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Mild, regiospecific hydrocarboxylation of alkynes catalyzed by nickel cyanide under phase transfer conditions

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Abstract

Phase transfer catalyzed reaction of alkynes (e.g., phenylacetylene) with carbon monoxide, aqueous base, toluene as the organic phase, and catalytic amounts of nickel cyanide as the metal catalyst and cetyltrimethylammonium bromide as the phase transfer agent, affords unsaturated acids (e.g., atropic acid) in reasonable yields. This regiospecific reaction occurs under mild conditions.

A significant development in metal carbonyl chemistry, following the discovery of nickel tetracarbonyl by Mond 100 years ago, was the carbonylation of alkynes and other unsaturated hydrocarbons induced by nickel complexes [1]. For example, the hydrocarboxylation [2*] of phenylacetylene to atropic acid can be effected by nickel tetracarbonyl (3.6/1.0 ratio of alkyne/Ni) and added hydroquinone. The carbonylation of alkynes (e.g., acetylene) is genuinely catalytic, but only at high pressures (e.g. 100 atm at 180 °C for 100 h) of carbon monoxide using a nickel halide as the catalyst. Nickel cyanide is relatively ineffective in this regard.

Phase transfer catalysis is a useful method for effecting metal catalyzed processes under exceptionally mild conditions [3,4]. Recent studies have demonstrated that nickel cyanide can catalyze the carbonylation of allyl halides [5], aryl iodides [6], and benzyl chlorides [7] to the corresponding acids, the latter reaction being promoted by lanthanide salts. The cyanotricarbonylnickelate anion is probably the key catalytic species in this reaction. We now wish to report that hydrated nickel cyanide can catalyze the hydrocarboxylation of alkynes under mild conditions using phase transfer methodology.

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* Reference numbers with asterisks indicate notes in the list of references.

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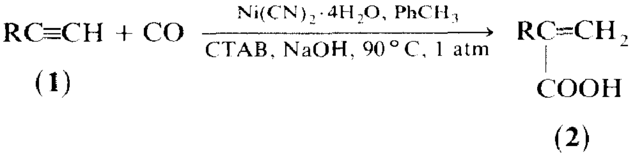
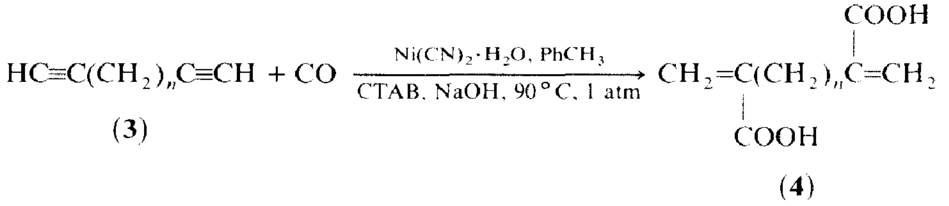
Results and discussion

Reaction of phenylacetylene (**1**, R = Ph) in toluene with carbon monoxide, 5*N* sodium hydroxide and catalytic amounts of hydrated nickel cyanide and cetyltrimethylammonium bromide (CTAB) as the phase transfer agent, for 3 h at 90 °C and 1 atm, afforded atropic acid (**2**, R = Ph) as the only product in an isolated yield of 62%. No cinnamic acid was detected in this reaction. The ratio of **1** to nickel catalyst was 10/1. Experiments using different concentrations of base (Table 1) indicate that similar yields of **2**, *R* = Ph, result using 1.0–7.5 *N* NaOH, with the rate of reaction being greater at higher base concentrations. Not only does the base concentration affect the rate of the reaction of the catalytically active nickel species with the substrate, but also the time needed to generate $Ni(CO)_3CN^-$ is longer at lower base concentrations (i.e., 60 min at 1.0–3.25 *N* NaOH vs. 30–35 minutes at 5.0–7.5 *N* NaOH).



$$\underset{(1)}{RC{\equiv}CH} + CO \xrightarrow[\text{CTAB, NaOH, 90°C, 1 atm}]{Ni(CN)_2\cdot 4H_2O,\ PhCH_3} \underset{(2)}{\underset{|\atop COOH}{RC}{=}CH_2}$$

The nickel catalyzed hydrocarboxylation reaction was applied to a variety of terminal alkynes forming unsaturated acids in fair to good yields (Table 1). Isomeric acids were isolated as by-products in several instances. The reaction is also useful for diynes including 1,7-octadiyne (**3**, *n* = 4) and 1,8-nonadiyne (**3**, *n* = 5). No carboxylic acids were formed when internal alkynes were used as reactants.



$$\underset{(3)}{HC{\equiv}C(CH_2)_nC{\equiv}CH} + CO \xrightarrow[\text{CTAB, NaOH, 90°C, 1 atm}]{Ni(CN)_2\cdot H_2O,\ PhCH_3} \underset{(4)}{CH_2{=}\underset{|\atop COOH}{C}(CH_2)_n\overset{COOH\atop |}{\underset{|\atop COOH}{C}}{=}CH_2}$$

The concentration of CTAB influences the reaction rate (Table 2), with 0.168–0.659 mmol of CTAB to 10 mmol of substrate and 1.0 mmol of $Ni(CN)_2\cdot 4H_2O$ being the best reaction conditions. At 1.0 mmol or higher concentrations of CTAB, the reaction is very slow while in the absence of the phase transfer agent, reaction does proceed but the yield of acid is significantly less.

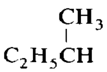
As in the carbonylation of benzylic chlorides promoted by lanthanide salts [7], most favorable results are obtained using quaternary ammonium salts having one long chain alkyl group such as CTAB or tetradecyltrimethylammonium bromide. Lower yields of atropic acid were observed when phenylacetylene was subjected to hydrocarboxylation with shorter chain tetraalkylammonium salts (Table 3).

Several solvents were used as the organic phase, of which toluene was the best. For example, while phenylacetylene afforded atropic acid in 62% yield when toluene was employed as the organic phase (reaction time of 3 h), the acid was isolated in 34% yield using 4-methyl-2-pentanone and in only 15% yield in the case of t-amyl alcohol (reaction time of 4 h).

A possible pathway for the hydrocarboxylation of alkynes in outlined in Scheme 1. As described previously [5], the first step may be generation of the cyanotri-

Table 1

Carbonylation of alkynes catalyzed by nickel cyanide under phase transfer conditions [a]

Alkyne	NaOH (N)	Reaction time [b] (h)	Product	Yield (%) GC	isolated
1, R = Ph	7.5	1	**2**[c]	95	
	6.25	3		93	(62)
	5	3		95	(62)
	3.25	4		90	(61)
	1	4		68	(35)
	1	18		95	
1, R = $PhCH_2CH_2$	3	5	**2**	50	
1, R =  $C_2H_5\overset{\overset{CH_3}{\vert}}{C}H$	6.25	6	**2**	95	
1, R = n-C_4H_9	5	5	**2**[c]	62	(30)[d]
1, R = n-C_5H_{11}	5	3.5	**2**[c]	70	(30)[e]
	3.75	22	**2**		(47)[f]
3, $n = 4$	6.25	6	**4**, $n = 4$	73	(68)
3, $n = 5$	5	8	**4**, $n = 5$	69	(65)

[a] Reaction conditions: 10 mmol alkyne, 1.0 mmol $Ni(CN)_2 \cdot 4H_2O$, 0.165 mmol CTAB, 20 ml $PhCH_3$, 20 ml NaOH, CO (1 atm.), 90 °C. [b] Reaction time is that following 30–45 min premixing of all components (except the substrate) needed to generate $Ni(CO)_3CN^-$. [c] Known compound (E.R.H. Jones, T.Y. Shen, and M.C. Whiting, J. Chem. Soc., (1950) 230). [d] $C_3H_7CH{=}C(CH_3)COOH$ was also isolated in 9% yield. [e] $C_4H_9CH{=}C(CH_3)COOH$ also formed in 15% yield. [f] $C_4H_9CH{=}C(CH_3)COOH$ also formed in 46% yield.

Table 2

Effect of the concentration of CTAB on the hydrocarboxylation of **1**, R = Ph[a]

CTAB (mmol)	Reaction time (h)	Isolated yield of atropic acid (%)
0.0824	3	49
0.165	3	62
0.329	2.5	55
0.659	2.4	48
1.0	5	–
0	5	27

[a] Reaction conditions: 10 mmol $PhC{\equiv}CH$, 1.0 mmol $Ni(CN)_2 \cdot 4H_2O$, CTAB, 20 ml $PhCH_3$, 20 ml 6.25 N NaOH, CO (1 atm), 90 °C.

Table 3

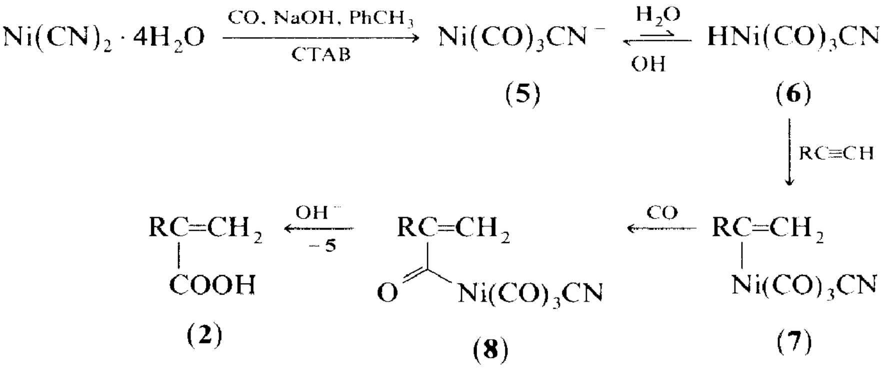
Effect of phase transfer catalyst on the hydrocarboxylation of **1**, R = Ph[a]

Phase transfer agent	Reaction time (h)	Isolated yield of atropic acid (%)
CTAB	3	62
$C_{14}H_{29}N(CH_3)_3^+\ Br^-$	4	59
$(C_8H_{17})_4N^+\ Br^-$	2	34
$(C_6H_{13})_4N^+\ Br^-$	3	20
$(C_4H_9)_4N^+\ HSO_4^-$	33	41

[a] Reaction conditions: 10 mmol $PhC{\equiv}CH$, 1.0 mmol $Ni(CN)_2 \cdot 4H_2O$, 0.165 mmol of phase transfer catalyst, 20 ml $PhCH_3$, 20 ml 6.25 N NaOH, CO (1 atm), 90 °C.

carbonylnickelate anion **5**. It is conceivable that protonation of the anion may occur, at least to a small extent, to give the nickel hydride **6**. Addition of **6** to the alkyne may afford the vinylnickel complex **7**. Carbonylation of the latter to form **8** followed by hydroxide ion induced carbon–nickel bond cleavage would produce the acid **2** and regenerate **5**.

Scheme 1



In conclusion, phase transfer catalysis enables one to realize the regiospecific hydrocarboxylation of alkynes to methylene acids under mild conditions. This reaction is simple, both in execution and work-up. While a number of publications have appeared on phase-transfer-catalyzed carbonylation reactions involving alkynes as substrates [8–10], the key step in such processes has been the addition of an acylmetal carbonyl to the reactant. The present reaction, which cannot involve such acylmetal complexes, is the first genuine example of hydrocarboxylation by phase transfer catalysis.

Experimental

General

Proton and carbon magnetic resonance spectra were recorded on a Varian XL-300 spectrometer. Mass spectral determinations were made using a VG 5050 micromass spectrometer. A Varian 3400 instrument was used for gas chromatographic analysis, with a column consisting of 10% OV-101 on Chromosorb W. Alkynes were purchased from Farchan Chemical Co., and were used as received.

General procedure for the hydrocarboxylation of alkynes

To a toluene (20 ml) solution containing 0.165 mmol of CTAB was added hydrated nickel cyanide (1.0 mmol) in sodium hydroxide (20 ml, see Table 1 for base concentration). The reaction mixture was stirred under carbon monoxide (1 atm) at 90 °C for 30–45 min. The alkyne (10 mmol) was then added, and stirring was continued for the period indicated in Tables 1–3 (reactions were followed by gas chromatography). After cooling to room temperature, the phases were separated, ice was added to the aqueous phase which was then acidified with 10% HCl and the acid was extracted with ether (3 × 25 ml). The combined ether extracts were washed with 20 ml of water, dried over $MgSO_4$, and then concentrated to give the acid. When mixtures of acids were formed, separation was achieved by distillation or preparative thick layer chromatography.

The mass spectra of the silylated derivatives gave molecular ion peaks in all cases. Proton and carbon magnetic resonance data follows:

2: R = Ph, ^{1}H NMR δ ($CDCl_3$): 6.01, 6.53 (d each, 2H, vinyl protons, *J* 1.1 Hz), 7.36 (m, 3H, *m*- and *p*-protons), 7.43 (m, 2H, *o*-protons); ^{13}C NMR δ($CDCl_3$): 127.46, 127.68, 127.77, 135.38 (aromatic carbons), 128.80 (CH_2), 139.91 (>C=), 171.47 (COOH).

2, R = $PhCH_2CH_2$: ^{1}H NMR δ($CDCl_3$); 2.62, 2.82 (t each, 4H, CH_2CH_2, *J* 7.8 Hz), 5.61, 6.30 (d each 2H, vinyl protons, *J* 1.1 Hz), 7.23 (m, 5H, Ph).

2, R = $C_2H_5CHCH_3$: ^{1}H NMR δ($CDCl_3$): 0.85 (t, 3H, CH_3CH_2, *J* 7.4 Hz), 1.06 (d, 3H, CH_3CH, *J* 6.9 Hz), 1.45 (m, 2H, CH_2CH_3), 2.58 (m, 1H, $CHCH_3$), 5.57, 6.28 (d each 2H, vinyl protons, *J* 1.1 Hz); ^{13}C NMR δ ($CDCl_3$): 11.67 (CH_3), 19.36 (CH_3), 28.63 (CH_2), 35.81 (CH), 125.18 (CH_2=), 145.01 (>C=), 172.98 (COOH).

2, R = n-C_4H_9: ^{1}H NMR δ($CDCl_3$): 0.92 (t, 3H, CH_3, *J* 7.3 Hz), 1.39 (m, 4H, $CH_3CH_2CH_2$), 2.29 (t, 2H, allylic CH_2, *J* 7.1 Hz), 5.62, 6.26 (d each 2H, vinyl protons, *J* 1.1 Hz).

2, R = n-C_5H_{11}: ^{1}H NMR δ($CDCl_3$): 0.89 (t, 3H, CH_3, *J* 7.0 Hz), 1.36 (m, 6H, $CH_3(CH_2)_3$), 2.27 (t, 2H, allylic CH_2, *J* 7.4 Hz), 5.62, 6.25 (d each, 2H, vinyl protons, *J* 1.3 Hz).

4, *n* = 4: ^{1}H NMR δ(DMSO-d_6): 1.34 (m, 4H, CH_2CH_2), 2.12 (m, 4H, allylic methylenes), 5.34, 5.95 (d each 4H, vinyl protons, *J* 1.4 Hz); ^{13}C NMR δ(DMSO-d_6) 27.36 (CH_2CH_2), 30.43 (allylic methylene carbons), 123.68 (CH_2=), 140.23 (>C=), 168.45 (acid carbons). Anal. Found: C, 60.43; H, 7.24. $C_{10}H_{14}O_4$ calcd.: C, 60.59; H, 7.12%.

4, *n* = 5: ^{1}H NMR δ($CDCl_3$): 1.40 (m, 6H, $CH_2CH_2CH_2$), 2.29 (t, 4H, allylic CH_2, *J* 7.5 Hz), 5.62, 6.26 (d each 2H, vinyl protons, *J* 1.20 Hz); ^{13}C NMR δ($CDCl_3$), 28.14, 28.67 ($CH_2CH_2CH_2$), 31.39 (allylic carbons), 126.83 (CH_2=), 139.92 (>C=), 172.56 (acid carbons). Anal. Found: 61.97; H, 7.54. $C_{11}H_{16}O_4$ calcd.: C, 62.25; H, 7.60%.

Acknowledgements

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