1a**	$NiBr_2$dme + 3 PPh_3	5	95	–
7	**1f**	$NiBr_2$dme + 2 PMDTA	1	90	5
8	**1f**	$NiBr_2$dme + 2 PMDTA	1 [b]	65	20
9	**1f**	$NiBr_2$dme + 2 PMDTA	5	80	15
10	**1f**	$Ni(bipy)_3(BF_4)_2$	1	85	10
11	**1f**	$Ni(bipy)_3(BF_4)_2$	5	45	35
12	**1f**	$NiBr_2$dme + 3 PPh_3	5	95	–

[a] At $T = 20°C$ [b] At $T = 60°C$

were monocarboxylic acids **2** and **3** (Scheme 1), resulting from the incorporation of one molecule of CO_2 into the conjugated system. PMDTA is an aliphatic tris-amine with the ability to show mono-, bis- or trischelation to the metal centre [13], and it is more basic and sterically more crowded than aromatic bipy. On the other hand, bipy has an important back-donation ability.

No reaction of **1a** occurred in the absence of Ni-complex and the enyne was quantitatively recovered after the electrolysis.

A change in the CO_2 pressure from 1 to 5 atm had a positive effect on the conversion of **1a** and **1f** when bipy was the ligand (compare entries 3,4 and 10,11), but only a small effect was observed with PMDTA (entries 1,2). The effect of the temperature increase from 20 to 60°C was important at 1 atm of CO_2 (entries 7,8) but negligible at 5 atm. The regioselectivity **2**:**3** was only slightly affected by the changes in the reaction conditions. However, the ratio **2**:**3** was dependent on the enyne substitution and on the nature of the ligand. Tables 2 and 3 present the results obtained for the carboxylation of **1a**–**1g** with Ni-PMDTA and Ni-bipy, respectively, as the catalytic systems.

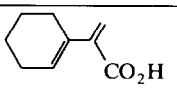
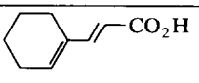
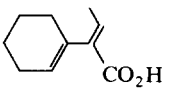
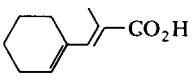
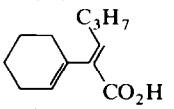
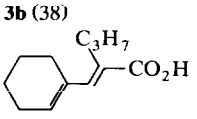
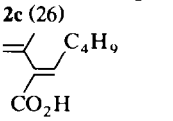
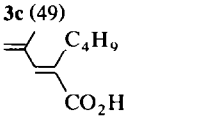
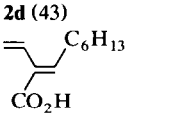
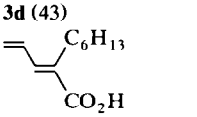
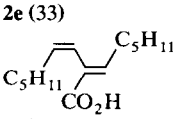
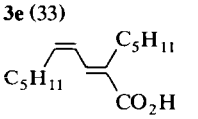
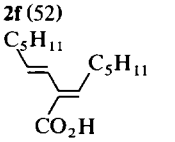
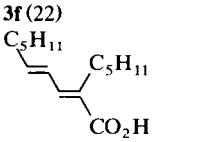
Carboxylations with Ni-PMDTA as the catalytic system

With PMDTA as the ligand (at 5 atm CO_2, 20°C), carboxylic acids **2** and **3** were formed in the ratio shown in Table 2. It is noteworthy that in all the examples examined a single CO_2 molecule was incorporated chemioselectively into the conjugated system in an hydrocarboxylation-type reaction, with exclusive addition to the triple bond.

The carboxylation of terminal enyne **1a** occurred regioselectively, the CO_2 becoming attached to the internal carbon of the triple bond. Isomers **2a** and **3a** were isolated in a 9:1 ratio. When the terminal alkynyl position of **1a** was substituted by a methyl or a propyl group, as in **1b** or **1c**, the reaction yielded, in the case of **1b**, **2b** and **3b** with loss of regioselectivity (**2b**/**3b** = 1). In the case of **1c**,

Table 2

Ni-PMDTA catalysed electrochemical carboxylation of 1,3-enynes at 20°C and 5 atm of CO_2

Entry	Enyne	Conversion (%)	Reaction products (% isolated yield) [a]		Ratio **2** **3**
1	**1a**	80	 **2a** (84)	 **3a** (9)	90 10
2	**1b**	40	 **2b** (38)	 **3b** (38)	50:50
3	**1c**	20	 **2c** (26)	 **3c** (49)	35 65
4	**1d**	70	 **2d** (43)	 **3d** (43)	50 50
5	**1e**	30	 **2e** (33)	 **3e** (33)	50 50
6	**1f**	20	 **2f** (52)	 **3f** (22)	70:30
7	**1g**	50	 **2g** (40)	 **3g** (40)	50:50

[a] For experimental conditions, see Experimental section. Yields refer to the amount of isolated methyl ester relative to the amount of enyne that has reacted

Table 3

$Ni(bipy)_3(BF_4)_2$ catalysed electrochemical carboxylation of 1,3-enynes at 20°C and 5 atm of CO_2

1 + CO_2 $\xrightarrow{\text{e, Ni-bipy (10\%)}}$ **2** + **3** + **4** (or **5**)

Entry	Enyne	Conversion (%)	Reaction products [a] (% isolated yield)	Ratio **2** **3**
1	**1a**	90	**2a** (68) + **3a** (7) + **5** (25)	90:10
2	**1b**	85 [b]	**2b** (38) + **3b** (21)	65 35
3	**1c**	40	**2c** (30) + **3c** (45) + **4c** (13)	40.60
4	**1d**	70	**2d** (36) + **3d** (36) + **4d** (7)	50.50
5	**1e**	45	**2e** (23) + **3e** (43) + **4e** (22)	35·65
6	**1f**	55	**2f** (38) + **3f** (25) + **4f** (27)	60 40
7	**1g**	55	**2g** (26) + **3g** (47) + **4g** (18)	35 65

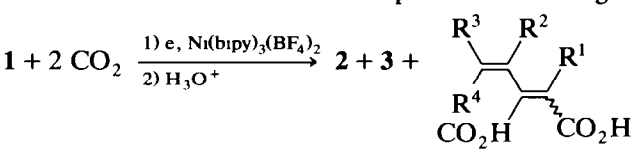
[a] See Table 2, note a. [b] In addition to **2b** and **3b**, diene from reduction of **1b** was formed in 29% yield

isomers **2c** and **3c** were formed with reversed regioselectivity (**2c**/**3c** ≅ 1/2) compared to **1a**. Each of these regioisomers is, however, a single stereoisomer, arising from *cis*-addition of H and CO_2H across the triple bond. This *cis*-stereoselectivity was found in all the examples that we examined.

Methylene derivatives **1d** and **1e** gave a 1:1 mixture of regioisomers. Both stereocontrolled (*Z*)- and (*E*)-6,8-tetradecaenynes **1f** and **1g** (prepared by selective reduction of the corresponding 1,3-diyne) were also carboxylated in order to examine the possibility of isomerization involving the conjugated double bond. The (*Z*)-isomer **1f** afforded **2f** and **3f** in a 7:3 ratio. The incorporation of CO_2 occurred in a stereocontrolled *cis*-addition on the triple bond as previously, without double bond isomerization involving the ene-part of the molecule. The (*E*)-enyne **1g** yielded both of the expected acids in a 1:1 mixture with no double bond equilibration.

Carboxylations with Ni-bipy as the catalytic system

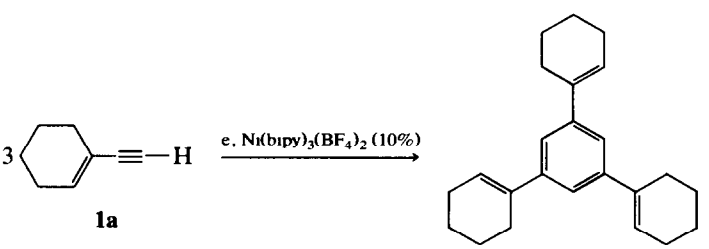
Table 3 shows the results obtained for the carboxylations catalysed by $Ni(bipy)_3(BF_4)_2$. Several differences from the results with the Ni-PMDTA systems are noteworthy. Better conversions are generally achieved under the same conditions. The main products are carboxylic acids **2** and **3**, but a double CO_2 incorporation was observed with several substrates (entries 3–7. This double carboxylation took place exclusively at the triple bond in a 1,2-addition, yielding unsaturated diacids of type **4** (eq. 1) in up to 27% (entry 6). A double carboxylation of electron-deficient alkynes by Ni-bipy, leading to saturated 1,2-diacids, has been observed previously [7b], but this is the first example of formation of maleic acid derivatives from C≡C in a one-step reaction starting from CO_2.



(1)

4

The terminal enyne **1a** gave carboxylic acid **2a** regioselectively (**2a**/**3a** = 9/1), as with Ni-PMDTA. However, with bipy as the ligand, a new compound **5** (not formed with PMDTA) was isolated in 25% yield. The product **5** results from cyclic trimerization of the yne-part of **1a**. Trimerization of alkynes in the presence of Ni^0 complexes is a known reaction, favoured in the case of terminal acetylenes [15]. When the electrolysis of **1a** in the presence of $Ni(bipy)_3(BF_4)_2$ (0.1 equiv.) was carried out in the absence of CO_2 (eq. 2), **5** was formed in 55% yield (35% of **1a** was recovered).



(2)

1a

5a (55%)

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

Cathode: $Ni^{II} + L + 2e \rightarrow LNi^{0}$

Scheme 2

This cyclization was not observed for internal enynes **1b–1g**.

The ratio **2**:**3** as a function of the enyne substitution showed the same trends as those observed with PMDTA. In the series **1a**, **1b** and **1c**, isomer **2** is very predominant in the case of terminal **1a**; the methyl-substituted **1b** reacts with loss of regioselectivity, and the propyl-substituted **1c** shows the reverse regiochemical behaviour, **3c** being the predominant isomer. This behaviour can be related to the electrocarboxylation of isolated triple bonds by Ni-bipy [7]: for terminal alkynes such as phenylacetylene a selective carboxylation of the 2-position is favoured, whereas in the case of phenylpropyne the regioselectivity is reversed.

Reaction mechanism

Consideration of the mechanism of the carboxylation may help understanding of the regiochemical outcome. The first step in the reaction is the electrochemical 2e reduction of Ni^{II} to Ni^{0} at the cathode. At the anode, consisting of a magnesium rod, the metal is oxidized into Mg^{2+} ions (Scheme 2). This is followed by coordination of the enyne and CO_2 to the LNi^{0} complex, as shown by cyclic voltammetry in the case of **1a** with Ni-bipy, shown in Fig. 1.

The reduction of $Ni(bipy)_3^{2+}$ to $Ni(bipy)_2$ in a DMF solution containing tetrabutylammonium tetrafluoroborate occurs reversibly at -1.2 V vs. SCE. This wave is followed by a one-electron reduction of the $Ni^{0}(bipy)_2$ at -1.9 V [16–18] as shown in curve a). The effect of the addition of 1 equiv. of **1a** is shown in curve b). The first wave is advanced to -1.15 V and becomes irreversible, and the

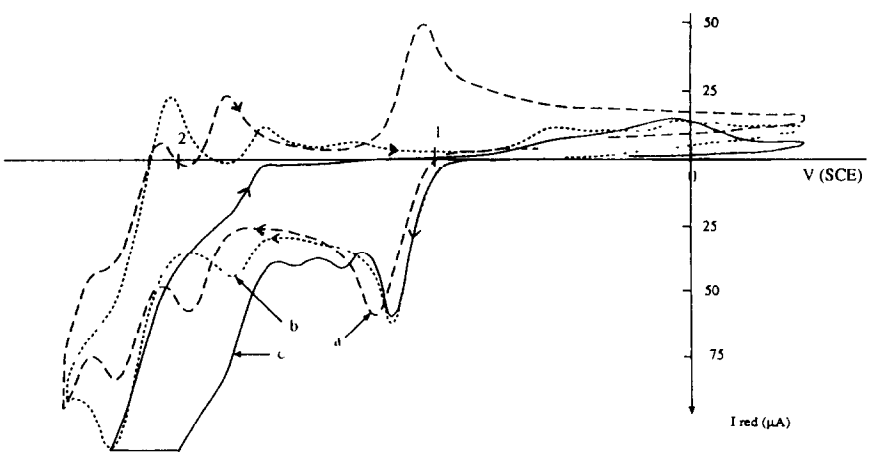


Fig. 1. Cyclic voltammograms obtained with freshly polished gold microelectrode (3 mm^2) at 20°C at a scan rate of 200 mV s^{-1} for a solution of $Ni(bipy)_3(BF_4)_2$ (0.3 mmol) in DMF (30 ml) containing 0.1 *M* tetrabutylammonium tetrafluoroborate as supporting electrolyte (a) Under argon (b) After addition of **1a** (0.3 mmol) (c) Solution as in (b) saturated with CO_2.

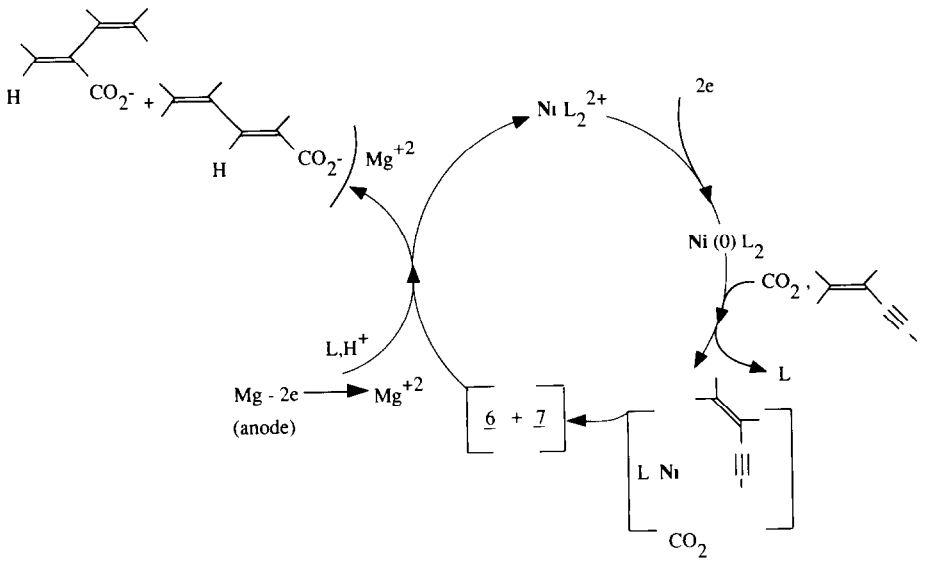


Fig 2 Proposed mechanistic cycle

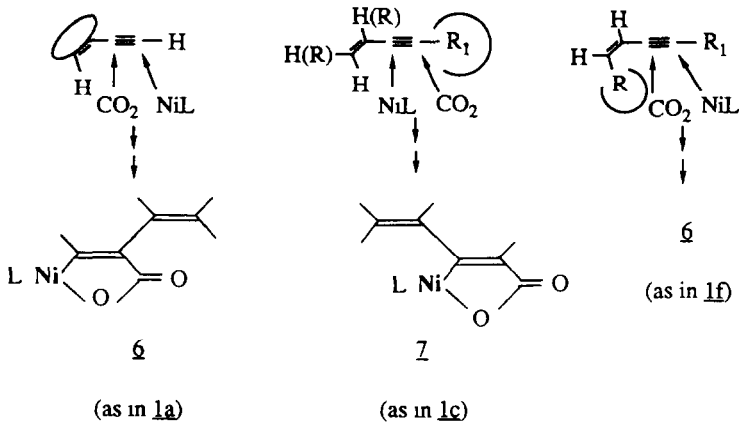
second wave at -1.9 V is shifted to -1.75 V, indicative of a rapid coordination of the enyne on the Ni^0 with a bipy-enyne exchange. In the presence of CO_2 (curve c)) the voltammogram exhibits a non-reversible Ni^{II}/Ni^0 transition at -1.15 V and an irreversible catalytic current at -1.6 V, these corresponding to the electron transfer to CO_2 coordinated to Ni-bipy. By analogy with the electrocarboxylation of monoalkynes by $Ni(bipy)_3(BF_4)_2$ [16] we suggest the formation of the new C–C bond via intermediate metallacycles of type **6** and **7** (Fig. 2). In the case of 4-octyne, an analogous metallacycle was isolated from the reaction [16]. In the presence of Mg^{2+} ions generated in the anodic oxidation process, the metallacycles are opened with formation of magnesium carboxylates and liberation of the nickel species into the catalytic cycle. The presence of the Mg^{2+} ions is essential for the catalytic reaction; the nickel is not recycled in the absence of these ions. The proton needed at the stage of cleavage of **6** and **7** comes from the supporting electrolyte or the DMF solvent [16].

The regiochemical outcome is controlled at the stage of metallacycle formation, and is essentially governed by steric factors, the metal occupying the less hindered part of the triple bond. When R^1 = H, intermediate **6** (leading to isomer **2**) strongly predominates (Scheme 3). The ratio of **7** (e.g. acid **3**) increases when R^1 provides more steric hindrance than the ene-portion.

A less effective coordination of CO_2 to the Ni-PPh_3 system could account for the low reactivity observed for enyne carboxylation when triphenylphosphine is used as the ligand.

Conclusion

We have presented the first example of incorporation of carbon dioxide into conjugated enyne derivatives catalysed by electrogenerated nickel complexes. For



Scheme 3. Predominant regioisomeric metallacycles **6** and **7** as a function of the steric hindrance of the enyne

both Ni-PMDTA and Ni-bipy systems studied, the electrocarboxylation involves a *cis* reductive addition of CO_2 to the yne-part of the molecule and enables the preparation of stereodefined doubly-unsaturated carboxylic acids of type **2** and **3**. The regiochemistry of the CO_2 incorporation parallels that in the electrocarboxylation of monoalkynes: terminal 1,3-enynes ($R^1 = H$) show high regio-control, in contrast to substituted derivatives (R^1 = alkyl).

Experimental section

All the chemicals employed were of reagent grade. Dimethylformamide (Prolabo) was distilled under argon from calcium hydride and copper sulphate under reduced pressure and was stored over 4A molecular sieves. Tetrabutylammonium tetrafluoroborate ($TBABF_4$, Fluka) was dried overnight at 70°C *in vacuo*. $Ni(bipy)_3(BF_4)_2$, **1**, was prepared as described in ref. 7a. Carbon dioxide was N45 (Alphagaz).

^1H and ^{13}C NMR spectra were recorded on a Bruker AC 200 E spectrometer and IR spectra on a Perkin Elmer 577 spectrophotometer. Mass spectra were obtained with a Finnigan ITD 800 spectrometer coupled to a Varian 300 chromatograph with DB-1 capillary column, either by electron impact or with CH_4 or NH_3 as the ionizing agent. Gas chromatography was performed on either a Intersmat IGC 120 chromatograph fitted with a Se-30 stainless steel (1/8 in–13 ft) column or a Delsi DI 200 instrument equipped with a 25 m DB-1 capillary column.

General electrolysis procedure

For carboxylations at atmospheric CO_2 pressure, the two electrode, single-compartment electrochemical cell was similar to that described previously [7a]. A closed stainless-steel cell was used for carboxylations at $P(CO_2) = 5$ atm. The anode was a cylindrical rod of magnesium (99.8, diameter 1 cm) surrounded by a carbon fibre cathode (apparent surface 20 cm^2). A DMF (40 ml) solution of nickel complex (either $Ni(bipy)_3(BF_4)_2$ [7a] (0.3 mmol) or $NiBr_2 \cdot dme$ (0.3 mmol) + PMDTA (0.6 mmol)), containing $^nBu_4N^+BF_4^-$ (0.3 mmol) and **1** (3 mmol) was

electrolysed under carbon dioxide (Alphagaz N45, 1 or 5 atm), at a constant intensity of 50 mA. Faradaic yields were in the range of 50–80% for reaction times of 5–7 h.

The reaction mixture was esterified directly in DMF by adding anhydrous K_2CO_3 (4 mmol) and iodomethane (8 mmol) and stirring the mixture at 50°C for 5 h. The solution was hydrolysed and extracted with Et_2O, and the organic layers washed with H_2O, dried over $MgSO_4$, and evaporated. The methyl esters corresponding to acids **2**, **3** and **4** were isolated by column chromatography (normal or flash on silica gel) with pentane/Et_2O mixtures as eluent.

Following the general electrolysis procedure, the carboxylic acid methyl esters were isolated in the yields reported in Tables 2 and 3.

*2-(cyclohex-1-ene)-prop-2-enoic acid methyl ester (**2a**).* ^{1}H NMR ($CDCl_3$) δ 5.97 (s, 1H), 5.72 (s, 1H), 5.48 (s, 1H), 3.77 (s, 3H), 2.17–2.12 (m, 4H), 1.75–1.54 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 168.31, 143.30, 133.17, 128.63, 119.16, 51.71, 26.19, 25.52, 22.39, 21.71; IR (neat, NaCl) 3100, 3020, 2940, 2860, 2820, 1720, 1630, 1610, 1590 cm^{-1}; GCMS (*m/e*, %) 166 (M^+, 100), 151(16.9), 135(26.6), 107(67.7); exact mass calcd. for $C_{10}H_{14}O_2$ 166.0994, found 166.0989.

*(E)-3-(cyclohex-1-ene)-prop-2-enoic acid methyl ester (**3a**).* ^{1}H NMR ($CDCl_3$) δ 7.29 (d, J = 15.8 Hz, 1H), 6.18 (s, 1H), 5.77 (d, J = 15.8 Hz, 1H), 3.75 (s, 3H), 2.22–2.14 (m, 4H), 1.76–1.56 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 168.57, 148.30, 138.92, 134.83, 114.04, 51.37, 26.39, 24.03, 21.96 (2C); IR (neat, NaCl) 3020, 2920, 2850, 2830, 1720, 1630, 1615 cm^{-1}; GCMS (*m/e*, %) 166(M^+, 100), 151(29.8), 135(38.7), 107(63.2); exact mass calcd. for $C_{10}H_{14}O_2$ 166.0994, found 166.0998.

*(2E)-2-(cyclohex-1-ene)-but-2-enoic acid methyl ester (**2b**).* ^{1}H NMR ($CDCl_3$) δ 6.84 (t, J = 7.1 Hz, 1H), 5.45 (s, 1H), 3.72 (s, 3H), 2.23–2.16 (m, 2H), 2.14–2.09 (m, 2H), 1.79 (d, J = 7.1 Hz, 3H), 1.75–1.62 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 167.76, 142.05, 134.86, 132.82, 127.41, 51.59, 28.48, 25.17, 22.71, 22.00, 15.05; IR (neat, NaCl) 3020, 2920, 2850, 2830, 1710, 1630; GCMS (*m/e*, %) 180(M^+, 100), 165(5.3), 149(33.5), 121(37.2); exact mass calcd. for $C_{11}H_{16}O_2$ 180.1150, found 180.1138.

*(2E)-2-methyl-3-(cyclohex-1-ene)-prop-2-enoic acid methyl ester (**3b**).* ^{1}H NMR ($CDCl_3$) δ 7.06 (s, 1H), 5.93 (s, 1H), 3.75 (s, 3H), 2.14–2.10 (m, 4H), 2.02 (s, 3H), 1.74–1.60 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 169.71, 137.90, 136.91, 133.79, 124.46, 51.76, 28.48, 25.97, 22.65, 21.71, 14.06; IR (neat, NaCl) 3020, 2920, 2850, 2830, 1715, 1620 cm^{-1}; GCMS (*m/e*, %) 180(M^+, 100), 165(5.8), 149(33.7), 121(72.0); exact mass calcd. for $C_{11}H_{16}O_2$ 180.1150, found 180.1145.

*(2E)-2-(cyclohex-1-ene)-hex-2-enoic acid methyl ester (**2c**).* ^{1}H NMR ($CDCl_3$) δ 6.74 (t, J = 7.6 Hz, 1H), 5.46 (s, 1H), 3.72 (s, 3H), 2.22–2.01 (m, 6H), 1.73–1.58 (m, 4H), 1.54–1.26 (m, 2H), 0.89 (t, J = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 169.61, 142.18, 134.85, 133.48, 129.68, 51.66, 29.69, 28.10, 26.06, 23.53, 22.75, 21.74, 14.15; IR (neat, NaCl) 3020, 2950, 2920, 2870, 2850, 1710, 1665, 1620 cm^{-1}; GCMS (*m/e*, %) 208(M^+, 73.5), 179(55.6), 177(11.7), 165(8.3), 149(10.5), 91(100); exact mass calcd. for $C_{13}H_{20}O_2$ 208.1463, found 208.1462.

*(2E)-2-propyl-3-(cyclohex-1-ene)-prop-2-enoic acid methyl ester (**3c**).* ^{1}H NMR ($CDCl_3$) δ 6.15 (s, 1H), 5.72 (s, 1H), 3.74 (s, 3H), 2.42 (t, J = 7.1 Hz, 2H), 2.23–2.02 (m, 4H), 1.71–1.57 (m, 4H), 1.52–1.23 (m, 2H), 0.86 (t, J = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 167.95, 143.24, 136.08, 133.23, 127.11, 51.66, 31.24, 28.84, 25.19, 22.75, 22.26, 22.02, 13.93; IR (neat, NaCl) 3020, 2950, 2920, 2870, 2850, 1715, 1660, 1620 cm^{-1}; GCMS (*m/e*, %) 208(M^+, 85.9), 179(31.9), 177(18.5), 149(45.9), 91(100); exact mass calcd. for $C_{13}H_{20}O_2$ 208.1463, found 208.1443.

*(2E)-2-(1-methylethenyl)-hept-2-enoic acid methyl ester (**2d**).* ^{1}H NMR ($CDCl_3$) δ 6.79 (t, J = 7.6 Hz, 1H), 5.07 (s, 1H), 4.77 (s, 1H), 3.74 (s, 3H), 2.19 (m, 2H), 1.88 (s, 3H), 1.38–1.17 (m, 4H), 0.91 (t, J = 6.5 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 167.25, 143.38, 139.93, 132.95, 118.94, 51.42, 30.90, 28.73, 22.84, 22.19, 13.57; IR (neat, NaCl) 3080, 3020, 2950, 2920, 2870, 2860, 1715, 1625 cm^{-1}; GCMS (*m/e*, %) 182(M^+, 22.0), 167(65.1), 153(29.4), 151(44.0), 139(77.1), 123(37.6), 107(100); exact mass calcd. for $C_{11}H_{18}O_2$ 182.1307, found 182.1308.

*(2E)-2-butyl-4-methyl-penta-2,4-dienoic acid methyl ester (**3d**).* ^{1}H NMR ($CDCl_3$) δ 7.09 (s, 1H), 5.16 (m, 2H), 3.75 (s, 3H), 2.47 (t, J = 7.3 Hz, 2H), 1.94 (s, 3H), 1.36–1.16 (m, 4H), 0.91 (t, J = 6.5 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 168.67, 140.47, 140.24, 132.26, 115.90, 51.42, 32.05, 26.99, 22.56, 22.29, 13.57; IR (neat, NaCl) 3080, 3020, 2950, 2920, 2870, 2860, 1715, 1625 cm^{-1}; GCMS (*m/e*, %) 182(M^+, 39.1), 167(11.8), 153(14.3), 151(19.9), 139(14.3), 125(30.4), 123(16.2), 79(100); exact mass calcd. for $C_{11}H_{18}O_2$ 182.1307, found 182.1297.

*(2E)-2-ethenyl-non-2-enoic acid methyl ester (**2e**).* ^{1}H NMR ($CDCl_3$) δ 6.33 (dd, J = 17.1 Hz, J = 10.9 Hz, 1H), 5.96 (t, J = 7.7 Hz, 1H), 5.24 (d, J = 17.0 Hz, 1H), 5.08 (d, J = 10.9 Hz, 1H); 3.80 (s, 3H), 2.33–2.23 (m, 2H), 1.42–1.28 (m, 8H), 0.88 (t, J = 6.5 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 168.38, 140.25, 132.79, 129.03, 114.48, 51.47, 31.55, 29.66, 28.84, 28.64, 22.51, 13.96; IR (neat, NaCl) 3090, 3010, 2950, 2920, 2870, 2850, 1725, 1630, 1590 cm^{-1}; GCMS (*m/e*, %) 196(M^+, 22.8), 165(12.6), 139(40.9), 137(10.2), 81(100); exact mass calcd. for $C_{12}H_{20}O_2$ 196.1463, found 196.1471.

*(2E)-2-hexyl-penta-2,4-dienoic acid methyl ester (**3e**).* ^{1}H NMR ($CDCl_3$) δ 7.15 (d, J = 11.4 Hz, 1H), 6.65 (ddd, J = 16.9 Hz, J = 11.4 Hz, J = 10.9 Hz, 1H), 5.56 (d, J = 16.9 Hz, 1H), 5.44 (d, J = 10.8 Hz, 1H), 3.76 (s, 3H), 2.41 (t, J = 7.9 Hz, 2H), 1.41–1.26 (m, 8H), 0.88 (t, J = 6.5 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 168.47, 138.45, 134.65, 132.00, 124.19, 51.63, 31.55, 29.57, 29.08, 26.93, 22.51, 13.96; IR (neat, NaCl) 3085, 3010, 2950, 2920, 2870, 2850, 1720, 1630, 1590 cm^{-1}; GCMS (*m/e*, %) 196(M^+, 36.6), 165(15.8), 153(26.7), 137(11.4), 125(20.5), 111(73.3), 67(100); exact mass calcd. for $C_{12}H_{20}O_2$ 196.1463, found 196.1462.

*2{(1E)-1-hexylidene}-(3Z)-non-3-enoic acid methyl ester (**2f**).* ^{1}H NMR ($CDCl_3$) δ 6.82 (t, J = 7.4 Hz, 1H), 5.92 (d, J = 11.4 Hz, 1H), 5.66 (dt, J = 11.3 Hz, J = 7.2 Hz, 1H), 3.74 (s, 3H), 2.27–2.12 (m, 2H), 1.92–1.82 (m, 2H), 1.46–1.26 (m, 12H), 0.88 (m, 6H); ^{13}C NMR ($CDCl_3$) δ 168.34, 144.62, 135.10, 128.78, 121.90, 51.64, 31.49, 31.44, 29.50, 29.02, 28.59, 28.02, 22.40 (2C), 13.91 (2C); IR (neat, NaCl) 3010, 2950, 2910, 2850, 1715, 1635, 1600 cm^{-1}; GCMS (*m/e*, %) 252(M^+, 20.7), 209(14.0), 195(31.1), 193(15.2), 41(100); exact mass calcd. for $C_{16}H_{28}O_2$ 252.2089, found 252.2104.

*(2E,4Z)-2-pentyl-deca-2,4-dienoic acid methyl ester (**3f**).* ^{1}H NMR ($CDCl_3$) δ 7.16 (d, J = 11.2 Hz, 1H), 6.33 (dd, J = 11.1 Hz, J = 11.1 Hz, 1H), 5.66 (dt, J = 11.3 Hz, J = 7.2 Hz, 1H), 3.76 (s, 3H), 2.38 (t, J = 6.8 Hz, 2H), 2.17–2.05 (m, 2H), 1.48–1.25 (m, 12H), 0.88 (m, 6H); ^{13}C NMR ($CDCl_3$) δ 169.15, 143.37, 138.87, 129.70, 125.70, 51.59, 33.15, 31.59, 31.28, 29.26, 28.51, 26.77, 22.40 (2C), 13.91 (2C); IR (neat, NaCl) 3010, 2950, 2910, 2850, 1710, 1630, 1600 cm^{-1}; GCMS (*m/e*, %) 252(M^+, 26.3) 221(14.3), 195(17.4), 181(100); exact mass calcd. for $C_{16}H_{28}O_2$ 252.2089, found 252.2071.

*(E,E)-2-hexylidene-non-3-enoic acid methyl ester (**2g**).* ^{1}H NMR ($CDCl_3$) δ 6.62 (t, J = 7.5 Hz, 1H), 6.11 (m, 1H), 6.06 (d, J = 15.1 Hz, 1H), 3.74 (s, 3H),

2.34–2.23 (m, 4H), 1.43–1.30 (m, 12H), 0.89 (t, $J = 6.8$ Hz, 6H); ^{13}C NMR ($CDCl_3$) δ 168.09, 142.11, 136.37, 129.88, 121.87, 51.48, 33.51, 31.46, 31.34, 31.28 (2C), 28.86, 22.42 (2C), 13.92 (2C); IR (neat, NaCl) 3020, 2950, 2920, 2870, 2860, 1710, 1640, 1600 cm^{-1}; GCMS (*m/e*, %) 252(M^+, 53.9), 221(14.8), 209(27.0), 195(41.7), 181(13.9), 79(100); exact mass calcd. for $C_{16}H_{28}O_2$ 252.2089, found 252.2076.

*(E,E)-2-pentyl-deca-2,4-dienoic acid methyl ester (**3g**).* ^{1}H NMR ($CDCl_3$) δ 7.15 (d, $J = 11.1$ Hz, 1H), 6.33 (dd, $J = 15.0$ Hz, $J = 11.1$ Hz, 1H), 6.04 (m, 1H), 3.74 (s, 3H), 2.41–2.30 (m, 2H), 2.17 (t, $J = 6.8$ Hz, 2H), 1.41–1.32 (m, 12H), 0.89 (t, $J = 6.8$ Hz, 6H); ^{13}C NMR ($CDCl_3$) δ 168.79, 143.39, 138.88, 129.71, 125.70, 51.48, 33.15, 31.59, 29.27, 28.61, 28.51, 26.77, 22.42 (2C), 13.92 (2C); IR (neat, NaCl) 3020, 2950, 2920, 2870, 2860, 1715, 1640, 1600 cm^{-1}; GCMS (*m/e*, %) 252(M^+, 21.1), 221(10.2), 195(8.8), 181(100); exact mass calcd. for $C_{16}H_{28}O_2$ 252.2089, found 252.2074.

*1,3,5-(tricyclohex-1-ene)-benzene (**5**).* ^{1}H NMR ($CDCl_3$) δ 7.23 (s, 3H), 6.09 (s, 3H), 2.43–2.39 (m, 6H), 2.22–2.17 (m, 6H), 1.83–1.60 (m, 12H); ^{13}C NMR ($CDCl_3$) δ 142.58, 137.20, 124.56, 120.43, 27.70, 25.84, 23.09, 22.19; IR (CCl_4, NaCl) 3020, 2920, 2850, 2830, 1630, 1580 cm^{-1}; GCMS (*m/e*, %) 318(M^+, 100), 237(11.1); exact mass calcd. for $C_{24}H_{30}$ 318.2348, found 318.2357.

*2-(cyclohex-1-ene)-3-propyl-buten-1,4-dioic acid dimethylester (**4c**).* ^{1}H NMR ($CDCl_3$) δ 5.63 (s, 1H), 3.76 (s, 3H), 3.69 (s, 3H), 2.40 (t, $J = 7.9$ Hz, 2H), 2.04 (m, 4H), 1.68–1.57 (m, 4H), 1.53–1.40 (m, 2H), 0.92 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 170.20, 167.90, 139.45, 138.12, 135.45, 127.89, 51.87, 51.59, 33.27, 27.73, 25.46, 22.52, 21.69, 21.53, 13.72; IR (neat, NaCl) 3030, 2950, 2920, 2870, 2850, 1730, 1720, 1660, 1610 cm^{-1}; GCMS (*m/e*, %) 266(M^+, 5.3), 265(11.1), 237(100), 235(41.5), 207(7.6); exact mass calcd. for $C_{15}H_{22}O_4$ 266.1518, found 266.1534.

*2-(1-methylethenyl)-3-butyl-buten-1,4-dioic acid dimethylester (**4d**).* ^{1}H NMR ($CDCl_3$) δ 5.19 (s, 1H), 4.94 (s, 1H), 3.79 (s, 3H), 3.75 (s, 3H), 2.37 (t, $J = 6.6$ Hz, 2H), 1.89 (s, 3H), 1.47–1.20 (m, 4H), 0.89 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 169.28, 167.35, 139.98, 139.27, 138.25, 117.21, 52.28, 52.17, 37.63, 30.62, 30.56, 22.62, 13.77; IR (neat, NaCl) 3080, 2960, 2920, 2870, 2860, 1730, 1720, 1650, 1625 cm^{-1}; GCMS (*m/e*, %) 225(M^+ – Me, 6.8), 209(32.3), 197(100), 181(6.4); exact mass calcd. for $C_{13}H_{20}O_4$ 240.1362, found 240.1375.

*2-ethenyl-3-hexyl-buten-1,4-dioic acid dimethyl ester (**4e**).* ^{1}H NMR ($CDCl_3$) δ 6.65 (dd, $J = 10.9$ Hz, $J = 17.4$ Hz, 1H), 5.55 (d, $J = 10.7$ Hz, 1H), 5.49 (d, $J = 17.4$ Hz, 1H), 3.85 (s, 3H), 3.76 (s, 3H), 2.44 (t, $J = 6.7$ Hz, 2H), 1.45–1.22 (m, 8H), 0.87 (t, $J = 6.8$ Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 168.72, 167.97, 139.97, 132.83, 129.52, 122.99, 52.24 (2C), 31.46, 29.12, 27.84, 22.49 (2C), 13.99; IR (neat, NaCl) 3090, 3020, 2950, 2920, 2870, 2850, 1735, 1720, 1655, 1620 cm^{-1}; GCMS (*m/e*, %) 223(M^+ – OMe, 100), 195(80.1), 183(42.2); exact mass calcd. for $C_{14}H_{22}O_4$ 254.1518, found 254.1513.

*2-{(1Z)-hept-1-enyl}-3-pentyl-buten-1,4-dioic acid dimethyl ester (**4f**).* ^{1}H NMR ($CDCl_3$) δ 5.97 (d, $J = 11.5$ Hz, 1H), 5.75 (dt, $J = 11.5$ Hz, $J = 7.3$ Hz, 1H), 3.77 (s, 3H), 3.76 (s, 3H), 2.33 (t, $J = 7.0$ Hz, 2H), 2.04–1.94 (m, 2H), 1.45–1.26 (m, 12H), 0.88 (t, $J = 6.7$ Hz, 6H); ^{13}C NMR ($CDCl_3$) δ 168.84, 168.56, 139.11, 138.16, 133.77, 121.38, 52.12 (2C), 31.54, 31.42, 29.96, 28.84, 28.61, 27.29, 22.42, 22.32, 13.94, 13.85; IR (neat, NaCl) 3015, 2950, 2920, 2870, 2850, 1735, 1725, 1620, 1585 cm^{-1}; GCMS (*m/e*, %) 279(M^+ – OMe, 68.4), 251(39.0), 221(42.1), 41(100); exact mass calcd. for $C_{18}H_{30}O_4$ 310.2144, found 310.2157.

*2-{(1E)-hept-1-enyl}-3-pentyl-buten-1,4-dioic acid dimethylester (**4g**).* ^{1}H NMR ($CDCl_3$) δ 6.32 (d, J = 15.8 Hz, 1H), 5.95 (dt, J = 15.8 Hz, J = 6.9 Hz, 1H), 3.85 (s, 3H), 3.75 (s, 3H), 2.41 (t, J = 6.9 Hz, 2H), 2.25–2.15 (m, 2H), 1.44–1.22 (m, 12H), 0.89 (t, J = 6.5 Hz, 6H); ^{13}C NMR ($CDCl_3$) δ 169.48, 167.61, 141.40, 141.23, 129.11, 123.32, 52.17, 52.09, 33.53, 31.60, 31.29, 28.76, 28.25, 27.54, 22.39, 22.35, 13.90 (2C); IR (neat, NaCl) 3025, 2950, 2920, 2870, 2850, 1735, 1715, 1625, 1595 cm^{-1}; GCMS (m/e, %) 309(M^+ – H, 24.2), 279(88.4), 251(74.6), 238(93.1), 221(100); exact mass calcd. for $C_{18}H_{30}O_4$ 310.2144, found 310.2162.

References

1 A Behr, Carbon Dioxide Activation by Metal Complexes, VCH, Weinheim,1988
2 D. Walther, Coord Chem Rev , 79 (1978) 135
3 P. Braunstein, D Matt and D Nobel, Chem. Rev , 88 (1988) 747
4 H Hoberg, D. Schaefer, G Burkhart, C Kruger and M J Romao, J. Organomet Chem , 266 (1984) 203
5 Y Inoue, Y Itoh, H Kazama and H. Hashimoto, Bull Chem. Soc Jpn., 53 (1980) 3329
6 D Walther, H Schonberg, E Dinjus and J Sieler, J Organomet Chem , 334 (1987) 377
7 (a) E Duñach and J. Périchon, J. Organomet Chem., 352 (1988) 239, (b) E Duñach, S Dérien and J Périchon, J Organomet Chem., 364 (1989) C33, (c) E Labbé, E Duñach and J Périchon, J Organomel Chem., 353 (1988) C51.
8 S Inoue and N Yamazaki, Organic and Bioorganic Chemistry of CO_2, Kodansha, Tokyo, 1982
9 G V M Sharma, B M Chondary, M.R. Sarma and K K Rao, J Org. Chem , 54 (1989) 2997
10 Y Wakatsuki, H Yamazaki, Y Maryama and I Shimizu, J. Chem Soc , Chem Commun , (1991) 261
11 R. Aksela and A.C Oehlschlager, Tetrahedron, 47 (1991) 1163
12 J F Normant, Tetrahedron Lett , (1982) 5151, see also ref 11
13 E Duñach and J. Périchon, Synlett, 1 (1990) 143
14 L Brandsma, Preparative Acetylenic Chemistry, 2nd ed , Elsevier, Amsterdam, 1988, and references therein
15 G Wilke, Pure Appl Chem , 50 (1978) 677
16 S Dérien, E Duñach and J Périchon, J Am Chem Soc , 113 (1991) 8447
17 S. Daniele, P Ugo, G Bontempelli and M Fiorani, J Electroanal Chem , 219 (1987) 259
18 L Garnier, Y Rollin and J Périchon, New J. Chem , 13 (1989) 53