Activation of Carbon Dioxide: Nickel-Catalyzed Electrochemical Carboxylation of Diynes

Sylvie Dérien,[†] Jean-Claude Clinet,[‡] Elisabet Duñach,[*,†] and Jacques Périchon[†]

Laboratoire d'Electrochimie, Catalyse et Synthèse Organique, C.N.R.S., UMR no. 28, 94320 Thiais, France, and Institut de Chimie Moléculaire d'Orsay, UA 255, Bat. 420, Université Paris-Sud, 91405 Orsay Cedex, France

Received September 28, 1992

The simultaneous activation of carbon dioxide and diynes by electrogenerated LNi(0) complexes (L = bpy, pentamethyldiethylenetriamine: PMDTA) enables the selective incorporation of one molecule of CO_2 into the unsaturated systems and the preparative-scale electrosyntheses of carboxylic acids. A series of nonconjugated diynes afforded selectively linear or cyclic adducts depending on the ligand. Diynes bearing both a terminal and an internal triple bond gave exclusive CO_2 incorporation into the terminal alkynyl group, regioselectively at the 2-position. The electrocarboxylation of 1,3-diynes with the Ni–PMDTA catalytic system yielded, regio- and stereoselectively, (*E*)-2-vinylidene-3-yne carboxylic acids in one step. The electrosyntheses were carried out in single-compartment cells fitted with a consumable magnesium anode, and utilized a catalytic amount of an air-stable Ni(II) complex as the catalyst precursor. Cyclic voltammetry studies revealed that both carbon dioxide and the diynes are able to coordinate to LNi(0)-generated species in DMF.

Introduction

The use and recycling of carbon dioxide as source of organic compounds via chemical reactions is receiving much attention, due to its undesirable accumulation in the atmosphere as well as the accelerated depletion of oil reserves. The fixation of CO_2 may also contribute to a better understanding of photosynthetic, bioorganic, and chemical processes.[1]

Only a few industrial processes are currently using CO_2:[2] synthesis of urea, acetylsalicylic acid via the Kolbe Smith reaction, production of cyclic carbonates, and methanol synthesis. These limited industrial applications are related to the fact that CO_2 is a thermodynamically stable and kinetically inert molecule.

The activation of CO_2 can be brought about through its coordination to transition metal complexes.[3,4] The simultaneous activation of CO_2 and unsaturated hydrocarbons by metal complexes represents an interesting possibility for creating new carbon–carbon bonds, thus allowing the utilization of CO_2 as a raw material in the synthesis of fine chemicals.

In particular, electron-rich Ni(0) complexes have shown interesting activity toward CO_2 incorporation into unsaturated hydrocarbons, such as alkynes, alkenes, and dienes, leading to the synthesis of carboxylic acids and esters.[5] These reactions are generally stoichiometric, and there are only a few catalytic and homogeneous processes resulting in CO_2 coupling reactions.[5a,b–7] Among conjugated systems, the Pd-, Ni-, and Rh-catalyzed carboxylations of 1,3-dienes have been thoroughly investigated.[1,2] Recently, the electrocarboxylation of 1,3-enynes has also been reported.[8]

We have been concerned with the fixation of CO_2 into unsaturated hydrocarbons via electrosynthesis. Electrochemical methodology applied to organic[9] and organometallic[10] chemistry is of considerable interest. Recently, a new electrochemical method has been developed, based on the use of sacrificial anodes in undivided cells.[11] This process associates the anodic oxidation of a metal such as Mg, Al, or Zn to the cathodic reduction of an organic substrate or a metal complex. Several applications concerning the reductive functionalization of organic halides have demonstrated the utility of this methodology.[11a]

Our electrochemical approach is based on the use of a catalytic amount of a Ni(II) salt as the starting material. Ni(0) complexes associated to the appropriate ligands, L, are generated "in situ" by a two-electron reduction. The electrogenerated $L_nNi(0)$ complexes are able to activate both CO_2 and an unsaturated hydrocarbon, resulting in the formation of a new C–C bond. Using undivided cells associated with a Mg anode, CO_2 (at a pressure of 1 atm) has been incorporated to several alkynes in a Ni–bpy (bpy

---

[*] Actual address: Lab, Chimie Moléculaire, URA 426, Université Nice-Sophia Antipolis, 06108 Nice Cedex 2, France.

[†] Laboratoire d'Electrochimie, Catalyse et Synthèse Organique.

[‡] Institut de Chimie Moléculaire d'Orsay.

(1) Inoue, S.; Yamazaki, N. *Organic and Bio-Organic Chemistry of Carbon Dioxide*; Kodansha Ltd.: Tokyo, 1982.

(2) Behr, A. *Carbon Dioxide Activation by Metal Complexes*; VCH: Weinheim, 1988.

(3) Aresta, M.; Forti, G. *Carbon Dioxide as a Source of Carbon*; Nato Asi Ser. C; Reidel: Dordrecht, 1987; Vol. 206.

(4) Sneeden, R. P. A. Reactions of Carbon Dioxide. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, U.K., 1982; Vol. 8.

(5) (a) Walther, D. *Coord. Chem. Rev.*, **1987**, *79*, 135 and references cited therein. (b) Braunstein, P.; Matt, D.; Nobel, D. *Chem. Rev.* **1988**, *88*, 747. (c) Hoberg, H.; Schaefer, D.; Burkhart, G.; Krüger, C.; Romao, M. J. *J. Organomet. Chem.* **1984**, *266*, 203 and references cited therein.

(6) Mahé, R.; Sasaki, Y.; Bruneau, C.; Dixneuf, P. H. *J. Org. Chem.* **1989**, *54*, 1518.

(7) Dérien, S.; Duñach, E.; Périchon, J. *J. Am. Chem. Soc.* **1991**, *113*, 8447.

(8) Dérien, S.; Clinet, J. C.; Duñach, E.; Périchon, J. *J. Organomet. Chem.* **1992**, *424*, 213.

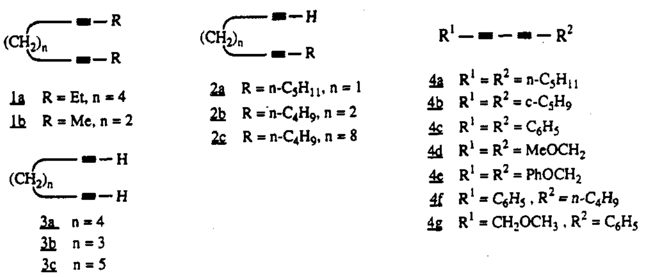
(9) (a) Baizer, M. M. *Tetrahedron* **1989**, *45*, 935 (Report 161). (b) Shono, T. *Tetrahedron* **1984**, *40*, 811 (Report 160). (c) Electrosynthesis involving CO_2: Silvestri, G. *NATO ASI Ser., Ser. C* **1987**, *206*, 339.

(10) (a) Grobe, J.; Scheider, B. H.; Zimmermann, H. Z. *Naturforsch., B: Anorg. Chem., Org. Chem.* **1984**, *39*, 957. (b) Lehmkuhl, H.; Mehler, K.; Hauschild, G. *Chem. Ber.* **1983**, *116*, 438. (c) Magdesieva, T. V.; Butin, K. P.; Reutov, O. A. *Russ. Chem. Rev. (Engl. Transl.)* **1988**, *57*, 864. (d) Torii, S. *Synthesis* **1986**, 873. (e) Efimov, O. N.; Strelets, V. V. *Coord. Chem. Rev.* **1990**, *99*, 15.

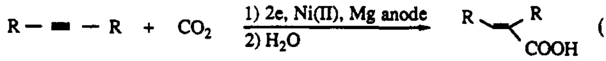
(11) (a) Chaussard, J.; Folest, J. C.; Nédélec, J. Y.; Périchon, J.; Sibille, S.; Troupel, M. *Synthesis* **1990**, *5*, 369. (b) Silvestri, G.; Gambino, S.; Filardo, G. *Acta Chem. Scand.* **1991**, *45*, 987.

0022-3263/93/1958-2578$04.00/0

Scheme I



= 2,2′-bipyridine) catalyzed hydrocarboxylation-type reaction leading to unsaturated carboxylic acids[7] (eq 1).



$$R-\equiv-R + CO_2 \xrightarrow[2)\ H_2O]{1)\ 2e,\ Ni(II),\ Mg\ anode} RCH{=}C(R)COOH \quad (1)$$

The present study is devoted to the electrochemical and synthetic aspects of this nickel-catalyzed electroreductive carboxylation applied to both conjugated and nonconjugated diynes. Several air-stable Ni(II) complexes such as $Ni(bpy)_3(BF_4)_2$ or $NiBr_2{\cdot}DME$ (DME = dimethoxyethane) associated to basic polyamines or to phosphines were used as the catalyst precursors. Preliminary results on the reactivity of 1,7-octadiyne[12] and 1,3-diynes[13] have already been reported. To our knowledge, no other electrochemical carboxylation of diynes has been described.

Diyne molecules have been extensively used for building polycyclic frameworks via intramolecular reactions.[14] In the presence of CO_2 under elevated pressures (superior to 50 atm), nonconjugated diynes have been reported to yield bicyclic pyrones by the use of air-sensitive nickel-phosphine complexes.[15]

Results

Electrochemical Studies. Nonconjugated Diynes. Internal 3,9-dodecadiyne, **1a**, and terminal 1,7-octadiyne, **3a** (Scheme I), were chosen as model compounds to study the electrochemical behavior of nonconjugated diynes in the presence of $Ni(bpy)_3(BF_4)_2$ and of CO_2 in dimethylformamide (DMF). Reduction of **1a** or **3a** alone occurs at less than −2.7 V vs SCE. At this potential we observe the reduction of the solvent. The results of cyclic voltammetry of $Ni(bpy)_3^{2+}$ solutions in DMF, containing tetrabutylammonium tetrafluoroborate as supporting electrolyte, are presented in Figure 1, curve a. The $Ni(bpy)_3^{2+}/Ni(bpy)_2$ + bpy reversible two-electron reducing process at −1.2 V is followed by a reversible one-electron reduction of $Ni(bpy)_2$ at −1.9 V (Scheme II) and the reduction of free bpy ligand at −2.2 V.[7] The addition of 0.5 and 1 equiv of **1a** causes a shift of the Ni(II)/Ni(0) reduction peak of curve a from −1.2 to −1.15 V as shown in curves b and c, Figure 1. The further Ni(0) complex reduction peak appears, respectively, at −1.85 and at −1.8 V for curves b and c instead of −1.9 V for curve a. Moreover, an increase of the peak intensity corresponding to the reduction of free bpy is observed at −2.2 V. In curve b, the intensity of the reoxidation peak of Ni(0) at −1.0 V decreases and a new reoxidation peak appears around −0.6 V. Upon addition of 1 equiv of **1a** per nickel (curve c), the Ni(II)/Ni(0) reduction peak becomes less reversible at the expense of a more intense reoxidation peak at −0.6 V.

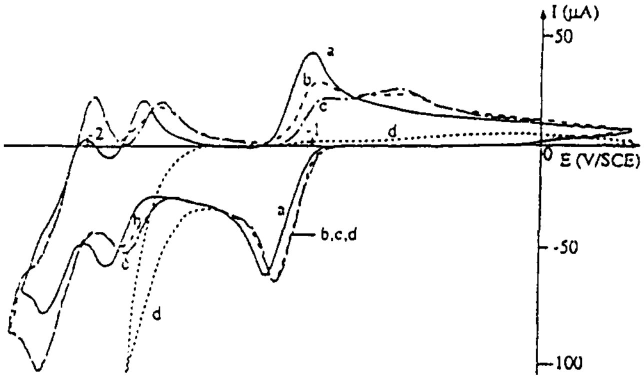
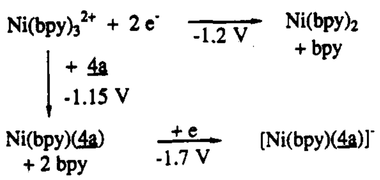


Figure 1. Cyclic voltammograms obtained with freshly polished gold microelectrode (3 mm^2) at 20 °C at a scan rate of 200 mV s^{-1} for a solution of $Ni(bpy)_3(BF_4)_2$ (0.3 mmol) in DMF (30 mL) containing 0.1 M tetrabutylammonium tetrafluoroborate as supporting electrolyte: (a) under argon; (b) after addition of 3,9-dodecadiyne, **1a** (0.15 mmol); (c) after addition of **1a** (0.3 mmol); (d) solution as in c saturated with CO_2.

Scheme II



Addition of CO_2 to the solution depicted by curve c results in a modified cyclic voltammogram, as illustrated by curve d, Figure 1. The new voltammogram exhibits a nonreversible Ni(II)/Ni(0) transition at −1.15 V and an irreversible catalytic current at −1.6 V. Earlier work has shown that the catalytic process observed in curve d is characteristic of the reduction of coordinated CO_2 in its conversion to a radical anion.[16]

Figure 2 presents the cyclic voltammograms of $Ni(bpy)_3^{2+}$ in the presence of terminal 1,7-octadiyne **3a** and CO_2. The addition of 0.25 and 0.5 equiv of **3a** to $Ni(bpy)_3^{2+}$ (curves b, c) induces a slight shift of the Ni(II)/Ni(0) transition from −1.2 to −1.15 V, with progressive irreversibility. No other reoxidation peak appears below +0.3 V. The reduction peak of the Ni(0) complex appears at −1.7 V with 0.5 equiv of **3a**. The addition of CO_2 (curve d) causes identical effects as for **1a**.

The comparison of Figures 1 and 2 concerning the reoxidation peaks of Ni(0) reveals that, for the same diyne concentration (diyne/Ni ratio of 1/2), the terminal diyne is more reactive than the internal one.

Conjugated Diynes. The cyclic voltammograms of a solution of $Ni(bpy)_3(BF_4)_2$ in the presence of 0.5 and 1 equiv of 6,8-tetradecadiyne, **4a** (Scheme I), and CO_2 are depicted in Figure 3. The Ni(II)/Ni(0) reduction peak is slightly displaced from −1.2 to −1.15 V and becomes progressively irreversible with the addition of **4a** (curves b, c). The reoxidation peak of Ni(0) is replaced by a peak

---

[12] Dérien, S.; Duñach, E.; Périchon, J. *J. Organomet. Chem.* **1990**, *385*, C43.

[13] Dérien, S.; Clinet, J. C.; Duñach, E.; Périchon, J. *J. Chem. Soc., Chem. Commun.* **1991**, 549.

[14] See, for example: (a) Trost, B. M.; Lautens, M.; Chan, C.; Jebaratnam, D. J.; Mueller, T. M. *J. Am. Chem. Soc.*, **1991**, *113*, 636 and references cited therein. (b) Vollhardt, K. P. C. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 539. (c) Nugent, W. A.; Thorn, D. L.; Harlow, R. L. *J. Am. Chem. Soc.* **1987**, *109*, 2788.

[15] Tsuda, T.; Morikawa, S.; Hasegawa, N.; Saegusa, T. *J. Org. Chem.* **1990**, *55*, 2878.

[16] (a) Daniele, S.; Ugo, P.; Bontempelli, G.; Fiorani, M. *Electroanal. Chem.* **1987**, *219*, 259. (b) Garnier, L.; Rollin, Y.; Périchon, J. *New J. Chem.* **1989**, *13*, 53.

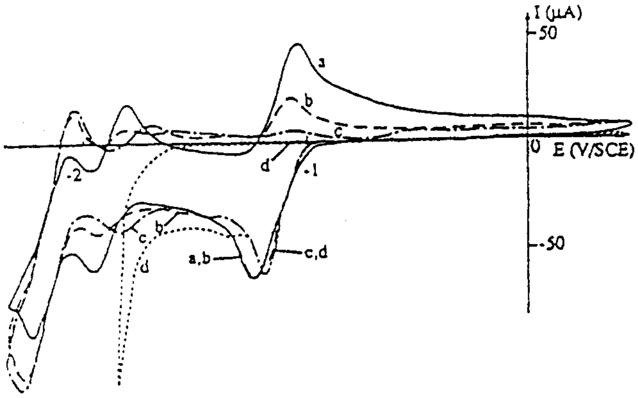


Figure 2. See Figure 1 for general conditions: (a) under argon; (b) after addition of 1,7-octadiyne, **3a** (0.075 mmol); (c) after addition of **3a** (0.15 mmol); (d) solution as in c saturated with CO_2.

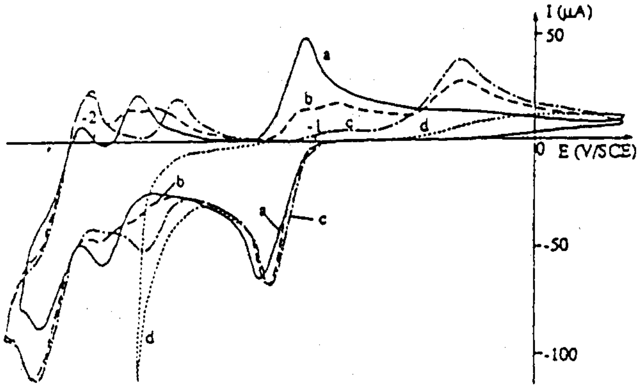


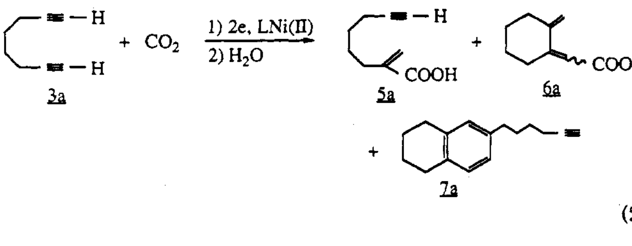
Figure 3. See Figure 1 for general conditions: (a) under argon; (b) after addition of 6,8-tetradecadiyne, **4a** (0.15 mmol); (c) after addition of **4a** (0.3 mmol); (d) solution as in c saturated with CO_2.

of equivalent intensity at −0.35 V. With a Ni/**4a** ratio of 1 the reversible reduction peak of the Ni(0) complex initially at −1.9 V (curve a) is replaced by a peak at −1.7 V which is also reversible (curve c). Bubbling CO_2 into the solution of curve c results in an irreversible catalytic current at −1.6 V (curve d) as for **1a** or **3a**.

Preparative-Scale Electrocarboxylations. The electrosyntheses were typically carried out in DMF in undivided cells fitted with a magnesium anode and a carbon fiber cathode, at constant intensity of 50 mA, with a diyne to Ni(II) ratio of 10/1. Only a low concentration of supporting electrolyte was required for these reactions (less than 10^{-2} M), in contrast to standard electrolyses.

α,ω-Diynes 3. No carboxylation of **3a** occurred in the absence of current. The reaction requires a continuous electrochemical generation and regeneration of the Ni(0) promoters and consumes 2–4 faradays per mol of diyne.

The $Ni(bpy)_3(BF_4)_2$-catalyzed electrocarboxylation of terminal **3a** at a CO_2 pressure of 1 atm afforded a mixture of linear and cyclic acids **5a** and **6a** accompanied by cyclic dimer **7a**, as depicted in eq 2. Electrolysis of **3a** with the Ni–bpy system in the absence of CO_2 gave bicyclic dimer **7a** alone in 10% yield, the remaining unreacted **3a** being recovered.

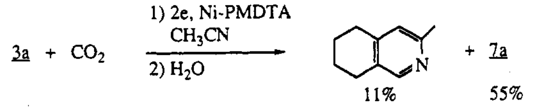


(2)

An adequate quantity of ligand, L, on nickel was essential for the reaction to occur: in the absence of L, the reduction of Ni(II) affords metallic nickel which could not be recycled. The nature of the ligand associated to nickel was found to strongly determine the rate of carboxylation versus oligomerization of the diyne, as well as the selectivity among the carboxylated products **5a** and **6a**. In the presence of $NiBr_2(PPh_3)_2$, the electrocarboxylation of **3a** formed very selectively dimer **7a** (70%), through a [2 + 2 + 2]-type cyclization. When L = phenantroline was used, the carboxylation led essentially to a mixture of dicarboxylated compounds (60% yield), through a double CO_2 incorporation. A selective monocarboxylation occurred with the aliphatic triamine ligand PMDTA (pentamethyldiethylenetriamine). At a CO_2 pressure of 5 atm, **3a** produced carboxylic acid **5a** with 98% selectivity. The alternative use of TMEDA (tetramethylethylene diamine) also favored isomer **5**. By contrast, with bpy as the ligand, and a CO_2 pressure of 5 atm, cyclic adduct **6a** became predominant. These results are summarized in Table I.

Other factors controlling the yield and selectivity of the CO_2 incorporation, such as the CO_2 pressure, the reaction temperature, or the nature of the electrodes were examined. A Mg/carbon fiber combination was found to be the best anode/cathode pair in terms of yield and regioselectivity in the carboxylation of **3a** with the Ni–PMDTA system. The use of an Al anode led to polymerization and a Zn anode resulted in an increase of dimer **7**. A Mg/nickel foam pair of electrodes afforded **7**, and the Mg/stainless steel pair formed 2,8-nonadiynoic acid in 40% yield (with 30% conversion).

A favorable reaction time was about 7 h for a 6 mmol scale reaction; further electrolysis did not form more CO_2 insertion products. The solvent also influenced the results: in acetonitrile, the carboxylation of **3a** led to the formation of **7a** (55%) together with substituted bicyclic pyridine (11%) (eq 3), with an overall low CO_2 incorporation (10% carboxylic acids). The synthesis of pyridine derivatives by cocyclization of nitriles and alkynes is a well-documented reaction normally catalyzed by Co complexes.[17]



(3)

The influence of the length of the carbon chain in the carboxylation of α,ω-diynes was examined with **3a** (n = 4), 1,6-heptadiyne, **3b** (n = 3), and 1,8-nonadiyne, **3c** (n = 5) (Scheme I). Both Ni–bpy and Ni–PMDTA catalytic systems led to a mixture of monocarboxylic acids from **3c**, with low conversion. Carboxylation of **3b** (Scheme III) with bpy as the ligand afforded selectively cyclic carboxylic acid **6b**, whereas with PMDTA, linear unsaturated acid **5b** was formed preferentially. The ratio of linear to cyclic carboxylic acids **5b**/**6b** (for n = 3), went from 7/93 with L = bpy to 83/17 with L = PMDTA. For **3a** (n = 4), under

---

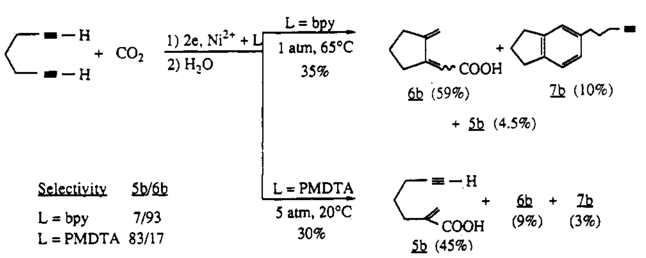
[17] (a) Bönnemann, H. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 505. (b) Naiman, A.; Vollhardt, K. P. C. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 708. (c) Vitulli, G.; Bertozzi, S.; Vignali, M.; Lazzaroni, R.; Salvadori, P. *J. Organomet. Chem.* **1987**, *326*, C33.

Table I. Electrocarboxylation of 3a: Influence of the Catalytic System and the Reaction Conditions

complex	reactn condns (atm, °C)	diyne convn (%)	product yield[a] (%) dimer 7a	product yield[a] (%) monocarboxylic acids 5, 6	selectivity[b] 5a/6a
$NiBr_2dme$ + 2 TMEDA	1, 65	88	20	40	50/15
$Ni(bipy)_3(BF_4)_2$	1, 65	100	30	60	25/50
$Ni(bipy)_3(BF_4)_2$	5, 20	90	15	50	25/65
$NiBr_2dme$ + 2 PMDTA	1, 65	80	20	30	80/20
$NiBr_2dme$ + 2 PMDTA	5, 20	50	6	60	98/2
$NiBr_2(PPh_3)_2$ + PPh_3	1, 65	50	70	5	

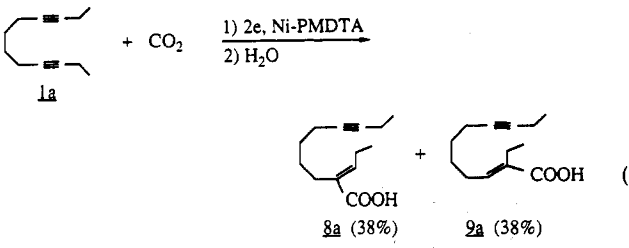
[a] Major products of the reaction; yields are expressed relative to the amount of converted diyne. [b] Selectivity calculated as the amount of 5a or 6a relative to the total amount of monocarboxylic acids.

Scheme III



comparable conditions, the ratios **5a**/**6a** were 33/67 for L = bpy and 98/2 for L = PMDTA.

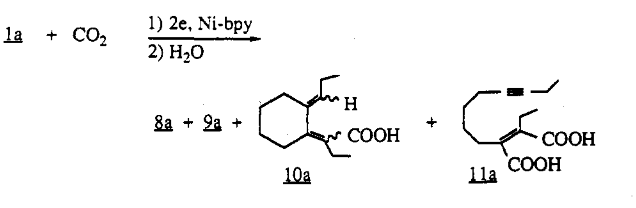
Nonconjugated Internal Diynes 1. The Ni–PMDTA-catalyzed CO_2 incorporation into diethyl-substituted **1a** (at P(CO_2) = 5 atm) yielded a 1:1 mixture of isomeric linear monocarboxylic acids **8a** and **9a** (eq 4). Less than



(4)

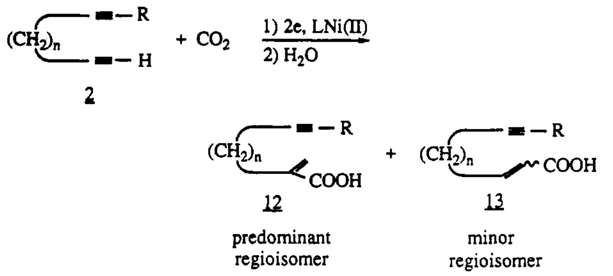
5% of **1a** was consumed in the absence of nickel complex or in the absence of CO_2. Similar reactivity was found for 2,6-octadiyne, **1b** (Table II), with a **8b**/**9b** ratio of 40/60.

Carboxylation of **1a** with $Ni(bpy)_3(BF_4)_2$ led to **8a** and **9a** and two other products: cyclic **10a** and dicarboxylic acid **11a** (eq 5). A single diacid was formed and was isolated



in 30% yield. **11a** arises from a cis-1,2-dicarboxylation of one of the triple bonds, the other triple bond remaining unreacted. With **1b**, the corresponding diacid **11b** was also formed in 15% yield. However, no cyclic adduct **10b** could be identified, possibly due to the strained four-membered-ring resulting cycle.

Carbon Dioxide Incorporation into Diynes 2. The electrocarboxylation of nonconjugated diynes containing both terminal and internal triple bonds led to carboxylic acids affecting exclusively the terminal unsaturation, in a totally chemospecific and highly regioselective reaction (eq 6). CO_2 was preferentially incorporated into the 2-position of the terminal unsaturation with both Ni–bpy and Ni–PMDTA catalytic systems (Table III). A 98/2 ratio of regioisomers **12**/**13** was reached with **2a**, and a

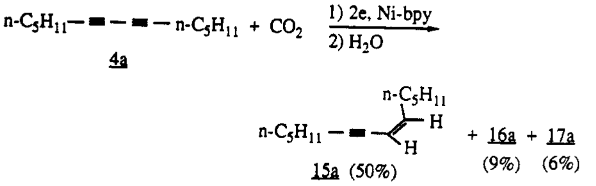


(6)

90/10 ratio was obtained with **2b**. With bpy as the ligand, some dicarboxylation took place as for diynes **1**, affecting only the terminal triple bond. Diacid **14c**, analogous to diacids **11**, was isolated in 20% yield. However, no bicyclic compounds analogous to **6** or **10** were isolated from the carboxylation of **2**.

Electrocarboxylation of Conjugated Diynes 4. The influence of several ligands on the activity of different catalytic systems in the electrocarboxylation of 6,8-tetradecadiyne, **4a**, was first examined.[13] No reaction occurred in the absence of the nickel catalyst, and 95% of **4a** could be recovered in the absence of CO_2 without polymerization, despite the conjugation present in the substrate.

With Ni–bpy. Unexpectedly, the electrocarboxylation of **4a** catalyzed by $Ni(bpy)_3(BF_4)_2$ at a CO_2 pressure of 5 atm led to enyne **15a** in 50% yield (eq 7). A single cis-



(7)

isomer was obtained in a stereoselective monoreduction reaction. In spite of the CO_2 pressure of 5 atm, only 15% carboxylation occurred, in contrast to the efficiency of the same catalytic system regarding alkyne carboxylation.[7] At P(CO_2) of 1 atm or without CO_2, **4a** was poorly reactive and was recovered in more than 80% yield.

When the carboxylation (P(CO_2) = 5 atm) was run in the presence of DMF containing D_2O (40:1), dideuterated enyne was isolated in 60% yield (Scheme IV). No deuterium incorporation was found when a classical electrocarboxylation was followed by hydrolysis with D_2O or D_2SO_4. Enyne **15b** was obtained in an analogous reaction of **4b** at P(CO_2) = 5 atm (conversion, 45%), in a 1:1 mixture with **16b** (R^1 = R^2 = c-C_5H_9, see Table IV).

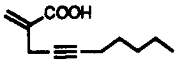
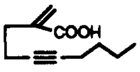
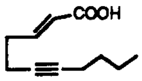
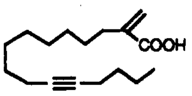
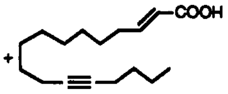
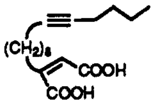
With Ni–PMDTA: Selective CO_2 Incorporation. Among the various ligands examined (TMEDA, PMDTA, PPh_3, PCy_3, bpy), PMDTA resulted in the best catalytic system in terms of yield and selectivity of the CO_2 incorporation into diynes **4** (Scheme I). In the presence

Table II. Electrocarboxylation of Nonconjugated Substituted Diynes

diyne	catalyst precursor	reactn condns (atm, °C)	diyne convn (%)	products[a] (% yield) monocarboxylic acids (8 + 9 + 10)	products[a] (% yield) dicarboxylic acid 11	selectivity 8/9/10
1a		5, 20	<5			
1a	$NiBr_2DME$ + 2 PMDTA	absence CO_2, 20	<5			
1a	$NiBr_2DME$ + 2 PMDTA	1, 65	30	5[b]		50/10/–
1a	$NiBr_2DME$ + 2 PMDTA	5, 20	20	75		50/50/–
1b	$NiBr_2DME$ + 2 PMDTA	5, 20	45	90		40/60/–
1a	$Ni(bipy)_3(BF_4)_2$	5, 20	55	65	30	40/30/30
1b	$Ni(bipy)_3(BF_4)_2$	5, 20	35	60	15	75/25/–

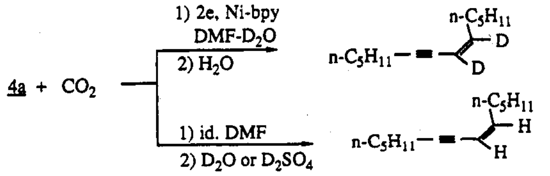
[a] Yields are expressed relative to the amount of converted diyne. [b] Diyne polymerization occurred.

Table III. Electrocarboxylation of Diynes 2, at $P(CO_2)$ = 5 atm, T = 20 °C

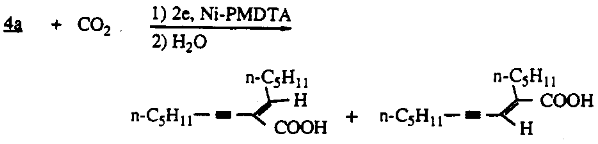
diyne	catalyst precursor	diyne convn	product yield[a] (%) monoacids	product yield[a] (%) diacids	major monocarboxylic acids[a] (%)	selectivity 12/13
2a	$NiBr_2DME$ + 2 PMDTA	75	80		 12a (63)	98/2
2b	$NiBr_2DME$ + 2 PMDTA	85	85		 12b (77) +  13b (8)	90/10
2c	$NiBr_2DME$ + 2 PMDTA	40	65		 12c (39) +  13c (19)	60/40
2a	$Ni(bipy)_3(BF_4)_2$	45	65	5	12a (63)	97/3
2b	$Ni(bipy)_3(BF_4)_2$	85	75	5	12b (56) 13b (11)	75/25
2c	$Ni(bipy)_3(BF_4)_2$	80	55	 14c (20)	12c (36) 13c (19)	65/35

[a] Yields are expressed relative to the amount of converted diyne.

Scheme IV



of Ni–PMDTA, **4a** afforded carboxylic acids **16a** and **17a**, in a selective monocarboxylation reaction (eq 8). For each



(8)

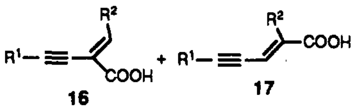
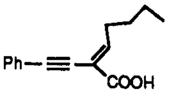
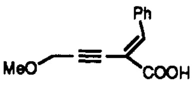
regioisomer, an exclusive cis-addition of H and CO_2H across one triple bond takes place, **16** and **17** being single stereoisomers. No isomerization occurred under the reaction conditions. The CO_2 incorporation and the regioselectivity were very dependent on the experimental conditions of CO_2 pressure and temperature, the best being found for $P(CO_2)$ = 5 atm at 20 °C.

Diynes **4a–4g** were carboxylated with the Ni–PMDTA system, and the results are gathered in Table IV. Diynes were prepared according to previously described procedures.[18] The optimal CO_2 pressure depended on the diyne nature and was examined for each diyne between 1 and 5 atm. Dicyclopentylbutadiyne, **4b**, afforded carboxylic acid **16b** in good yield and 97% regioselectivity. Diphenylbutadiyne gave a single isomer **16c** isolated in 40% yield. Its *p*-tolyl analog, very reactive, resulted in a 1:1 mixture of mono- and dicarboxylated products. When the more polar methoxymethyl or phenoxymethyl substituents were used, e.g., **4d**, **4e**, one carboxylic acid was

---

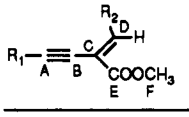
[18] Brandsma, L. In *Preparative Acetylenic Chemistry*, 2nd ed.; Elsevier: Amsterdam, 1988.

Table IV. Electrocarboxylation of 1,3-Diynes, Catalyzed by the Ni–PMDTA System, at 20 °C

diyne	PCO_2 (atm)	diyne convn	products (yield,[a] %)  16 + 17	selectivity[b] 16/17
4a	5	85%	**16a** (58) + **17a** (25)	70/30
4b	5	70%	**16b** (86)	97/3
4c	5	100%	**16c** (40)[c]	100/0
4d	5	100%	**16d** (20)[c]	98/2
4d	1	75%	**16d** (60)	98/2
4e	5	40%	**16e** (88)	98/2
4f	1	95%	**16f** (37) + **17f** (16) +  **16'f** (3)	71/29[d]
4g	5	90%	**16g** (50) +  **16'g** (11)	100/0[d]

[a] Yields are expressed relative to the amount of converted diyne. [b] Selectivity as a ratio of internal versus terminal monocarboxylic acid regioisomers, see **16a**/**17a**, eq 8. [c] The rest of the diyne was polymerized. [d] Regioselectivity **16f**/**16'f**:93/7; **16g**/**16'g**:82/18.

Table V. ^{13}C NMR Chemical Shifts of Compounds 16a–16g (TMS as Internal Standard)

products 	δ ^{13}C(ppm)					
	C_A	C_B	C_C	C_D	C_E	C_F
16a	73.84	96.88	116.93	151.81	165.28	51.76
16b	73.61	101.00	115.49	156.86	165.79	52.12
16c	85.17	97.98	112.76	145.53	166.08	52.75
16d	78.71	93.64	116.56	149.27	164.00	52.34
16e	79.31	93.81	116.61	149.17	164.30	52.75
16f	77.02	100.18	113.33	144.42	166.57	52.66
17g	81.79	97.71	117.34	148.64	164.30	52.53

formed from each diyne, regio- and stereoselectively. In the case of **4d**, the best yield of **16d** was obtained at $P(CO_2)$ = 1 atm. At higher CO_2 pressure, the diyne was totally converted but some polymerization occurred.

The reactivity of two dissymmetrically substituted diynes such as **4f** and **4g** was also examined. In the case of **4f** three carboxylic acids were isolated: **16f**, **17f**, and traces of **16f'**. The CO_2 incorporation mainly occurred on the phenyl side (93%), the major regioisomer being **16f**. The electrocarboxylation of **4g** afforded carboxylic acids **16g** and **16g'**: both compounds have the carboxy groups in the internal position of the diyne. However, in contrast to **4f**, here the CO_2 is preferentially bound to the methoxymethyl site, with a **16g**/**16g'** ratio of 82/12.

Structural NMR Assignments of Carboxylated Diynes 4. The carboxylic acids formed in the Ni–PMDTA electrocarboxylation of 1,3-diynes are new compounds and were isolated as methyl esters. We used combined ^1H and ^{13}C NMR techniques to determine the regio- and stereochemistry of the CO_2 incorporation onto the different acetylenic carbons and to assign the C_A–C_F chemical shifts (Table V). As determined for many α,β-unsaturated esters, the CO_2Me function induces a ^1H NMR shift difference of about 0.6 ppm on the chemical shift of the vinyl proton, depending on their relative cis or trans stereochemistry. The higher field for the vinyl H corresponds to the (*E*)-configuration, e.g., a cis H–CO_2H relationship. The chemical shift of the sp and sp^2 carbons C_A–C_D was examined by ^{13}C DEPT associated to totally coupled ^{13}C spectra. The chemical shift difference between sp carbons C_A and C_B was found to be ≈20 ppm, the upfield signal corresponding to C_B.

The chemical shift of C_A varies from 73 to 85 ppm as a function of the polarity of the α substituent R^1. Low values of δ correspond to alkyl substituents, and high values are obtained when a phenyl group is present. By contrast, δ of C_B appears at 97–100 ppm for either alkyl or aryl groups. C_B chemical shift lowers to 93 ppm in the presence of a β-methoxymethyl or phenoxymethyl substituent (**16d**, **16e**). The chemical shift of quaternary C_C bearing the ester group varies only slightly around 115 ppm, the lower values being for phenyl substituents. The influence of the phenyl group is more important on the δ of C_D: 145 ppm with a phenyl group in the α position and up to 156 ppm when R^2 is an alkyl substituent. The chemical shift of C_D diminishes with the polarity of R^2; this effect is reversed as compared to C_A.

The chemical shift of the methyl group and the carboxylate of the ester functions (C_F, C_E) present small variations, though a phenyl vinyl group slightly shifts C_E upfield.

Discussion

Electrochemistry. The electrochemical method enables the use of a Ni(II) catalyst precursor for the preparative-scale carboxylation, in situ electrogenerated low-valent L_nNi complexes being the effective catalysts. For Ni–bpy and 4-octyne we have demonstrated that $Ni(bpy)_2$ was able to coordinate both the carbon dioxide and the alkyne.[7] The reaction involves the Ni(II)/Ni(0) transition and can be run at a potential of –1.2 to –1.4 V. The interaction of diynes **1a**, **3a**, and **4a** with $Ni(bpy)_2$ (Figures 1–3) is shown by a slight shift from –1.2 to –1.15 V of the $Ni(bpy)_3^{2+}/Ni(bpy)_2$ reduction peak, which becomes less or even nonreversible. This is indicative of a fast chemical reaction between the diyne and electrogenerated $Ni(bpy)_2$ (Scheme II).

The interaction of Ni(0) with **1a** or **4a** is also ascertained by the presence of new reoxidation peaks of Ni(0) to Ni(II) at −0.6 and −0.35 V, respectively. Figure 3, curve c, exhibits this reoxidation peak with an intensity equivalent to that of the initial peak (curve a) for a Ni/**4a** ratio of 1, suggesting a new 1/1 complex. The bpy/**4a** ligand exchange is corroborated by the potential change of the Ni(0) reduction peak from −1.9 V in curve a to −1.7 V in curve c. Moreover, the increase of free bpy in solution is reflected by the increase of its reduction peak at −2.2 V. Mono- and dinuclear Ni(0) complexes of butadiyne have been isolated for L = alkyldiphosphines.[19] For **1a** or **3a** the fast diyne–bpy exchange reaction allows the new Ni(0) reduction peak to be present at −1.75 and at −1.70 V, respectively.

A Ni/**3a** molar ratio of 2/1 led to an irreversible Ni(II)/Ni(0) transition (Figure 2, curve c), indicative of a fast chemical reaction. However, in a preparative-scale electrolysis of **3a** and $Ni(bpy)_3(BF_4)_2$ run in the absence of CO_2 under argon (in a 10/1 molar ratio of **3a**/Ni(II)), the dimer **7a** was isolated in only a 10% yield, together with unreacted **3a**. A stoichiometric reaction occurs, without the nickel species being recycled. Electrogenerated $Ni(bpy)_2$ in DMF is, therefore, not a suitable catalyst for diyne dimerization, in spite of the diyne coordination which takes place according to cyclic voltammetry. The electrochemical curves obtained for **1a** (Figure 1) exhibit a less important shift of the reduction peak of the Ni(0) complexes (from −1.9 to −1.8 V) as compared to that of **3a**, with a partial reversibility of the Ni(II)/Ni(0) transition. The new reoxidation peak at −0.6 V can be assigned to the oxidation of a Ni(**1a**)(bpy) type of complex, in which the diyne is simply coordinated to the nickel center. The electrochemical behavior of **1a** and **3a** can be compared to that found for 4-octyne and 1-octyne, respectively,[7,20] with a higher reactivity of electrogenerated $Ni(bpy)_2$ toward terminal diynes, as compared to internal diynes.

The electrochemical behavior can be related to the reactivity of these molecules with CO_2. Almost complete conversion of **3a** was achieved at 20 °C under a CO_2 pressure of 5 atm (Table I) as compared to 55% for **1a** under the same conditions (Table II). Cyclic dimers such as **7a** (eq 2) were formed with **3a**, whereas no di- or trimerization products could be observed with **1a**. Moreover, diynes possessing a terminal —C≡CH and an internal —C≡C— incorporate CO_2 exclusively at the monosubstituted triple bond (eq 6).

The direct electroreduction of CO_2 occurs at rather negative potentials (−2.2 to −2.8 V) and forms oxalate, formate, carbonate, and/or CO.[21] In the presence of a transition metal complex, the CO_2 electroreduction may become more selective and can be effected at less negative potentials.[22] In the presence of Ni–bpy systems[7,16] the Ni(II)/Ni(0) reducing peak at −1.2 V (Figure 1, curve a) becomes irreversible when bubbling CO_2 (curve d), whereas a catalytic wave appears at −1.6 V. This catalytic process is assigned to the reduction of coordinated CO_2 to its anion radical. The preparative-scale electrolysis of CO_2 in DMF, in the presence of $Ni(bpy)_3(BF_4)_2$ at −1.6 to −1.7 V, led to a mixture of oxalate, CO, and carbonate as a result of two competitive reactions of the anion radical of CO_2.[7]

The voltammograms for solutions of either **1a**, **3a**, or **4a** with CO_2 exhibit identical features: catalytic wave at −1.6 V and irreversible Ni(II)/Ni(0) transition. The catalytic wave can be associated with the electron transfer to a Ni(diyne)(bpy)(CO_2)-type complex.

The electrochemical studies show that diynes and carbon dioxide are able separately to coordinate to Ni(0)-generated species in DMF, but no additional information concerning their relative reactivity could be inferred from the voltammograms.

Carboxylations of Nonconjugated Diynes. When Ni(0) complexes are in the presence of both diynes and CO_2, several possibilities can be contemplated: (I) the preferential coordination of the diyne leading to oligomerization or reduction; (II) the preferential coordination of CO_2 with the formation of its reduction products, with poor diyne conversions, and (III) a predominant 1:1 coordination of both the diyne and CO_2 affording heterocoupling products. The relative electron density and the steric hindrance on the metal center will determine the results of the competition between CO_2 and the diyne for coordination. An important dependence of the product on the ligand's nature has already been reported for the electrocarboxylation of 1-octyne.[23]

In the case of nonconjugated diynes, with L = PPh_3, the nickel complex has poor affinity for CO_2, and a [2 + 2 + 2] type cyclization of the diyne occurs preferentially: **7a** is thus formed with an excellent selectivity from **3a**, as shown in Table I. No dimers were formed from diynes **1** or **2**, probably due to steric reasons.

With PMDTA as the ligand, with possible bis- or trischelation and no back-bonding, the LNi(0) complex is more electron-rich and the ability to coordinate CO_2 increases.[24] A 1:1 coordination of a triple bond and a molecule of CO_2 is preferred. Carboxylic acids **5**, are selectively formed from diynes **3** (eq 2), and acids **12** from diynes **2** (eq 6), with the regioselective functionalization of the 2-position of terminal diynes.

With bpy as the ligand, the electron density of the Ni(0) complex is intermediate between Ni–PPh_3 and Ni–PMDTA. A preference for cyclic products, e.g., **6** and **10** (eqs 2 and 5) was observed. For terminal **3a** and **3b**, cyclic **6a** and **6b** were formed in 70% (n = 4) and 93% (n = 3) regioselectivity among carboxylated compounds. For internal **1a**, a 70/30 ratio of linear to cyclic carboxylic acids was attained. Moreover, **1a** led to dicarboxylic acid **11a** with a 30% yield (eq 5). This double CO_2 incorporation into one of the triple bonds giving maleic acid derivatives was essentially found with the Ni–bpy system. It is to be noted that only one triple bond was doubly functionalized by CO_2, the second triple bond remaining unreacted.

We propose a mechanism similar to that operating in the electrocarboxylation of alkynes by Ni–bpy.[7] At the anode, the oxidation of the magnesium metal gives rise to Mg^{2+} ions in solution. Ni(II) is reduced to Ni(0) species at the cathode (Scheme V). The in situ formed LNi(0) species coordinates a C≡C and CO_2 to form a metallacycle of type **18** or **18′**. Such metallacycles have been chemically prepared from disubstituted alkynes and $Ni(COD)_2$,[5c] and isolated in the electrocarboxylation of 4-octyne.[7] The nickelacycle is then opened in the presence of Mg^{2+} ions and an appropriate source of protons (such as the residual

---

[19] Bonrath, W.; Pörschke, K. R.; Wilke, G., Angermund, K.; Krüger, C. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 833.

[20] Dérien, S. Thèse de Doctorat, Université Paris XI-Orsay, 1991.

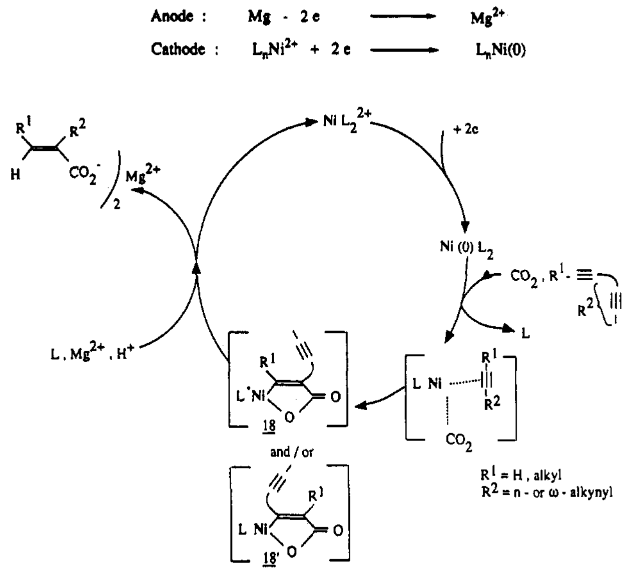
[21] Amatore, C.; Savéant, J. M. *J. Am. Chem. Soc.* **1981**, *103*, 5021.

[22] (a) Beley, M.; Collin, J. P.; Ruppert, R.; Sauvage, J. P. *J. Chem. Soc., Chem. Commun.* **1984**, 1315; (b) *J. Am. Chem. Soc.* **1986**, *108*, 7461. (c) Amatore, C.; Jutand, A. *J. Am. Chem. Soc.* **1991**, *113*, 2819.

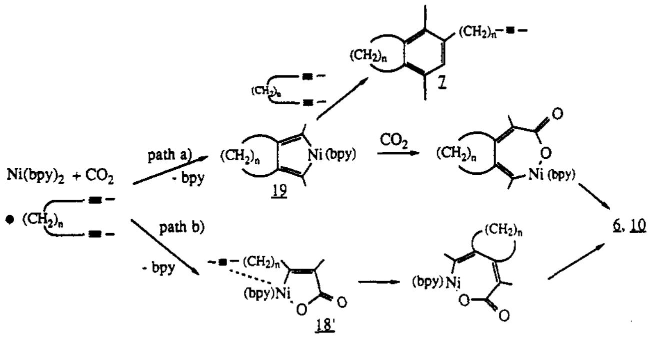
[23] Labbé, E.; Duñach, E.; Périchon, J. *J. Organomet. Chem.* **1988**, *353*, C51.

[24] Duñach, E.; Périchon, J. *Synlett* **1990**, *1*, 143.

Scheme V

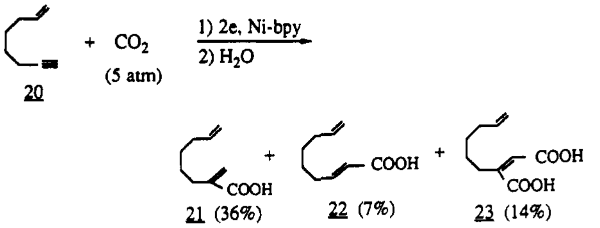


Scheme VI



water, the supporting electrolyte, or the DMF solvent) to afford magnesium carboxylates, hydrolyzed at the end of the reaction. The mechanistic cycle proposed in Scheme V explains the formation of linear unsaturated carboxylic acids **5**, **8**, **9**, **12**, and **13**. The regioselectivities attained for **8**/**9** or **12**/**13** strongly depend on R^1. When R^1 = H (as in eq 6), the high regiocontrol can be explained by steric reasons ($R^2 \gg R^1$ and therefore **12** ≫ **13**), the nickel occupying the less hindered side of the metallacycle, e.g., **18**. When R^1 = alkyl, and R^2 = alkynyl, isomeric **18** and **18′** are formed in ratios depending on the relative steric hindrance of both substituents and on the other ligands on nickel.

The formation of cyclic carboxylic acids **6** and **10** (essentially by Ni–bpy, eqs 2 and 5), involves the coordination and functionalization of both triple bonds to the nickel center. Two different pathways may be considered (Scheme VI): path a, a preferential first coordination of both triple bonds to Ni(0) with formation of metallacyclopentadiene derivative **19**, followed by CO_2 insertion, and path b, the formation of a first oxanickelacycle **18** or **18′** as in Scheme V, followed by intramolecular insertion of the second C≡C bond. For steric reasons, between **18** and **18′**, only the **18′** isomer may undergo further intramolecular cyclization. When R^1 = H (**18** ≫ **18′**), path b does not explain the selective formation of cyclic acids **6** because of the expected low ratio of **18′** versus **18**. The insertion of a second diyne molecule into intermediates **19** yields bicyclic aromatic derivatives **7**, byproducts in the carboxylation of **3**. Path a seems therefore to better explain the experimental results. In order to further discriminate between paths a and b we examined the reactivity of 1-octen-7-yne, **20**, a terminal enyne analog to **3a**, in the presence of the Ni–bpy system (eq 9). If a



(9)

mechanism following path b in Scheme VI was operating, cyclic compounds should be formed. Path a should be less favored for **20** as compared to **3a**, according to the lower reactivity of enynes to form metallacyclopentenes as compared to 1,7-diynes.[25] The Ni-bpy-catalyzed electrocarboxylation of **20** afforded linear **21** and **22** in 43% yield and 83/17 regioselectivity. No reactivity implicated the C=C, and no cyclic products analogs to **6a** or **7a** were observed. The electrocarboxylation with Ni–PMDTA yielded **21** and **22** in 70% yield and 80/20 regioselectivity.[26] The absence of cyclized products in the carboxylation of **20** is an indication favoring path a. Moreover, it provides an indication on the ionic nature of the nickel–carbon bond cleavage in **18** and analogs. If a radical cleavage was to be operating, cyclic compounds derived from **20** would be expected through a facilitated radical–olefin coupling.[27]

We conclude that, for a given diyne, the ligand on nickel determines the main reaction pathway. With L = PPh_3, cyclic products **7** are formed. With L = bpy, a competition between metallacycles **18** and **19** leads to a mixture of cyclic and linear acids, with some dicarboxylation. With L = PMDTA, the 1:1 coordination of diyne and CO_2 affords selectively linear carboxylic acids. The reactivity of nonconjugated diynes with CO_2 follows the order Ni–PMDTA > Ni–bpy > Ni–PPh_3. A similar tendency has been proposed for the oxidative addition of C–Cl bonds to Ni(0).[28]

Despite different reactivities, both Ni–PMDTA and Ni–bpy systems mainly afforded monocarboxylic acids with nonconjugated diynes, with the net result of a hydrocarboxylation-type reaction affecting one of the triple bonds. No formation of bicyclic pyrones was observed for any of the catalytic systems tested.

Conjugated Diynes. The Ni–PMDTA system enables a highly regio- and stereoselective CO_2 incorporation into conjugated diynes **4** (Table IV). The new C–C bond is preferentially, or exclusively, formed on the internal position of the diyne unit, e.g., **16**. The incorporation of H and CO_2H across the triple bond occurs exclusively in a cis mode. This method thus enables the short and efficient synthesis of substituted (*E*)-2-vinylidene-3-yne carboxylic acids.

We propose the formation of the isomeric metallacycles **24** and **25** (Scheme VII). The unsaturated magnesium carboxylates derived from **25** and **25** accumulate during the electrolysis and deactivate the conjugated triple bond toward further CO_2 incorporation. Moreover, the magnesium carboxylates did not undergo *E*/*Z* isomerization,

---

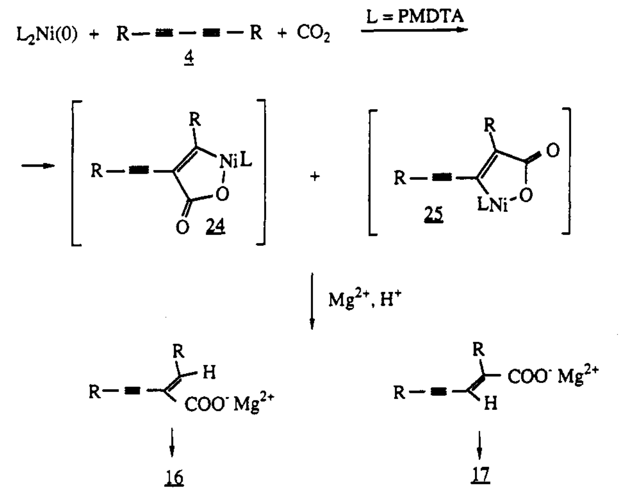
(25) Negishi, E. *Acc. Chem. Res.* **1987**, *20*, 65.

(26) Dérien, S.; Clinet, J. C.; Duñach, E.; Périchon, J. *Tetrahedron* **1992**, *48*, 5235.

(27) Giese, B. In *Radicals in Organic Synthesis: Formation of Carbon Carbon Bonds*; Pergamon Press: Oxford, 1986.

(28) Wenschuh, E.; Zimmering, R. Z. *Chem.* **1987**, *27*, 448.

Scheme VII

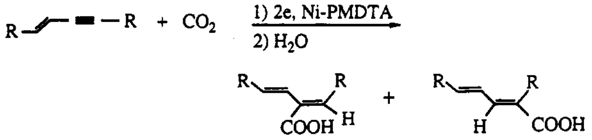


even in the presence of Ni(0), although such species are known to catalyze double-bond isomerization.[7,29]

Both electronic and steric effects are responsible for the observed product ratios. Electronically, we favor the nickel conjugation in metallacycle **24** over its cross-conjugation in isomer **25**. The steric hindrance of the R group also influences the regioselectivity: by switching R = n-C_5H_{11} in **4a** and R = c-C_5H_9 in **4b**, the ratio **16**/**17** rises from 70/30 to 93/3 (Table IV). For R = Ph, $MeOCH_2$, or $PhOCH_2$, isomer **16** is formed almost exclusively.

The two examples of dissymmetrically substituted diynes, **4f** and **4g**, pointed out that the competition between phenyl, n-butyl, and methoxymethyl substituents to direct CO_2 fixation is $MeOCH_2$ > Ph > alkyl. The competition favors the more polar substituent side for the carboxylation, with a $MeOCH_2$/Ph ratio of 82/18 and a Ph/n-butyl ratio of 93/7.

A related single CO_2 incorporation into conjugated systems has been observed in the electrocarboxylation of 1,3-enynes (eq 10).[8] Only the triple bond was carboxylated



(10)

in a cis hydrocarboxylation reaction. For the Ni–PMDTA system and R = n-C_5H_{11} (P = 5 atm, 20 °C), both regioisomers were formed in a 1:1 ratio without double-bond isomerization or dicarboxylation. However, conjugated dienes such as 1,4-diphenylbutadiene led preferentially to a 1,4-bis carbon dioxide incorporation.[26]

A remarkable dependence of the reaction products on the catalytic system was also observed for conjugated diynes. With L = PPh_3, no diyne conversion was obtained at 1 or 5 atm of CO_2. When L = bpy, the carboxylation of **4a** afforded regio- and stereoselectively enyne **15a** in 50% yield (eq 7), with less than 15% carboxylic acids (at $P(CO_2)$ = 5 atm). This result was surprising, considering that the Ni–bpy system was effective for other alkyne carboxylations.[7] Enyne **15** resulted from a cis reduction of one of the triple bonds under CO_2. The proton source is the electrolytic medium (residual water, supporting electrolyte, DMF) according to the tests of deuterium incorporation summarized in Scheme IV. This cis-hydrogenation has some analogy to the Zn/MeOH reduction of alkynes or enynes.[30] Electrochemically, this reduction is interesting from the point of view of the chemoselective monohydrogenation of a conjugated diyne system, as well as from the point of view of the stereoselectivity. Direct electrochemical reduction of triple bonds often leads to nonselective reactions.[31] The electrochemical Ni–bpy-catalyzed cis-reduction of 1,3-diynes to 1,3-enynes is an example of high substrate selectivity (1,3-enynes being carboxylated but not reduced) and constitutes, as well, an example of CO_2 enhancement of the catalytic reduction activity. Small changes of the catalytic structure may have significant effects on the activity and selectivity of hydrogenation reactions.[32] A CO_2 enhancement of butadiene oligomerization has already been reported for Pd complexes.[33]

Conclusions

The nickel-catalyzed electrochemical method for the functionalization of unsaturated hydrocarbons has been applied to several diynes with various catalytic systems. Albeit the presence of two C≡C unsaturations, a single CO_2 incorporation was generally observed. Unsaturated monocarboxylic acids were the main reaction products, as a result of a cis hydrocarboxylation-type reaction affecting only one of the triple bonds. The regio- and stereoselectivities were very dependent on the diyne structure and on the catalytic system.

The Ni–PMDTA system enables a highly selective CO_2 incorporation into conjugated diynes leading to substituted (E)-2-vinylidene-3-yne carboxylic acids, in one step. This catalytic system is also regioselective toward the functionalization of the 2-position of diynes bearing terminal ≡C–H bonds. The Ni–bpy system favors the formation of cyclic derivatives in nonconjugated systems and induces a cis reduction in conjugated diynes.

This study constitutes a further example of CO_2 activation resulting in the formation of new C–C bonds. The electrosyntheses were carried out under mild conditions (CO_2 pressure of 1–5 atm, T = 20–60 °C) utilizing Ni(II) salts as catalyst precursors in an easy electrochemical setup.

Experimental Section

Reagents and Chemicals. All the chemicals employed were of reagent-grade quality. Dimethylformamide (Prolabo) was distilled under argon from calcium hydride and copper sulfate under reduced pressure and was dried over 4-Å molecular sieves. Tetrabutylammonium tetrafluoroborate (Fluka) was dried by heating overnight at 70 °C in vacuo. $Ni(bpy)_3(BF_4)_2$ was prepared according to ref 34. $NiBr_2$·DME (Alfa) was used directly, added to PMDTA in the electrolytic solution. Metals used as the anode were magnesium rod (99.8%, diameter 1 cm, Prolabo), zinc, and aluminum rods (Alfa). The cathodes were of carbon fiber, stainless steel, or nickel foam (Alfa). Other reagents were obtained commercially and used as supplied. Carbon dioxide was N45 (Alphagaz). The electrolyses in the absence of CO_2 were run under argon atmosphere.

---

(29) Kanai, H.; Choe, S. B.; Klabunde, K. J. *J. Am. Chem. Soc.* **1986**, *108*, 2019.

(30) (a) Chou, W. N.; Clark, D. L.; White, J. B. *Tetrahedron Lett.* **1991**, *32*, 299. (b) Shosenji, H.; Nakano, Y.; Yamada, K. *Chem. Lett.* **1988**, *6*, 1033.

(31) Utley, J. H. P.; Lines, R. The electrochemistry of the carbon-carbon triple bond. In *The Chemistry of the Carbon–Carbon Triple Bond*; Patai, S., Ed.; Wiley and Sons: New York, 1978; Part 2, Chapter 7.

(32) Maier, N. F. *Katalyse* **1989**, *118*, 243.

(33) Kohnle, J. F.; Slaugh, L. H.; Nakamaye, K. L. *J. Am. Chem. Soc.* **1969**, *91*, 5904.

(34) Duñach, E.; Périchon, J. *J. Organomet. Chem.* **1988**, *352*, 239.

Cells and Instrumentation. For carboxylations at atmospheric CO_2 pressure, the electrochemical one-compartment cell is a cylindrical glass vessel of ≈50 mL volume, such as that described in ref 11a, equipped with a carbon fiber cathode (20 cm^2) and a magnesium rod (immersed to 3 cm) anode. A closed stainless-steel cell was used for carboxylations at $P(CO_2) = 5$ atm. Cyclic voltammetric experiments were performed with the aid of Solea Tacussel conventional equipment and were carried out at 25 °C by utilizing a gold microelectrode (Tacussel). All potentials are quoted with respect to the saturated calomel electrode (SCE). Intensiostatic electrolyses were carried out by using a stabilized constant current supply (Sodilec, EDL 36.07).

^1H and ^{13}C NMR spectra were recorded on a Bruker AC 200 E spectrometer. Infrared spectra were recorded on a Perkin-Elmer 577 spectrophotometer. Mass spectra were obtained on a Nermag R-10-10 (Orsay, France) or a Finnigan ITD 800 spectrometer coupled to a Varian 300 chromatograph with a 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 an Intersmat IGC 120 chromatograph with a SE-30 stainless steel ($^1/_8$-in. × 13-ft) column or a Delsi DI 200 chromatograph equipped with a 25-m DB-1 capillary column. Products were isolated by flash silica gel (230–240 mesh) column chromatography. Elemental analyses and high resolution mass spectra were performed by the Service de Microanalyse du CNRS, Lyon, France.

General Electrolysis Procedure. A DMF (40 mL) solution of nickel complex (either $Ni(bpy)_3(BF_4)_2$ (0.3 mmol) or $NiBr_2 \cdot DME$ (0.3 mmol) + PMDTA (0.6 mmol)), containing $n\text{-}Bu_4N^+BF_4^-$ (0.3 mmol) and the diyne (3 mmol) was electrolyzed under carbon dioxide (1 or 5 atm). A current of 50 mA was applied between the electrodes connected to a DC power supply (apparent cathodic current density of 0.25 A dm^{-2}, applied voltage ca. 3–15 V), with passage of 2–4 F/mol of diyne, for reaction times of 5–7 h.

The reaction mixture was esterified directly in DMF by adding anhydrous K_2CO_3 (4 mmol) and methyl iodide (8 mmol) and stirring the mixture at 50 °C for 5 h. The solution was hydrolyzed with 50 mL of 0.1 N HCl solution 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 carboxylic acids were isolated by flash chromatography on silica gel with pentane/Et_2O mixtures as eluent. The products were analyzed by NMR and IR spectrometry, mass spectroscopy, and GLC. The following compounds were identified by comparison of their physical and spectral data with those given in the cited references: **6a**,[35] **6b**,[36] **7a**,[37] **7b**,[38] **13b**,[39] **21**,[8] **22**,[8] **23**.[8] For new compounds:

2-Methylene-7-octynoic acid methyl ester, 5a: ^1H NMR ($CDCl_3$) δ 6.15 (s, 1 H), 5.55 (s, 1 H), 3.75 (s, 3 H), 2.36–2.29 (m, 1 H), 2.25–2.17 (m, 2 H), 1.96 (t, $J = 2.6$ Hz, 1 H), 1.67–1.56 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 167.46, 140.13, 124.63, 84.07, 68.28, 51.60, 31.17, 27.80, 27.24, 18.05; IR (neat) 3300, 3100, 2950, 2930, 2850, 2120, 1725, 1630 cm^{-1}; MS 166 (M), 165, 151, 135, 107, 79 (base). Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 72.17; H, 8.55.

2-Methylene-6-heptynoic acid methyl ester, 5b: ^1H NMR ($CDCl_3$) δ 6.18 (s, 1 H), 5.59 (s, 1 H), 3.76 (s, 3 H), 2.43 (t, $J =$ 7.4 Hz, 2 H), 2.22 (td, $J = 7.2, 2.6$ Hz, 2 H), 1.98 (t, $J = 2.6$ Hz, 1 H), 1.79–1.64 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 167.31, 139.64, 125.42, 84.12, 68.66, 51.76, 30.81, 27.00, 17.74; IR (neat) 3300, 3100, 2990, 2950, 2920, 2870, 2840, 2120, 1720, 1630 cm^{-1}; MS 152 (M), 151, 137, 121, 93 (base). Anal. Calcd for $C_9H_{12}O_2$: C, 71.03; H, 7.95. Found: C, 71.08; H, 7.97.

(*E*)-2-Propylidene-7-decynoic acid methyl ester, 8a: ^1H NMR ($CDCl_3$) δ 6.72 (t, $J = 7.5$ Hz, 1 H), 3.73 (s, 3 H), 2.37–2.09 (m, 8 H), 1.62–1.45 (m, 4 H), 1.15–0.89 (m, 6-H); ^{13}C NMR ($CDCl_3$) δ 168.52, 141.86, 131.48, 82.31, 79.17, 51.47, 28.61, 27.90, 27.77, 19.97, 18.45, 14.27, 13.84, 12.32; IR (neat) 3020, 2970, 2940, 2930, 2870, 2850, 2200, 1710, 1640 cm^{-1}; MS 222 (M), 193, 191, 163, 67 (base); exact mass calcd for $C_{14}H_{22}O_2$ 222.1620, found 222.1609.

(*E*)-2-Ethylidene-5-heptynoic acid methyl ester, 8b: ^1H NMR ($CDCl_3$) δ 6.87 (q, $J = 7.2$ Hz, 1 H), 3.66 (s, 3 H), 2.50–2.39 (m, 2 H), 2.30–2.08 (m, 2 H), 1.70–1.66 (m, 6 H); ^{13}C NMR ($CDCl_3$) δ 167.68, 138.92, 131.33, 78.28, 75.61, 51.35, 28.16, 25.83, 17.90, 14.17; IR (neat) 3010, 2980, 2950, 2920, 2850, 2210, 1715, 1650 cm^{-1}; MS 166 (M), 151, 135, 107 (base); exact mass calcd for $C_{10}H_{14}O_2$ 166.0994, found 166.0982.

(*E*)-2-Ethyl-2-undecen-8-ynoic acid methyl ester, 9a: ^1H NMR ($CDCl_3$) δ 6.74 (t, $J = 7.5$ Hz, 1 H), 3.73 (s, 3 H), 2.37–2.09 (m, 8 H), 1.62–1.45 (m, 4 H), 1.15–0.89 (m, 6 H); ^{13}C NMR ($CDCl_3$) δ 168.68, 144.30, 133.93, 82.19, 79.42, 51.47, 28.79, 28.43, 26.08, 21.80, 18.45, 14.27, 13.28, 12.32; IR (neat) 3015, 2970, 2940, 2930, 2870, 2850, 2200, 1715, 1630 cm^{-1}; MS 222 (M), 207, 193, 191, 163, 67 (base); exact mass calcd for $C_{12}H_{17}O_2$ ($M - C_2H_5$) 193.1229, found 193.1235.

(*E*)-2-Methyl-2-octen-6-ynoic acid methyl ester, 9b: ^1H NMR ($CDCl_3$) δ 6.70 (t, $J = 7.0$ Hz, 1 H), 3.65 (s, 3 H), 2.30–2.08 (m, 4 H), 1.77 (s, 3 H), 1.70–1.66 (m, 3 H); ^{13}C NMR ($CDCl_3$) δ 168.25, 140.32, 128.35, 77.71, 76.05, 51.47, 28.16, 18.19, 17.90, 12.28; IR (neat) 3020, 2990; 2950, 2920, 2860, 2230, 1720, 1650 cm^{-1}; MS 166 (M), 151 (base), 135, 107; exact mass calcd for $C_{10}H_{14}O_2$ 166.0994, found 166.1007.

2-[2-(Propylidene)cyclohexylidene]butanoic acid methyl ester, 10a: ^1H NMR ($CDCl_3$) δ 5.13 (t, $J = 7.3$ Hz, 1 H), 3.60 (s, 3 H), 2.36–2.09 (m, 6 H), 1.98 (t, $J = 7.5$ Hz, 2 H), 1.65–1.48 (m, 4 H), 1.14–0.81 (m, 6 H); ^{13}C NMR ($CDCl_3$) δ 172.20, 146.12, 140.15, 127.72, 125.94, 50.81, 30.77, 28.91, 27.44, 27.04, 22.75, 20.57, 13.38, 12.20; IR (neat) 3015, 2980, 2930, 2850, 1710, 1640 cm^{-1}; MS 222 (M), 193 (base), 191; exact mass calcd for $C_{14}H_{22}O_2$ 222.1620, found 222.1591.

2-(5-Octynyl)-3-ethyl-1,4-butenedioic acid dimethyl ester, 11a: ^1H NMR ($CDCl_3$) δ 3.75 (m, 6 H), 2.43–2.32 (m, 4 H), 2.19–2.08 (m, 4 H), 1.5 (m, 4 H), 1.13–1.02 (m, 6 H); ^{13}C NMR ($CDCl_3$) δ 169.00, 168.89, 139.21, 136.88, 81.87, 78.57, 51.88 (2C), 28.67, 28.50, 27.27, 22.68, 18.23, 14.15, 12.59, 12.20; IR (neat) 2960, 2930, 2870, 2850, 2210, 1735, 1720, 1635 cm^{-1}; MS 251 ($M - C_2H_5$), 250, 221, 190 (base); exact mass calcd for $C_{15}H_{21}O_3$ (M − OMe) 249.1491, found 249.1485.

2-(3-Pentynyl)-3-methyl-1,4-butenedioic acid dimethyl ester, 11b: ^1H NMR ($CDCl_3$) δ 3.69 (s, 3 H), 3.68 (s, 3 H), 2.48 (t, $J = 7.5$ Hz, 2 H), 2.26–2.21 (m, 2 H), 1.94 (s, 3 H), 1.68 (t, $J = 2.5$ Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 168.97, 168.81, 138.40, 135.87, 77.78, 77.20, 52.13, 52.00, 30.80, 30.72, 29.00, 17.44; IR (neat) 2950, 2920, 2850, 2230, 1735, 1720, 1640 cm^{-1}; MS 209 (M − Me), 193, 165, 161, 133 (base); exact mass calcd for $C_{12}H_{16}O_4$ 224.1049, found 224.1034.

2-Methylene-4-decynoic acid methyl ester, 12a: ^1H NMR ($CDCl_3$) δ 6.22 (m, 1 H), 5.95 (m, 1 H), 3.68 (s, 3 H), 3.12 (m, 2 H), 2.13–2.07 (m, 2 H), 1.45–1.26 (m, 6 H), 0.83 (t, $J = 6.7$ Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 166.44, 136.07, 125.46, 84.13, 75.33, 51.60, 30.86, 28.46, 22.00, 21.63, 18.49, 13.71; IR (neat) 3100, 3020, 2990, 2950, 2930, 2860, 2250, 1735, 1630 cm^{-1}; MS 194 (M), 179, 137, 123, 109, 95 (base). Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 74.07; H, 9.42.

2-Methylene-5-decynoic acid methyl ester, 12b: ^1H NMR ($CDCl_3$) δ 6.20 (s, 1 H), 5.63 (s, 1 H), 3.74 (s, 3 H), 2.47 (t, $J =$ 7.5 Hz, 2 H), 2.37–2.29 (m, 2 H), 2.13–2.09 (m, 2 H), 1.50–1.29 (m, 4 H), 0.89 (t, $J = 6.9$ Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 166.92, 138.61, 125.64, 80.88, 78.52, 51.44, 31.41, 30.94, 21.64, 18.11, 17.89, 13.31; IR (neat) 3090, 2950, 2930, 2870, 2850, 2180, 1720, 1630 cm^{-1}; MS 195 (M + 1); 179, 165, 163, 151, 137 (base), 135. Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 74.05; H, 9.45.

2-Methylene-11-hexadecynoic acid methyl ester, 12c: ^1H NMR ($CDCl_3$) δ 6.12 (m, 1 H), 5.60 (m, 1 H), 3.75 (s, 3 H), 2.28–2.12 (m, 6 H), 1.42–1.30 (m, 16 H), 0.93–0.85 (m, 3 H); ^{13}C NMR ($CDCl_3$) δ 168.49, 141.31, 124.32, 80.02, 79.91, 51.60, 31.80, 31.20, 29.24, 29.07 (2C), 28.73, 28.30, 21.85 (2C), 18.66, 18.36, 13.55; IR (neat) 3090, 2990, 2950, 2930, 2870, 2850, 2250, 1710, 1630 cm^{-1}; MS (C.I., $i\text{-}C_4H_{10}$) 279 (M + 1), 248, 220, 81 (base); exact mass calcd for $C_{18}H_{30}O_2$ 278.2246, found 278.2230.

(*E*)-2-Heptadecen-12-ynoic acid methyl ester, 13c: ^1H NMR ($CDCl_3$) δ 6.97 (dt, $J = 15.6, 7.0$ Hz, 1 H), 5.82 (dt, $J = 15.7,$ 1.6 Hz, 1 H), 3.73 (s, 3 H), 2.21–2.11 (m, 6 H), 1.46–1.30 (m, 16

---

(35) Frosch, J. V.; Harrison, I. T.; Lythgve, B.; Sakensa, A. K. *J. Chem. Soc., Perkin Trans. 1* **1974**, 2005.

(36) Chiusoli, G. P.; Costa, H.; Pergreffi, P.; Reverberi, S.; Salerno, G. *Gazz. Chim. Ital.* **1985**, *115*, 691.

(37) Herbert, A. J.; Dale, J. *J. Chem. Soc.* **1965**, 3160.

(38) Grigg, R.; Scott, R.; Stevenson, P. *J. Chem. Soc., Perkin Trans. 1* **1988**, 1357.

(39) Mitsudo, T.; Nakagawa, Y.; Watanabe, K.; Hori, Y.; Misawa, H.; Watanabe, H.; Watanabe, Y. *J. Org. Chem.* **1985**, *50*, 565.

H), 0.94–0.87 (m, 3 H); ^{13}C NMR ($CDCl_3$) δ 166.65, 149.87, 121.42, 80.23, 80.11, 51.26, 32.16, 31.22, 29.27, 29.19, 29.08 (2C), 28.73, 28.67, 21.88, 18.68, 18.39, 13.59; IR (neat) 3020, 2950, 2920, 2850, 2220, 1730, 1650 cm^{-1}; MS (C.I., i-C_4H_{10}) 279 (M + 1), 248, 220, 81 (base); exact mass calcd for $C_{17}H_{27}O$ (M − OMe) 247.2062, found 247.2085.

2-(9-Tetradecynyl)-1,4-butenedioic acid dimethyl ester, 14c: ^{1}H NMR ($CDCl_3$) δ 5.73 (t, J = 1.3 Hz, 1 H), 3.76 (s, 3 H), 3.65 (s, 3 H), 2.28 (dt, J = 6.8, 1.2 Hz, 2 H), 2.07–2.04 (m, 4 H), 1.39–1.19 (m, 16 H), 0.87–0.80 (m, 3 H); ^{13}C NMR ($CDCl_3$) δ 169.40, 165.40, 150.98, 118.99, 80.19, 80.07, 52.27, 51.75, 34.36, 31.24, 29.11 (2C), 28.92, 28.82, 28.72, 26.89, 21.89, 18.70, 18.40, 13.59; IR (neat) 3010, 2960, 2940, 2920, 2850, 2220, 1735, 1725, 1650 cm^{-1}; MS (C.I., i-C_4H_{10}) 337 (M + 1), 306 (base), 288, 246, 218; exact mass calcd for $C_{20}H_{32}O_4$ 336.2301, found 336.2319.

(*E*)-2-Hexylidene-3-nonynoic acid methyl ester, 16a: ^{1}H NMR ($CDCl_3$) δ 7.16 (t, J = 7.7 Hz, 1 H), 3.78 (s, 3 H), 2.52–2.35 (m, 4 H), 1.62–1.26 (m, 12 H), 0.89 (t, J = 6.3 Hz, 6 H); ^{13}C NMR ($CDCl_3$) δ 165.28, 151.81, 116.93, 96.88, 73.84, 51.76, 31.14, 30.67, 30.25, 28.00, 27.44, 22.06, 21.84, 19.15, 13.53 (2 C); IR (neat) 2960, 2930, 2860, 2220, 1730, 1610 cm^{-1}; MS 250 (M), 235, 219, 191, 91 (base). Anal. Calcd for $C_{16}H_{26}O_2$: C, 76.75; H, 10.47. Found: C, 76.61; H, 10.43.

(*E*)-2-Cyclopentylmethylene-4-cyclopentyl-3-butynoic acid methyl ester, 16b: ^{1}H NMR ($CDCl_3$) δ 7.04 (d, J = 9.8 Hz, 1 H), 3.77 (s, 3 H), 3.10–2.98 (m, 1 H), 2.87–2.80 (m, 1 H), 1.98–1.89 (m, 4 H), 1.84–1.57 (m, 10 H), 1.44–1.26 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 165.79, 156.86, 115.49, 101.00, 73.61, 52.12, 41.17, 33.74 (2 C), 32.49 (2 C), 30.89, 25.53, 24.81 (2 C); IR (neat) 2950, 2910, 2860, 2220, 1750, 1610 cm^{-1}; MS 246 (M), 231, 215, 187 (base). Anal. Calcd for $C_{16}H_{22}O_2$: C, 78.01; H, 9.00. Found: C, 78.15; H, 9.04.

(*E*)-2-(Phenylmethylene)-4-phenyl-3-butynoic acid methyl ester, 16c: ^{1}H NMR ($CDCl_3$) δ 8.10–8.05 (m, 2 H), 7.96 (s, 1 H), 7.58–7.53 (m, 2 H), 7.45–7.32 (m, 6 H), 3.89 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 166.08, 145.53, 134.35, 131.52, 130.59, 130.42 (2 C), 128.71, 128.46 (2 C), 128.36 (2 C), 122.83, 112.76, 97.98, 85.17, 52.75; IR (neat) 3060, 3020, 2950, 2200, 1720, 1600, 1590, 1490 cm^{-1}; MS 262 (M), 247, 231, 203, 105 (base). Anal. Calcd for $C_{18}H_{14}O_2$: C, 82.42; H, 5.38. Found: C, 82.38; H, 5.31.

(*E*)-2-(Methoxyethylidene)-5-methoxy-3-pentynoic acid methyl ester, 16d: ^{1}H NMR ($CDCl_3$) δ 7.28 (t, J = 5.9 Hz, 1 H), 4.32 (d, J = 5.8 Hz, 2 H), 4.32 (s, 2 H), 3.81 (s, 3 H), 3.43 (s, 3 H), 3.39 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 164.00, 149.27, 116.56, 93.64, 78.71, 70.25, 59.94, 58.38, 57.35, 52.34; IR (neat) 2980, 2930, 2890, 2820, 2210, 1725, 1620 cm^{-1}; MS 167 (M − OMe), 166 (base), 151; MS (C.I., i-C_4H_{10}) 199 (M + 1), 167 (base). Anal. Calcd for $C_{10}H_{14}O_4$: C, 60.60; H, 7.12. Found: C, 60.76; H, 7.15.

(*E*)-2-(2-Phenoxyethylidene)-5-phenoxy-3-pentynoic acid methyl ester, 16e: ^{1}H NMR ($CDCl_3$) δ 7.22 (t, J = 7.0 Hz, 1 H), 7.00–6.72 (m, 10 H), 4.84 (s, 2 H), 4.70 (d, J = 7.0 Hz, 2 H), 3.73 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 164.30, 157.61, 157.07, 149.17, 129.42 (2 C), 129.34, 121.55, 121.18, 120.19, 116.61, 115.23 (2 C), 114.89, 114.36, 93.81, 79.31, 65.72, 55.99, 52.75; IR (neat) 3070, 3040, 2950, 2840, 2250, 1700, 1600, 1590, 1500, 1490 cm^{-1}; MS 263 (M − COOMe), 229, 197, 169, 77, 65 (base). Anal. Calcd for $C_{20}H_{18}O_4$: C, 74.52; H, 5.63. Found: C, 74.55; H, 5.65.

(*E*)-2-(Phenylmethylene)-3-octynoic acid methyl ester, 16f: ^{1}H NMR ($CDCl_3$) δ 8.06–8.01 (m, 2 H), 7.85 (s, 1 H), 7.42–7.30 (m, 3 H), 3.86 (s, 3 H), 2.53 (t, J = 6.8 Hz, 2 H), 1.73–1.42 (m, 4 H), 0.96 (t, J = 7.1 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 166.57, 144.42, 134.54, 130.26, 130.15 (2 C), 128.31 (2 C), 113.33, 100.18, 77.02, 52.66, 30.38, 22.00, 19.65, 13.57; IR (neat) 3060, 3020, 2960, 2930, 2870, 2220, 1720, 1600, 1570, 1490 cm^{-1}; MS 242 (M), 227, 211, 199 (base), 183. Anal. Calcd for $C_{16}H_{18}O_2$: C, 79.31; H, 7.49. Found: C, 79.18; H, 7.44.

(*E*)-2-(Phenylethynyl)-4-methoxy-2-butenoic acid methyl ester, 16g: ^{1}H NMR ($CDCl_3$) δ 7.53–7.48 (m, 2 H), 7.36–7.28 (m, 4 H), 4.40 (d, J = 5.9 Hz, 2 H), 3.83 (s, 3 H), 3.40 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 164.30, 148.64, 131.51 (2 C), 128.78, 128.26 (2 C), 122.30, 117.34, 97.71, 81.79, 70.52, 58.58, 52.53; IR (neat) 3050, 2950, 2930, 2820, 2220, 1730, 1620, 1600, 1490 cm^{-1}; MS 230 (M), 215 (base), 199, 171. Anal. Calcd for $C_{14}H_{14}O_3$: C, 73.03; H, 6.13. Found: C, 72.88; H, 6.15.

Supplementary Material Available: ^{1}H NMR spectra for compounds **8a**, **8b**, **9a**, **9b**, **10a**, **11a**, **11b**, **12c**, **13c**, and **14c** (10 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from ACS; see any current masthead page for ordering information.