Nickel- and Phase-Transfer-Catalyzed Carboxylation of Propargyl and Allenyl Halides

Henri Arzoumanian,* Fabienne Cochini, Didier Nuel, and Noé Rosas†

Ecole Nationale Supérieure de Synthèses, de Procédés et d'Ingéniérie Chimiques d'Aix-Marseille, URA du CNRS 1410, Université d'Aix-Marseille III, 13397 Marseille, France

Received November 30, 1992

Propargyl and allenyl halides are carbonylated in the presence of $Ni(CN)_2$ under phase-transfer conditions (4-methyl-2-pentanone, 5 N NaOH, tetraalkylammonium halide) at room temperature or slightly above and atmospheric pressure of CO to give allenic monoacids or unsaturated diacids with high regio- and stereoselectivities. It is shown that the monoacid is first obtained followed by a slower second carbonylation. Propargyl halides react catalytically whereas allenyl halides necessitate the presence of excess KCN. This is rationalized in terms of two different mechanisms; in the former case, the nickel catalyst plays the role of a true nucleophile, and in the latter the nickel center undergoes an oxidative addition/reductive elimination sequence facilitated by the high trans influence of cyano groups.

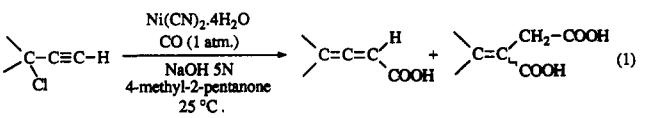
Introduction

Carbonylation of organic substrates mediated by transition metal complexes using the technique of phase-transfer catalysis is a well-studied reaction.[1] Although the metals most commonly used have been cobalt[2,3] and iron,[4,5] nickel has aroused increasing interest in recent years since Alper and co-workers showed that $Ni(CN)_2$ can advantageously replace $Ni(CO)_4$ and become a versatile and much safer carbonylation catalyst.[6] This has been an incentive to revisit the rich field of carbonylation reactions catalyzed by $Ni(CO)_4$ developed in the 1950's[7-15] with the endeavor to obtain new reactivities and selectivities.

This report concerns the nickel cyanide-catalyzed carbonylation, under phase-transfer conditions, of propargyl and allenyl halides to give mono and/or dicarboxylic acids.

Results and Discussion

Propargyl Halides. Stoichiometric carbonylation of alkynols[11,15] or propargyl halides[12] with nickel tetracarbonyl have been reported to give a monocarboxylated product, whereas nickel cyanide, under phase-transfer conditions, transformed alkynols exclusively into dicarboxylic acids.[16] More recently we showed in a preliminary note that propargyl halides are catalytically carbonylated under very mild phase-transfer conditions with $Ni(CN)_2$ to give either mono or dicarboxylic acids.[17]



(1)

We have now extended this reaction to variously substituted propargyl halides and showed its general character. The results given in Table I lead to the following comments:

The reaction proceeds by two successive carbonylations, the first one occurring at the terminal carbon to give an allenyl derivative followed by a slower second step to give the observed 1,2-dicarboxylic acid. This second carbonylation could plausibly occur either via a concerted base cleavage and intramolecular nickel attack onto the center carbon of the allene moiety or simply by a prior formation of an allenic acid followed by its carbonylation. No definite distinction could be established between these two possible routes.[17]

The high stereoselectivities observed are indicative of a sterically demanding pathway; this is supported by the stereochemical inversion observed by changing the nature of the transfer agent and its consequence on the steric requirement of the nickelate ion-pair catalyst. This steric requirement is corroborated by the difficulty to achieve a dicarbonylation with trisubstituted propargyl halides.

Finally, bromides react at a slightly slower rate than chlorides.

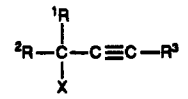
A plausible mechanism (Scheme I) taking into account all these observations features a nickel complex which acts as a nucleophile through an S_N2' mechanism.[19]

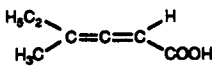
† On sabbatical leave from Instituto de Quimica, UNAM, Mexico.

(1) Petrignani, J. F. In *The Chemistry of the Metal-Carbon Bond*; Hartley, F. R. Ed.; Wiley: New York, 1989; Vol. 5, Chapter 3.
(2) Alper, H.; Des Abbayes, H. *J. Organometal. Chem.* **1977,** *134,* C11.
(3) Cassar, L.; Foa, M. *J. Organometal. Chem.* **1977,** *134,* C15.
(4) Kimura, Y.; Tomita, Y.; Nakanishi, S.; Otsuji, Y. *Chem. Lett.* **1979,** 321.
(5) Tanguy, G.; Weinberger, B.; Des Abbayes, H. *Tetrahedron Lett.* **1984,** 5529.
(6) Joo, F.; Alper, H. *Organometallics* **1985,** *4,* 1775.
(7) Reppe, W. *Recent Developments in the Chemistry of Acetylene and Carbon Monoxide*; Springer-Verlag: Berlin, 1949.
(8) Reppe, W. *Liebigs Ann. Chem.* **1953,** *582,* 1.
(9) Jones, E. R. H.; Shen, T. Y.; Whiting, M. C. *J. Chem.* Soc. **1950,** 230.
(10) Jones, E. R. H.; Shen, T. Y.; Whiting, M. C. *J. Chem.* Soc. **1951,** 48.
(11) Jones, E. R. H.; Whitham, G. H.; Whiting, M. C. *J. Chem.* Soc. **1957,** 4628.
(12) Chiusoli, G. P. *Chim. Indus. (Milan)* **1959,** *41,* 506.
(13) Chiusoli, G. P. *Chim. Indus. (Milan)* **1959,** *41,* 513.
(14) Rosenthal, R. W.; Schwartzman, L. H. *J. Org. Chem.* **1959,** *24,* 836. Rosenthal, R. W.; Schwartzman, L. H.; Greco, N. P.; Proper, R. *J. Org. Chem.* **1963,** *28,* 2835.
(15) Corey, E. J.; Hegedus, L. S. *J. Am. Chem. Soc.* **1969,** *91,* 1233.
(16) Satyanarayana, N.; Alper, H. *Organometallics* **1991,** *10,* 804.
(17) Arzoumanian, H.; Cochini, F.; Nuel, D.; Petrignani, J. F.; Rosas, N. *Organometallics* **1992,** *11,* 493.
(18) Tsiji, J.; Sugiura, T.; Minami, I. *Tetrahedron Lett.* **1986,** 731.
(19) In Scheme I, the direct conversion of **6** to **7** can alternatively be described by a 1,3-metal shift to give a vinylketene[20] prior to ^-OH attack. We thank one of the reviewers for making this suggestion.
(20) Wouters, J. M. A.; Avis, M. W.; Elsevier, C. J.; Kyriakidis, C. E.; Stam, C. H. *Organometallics* **1990,** *9,* 2203.

0276-7333/93/2312-1871$04.00/0

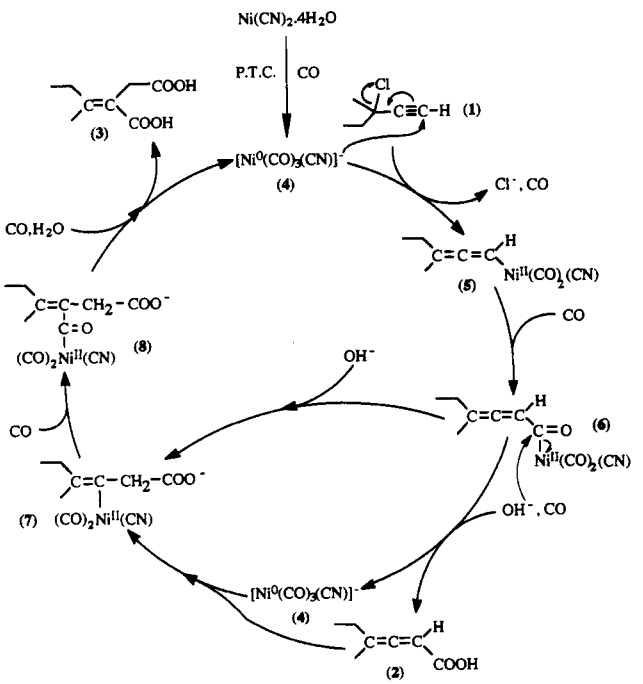
Table I. Carbonylation of Propargyl Halides[a]



R^1	R^2	R^3	X	temp, °C	time, h	yield,[b] %	product distribution, % monoacid	product distribution, % diacid (*E*/*Z*)
C_2H_5	CH_3	H	Cl (**1**)	25	1	94	87 (**2**)	13 (5/95)[c] (**3**)
C_2H_5	CH_3	H	Cl (**1**)	60	1	92	61 (**2**)	39 (**3**)
C_2H_5	CH_3	H	Cl (**1**)	95	1	91	24 (**2**)	76 (7/93) (**3**)
C_2H_5	CH_3	H	Cl (**1**)	25	5	93	79 (**2**)	21 (**3**)
C_2H_5	CH_3	H	Cl (**1**)	25	24	94	36 (**2**)	64 (**3**)
C_2H_5	CH_3	H	Cl (**1**)	25	48	96	–	100 (9/91) (**3**)
C_2H_5	CH_3	H	Br (**9**)	25	48	94	13 (**2**)	87 (10/90) (**3**)
C_2H_5	CH_3	H	Cl (**1**)[d]	25	48	94	5 (**2**)	95 (10/90) (**3**)
C_2H_5	CH_3	H	Cl (**1**)[e]	25	48	71	52 (**2**)	48 (88/12) (**3**)
CH_3	CH_3	H	Cl (**10**)	25	1	71	48 (**11**)	52 (**12**)[f]
H	H	H	Cl (**13**)	65	2	85	15[g] (**14**)	85 (**15**)
H	H	H	Br (**16**)	65	2	68	32[g] (**14**)	68 (**15**)[h]
C_5H_{11}	H	H	Cl (**17**)	25	4	90	95 (**18**)[i]	5 (**19**)
c-C_6H_{10}		H	Cl (**20**)	25	6	92	85 (**21**)	15 (**22**)[j]
i-C_4H_9	CH_3	n-C_3H_7	Cl (**23**)	25	8	75	100 (**24**)	–
C_2H_5	CH_3	n-C_4H_9	Cl (**25**)	25	6	89	100 (**26**)	–
i-C_4H_9	CH_3	n-C_4H_9	Cl (**27**)	25	24	95	100 (**28**)	–
				25	24	94	–	100 (12/88) (**3**)

[a] Reaction conditions: propargyl halide (14 mmol), 4-methyl-2-pentanone (50 mL), 5 N NaOH (20 mL), $Ni(CN)_2{\cdot}4H_2O$ (1.0 mmol), tetrabutylammonium bromide (0.3 mmol), CO (1 atm), 25 °C. [b] Isolated yields. [c] Ratio established by ^1H NMR and based on reported data.[16] [d] Phase-transfer agent: tetrabutylammonium chloride. [e] Phase-transfer agent: cetyltrimethylammonium bromide. [f] Known compound (Tsuji, T.; Nogi, T. Jpn. Pat. 6809,046, Apr 1968; *Chem. Abstr.* **1968**, *70*, 19808w). [g] Could not be obtained in pure form.[18] Estimated from the yield of isolated diacid. [h] Commercially available compound. [i] Known compound (Clinet, J. C.; Linstrumelle, G. *Synthesis* **1981**, 875). [j] Known compound (Nogi, T.; Tsuji, T. *Tetrahedron* **1969**, *25*, 4099).

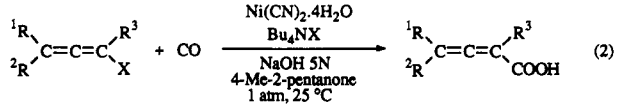
Scheme I. Catalytic Cycle for the Carbonylation of Propargyl Halide 1



Another route remained, however, possible: one in which the propargyl halide was rearranged to an allenyl halide prior to carbonylation. Various substituted haloallenes were thus synthesized and submitted to the same experimental conditions.

Haloallenes. Carbonylation under phase-transfer conditions mediated by cobalt,[21] manganese,[22] or nickel[23] have been reported for allenes to give, respectively, α,β-unsaturated hydroxy ketones, α,β-unsaturated ketones, or β,γ-unsaturated acids. Carbonylation of allenyl halides, on the other hand, have only been studied under classical homogeneous conditions catalyzed by Pd or Pt, yielding as the major product cyclic dicarbonylated species.[20,24]

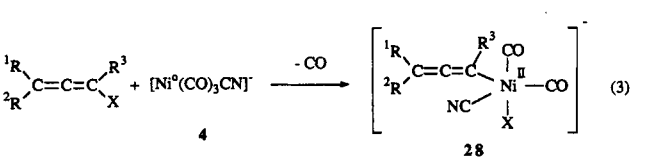
When submitted to the same mild phase-transfer conditions in the presence of $Ni(CN)_2$, haloallenes were transformed to allenic acids with high regioselectivity.



(2)

This is analogous to the initial step of propargyl halide carbonylation with the main difference that the reaction proceeded only to a 11% yield based on allenyl halide and then stopped. Doubling the ratio nickel/substrate resulted simply in the formation of twice the amount of allenic acid (20%).

Assuming that the active species is the $[Ni^0(CO)_3CN]^-$ anion for both type of substrate, the nucleophilic attack onto the allenic halide (comparable to a vinylic halide) would be expected to be more difficult and it seems more feasible that the reaction would rather proceed via an oxidative addition to give an allenylnickel(II) (**28**).



(3)

(21) Gambarotta, S.; Alper, H. *J. Org. Chem.* **1981**, *46*, 2142.
(22) Satyanarayana, N.; Alper, H. *J. Chem. Soc., Chem. Commun.* **1991**, 8.
(23) Satyanarayana, N.; Alper, H.; Amer, I. *Organometallics* **1990**, *9*, 284.
(24) Trieu, N. D.; Elsevier, C. J.; Vrieze, K. *J. Organometal. Chem.* **1987**, *325*, C23.

Table II. Carbonylation of Haloallenes[a]

R^1	R^2	R^3	X	[KCN]/[Ni]	reaction time, h	yield, %[b]
C_2H_5	CH_3	H	Br (**32**)	–	1	11 (**2**)
C_2H_5	CH_3	H	Br (**32**)	*c*	1	20 (**2**)
C_2H_5	CH_3	H	Br (**32**)	–	48	13 (**2**)
C_2H_5	CH_3	H	Br (**32**)	14	48	73 (**2**) (+9% diacid **3**)
C_2H_5	CH_3	H	Cl (**33**)	2.7	48	10 (**2**)
C_2H_5	CH_3	H	Cl (**33**)	6.7	48	20 (**2**)
C_2H_5	CH_3	H	Cl (**33**)	10	48	69 (**2**) (+5% diacid **3**)
C_2H_5	CH_3	H	Cl (**33**)	14	48	80 (**2**) (+7% diacid **3**)
C_2H_5	CH_3	H	Cl (**33**)	17	48	64 (**2**) (+6% diacid **3**)
C_2H_5	CH_3	H	Cl (**33**)	21	48	15 (**2**)
C_2H_5	CH_3	H	Cl (**33**)	28	48	0
C_2H_5	CH_3	H	Cl (**33**)	14[d]	48	50 (**2**)
CH_3	CH_3	H	Br (**34**)	14	48	61 (**11**)
CH_3	CH_3	H	Cl (**35**)	14	48	69 (**11**)
C_6H_5	CH_3	H	Br (**36**)	14	48	70 (**37**)[e]
C_2H_5	CH_3	n-C_4H_9	Cl (**38**)	14	48[f]	82 (**26**)
i-C_4H_9	CH_3	n-C_3H_7	Cl (**39**)	14	48[f]	85 (**24**)
i-C_4H_9	CH_3	n-C_4H_9	Cl (**40**)	14	48[f]	80 (**28**)

[a] Reaction conditions: haloallenes (14 mmol), 4-methyl-2-pentanone (50 mL), 5 N NaOH (25 mL), $Ni(CN)_2 \cdot 4H_2O$ (1.0 mmol), tetrabutylammonium bromide (0.3 mmol), CO (1 atm), 25 °C. [b] Isolated yield based on substrate. [c] $Ni(CN)_2 \cdot 4H_2O$ (2.0 mmol). [d] KNCO. [e] Known compound (Shingu, K.; Hagishita, S.; Nakayama, M. *Tetrahedron Lett.* **1967**, 4371). [f] Reaction temp: 55 °C.

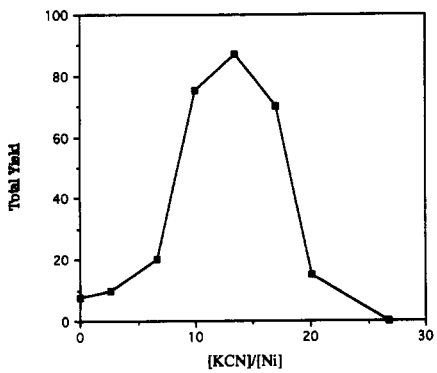
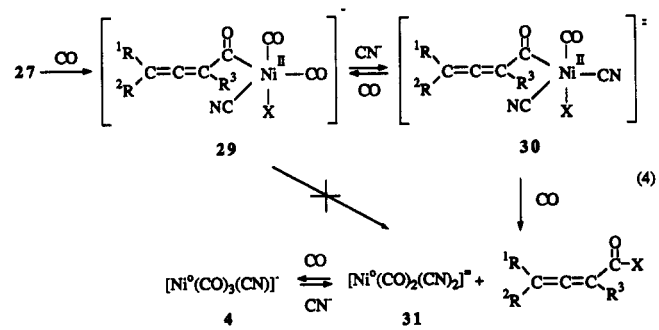


Figure 1. Dependence of added KCN on the overall yield of carbonylation of **2**.

Upon CO insertion, the acylnickel(II) intermediate **29** cannot be base-hydrolyzed as **6** in Scheme I and must undergo a reductive elimination in order to regenerate the active Ni(0) anion (**4**). Apparently, under the reaction conditions, this does not occur. Such reductive elimination are often accelerated by the presence of high trans-effect ligands, and cyano groups are known to have a strong trans influence.[25] However the intermediate **29** bears only one cyano group and this seems not to be enough to induce the reductive elimination. It was thus conceivable that increasing the number of cyano ligands in the coordination sphere of nickel could be a way to facilitate this reduction. This was indeed shown to be the case.

When the reaction was repeated in the presence of excess KCN (KCN/Ni = 10) the yield was increased nearly 9-fold and was now comparable with the results obtained with propargylic substrates. This was tested on several haloallenes and the results given in Table II show its general character. The presence of this trans effect was corroborated when KCN was replaced by KCNO (lower trans influence)[25] yielding, as expected, less allenic acid. Furthermore, it was shown that the amount of KCN was critical as illustrated in Figure 1. When the amount of added KCN was low, the increase in yield of allenic acid was insignificant; on the other hand, when the amount was too high, no carbonylation was observed. This can be rationalized in terms of two equilibria illustrated below (eq 4).



At low concentration of CN^- the equilibrium between the two Ni(II) complexes lies to the left and thus explains the low yield of reductive elimination product, whereas at high concentration of CN^- the equilibrium between the two Ni(0) species lies to the right and diminishes drastically the concentration of the active nickel tricarbonyl anion (**4**) catalyst. This indicates that under our reaction conditions the dianion **31** cannot perform the carbonylation of allenyl halides. Supporting evidence for this is the reported *stoichiometric* character of the dianion **31** in the carbonylation of benzyl bromide.[26,27]

Conclusions

The study reported here describes the regio- and stereoselective nickel- and phase-transfer-catalyzed carbonylation of variously substituted propargyl and allenyl halides. The products obtained are always either mono or dicarboxylic acids; however, it is shown that the mechanism differs for the two types of substrates. This puts an emphasis on the importance of the anionic character of the carbonylation catalyst, compared with an

(25) Cotton, F.; Wilkinson, G. *Advanced Inorganic Chemistry*, 4th ed.; John Wiley and Sons; New York, 1980; p 1200.

(26) Hashimoto, I.; Tsuruta, N.; Ryang, M.; Tsutsumi, S. *J. Org. Chem.* **1970**, *35*, 3748.

(27) del Rosario, R.; Stuhl, L. S. *Tetrahedron Lett.* **1982**, 3999.

analogous classical homogeneous catalytic system, and its direct consequence on the reaction pathway taken whether the substrate is a good or a poor electrophile (e.g. propargylic or allylic vs allenic or vinylic systems). This study constitutes also an interesting example of the influence of the trans effect on reactivity.

Experimental Section

General Comments. Unless otherwise noted, all materials were obtained from commercial suppliers and used without further purification. NMR spectra were recorded on a Bruker AC-100 or a Bruker AMX-400 spectrometer. The chemical shifts (ppm) were determined relative to $(CH_3)_4Si$. IR spectra were recorded on a Nicolet MX5 spectrometer. Thin-layer or column chromatography was performed on silica gel (Merck). Reactions were done in a 100-mL double-walled, thermostated reactor equipped with magnetic stirrer and inlet tube for gas bubbling. 3-Methyl-1-pentyn-3-ol, 2-methyl-3-butyn-2-ol, 2-phenyl-3-butyn-2-ol, propargyl bromide, and propargyl chloride were commercial products. The other propargyl alcohols[28] and propargyl halides[29] were prepared according to published methods. Haloallenes bearing alkyl subtituents were obtained by halogenation of the propargyl alcohols using either the CuX/HX system[30] or the $SOCl_2$ method.[31] For the haloallene with phenyl substituent the method developed by Elsevier et al.[32] using $LiCuX_2$ as chlorinating agent gave the best results.

General Procedure for the Nickel Cyanide- and Phase-Transfer-Catalyzed Carbonylation of Propargyl Halides. 4-Methyl-2-pentanone (50 mL) and 5 N NaOH (20 mL) were degassed and saturated with CO under atmospheric pressure before $Ni(CN)_2{\cdot}4H_2O$ (1.0 mmol) and tetrabutylammonium bromide (0.3 mmol) were introduced and the mixture kept at room temperature overnight with stirring while CO was slowly (2–3 mL/min) bubbled through the solution. To the yellow-colored two-phase mixture was then added 14 mmol of propargyl halide. Stirring and flow of CO were maintained for the desired time and at a given temperature. Separation of the aqueous phase and acidification (pH ≈ 1) (**Caution** when excess KCN is used), followed by extraction with diethyl ether (2 × 25 mL), drying ($MgSO_4$) of the combined extracts, and rotary evaporation yielded the products. Either recrystallization (methanol/diethyl ether, 50/50) for the diacid or distillation for the monoacid gave analytically pure samples. Unless otherwise stated, products were known materials and had spectral and physical characteristics in accordance with literature values.

General Procedure for the Nickel Cyanide- and Phase-Transfer-Catalyzed Carbonylation of Haloallenes. 4-Methyl-2-pentanone (50 mL) and 5 N NaOH (25 mL) were degassed and saturated with CO under atmospheric pressure. $Ni(CN)_2{\cdot}4H_2O$ (1.0 mmol) and tetrabutylammonium bromide (0.3 mmol) were introduced and the mixture kept at room temperature overnight with stirring while CO was slowly (2–3 mL/min) bubbled through the solution. To the yellow-colored two-phase mixture were then added 14 mmol of haloallene and 0.5 g of KCN. Stirring and flow of CO were maintained for the desired time and at a given temperature. Separation of the aqueous phase and acidification (pH ≈ 1) (**Caution** when excess KCN is used), followed by extraction with diethyl ether (2 × 25 mL), drying ($MgSO_4$) of the combined extracts, and rotary evaporation yielded the products. Either recrystallization (methanol/diethyl ether, 50/50) for the diacid or distillation for the monoacid gave analytically pure samples. Unless otherwise stated, products were known materials and had spectral and physical characteristics in accordance with literature values.

3-Methyl-4-nonyn-3-ol:[28] ^{1}H NMR (100 MHz, $CDCl_3$) 0.94 (t, 7 Hz, 3 H, $CH_3(CH_2)_2$), 1.01 (t, 7 Hz, 3 H, CH_3CH_2), 1.44 (s, 3 H, CH_3COH), 1.6 (m, 4 H, $CH_3CH_2CH_2$), 1.67 (q, 7 Hz, 2 H, CH_3CH_2COH), 2.19 (t, 7 Hz, 2 H, $CH_3(CH_2)_2CH_2$), 2.52 (s, 1 H, OH); $\{^1H\}^{13}C$ NMR (25 MHz, $CDCl_3$) 9.2, 13.6 (CH_3); 18.3, 21.9 (CH_2); 29.7 (CH_3); 30.9, 36.9 (CH_2); 68.7 (COH); 83.6, 84.1 (C≡C).

3-Chloro-3-methyl-4-nonyne (25): ^{1}H NMR (100 MHz, $CDCl_3$) 0.84 (t, 7 Hz, 3 H, $CH_3(CH_2)_2$), 1.08 (t, 7 Hz, 3 H, CH_3CH_2), 1.42 (m, 4 H, $CH_3CH_2CH_2$), 1.74 (s, 3 H, CH_3CCl), 1.68 (q, 7 Hz, 2 H, CH_3CH_2CCl), 2.17 (t, 7 Hz, 2 H, $CH_3(CH_2)_2CH_2$); $\{^1H\}^{13}C$ NMR (25 MHz, $CDCl_3$) 10.1, 13.6 (CH_3); 18.4, 21.9, 30.6 (CH_2); 33.2 (CH_3); 39.6 (CH_2); 64.1 (CCl); 81.9 (C≡C).

2,4-Dimethyl-5-nonyn-4-ol:[28] ^{1}H NMR (100 MHz, $CDCl_3$) 0.97 (t, 7 Hz, 3 H, $CH_3(CH_2)_2$), 1.01 (d, 7 Hz, 6 H, $(CH_3)_2CH$), 1.46 (s, 3 H, CH_3COH), 1.54 (m, 5 H, $(CH_3)_2CH$ and $CH_3(CH_2)_2CH_2$), 2.13 (t, 7 Hz, 2 H, $CH_2C{=}C$), 2.16 (s, 1 H, OH); $\{^1H\}^{13}C$ NMR (25 MHz, $CDCl_3$) 13.3 ($CH_3(CH_2)_2$); 20.5, 22.0 (CH_2); 24.0, 24.2 ($(CH_3)_2CH$); 25.0 (CH_3); 31.1 (CH); 52.0 ($CH_2C{=}C$); 67.9 (COH); 83.3, 84.7 (C≡C).

4-Chloro-2,4-dimethyl-5-nonyne (23): ^{1}H NMR (100 MHz, $CDCl_3$) 0.91 (t, 7 Hz, 3 H, $CH_3(CH_2)_2$), 1.03 (d, 7 Hz, 6 H, $(CH_3)_2CH$), 1.53 (sext, 7 Hz, 2 H, $CH_3CH_2CH_2$), 1.82 (s, 3 H, CH_3CCl), 1.84 (m, 3 H, $(CH_3)_2CHCH_2$), 2.21 (t, 7 Hz, 2 H, $CH_2C{\equiv}C$); $\{^1H\}^{13}C$ NMR (25 MHz, $CDCl_3$) 13.4 ($CH_3(CH_2)_2$), 20.8, 21.5 (CH_2), 24.0, 24.1 ($(CH_3)_2CH$); 28.3 (CH_3); 34.6 (CH); 54.6 ($CH_2C{\equiv}C$); 63.0 (CCl); 82.8, 86.1 (C≡C).

2,4-Dimethyl-5-decyn-4-ol:[28] ^{1}H NMR (400 MHz, $CDCl_3$) 0.83 (t, 7 Hz, 3 H, $CH_3(CH_2)_2$), 0.92 (d, 7 Hz, 3 H, $(CH_3)_2CH$), 0.93 (d, 7 Hz, 3 H, $(CH_3)_2CH$), 1.37 (m, 4 H, CH_2), 1.38 (s, 3 H, CH_3COH), 1.49 (m, 2 H, $(CH_3)_2CHCH_2$), 1.85 (non, 7 Hz, 1 H, $(CH_3)_2CH$), 2.11 (t, 7 Hz, 2 H, $CH_3(CH_2)_2CH_2C{\equiv}C$), 2.15 (s, 1 H, OH); $\{^1H\}^{13}C$ NMR (25 MHz, $CDCl_3$) 13.5 ($CH_3(CH_2)_2$); 18.3, 21.9 (CH_2); 24.1, 24.3 ($(CH_3)_2CH$); 25.1 (CH_3); 30.8 (CH_2); 31.2 (CH); 52.1 ($CH_2C{\equiv}C$); 68.1 (COH); 83.7, 84.5 (C≡C).

4-Chloro-2,4-dimethyl-5-decyne (27): ^{1}H NMR (100 MHz, $CDCl_3$) 0.91 (t, 7 Hz, 3 H, $CH_3(CH_2)_2$), 1.02 (d, 7 Hz, 6 H, $(CH_3)_2CH$), 1.55 (m, 4 H, $CH_3(CH_2)_2CH_2$), 1.83 (s, 3 H, CH_3CCl), 1.85 (m, 3 H, $(CH_3)_2CHCH_2$), 2.20 (t, 7 Hz, 2 H, $CH_2C{\equiv}C$); $\{^1H\}^{13}C$ NMR (25 MHz, $CDCl_3$) 13.6 ($CH_3(CH_2)_2$); 18.4, 21.8 (CH_2); 24.0, 24.1 ($(CH_3)_2CH$); 27.6 (CH_3); 30.5 (CH_2); 34.6 (CH); 54.6 ($CH_2C{\equiv}C$); 63.0 (CCl); 82.6, 86.2 (C≡C).

6-Chloro-2,4-dimethylnona-4,5-diene (39): ^{1}H NMR (100 MHz, $CDCl_3$) 0.96 (t, 7 Hz, 3 H, $CH_3(CH_2)_2$), 1.01 (d, 7 Hz, 6 H, $(CH_3)_2CH$), 1.72 (s, 3 H, $CH_3C{=}$), 1.76 (m, 5 H), 2.18 (m, 2 H, $CH_3(CH_2)_2CH_2$); $\{^1H\}^{13}C$ NMR (25 MHz, $CDCl_3$) 13.5 ($CH_3(CH_2)_2$), 18.9 ($CH_3C{=}$); 21.3 ($CH_3CH_2CH_2$); 22.4, 22.5 ($(CH_3)_2CH$); 26.2 ($(CH_3)_2CH$); 28.7 (CH_2); 47.4 ($(CH_3)_2CHCH_2$); 104.1, 107.9 ($C{=}C{=}C$); 198.2 ($C{=}C{=}C$).

6-Chloro-2,4-dimethyldeca-4,5-diene (40): ^{1}H NMR (100 MHz, $CDCl_3$) 0.95 (t, 7 Hz, 3 H, $CH_3(CH_2)_2$), 1.01 (d, 7 Hz, 6 H, $(CH_3)_2CH$), 1.71 (s, 3 H, $CH_3C{=}$), 1.77 (m, 7 H), 2.21 (m, 2 H, $CH_3(CH_2)_2CH_2$); $\{^1H\}^{13}C$ NMR (25 MHz, $CDCl_3$) 13.5 ($CH_3(CH_2)_2$); 19.7 ($CH_3C{=}$); 21.6 ($CH_3CH_2CH_2$); 22.4, 22.5 ($(CH_3)_2CH$); 25.2 ($(CH_3)_2CH$); 28.7, 29.3 (CH_2); 49.8 ($(CH_3)_2CHCH_2$); 103.8, 108.4 ($C{=}C{=}C$); 196.3 ($C{=}C{=}C$).

Hexylidenebutanedioic acid (19): ^{1}H NMR (100 MHz, $CDCl_3$) 0.91 (t, 7 Hz, 3 H, CH_3), 1.29 (m, 6 H, $(CH_2)_3$), 2.10 (q, 7 Hz, 2 H, $CH_2C{=}$), 3.19 (s, 2 H, CH_2COOH), 6.77 (t, 7 Hz, 1 H, $HC{=}C$), 12.21 (s, 2 H, COOH); $\{^1H\}^{13}C$ NMR (25 MHz, $CDCl_3$) 13.9 (CH_3); 21.9, 27.7, 28.1, 30.9, 32.0 (CH_2); 126.7 ($HC{=}$); 144.0 ($=CCOOH$); 168.1, 172.0 (COOH). Anal. Calcd for $C_{10}H_{16}O_4$: C, 59.98; H, 8.05. Found: C, 59.65; H, 8.47.

4,6-Dimethyl-2-propylhepta-2,3-dienoic acid (24): IR selected ν (cm^{-1}) 3100(br), 1957(m), 1681(s); ^{1}H NMR (400 MHz, $CDCl_3$) 0.92 (t, 7 Hz, 3 H, $CH_3(CH_2)_2$), 0.94 (d, 7 Hz, 3 H, $(CH_3)_2$-

(28) Crandall, J. K.; Conover, W. W.; Komin, J. B.; Machleder, W. H. *J. Org. Chem.* **1974**, *39*, 1723. Jones, E. R. H.; Skattebøl, L.; Whiting, M. C. *J. Chem. Soc.* **1956**, 4765. Brandsma, L. *Preparative Acetylenic Chemistry*, 2nd ed.; Elsevier: New York, 1988.

(29) Vogel, A. I. *Textbook of Practical Organic Chemistry*, 5th ed.; Longman: New York, 1989; p 505.

(30) Jacobs, T. L.; Brill, W. F. *J. Am. Chem. Soc.* **1953**, *75*, 1314. Mkryan, G. M.; Papazyan, N. A.; Arsenyan, G. B.; Avetisyan, E. A.; Zhurba, V. F.; Nazaryan, A. A. *J. Org. Chem. USSR* **1971**, *7*, 2562. Black, D. K.; Landor, S. R.; Patel, A. N.; Whiter, P. F. *Tetrahedron Lett.* **1963**, *8*, 483.

(31) Patel, A. N. *J. Org. Chem. USSR* **1977**, *13*, 1902. Muscio, O. J., Jr.; Jun, Y. M.; Philip, J. B., Jr. *Tetrahedron Lett.* **1978**, *27*, 2379.

(32) Elsevier, C. J.; Vermeer, P.; Gedanken, A.; Runge, W. *J. Org. Chem.* **1985**, *50*, 364. Elsevier, C. J.; Meijer, J.; Tadema, G.; Stehouwer, P. M.; Bos, J. T., II; Vermeer, P. *J. Org. Chem.* **1982**, *47*, 2194.

CH), 0.96 (d, 7 Hz, 3 H, $(CH_3)_2CH$), 1.47 (m, 2 H, $CH_3CH_2CH_2$), 1.76 (s, 3 H, CH_3C=), 1.77 (n, 1 H, $(CH_3)_2CH$), 1.96 (m, 2 H, $(CH_3)_2CHCH_2$), 2.18 (m, 2 H, $CH_3CH_2CH_2$), 12.10 (s, 1 H, COOH); {^{1}H}^{13}C NMR (100 MHz, $CDCl_3$) 13.45 ($CH_3(CH_2)_2$); 17.81 (CH_3C=); 21.28 ($CH_3CH_2CH_2$); 22.29, 22.32 ($(CH_3)_2CH$); 26.09 ($(CH_3)_2CH$); 30.42 ($CH_3CH_2CH_2$); 42.80 ($(CH_3)_2CHCH_2$); 97.96, 102.47 (C=C=C); 173.73 (COOH); 209.19 (C=C=C). Anal. Calcd for $C_{12}H_{20}O_2$: C, 73.43; H, 10.27. Found: C, 73.41; H, 10.20.

2-Butyl-4-methylhexa-2,3-dienoic acid (26): ^{1}H NMR (400 MHz, $CDCl_3$) 0.90 (t, 7 Hz, 3 H, CH_3), 1.03 (t, 7 Hz, 3 H, CH_3), 1.38 (m, 4 H, $CH_3(CH_2)_2$), 1.79 (s, 3 H, CH_3C=), 2.07 ((AB) part of an ABX_3 multiplet, 2 H, CH_3CH_2C=), 2.21 (t, 7 Hz, 2 H, $CH_3CH_2CH_2C$=), 11.50 (s, 1 H, COOH); {^{1}H}^{13}C NMR (100 MHz, $CDCl_3$) 13.90, 12.00 (CH_3); 22.30 (CH_3C=); 17.9, 26.8, 28.2 ($CH_3CH_2CH_2$); 22.29, 22.32, 30.50 (CH_2); 99.90, 106.00 (C=C=C); 174.10 (COOH); 208.60 (C=C=C). Anal. Calcd for $C_{11}H_{18}O_2$: C, 72.49; H, 9.95. Found: C, 72.51; H, 10.05.

2-Butyl-4,6-dimethylhepta-2,3-dienoic acid (28): IR selected ν (cm^{-1}) 3100(br), 1957(m), 1681(s), ^{1}H NMR (400 MHz, $CDCl_3$) 0.92 (dd, 7 and 8 Hz, 3 H, $CH_3(CH_2)_3$, 0.94 (d, 7 Hz, 3 H, $(CH_3)_2CH$), 0.96 (d, 7 Hz, 3 H, $(CH_3)_2CH$), 1.44 (m, 4 H, $CH_3(CH_2)_2CH_2$), 1.75 (s, 3 H, CH_3C=), 1.77 (n, 1 H, $(CH_3)_2CH$), 1.94 (m, 2 H, $(CH_3)_2CHCH_2$), 2.20 (m, 2 H, $CH_3(CH_2)_2CH_2$), 10.50 (s, 1 H, COOH); {^{1}H}^{13}C NMR (25 MHz, $CDCl_3$) 13.59 ($CH_3(CH_2)_2$); 17.73 (CH_3C=); 21.90 ($CH_3CH_2CH_2$); 22.20, 22.32 ($(CH_3)_2CH$); 26.0 ($(CH_3)_2CH$); 28.0, 30.20 ($CH_3CH_2(CH_2)_2$); 42.70 ($(CH_3)_2CHCH_2$); 98.15, 102.24 (C=C=C); 173.00 (COOH); 209.90 (C=C=C). Anal. Calcd for $C_{13}H_{22}O_2$: C, 74.24; H, 10.54. Found: C, 74.14; H, 10.59.

OM9207572