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Synthesis of Propiolic Acids *via* Copper-Catalyzed Insertion of Carbon Dioxide into the C–H Bond of Terminal Alkynes

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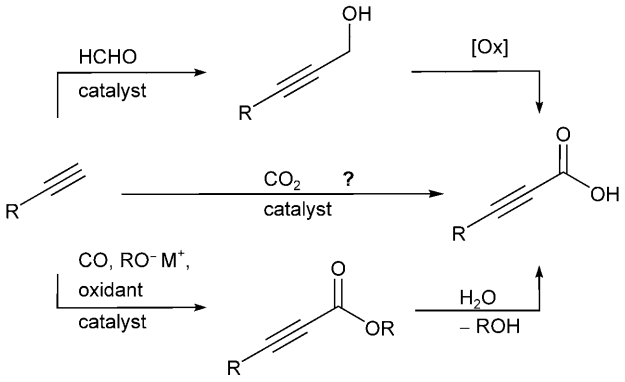
Abstract: A highly effective copper catalyst has been developed that promotes the insertion of carbon dioxide into the C–H bond of terminal alkynes under unprecedentedly mild conditions. For the first time, propiolic acids can thus be synthesized in excellent yields from alkynes and carbon dioxide in the presence of the mild base cesium carbonate. The catalyst, (4,7-diphenyl-1,10-phenanthroline)bis[tris(4-fluorophenyl)phosphine]-copper(I) nitrate, is easy accessible and relatively stable against air and water.

Keywords: carbon dioxide fixation; catalysis; C–H activation; copper; propiolic acids



Scheme 1. Known and proposed propiolic acid syntheses.

Propiolic acids are versatile synthetic intermediates, for example, in cycloaddition or hydroarylation reactions that give access to various heterocyclic derivatives including coumarins, flavones and 3-arylidene-2-oxindole derivatives.[1] Furthermore, they can be used in decarboxylative cross-couplings for the preparation of alkynylarenes or aminoalkynes.[2]

Traditionally, such compounds are synthesized in two-step processes from the corresponding alkynes. Most effective are the addition of alkynes to formaldehyde and subsequent oxidation of the resulting propargylic alcohol,[3] and the oxidative carbonylation of alkynes (Scheme 1).[4] The disadvantages of these routes lie in the C_1 building blocks employed, namely the relatively high cost of formaldehyde, and the toxicity and difficult handling of carbon monoxide.

Other synthetic approaches include the carbonylation of unstable and commercially unavailable alkynyl halides,[5] and the lithiation of 1-alkynes followed by quenching with chloroformate. Preformed alkynyl-metal species have also been coupled with CO_2 either directly or in the presence of transition metal catalysts. Examples are the direct carboxylation of alkynylmagnesium or -lithium reagents,[6] and the nickel- or palladium-catalyzed alkylative carboxylation of alkynes using organozinc reagents under a CO_2 atmosphere.[7] This synthetic strategy is attractive in that it makes use of abundant carbon dioxide as the C_1 building block.[8] However, it requires the synthesis of expensive and sensitive organometallic reagents.[9]

The optimum strategy both from economical and ecological standpoints would be a one-step catalytic carboxylation of terminal alkynes with CO_2 under C–H functionalization (Scheme 1).

Metal-mediated C–H functionalizations have received enormous attention within the last years, and great progress has been achieved.[10] The key challenge in this reaction type is to activate the normally non-acidic C–H bond to an extent that the proton can be abstracted by bases which are many orders of magnitude weaker than the intermediate carbon nucleophiles. For the C–H bonds of arenes, this has been achieved, for example, with palladium, rhodium, ruthenium, gold, and copper catalysts. Alkyne C–H activations have been described in the context of oxidative dimerizations,[11] coupling reactions of alkynes with arenes,[12] and alkynylations of aldehydes.[13]

Stoichiometric investigations suggest that CO_2 can insert into the Cu–C bond of preformed alkynylcuprates.[14] However, the reverse reaction, a decarboxylation of the resulting copper propiolates, proceeds rapidly even at low temperatures (35 °C). As the operating temperatures of known (de)carboxylation catalysts is much higher than that ($\geq$100 °C), it has so far been possible to perform catalytic carboxylation reactions only when the products are continuously removed by a trapping reaction.[15]

In the course of our work on decarboxylative coupling reactions,[16] we found phenanthroline/copper complexes to be highly active catalysts for the extrusion of CO_2 from aromatic carboxylic acids.[17] It appeared reasonable to assume that these catalysts might set new standards also for the reverse reaction, the insertion of CO_2 into C–H bonds.

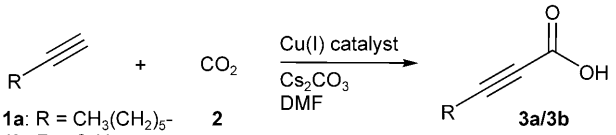
We probed this hypothesis using the model reaction of 1-octyne (**1a**) with carbon dioxide according to the scheme in Table 1. Indeed, using 1 mol% of a copper(I) phenanthroline complex as the catalyst, modest turnover was observed already at ambient CO_2 pressure in the presence of 2 equivalents of the mild base Cs_2CO_3 at 100 °C (Table 1, entry 1).

The yield was substantially increased when using copper/4,7-diphenyl-1,10-phenanthroline complexes as catalysts, which are also the most active protodecarboxylation catalysts (entries 2 and 3). The use of preformed phenanthroline phosphine copper(I) nitrate complexes, which are easily accessible on a multigram scale as well as being air-stable and easy to handle, was also beneficial.

A stepwise reduction of the reaction temperatures from 100 to 50 °C led to a step-up in the yields using catalyst **I**, which confirms that at higher temperatures, the equilibrium is shifted towards the starting materials (entries 4 and 5). At 50 °C, near-quantitative turnover was achieved; below this temperature, the yield dropped as the reaction rate became too low. Under optimized conditions, the amount of base could be reduced further, from 2.0 to 1.2 equivalents (entry 6).

We next evaluated the reaction of phenylacetylene (**1b**) as a particularly challenging substrate. Its corresponding carboxylate is so labile towards decarboxylation that it is present in only 65% in the equilibrium mixture under the previously optimized conditions (entry 7). A further reduction of the temperature did not improve the yields but, rather, led to sluggish turnover even when increasing the CO_2 pressure to 5 bar (entry 8). An even more active catalyst was clearly needed for this and related substrates. We therefore systematically varied the ligands in the phenanthroline phosphine Cu(I) nitrate complexes (Figure 1) and, for better comparison of their activities, tested them at incomplete conversions by reducing the reaction times (entries 9–18).

Table 1. Development of the catalyst system.[a]

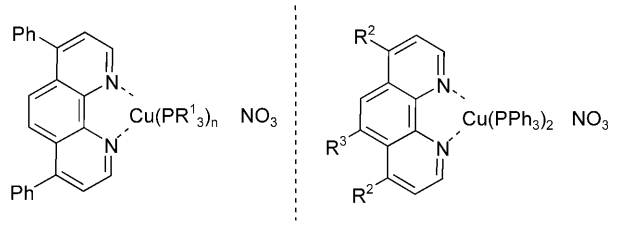


Entry	**1**	Cu(I) catalyst	CO_2 [bar]	*T* [°C]	*t* [h]	Yield [%]
1	**1a**	CuI/Phen	1	100	8	52
2	**1a**	CuI/diPhPhen	1	100	8	64
3	**1a**	**I**	1	100	8	74
4	**1a**	**I**	1	80	8	80
5	**1a**	**I**	1	50	8	92
6[b,c]	**1a**	**I**	1	50	8	93
7[c]	**1b**	**I**	1	50	8	65
8[c]	**1b**	**I**	5	35	8	85
9[c]	**1b**	**I**	5	35	2	52
10[c]	**1b**	**II**	5	35	2	53
11[c]	**1b**	**III**	5	35	2	43
12[c]	**1b**	**IV**	5	35	2	43
13[c]	**1b**	**V**	5	35	2	49
14[c]	**1b**	**VI**	5	35	2	52
15[c]	**1b**	**VII**	5	35	2	46
16[c]	**1b**	**VIII**	5	35	2	22
17[c]	**1b**	**IX**	5	35	2	58
18[c]	**1b**	**X**	5	35	2	85
19[c]	**1b**	**X**	5	35	8	99
20	**1a**	**X**	5	35	8	9
21	**1a**	–	5	35	8	0
22[d]	**1a**	**I**	5	35	8	0
23[c]	**1b**	**I**	5	35	8	0
24[c,d]	**1b**	**X**	5	35	8	0

[a] *Reaction conditions:* 1.0 mmol alkyne **1**, 1 mol% Cu(I) source, 1 mol% ligand, 2.0 mmol Cs_2CO_3, 3.0 mL DMF. Yields determined by GC analysis of the methyl esters generated by treatment of the crude mixture with methyl iodide, and using *n*-tetradecane as the internal standard. DMF = *N,N*-dimethylformamide; Phen = 1,10-phenanthroline; diPhPhen = 4,7-diphenyl-1,10-phenanthroline.
[b] 2 mol% Cu(I) source.
[c] 1.2 mmol Cs_2CO_3.
[d] Without CO_2.

The results confirmed 4,7-diphenyl-1,10-phenanthroline to be the most effective *N,N*-ligand. Among the phosphines tested, the moderately electron-rich tris(4-fluorophenyl)phosphine was optimal (entry 18). Both sterically crowded (e.g., JohnPhos) and particularly electron-rich phosphines (e.g., tricyclohexylphosphine) were inferior. The best catalyst, 4,7-diphenyl-1,10-phenanthroline)bis[tris(4-fluorophenyl)phosphine]copper(I) nitrate (**X**) led to an 85% yield of the product **3b** after 2 h, and near quantitative yields after 8 h (entries 18 and 19).

A control experiment showed that these conditions are optimal only for aryl-substituted alkynes, while for alkyl-substituted alkynes, the previous system



I: $R^1 = C_6H_5$; n = 2
V: R^1 = 4-MeO-C_6H_4; n = 2
VI: R^1 = 4-Me-C_6H_4; n = 2
VII: R^1 = Cy; n = 2
VIII: R^1 = JohnPhos; n = 1
IX: R^1 = 4-Cl-C_6H_4; n = 2
X: R^1 = 4-F-C_6H_4; n = 2

II: R^1, R^2 = H
III: R^2 = Cl; R^3 = H
IV: R^2 = H; $R^3 = NO_2$

Figure 1. Copper(I) complexes employed for optimizing the catalyst system; JohnPhos = 2-(di-*tert*-butylphosphino)biphenyl.

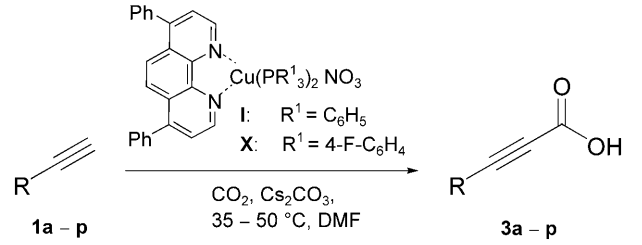
(entry 20) remains the best. Further experiments confirmed that for both protocols the carboxylation works only in the presence of copper, and that carbonate salts alone are not sufficient as sources of CO_2 (entries 21–24).

Having thus identified a complementary set of effective protocols, we next tested the generality of the new carboxylation reaction by applying it to various terminal alkynes. As can be seen from Table 2, the first catalyst system allows the smooth conversion of various alkyl-substituted alkynes, whereas the second is generally applicable to a broad range of aryl-substituted alkynes. The corresponding propiolic acids were isolated by crystallization. Alternatively, they were converted into esters and purified by column chromatography, the latter method serving to verify that moderate yields were caused primarily by non-optimized crystallization procedures. Only in some cases, e.g., when the products contained basic nitrogen heterocycles (**3m**), the free acids could not be isolated and had to be converted into esters to allow their separation from the reaction mixture.

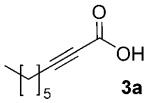
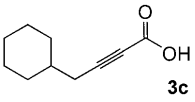
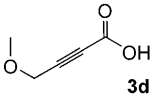
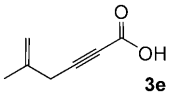
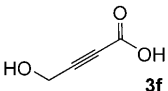
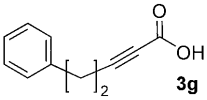
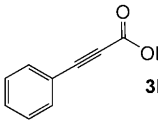
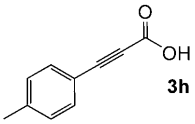
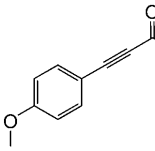
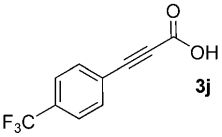
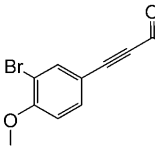
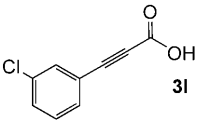
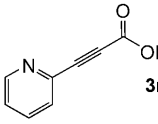
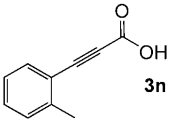
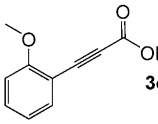
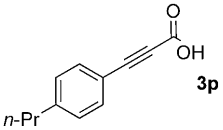
Due to the mild conditions, many functional groups including ethers, halogens, trifluoromethyl and alkenyl groups were tolerated. Unprotected NH or OH groups appeared to be incompatible with the procedure.[18] However, products with free hydroxy groups such as **3f** can be accessed starting from the corresponding silyl ethers, as the TMS groups is cleaved during the reaction work-up.

We assume that the reaction starts with the coordination of the copper to the alkyne, acidifying the sp^3-H and allowing deprotonation by the added base under formation of an alkynyl copper complex. It is reasonable to assume that the phosphine ligand dissociates in the course of these reaction steps. In the next step, the CO_2 inserts into the C–Cu bond. Final-

Table 2. Carboxylation of terminal alkynes.[a]

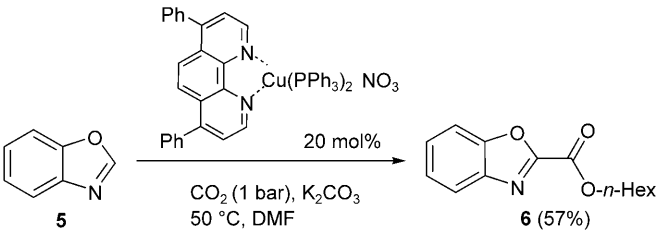


1a – p **3a – p**

Product	Yield [%]	Product	Yield [%]
 **3a**	95	 **3c**	85 (96)
 **3d**	62 (87)	 **3e**	97
 **3f**	(67)[b]	 **3g**	73 (87)
 **3b**	98	 **3h**	99
 **3i**	81	 **3j**	99
 **3k**	63 (84)	 **3l**	86
 **3m**	(75)	 **3n**	87
 **3o**	73 (86)	 **3p**	62 (85)

[a] *Reaction conditions: Method A*: alkyl-substituted alkynes: 1.0 mmol of alkyne **1**, 2 mol% of Cu(I) source, 1.2 mmol of Cs_2CO_3, CO_2 (1 bar), 3.0 mL of DMF, 50 °C, 16 h. *Method B*: (hetero-)aryl-substituted alkynes: 1.0 mmol of alkyne **1**, 1 mol% of Cu(I) source, 1.2 mmol of Cs_2CO_3, CO_2 (5 bar), 3.0 mL of DMF, 35 °C, 16 h; isolated yields. Yields in parentheses correspond to the *n*-hexyl esters generated by treatment of the crude mixture with 2.0 mmol of 1-bromohexane. For further details see Supporting Information.

[b] Using (2-propynyloxy)trimethylsilane **1f** as the starting material.



Scheme 2. Carboxylation of a heterocyclic C–H bond.

ly, the carboxylate ion is replaced by an alkyne molecule or, alternatively, by the phosphine.

The catalysts also allow the carboxylation of heterocycles that have a similar pK_a to alkynes (Scheme 2). However, we discontinued these investigations when a publication appeared in which Nolan et al. disclosed a mechanistically related carbene gold hydroxide-catalyzed carboxylation of heterocycles.[19] Their work suffices to demonstrate that the reaction concept outlined herein is not limited to alkynes but is likely to open up general perspectives for carboxylic acid synthesis.[20]

In conclusion, new copper-based carboxylation catalysts have been developed. By lowering the activation barrier for the carboxylation of terminal alkynes, the carboxylation/decarboxylation equilibrium can be shifted towards the carboxylated products to an extent that an isolation of free propiolic acids is possible for the first time.

Experimental Section

General Procedure for the Synthesis of Copper Phosphine Complexes

An oven-dried, nitrogen-flushed, 50-mL Schlenk tube was charged with 2.00 mL of EtOH and heated to reflux. Under an N_2 atmosphere, the phosphine (3.00 mmol) was then slowly added until it completely dissolved. To this, copper(II) nitrate trihydrate (242 mg, 1.00 mmol) was added, portionwise, over 20 min. After complete addition, the reaction mixture was stirred under reflux for 30 min. During this time a gradual formation of a precipitate was observed. The resulting solid was collected by filtration, washed sequentially with EtOH (2×10.0 mL) and cold (0 °C) Et_2O (2×10.0 mL), transferred to a flask, and dried at 2×10^{-3} mmHg to provide the corresponding phosphine copper complexes.

General Procedure for the Synthesis of Copper(I) Mixed-Ligand Nitrate Complexes (Figure 1)

An oven-dried, nitrogen-flushed, 50-mL Schlenk tube was charged with the copper phosphine complex (1.00 mmol) and 10.0 mL of $CHCl_3$. To this, the phosphine (1.00 mmol) was added the mixture was stirred until all materials were completely dissolved. Then, a solution of the N-ligand (1.00 mmol) in 2 mL of $CHCl_3$ was gradually added over 30 min. After stirring the reaction mixture for 30 min at room temperature, the $CHCl_3$ was removed under vacuum to afford a yellow solid which was further purified by recrystallization from CH_2Cl_2 and Et_2O, yielding the corresponding copper(I) complexes.

Synthesis of (4,7-Diphenyl-1,10-phenanthroline)bis-[tris(4-fluorophenyl)phosphine]copper(I) Nitrate (X)

Complex **X** was prepared from bis[tris(4-fluorophenyl)phosphine]copper(I) nitrate (**XVII**) (758 mg, 1.00 mmol), 4,7-diphenyl-1,10-phenanthroline (339 mg, 1.00 mmol) and tris(4-fluorophenyl)phosphine (316 mg, 1.00 mmol) affordding **X** as a yellow solid; yield: 1.40 g (97%). ^{31}P NMR (162 MHz, $CDCl_3$): $\delta = 19.84$ (s, 2P); anal. calcd. for $C_{60}H_{40}CuF_6N_3O_3P_2$: C 66.1, H 3.7, N 3.8; found: C 65.4, H 3.8, N 4.0.

General Procedure for the Carboxylation of Terminal Alkyl-Substituted Alkynes (Table 2)

An oven-dried, nitrogen-flushed, 10-mL vessel was charged with (4,7-diphenyl-1,10-phenanthroline)bis(triphenylphosphine)copper(I) nitrate (**I**) (19.7 mg, 0.02 mmol) and cesium carbonate (782 mg, 2.00 mmol). Under an atmosphere of nitrogen, the degassed DMF (3.00 mL) was added and the mixture was stirred at room temperature for 5 min. After purging the reaction vessel with CO_2, the alkyne (**1a**, **1c–g**) (1.00 mmol) was added *via* syringe. The resulting mixture was stirred for 12 h at 50 °C at ambient CO_2 pressure. At the end of the reaction time, the mixture was cooled down to room temperature, diluted with H_2O and extracted with *n*-hexane (3×20.0 mL). Then the aqueous layer was acidified with aqueous HCl (1 N, 10.0 mL) to afford a colorless solid which was further purified by recrystallization from H_2O and EtOH. In those cases where no solid was formed, the aqueous layer was further extracted with ethyl acetate ($3\times$ 20.0 mL). The combined organic layers were washed with a dilute aqueous solution of LiCl and brine, dried over $MgSO_4$, filtered and the volatiles were removed under vacuum to afford the corresponding acids **3a**, **3c–g** which were further purified by recrystallization from H_2O and EtOH.

General Procedure for the Carboxylation of Terminal Aryl-Substituted Alkynes (Table 2)

An oven-dried, nitrogen-flushed, 5-mL vessel was charged with the (4,7-diphenyl-1,10-phenanthroline)bis[tris(4-fluorophenyl)phosphine]copper(I) nitrate **X** (10.9 mg, 0.01 mmol) and cesium carbonate (391 mg, 1.20 mmol). Under an atmosphere of nitrogen, the degassed DMF (3.00 mL) was added and the mixture was stirred at room temperature for 5 min. After flushing the reaction vessel with CO_2, the alkyne (**1b**, **1h–p**) (1.00 mmol) was added *via* syringe. The reaction vessel was then placed in a steel autoclave, and pressurized with CO_2 (5 bar). The reaction mixture was stirred at 35 °C for 12 h. At the end of the reaction time, the autoclave pressure was released. The reaction mixture was diluted with H_2O (2.00 mL) and extracted with *n*-hexane (3×20.0 mL). The aqueous layer was acidified with aqueous HCl (1 N, 10.0 mL) to afford a colorless solid which was further purified by recrystallization from H_2O and EtOH. In those cases where no solid was formed, the aqueous layer

was futher extracted with ethyl acetate (3×20.0 mL). The combined organic layers were washed with a dilute aqueous solution of LiCl and brine, dried over $MgSO_4$, filtered and the volatiles were removed under vacuum to afford the corresponding acids **3b**, **3h–p** which were further purified by recrystallization from H_2O and EtOH.

Preparative-Scale Synthesis of 1-α-Nonynoic Acid (3a)

An oven-dried, nitrogen-flushed, 100-mL vessel was charged with (4,7-diphenyl-1,10-phenanthroline)bis(triphenylphosphine)copper(I) nitrate (**I**) (590 mg, 0.60 mmol) and cesium carbonate (11.7 g, 36.0 mmol). Under a nitrogen atmosphere, degassed DMF (50 mL) was added, and the mixture was stirred at room temperature for 5 min. After flushing the reaction vessel three times with CO_2, 1-octyne **1a** (4.47 mL, 30.0 mmol) was added *via* syringe. The resulting mixture was stirred at 50 °C under an ambient CO_2 pressure for 16 h. Once the reaction was complete, the mixture was cooled to room temperature, diluted with H_2O and extracted with *n*-hexane (3×20 mL). The aqueous layer was then acidified with aqueous HCl (1 N, 100 mL) and extracted with ethyl acetate (3×60 mL). The combined organic layers were washed with a dilute aqueous LiCl solution and brine, dried over $MgSO_4$, filtered, and the volatiles were removed under vacuum. The residue was purified by filtration over silica gel (500 mg) eluting with ethyl acetate/hexane 1:5, to afford **3a** as a colorless oil; yield: 4.6 g (97%). The spectroscopic data (NMR, IR) matched those reported in the literature for 1-α-nonyoic acid (**3a**) [CAS: 1846–70–4].

For full experimental procedures, see the Supporting Information.

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