

1,5,7-Triazabicyclo[4.4.0]dec-1-ene-Mediated Acetylene Dicarboxylation and Alkyne Carboxylation Using Carbon Dioxide

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Direct carboxylation of acetylene with CO₂ was carried out in the presence of 1,5,7-triazabicyclo[4.4.0]dec-1-ene (TBD); subsequent reduction of dicarboxylated acetylene produces commercially valuable succinate salts. This metal-free car-

boxylation has potential economic and environmental impact by utilizing non-petroleum feedstocks (acetylene) and CO₂ and by producing valuable chemical feed stocks.

Introduction

Various carbon-capture, storage, and utilization technologies have emerged to reduce atmospheric carbon dioxide (CO₂) concentrations to address global warming.^[1] Reactions that convert captured CO₂ into value-added chemical products are attractive to the chemical sector because the mass production of CO₂-incorporated products would utilize large amounts of CO₂ and even potentially provide significant benefits by reducing the use of petroleum as a chemical resource. Therefore, extensive research has been conducted on CO₂ conversion processes such as CO₂/epoxide copolymerization^[2,3] and the fixation of CO₂ to valuable small organic molecules.^[4–7]

One CO₂ conversion reaction, the transition-metal-catalyzed direct carboxylation of terminal alkynes, provides synthetically useful propiolic acid derivatives under relatively mild reaction conditions.^[6,8,9] Compared to classical methods using *n*-butyllithium or Grignard reagents, the transition-metal-catalyzed coupling of alkynes and CO₂ eliminates synthetic steps involving sensitive organometallic bases. Despite these advantages, previously reported transition-metal-catalyzed carboxylations use a large amount of carbonate bases (K₂CO₃ and Cs₂CO₃) and toxic transition-metal complexes. The use of simple and stable organic bases in the absence of transition-metal complexes and inorganic salts would provide a more cost-effective and environmen-

tally benign process. In addition, previously reported carboxylation conditions have not been applied to acetylene gas. Production of economically valuable basic reagents should aim to directly convert CO₂. Therefore, this study investigated the organic base mediated carboxylation of acetylene to produce commercially valuable chemicals.

Since its discovery in 1836, acetylene has been commercially produced from coal. Other than burning acetylene for welding, acetylene is mostly used in the production of 1,4-butanediol and vinyl chloride, which are transformed into various chemical products including polymers.^[10] The organic base mediated carboxylation of acetylene and subsequent reduction produces succinic acid, which is an important building block in biodegradable polymers [polybutylene succinate (PBS) and polybutylene succinate adipate (PBSA)].^[11] The increasing price of petroleum and the high environmental load of synthesizing succinic acid from crude oil suggest that this acetylene carboxylation/reduction protocol could serve as an alternative non-petroleum method to produce succinic acid that is both economical and contributes to utilizing CO₂. In addition to 1,4-butanediol and vinyl chloride, this method expands the utility of acetylene to produce polymer feedstocks.

Results and Discussion

The carboxylation of acetylene from CO₂ requires a base to deprotonate acetylene and a thermodynamically stable CO₂ activator. To meet such requirements, guanidine- and amidine-type organic bases, which are basic enough to deprotonate alkynes and known to form CO₂ adducts, were used for acetylene carboxylation.^[12,13] A solution of the base dissolved in dimethylacetamide (DMAc) was added to a 50 mL stainless-steel autoclave equipped with a magnetic stirring bar. The autoclave was charged with acetylene and CO₂, and the reaction was carried out at 100 °C. Subsequent to carboxylation, the crude material was exposed to

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Pd/C-catalyzed hydrogenation (1 atm of H₂) to provide succinate 1,5,7-triazabicyclo[4.4.0]dec-1-ene (TBD) salts. As shown in Table 1, organic bases known to form CO₂ adducts did not function for acetylene carboxylation except for TBD and 1,8-diazabicycloundec-7-ene (DBU). TBD is known to form CO₂ adducts and is a strong base that is widely used in various organic reactions.^[14,15] To optimize the TBD-mediated carboxylation, the acetylene ratio, CO₂ pressure, and reaction time were varied (Table 1, entries 1–4). Initially, 3 bar of acetylene and 5 bar of CO₂ were applied to the TBD solution, and this resulted in a 58% yield of **1b**. An increase in the pressure of CO₂ to 12 bar increased the yield of **1b** to 65%, but any further increase in this pressure resulted in lower yields. After increasing the concentration and reaction time, the yield of **1b** increased to 95% (Table 1, entry 4). The carboxylation of acetylene in the presence of DBU gave no CO₂-incorporated product under the optimized conditions with TBD (Table 1, entry 5). On the basis of previous studies on guanidine–CO₂ adducts and amidine–CO₂ adducts, the thermal stability to release CO₂ from the base–CO₂ adduct differs according to the base; thus, a lower temperature (50 °C) was applied to the DBU-mediated reaction to afford propionic acid in 49% yield (the monocarboxylation product) after reduction.^[12a,12f] Although the reaction of acetylene and CO₂ takes place in the presence of DBU, the dicarboxylation necessary to form succinic acid did not occur. In addition to organic bases, previously reported alkyne carboxylation conditions were applied for acetylene carboxylation. Neither copper(I) complex catalyzed conditions in combination with Cs₂CO₃ and K₂CO₃ nor inorganic base (Cs₂CO₃) me-

Table 1. Carboxylation of acetylene.^[a]

Entry	CO ₂ [bar]	Base	Time [h]	Yield [%]
1	5	TBD	18	58 ^[b]
2	12	TBD	18	65 ^[b]
3	12	TBD	18	66 ^[c]
4	12	TBD	42	95 ^[c]
5	12	DBU	18	0 ^[d]
6	12	TMG	18	0
7	12	DPG	18	0
8	12	DMAP	18	0
9	12	TEA	18	0

TBD: 1,5,7-triazabicyclo[4.4.0]dec-1-ene
 DBU: 1,8-diazabicycloundec-7-ene
 TMG: 1,3,5-trimethylguanidine
 DPG: 1,3-diphenylguanidine
 DMAP: 4-dimethylaminopyridine
 TEA = triethylamine

[a] Reaction conditions: acetylene, CO₂, organic base (2 mmol), DMAc (4 or 2 mL). The yield of succinic acid was calculated on the basis of the amount of base as a limiting reagent. [b] DMAc (4 mL). [c] DMAc (2 mL). [d] No product at 100 °C, propionic acid (49%) at 50 °C.

diated conditions induced the carboxylation of acetylene.^[6f–6i]

After optimizing the carboxylation of acetylene, phenylacetylene was subjected to the TBD-mediated carboxylation conditions to compare reactivities (Table 2). The carboxylation product, phenylpropionic acid, was obtained in high yield (83%) in the absence of solvent after a relatively short reaction time (6 h; Table 2, entries 1–3). In the presence of DMAc as the solvent, the yield decreased to 39% (Table 2, entry 4). In addition to TBD, DBU promoted the carboxylation of phenylacetylene to afford the product in 65% yield (Table 2, entry 5).^[16] However, other organic bases did not induce the desired CO₂ carboxylation (Table 2, entries 7–10). Compared to acetylene (**1a**), alkyne **2a** forms carboxylated products in shorter reaction times in the absence of solvent.

Table 2. Carboxylation of phenylacetylene.^[a]


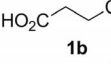

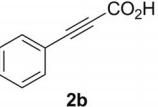
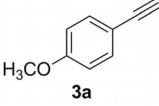
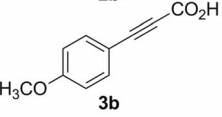

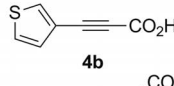
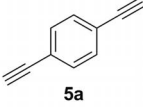
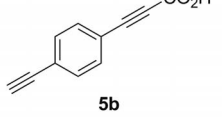
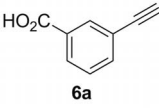
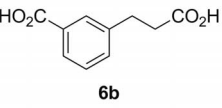

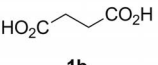

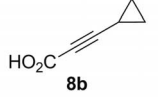
Entry	Base	Time [h]	Yield [%]
1	TBD	3	60 ^[b]
2	TBD	6	83 ^[b]
3	TBD	18	54 ^[b]
4	TBD	6	39 ^[c]
5	DBU	3	65 ^[b]
6	DBU	6	40 ^[b]
7	TMG	6	0 ^[b]
8	DPG	6	0 ^[b]
9	DMAP	6	0 ^[b]
10	TEA	6	0 ^[b]

[a] Reaction conditions: CO₂, phenylacetylene (2 mmol), organic base (4 mmol), no solvent or DMAc (2 mL). [b] Neat. [c] DMAc (2 mL).

On the basis of the results obtained in the carboxylation of acetylene and phenylacetylene, TBD is considered the most appropriate organic base to induce coupling with CO₂, and the solvent or neat conditions for the different reaction times are chosen according to the substituent on the alkynes. As shown in Table 3, aromatic alkynes, carboxylic acid substituted alkynes, and aliphatic alkynes underwent carboxylation. The carboxylation results of **1a** and **2a** are shown in Tables 1 and 2, respectively, and the isolation yields of free acids **1b** and **2b** are reported in Table 3 (entries 1 and 2). Aromatic alkynes **3a–6a** gave good yields of the carboxylic acid derivatives using methods A and B (Table 3, entries 3–6). Compound **5a**, possessing two acetylene units, was converted into monocarboxylic acid **5b** (Table 3, entry 5). Benzoic acid derivative **6a** underwent carboxylation, and dicarboxylic acid **6b** was isolated after hydrogenation (Table 3, entry 6).^[17] Propionic acid (**7a**), which is considered an intermediate of acetylene carboxylation, was transformed into acetylene dicarboxylic acid by using method B. The yield was determined following hydrogen-

ation (Table 3, entry 7). Cyclopropyl-substituted alkyne **8a** required a longer reaction time and provided carboxylic acid **8b** in 41% yield (Table 3, entry 8).

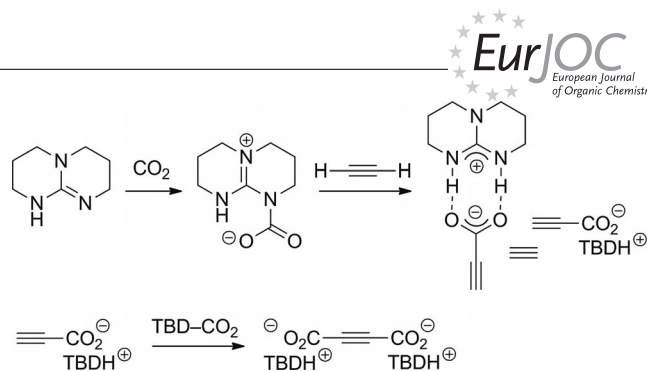
Table 3. Examples of TBD-mediated alkyne carboxylation.

Entry	Reactant	Product	Method ^[a]	Time [h]	Yield [%]
1			B	42	94
2			A	6	76 ^[b]
3			A	6	72
4			A	6	63
5			B	2	44
6			B	18	81
7			B	6	63
8			B	42	41

[a] Method A: No solvent (neat), 100 °C; method B: DMAc (1 M), 100 °C. [b] After sequential hydrogenation, 3-phenylpropanoic acid was obtained in 74% yield.

The proposed reaction mechanism is described in Scheme 1. Acetylene carboxylation is initiated by the formation of an TBD–CO₂ adduct, which undergoes nucleophilic addition of acetylene to afford a propiolate–TBD salt. Although TBD-mediated CO₂ additions to alcohols and amines have been reported previously, the TBD-mediated carboxylation of acetylene is reported here for the first time.^[12g] The second carboxylation of the propiolate–TBD salt occurs with the TBD–CO₂ adduct to provide the acetylene dicarboxylate–TBD salt.

Interestingly, the carboxylation of acetylene is not only controlled by basicity. Despite the similar basicities of amidine and guanidine bases (TBD, DBU, TMG, and DPG), their reactivities with acetylene to form acetylene dicarboxylic acid are completely different. The TBD-mediated reaction provides acetylene dicarboxylation, whereas the DBU-mediated reaction forms the acetylene monocarboxylation product. Other than TBD and DBU, strongly basic guanidine bases (i.e., TMG and DPG) did not produce the desired results. Key factors in this reaction are the



Scheme 1. Reaction mechanism.

reactivities of the base–CO₂ complexes towards acetylene as well as the ease with which the base–CO₂ adduct can be formed.^[12a,12e,12f]

Conclusions

We have presented the organic base (TBD)-mediated carboxylation of acetylene and alkynes under conditions that are free of transition metals, inorganic salts, and organometallic reagents, and importantly, the reaction consumes CO₂. Depending on the substituent on the alkyne, the reaction proceeds without the need of a solvent. As an efficient carboxylating agent, TBD–CO₂ adducts converted a range of alkyne derivatives—including acetylene—into carboxylic acids. Notably, acetylene dicarboxylate formed from acetylene and CO₂ can be transformed into succinic acid, which is a commercially attractive compound. This TBD-mediated carboxylation would provide a cost-effective protocol for the synthesis of succinic acid by utilizing non-petroleum feedstocks (CO₂ and acetylene). In addition to economic benefits, our proposed process utilizes CO₂; it therefore has the potential to incorporate large quantities of CO₂ through the mass production of various chemical products from acetylene dicarboxylic acid.

Experimental Section

General Procedure for the TBD-Mediated Acetylene Carboxylation with CO₂: An autoclave reactor was charged with a solution of TBD (286 mg, 2 mmol) in DMAc (2 mL) under pressure of acetylene (3 bar) and CO₂ (12 bar). The mixture was allowed to react for the indicated time at 100 °C. After the reaction was complete, the product was concentrated at the reduced pressure. Pd/C (10%, 60 mg) was added to a methanol solution (5 mL) of the crude material, which was stirred under a H₂ atmosphere for 18 h. The mixture was filtered, and the solvent was removed under reduced pressure to afford TBD–succinate salts. To isolate the free acid, the TBD–carboxylate salts were purified by column chromatography (chloroform, EtOH, and AcOH mixtures) to afford **1b** to **8b**. Highly pressurized neat acetylene may be explosive; thus, solvent must be used in this reaction. No parts of the autoclave may contain copper or silver for safe use.

Supporting Information (see footnote on the first page of this article): Experimental procedures and copies of the ¹H NMR and ¹³C NMR spectra.

Acknowledgments

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