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Carboxylation

The Renaissance of an Old Problem: Highly Regioselective Carboxylation of 2-Alkynyl Bromides with Carbon Dioxide

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Abstract: A steric effect-controlled, zinc-mediated carboxylation of different 2-alkynyl bromides under an atmospheric pressure of CO_2 has been developed by careful tuning of different reaction parameters, including the metal, solvent, temperature, and additive. 2-Substituted 2,3-allenoic acids were afforded from primary 2-alkynyl bromides, whereas the carboxylation of secondary 2-alkynyl bromides yielded 3-alkynoic acids in decent yields. A rationale for the observed regioselectivity has been proposed.

Despite its extensive applications in constructing various different kinds of heterocyclic compounds,[1–5] synthetic approaches towards 2,3-allenoic acids are still underdeveloped. The established approach is hydrolysis of 2,3-allenoates, but this method suffers from poor atom- or step-economy, the use of toxic carbon monoxide, and unsatisfying regioselectivity between the allenoic acid and 3-alkynoic acid in some cases (Scheme 1 a).[1c,6–8] We envisioned that the carboxylation of propargylic derivatives with carbon dioxide would be the most straightforward approach for the synthesis of allenoic acids.[9] Interestingly, despite comprehensive studies on the reaction of propargylic/allenylic metallic species with aldehydes and ketones,[10,11] no careful study of this reaction with CO_2 has, to our knowledge, been reported to date.[12] For the reaction of aldehydes or ketones, controlling the selectivity between allenylic and propargylic alcohols is always a challenge; the structures of propargylic derivatives and carbonyl compounds codetermined the selectivity.[10b,11b] In Al-, In-, and Ga-mediated reactions, terminal propargylic bromides selectively afforded homopropargylic alcohols, whereas non-terminal 2-alkynyl bromides selectively produced 2,3-allenyl alcohols (Scheme 1 b).[10] However, in zinc-mediated reactions, the selectivity control has not yet been established.[11a,13] Herein we report such a carboxylation of 2-alkynyl bromides in the presence of CO_2 and zinc with an excellent regioselectivity by applying the steric effect of R^2, demonstrating a completely different regioselectivity control to that with aldehydes or ketones (R^1; Scheme 1 c).

Our initial attempt at the reaction of 2-heptynylic bromide **1 a** and indium powder with CO_2 (provided by a balloon), mediated with LiCl in THF led to a complicated product mixture (Table 1, entry 1). Screening of other metal powders, including Mn, Al and Bi, failed to yield either allenoic acid **2 a** or 3-alkynoic acid **3 a** with recovery of starting material **1 a** (Table 1, entries 2–4). After some trial and error, we observed that the reaction of **1 a** with CO_2 mediated by zinc powder afforded 61 % yield of allenoic acid **2 a**. However, 3-heptynoic acid **3 a** was also formed in 17 % yield, as confirmed by ^{1}H NMR spectroscopic analysis of the crude product (Table 1, entry 5). The reaction in DMF or DMSO gave lower yields and selectivities to **2 a**/**3 a** (Table 1, entries 6 and 7). Ethereal solvents such as dioxane and methyl *tert*-butyl ether (MTBE) gave a higher selectivity to **2 a**/**3 a**, albeit with unsatisfactory yields (Table 1, entries 8 and 9). Pleasingly, a dramatic solvent effect was observed when dimethyl ether (DME) was used; allenoic acid **2 a** was afforded in 73 % yield with an allene/alkyne (**2 a**/**3 a**) selectivity of 6:1 (Table 1, entry 10). Replacing LiCl with LiOAc gave much lower yields (Table 1, entry 11). Finally, it was exciting to observe that the ratio between allene **2 a** and alkyne **3 a** was improved to $>$99:1 when the reaction was run at 65 °C in the presence of LiCl, affording **2 a** in 71 % yield (Table 1, entries 12 and 13). The yield dropped to 59 % in the absence of LiCl at 65 °C, with a similar regioselectivity (Table 1, entry 14).

After this optimization, the carboxylation of various different primary 2-alkynyl bromides was tested with typical results given in Table 2. 2-Alkyl-substituted 2,3-allenoic acids **2 a**–**d** were afforded exclusively in moderate to good yields (Table 2, entries 1–4). The carboxylation reaction may be easily scaled up to 100 mmol, affording 10 g of **2 a** in a yield of 71 % with a selectivity of $>$99:1, showing its practicality (Table 2, entry 1). The introduction of a bulkier isobutyl group and a CH_2CH_2Ph group did not affect the yield or selectivity (Table 2, entries 5 and 6). Synthetically useful functional groups, such as halides (F and Cl) and OMe, were tolerated. Allyl or benzyl group-substituted 2-alkynyl bromides **1 j** and **1 k** also gave the corresponding terminal allenoic acids **2 j** and **2 k** in moderate yields under the optimized conditions (Table 2, entries 10 and 11).

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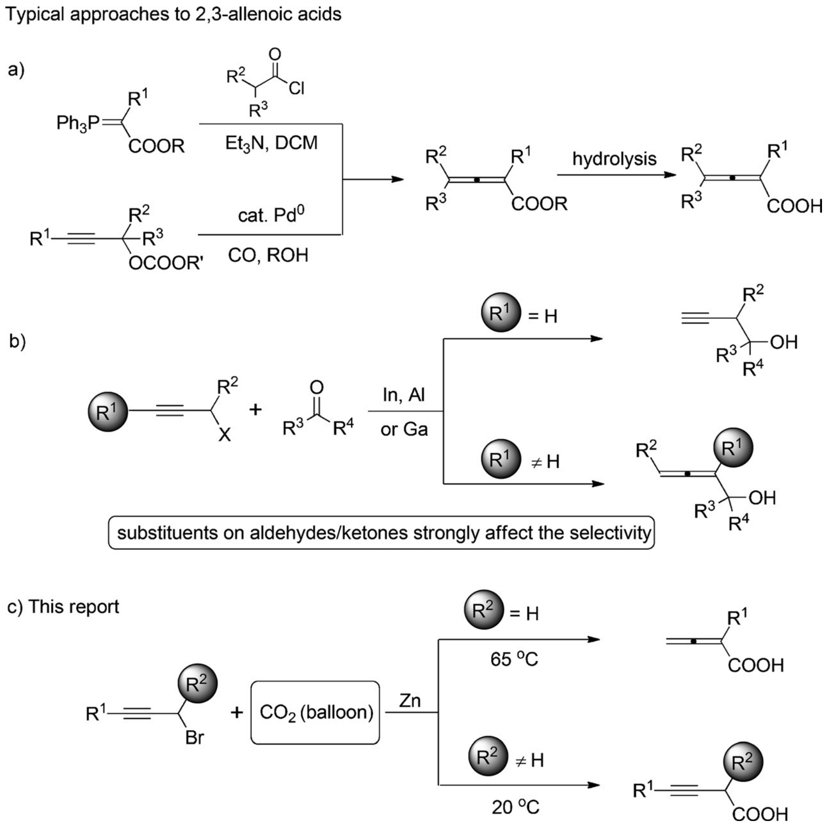


Scheme 1. Classical methodologies (a, b) and the CO_2-based approach to synthesis of 2,3-allenoic acids (c).

2-Butyl-2,3-butadienoic acid **2a** could easily be transformed to benzyl allenoate **2aa** and allenoyl amide **2ab**.[14] Furanone **2ac** was obtained from a palladium-catalyzed cyclization–allylation process[3g] and the reaction of **2a** with diethyl azodicarboxylate (DEAD) and Ph_3P yielded the pyrazolone **2ad** in 80% yield (Scheme 2).[4]

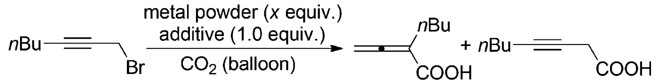
To our surprise, when secondary 2-alkynyl bromides were applied at 20 °C (Table 3), the selectivity was reversed: 3-alkynoic acids were formed with merely a trace amount of 2,3-allenoic acids.[15] 4-Phenyl-3-butynoic acid **3l** was afforded in 64% yield (Table 3, entry 1). The carboxylation worked smoothly with different non-terminal secondary 2-alkynyl bromides **1m–s** (Table 3, entries 2–8). Chloride and trimethylsilyl (TMS) substituents survived under the optimized conditions (Table 3, entries 9 and 10). Allyl-substituted propargylic bromide **1v** was also successfully converted (Table 3, entry 11). Even a terminal C≡C triple bond was tolerated to yield the terminal 3-alkynoic acid **3w** in 46% yield (Table 3, entry 12).

It is worth mentioning that 3-alkynoic acids **3** could be easily transformed into trisubstituted 2,3-allenoic acids **4** by a KOH-mediated rearrangement: **4n** and **4p** were afforded in decent yields, which addresses the concern of the scope limitation for the synthesis of allenoic acids shown in Table 2 (Scheme 3).

A mechanistic rationale for the observed regioselectivity is depicted in Scheme 4. We proposed that LiCl accelerates the reaction by forming a RZnX·LiCl complex in zinc-mediated reactions, thus also increasing the solubility of the metallic species.[16] The reaction of propargyl or allenyl zinc species with a carbonyl functionality most likely proceeds by a cyclic S_E2'-type process of the allenyl or propargylic species with CO_2.[13] With a primary propargylic bromide, the in situ-formed propargylic zinc reagent would react with CO_2 via a cyclic transition state **IM-1** to give the allenoic acids **2**; for the secondary 2-alkynyl bromide, a cyclic transition state involving allenyl intermediate **IM-2** would give the 3-alkynoic acid **3**. The steric effect of the R^2 group determines the equilibrium between the propargyl zinc species and the allenyl zinc intermediate.[17,18]

In summary, a highly selective carboxylation of readily available propargylic bromides mediated by zinc powder under 1 atm CO_2 was developed with the regioselectivity controlled by the steric effects of the 2-alkynyl bromides: 2-substituted 2,3-allenoic acids were afforded from primary 2-alkynyl bromides, whereas secondary bromides yielded 2-alkynoic acids under mild reaction conditions. The nature of the R^2 group has

Table 1. Optimization of the reaction conditions: carboxylation of 2-heptynyl bromide.[a]

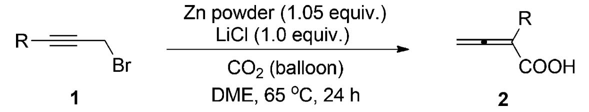


1a **2a** **3a**

Entry	Metal powder (equiv)[b]	Solvent	Additive	T [°C]	Yields [%][c] 2a	3a	1a
1	In (0.70)	THF	LiCl	20	complicated		
2	Al (0.70)	THF	LiCl	20	–	–	66
3	Bi (0.70)	THF	LiCl	20	–	–	24
4	Mn (1.05)	THF	LiCl	20	–	–	74
5	Zn (1.05)	THF	LiCl	20	61	17	–
6	Zn (1.05)	DMF	LiCl	20	40	26	3
7	Zn (1.05)	DMSO	LiCl	20	37	23	–
8	Zn (1.05)	MTBE	LiCl	20	37	3	9
9	Zn (1.05)	dioxane	LiCl	20	17	2	2
10	Zn (1.05)	DME	LiCl	20	73	13	–
11	Zn (1.05)	DME	LiOAc	20	58	11	–
12	Zn (1.05)	DME	LiCl	60	72	2	–
13	Zn (1.05)	DME	LiCl	65	71	<1	–
14	Zn (1.05)	DME	–	65	59	<1	–

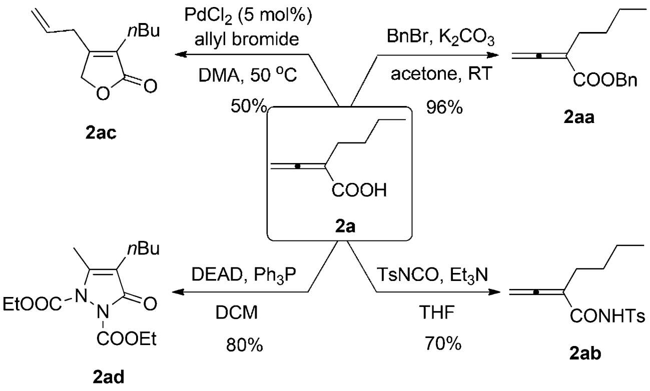
[a] Reaction conditions: **1a** (1.0 mmol), metal powder, and additive (1.0 mmol) under a CO_2 (balloon) atmosphere in anhydrous solvent (5 mL). [b] All metal powders were washed sequentially with 3 M HCl, acetone, and Et_2O for 3 times each and dried under vacuum before use. [c] NMR yield.

Table 2. Substrates scope of primary 2-alkynyl bromides.[a,b]



Entry	R	Yield of **2** [%][c]
1	n-C_4H_9 (**1a**)	71 (71)[d] (**2a**)
2	n-C_6H_{13} (**1b**)	67 (**2b**)
3	n-C_8H_{17} (**1c**)	60 (**2c**)
4	n-$C_{10}H_{21}$ (**1d**)	58 (**2d**)
5	i-C_4H_9 (**1e**)	61 (**2e**)
6	CH_2CH_2Ph (**1f**)	60 (**2f**)
7	$CH_2CH_2CH_2F$ (**1g**)	57 (**2g**)
8	$CH_2CH_2CH_2Cl$ (**1h**)	53 (**2h**)
9	$CH_2CH_2CH_2OMe$ (**1g**)	52 (**2i**)
10	allyl (**1j**)	60 (**2j**)
11	Bn (**1k**)	45 (**2k**)

[a] Reaction conditions (unless otherwise stated): 2-alkynyl bromide (1.0 mmol) and zinc powder (1.05 mmol) under CO_2 (balloon) in anhydrous DME (5 mL) at 65 °C. [b] Zinc powder was treated sequentially with 3 M HCl, and then washed with acetone and Et_2O for 3 times each and dried under vacuum before use. [c] Yields refer to isolated products. [d] Value in parentheses refers to reaction conducted on a 100 mmol scale.

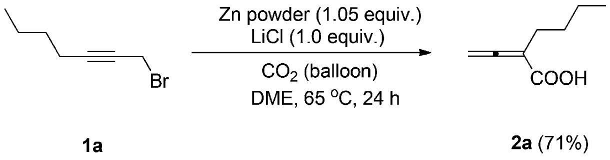


Scheme 2. Derivatization of 2-butyl-2,3-butadienoic acid **2a**.

a profound effect on the structure of the in situ-generated zinc reagents, which react with CO_2 via a S_E2'-type cyclic intermediate to afford the allenoic or 3-alkynoic acids. Further studies on the reaction are still ongoing in our group.

Experimental Section

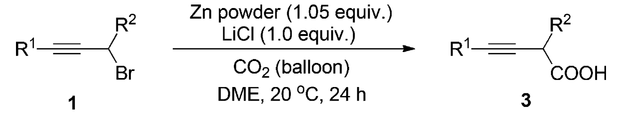
Synthesis of 2-butyl-2,3-allenoic acid (2a)



1a
100 mmol

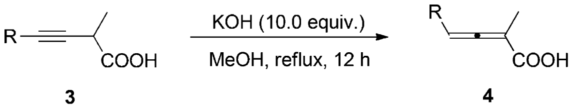
2a (71%)

Table 3. Substrate scope of secondary propargylic bromides.[a,b]



Entry	R^1	R^2	Yield of **3** [%][c]
1	Ph	Me (**1l**)	61 (**3l**)
2	n-C_4H_9	Me (**1m**)	58 (**3m**)
3	n-C_6H_{13}	Me (**1n**)	63 (**3n**)
4	n-C_8H_{17}	Me (**1o**)	73 (**3o**)
5	n-$C_{10}H_{21}$	Me (**1p**)	71 (**3p**)
6	t-C_4H_9	Me (**1q**)	70 (**3q**)
7	Cy	Me (**1r**)	80 (**3r**)
8	CH_2CH_2Ph	Me (**1s**)	57 (**3s**)
9	$CH_2CH_2CH_2Cl$	Me (**1t**)	65 (**3t**)
10	TMS	Me (**1u**)	62 (**3u**)
11	allyl	Me (**1v**)	61 (**3v**)
12	H	n-C_4H_9 (**1w**)	46 (**3w**)[d]
13	t-C_4H_9	Et (**1x**)	57 (**3x**)

[a] Reaction conditions (unless otherwise stated): 2-alkynyl bromide (1.0 mmol) and zinc powder (1.05 mmol) under CO_2 (balloon) in anhydrous DME (5 mL) at 20 °C. [b] Zinc powder was treated sequentially with 3 M HCl, and then washed with acetone and Et_2O 3 times each and dried under vacuum before use. [c] Yields refer to isolated products. [d] Reaction conducted at 65 °C.

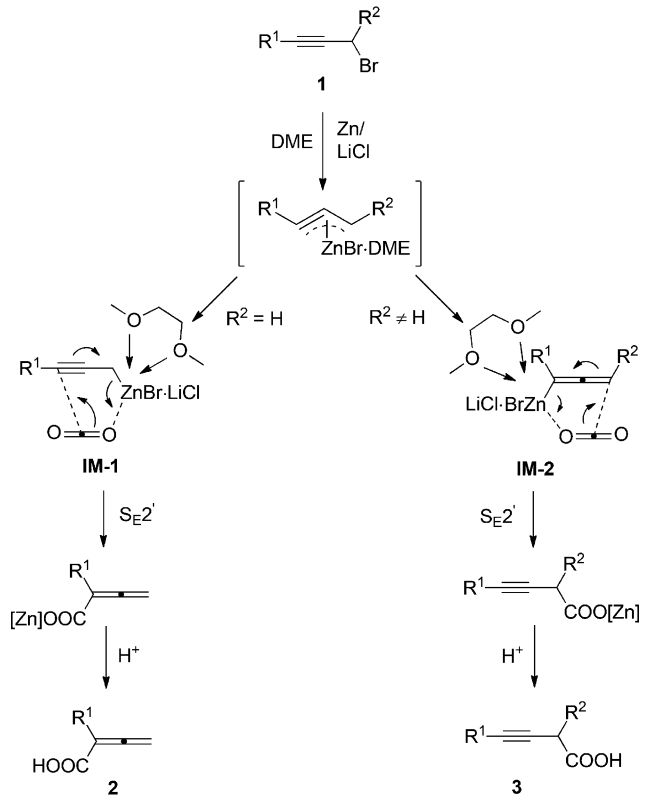


R = n-C_6H_{13}, yield: 72%, **4n**
R = n-$C_{10}H_{21}$, yield: 70%, **4p**

Scheme 3. Synthesis of trisubstituted 2,3-allenoic acids by KOH-mediated rearrangement of 3-alkynoic acids.

To a flame-dried 25 mL Schlenk tube equipped with a magnetic stirring bar were added zinc powder (68.7 mg, 1.05 mmol) and anhydrous LiCl (42.6 mg, 1.00 mmol) inside a glove box. The Schlenk tube was then dried under vacuum with a heat gun. **1a** (175.3 mg, 1.00 mmol) and DME (5 mL) were then added sequentially under Ar atmosphere. The mixture was then frozen with a liquid nitrogen bath and the tube's argon atmosphere was completely replaced with CO_2 via a balloon. The Schlenk tube was then allowed to stand until the mixture thawed and the resulting mixture was stirred at 65 °C for 24 h. The resulting mixture was then quenched with 3 M aqueous HCl (10 mL) and the aqueous layer was extracted with ethyl acetate (5×10 mL). The combined organic layer was washed with brine (30 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated. The crude product was purified by column chromatography on silica gel (gradient elution: 5:1 petroleum ether/ethyl acetate to 20:1 dichloromethane/methanol) to afford **2a** as a white solid (99.5 mg, 0.71 mmol, 71 %). M.p. 70–72 °C (petroleum ether); ^1H NMR (300 MHz, $CDCl_3$) $\delta = 10.42$ (bs, 1H, COOH), 5.19 (t, $J = 3.2$ Hz, 2H, $CH_2=$), 2.27–2.15 (m, 2H, CH_2), 1.52–1.28 (m, 4H, 2× CH_2), 0.91 ppm (t, $J = 7.2$ Hz, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) $\delta =$ 214.8, 173.0, 100.0, 79.2, 30.0, 27.4, 22.1, 13.8 ppm; MS (ESI) 457 $[(3M-2H+K)^-]$, 301 $[(2M-2H+Na)^-]$, 235 $[(2M-CO_2-H)^-]$, 139 $[(M-H)^-]$; IR (neat) $\tilde{\nu} = 3600$–2200 (br), 1957, 1913, 1673, 1458, 1415, 1375, 1334, 1289, 1264, 1241, 1123, 1074, 1053, 1005 cm^{-1}.

To a flame-dried 2 L three-necked flask equipped with a magnetic stirring bar were added zinc powder (6.87 g, 105 mmol) and anhydrous LiCl (4.24 g, 100 mmol) inside a glove box. DME (500 mL)



Scheme 4. Rationale for the observed regioselectivity.

and **1a** (17.51 g, 100 mmol) were then added sequentially under Ar atmosphere. The mixture was then frozen with a liquid nitrogen bath and the flask's argon atmosphere was completely replaced with CO_2 via a balloon. The reaction flask was then allowed to stand until the mixture thawed and the resulting mixture was stirred at 65 °C for 12 h. A new CO_2 balloon was equipped and the mixture was stirred at 65 °C for another 12 h. The mixture was quenched with 3 M aqueous HCl (500 mL) and the aqueous layer was extracted with ethyl acetate (5×150 mL). The combined organic layer was washed with brine (500 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated. The crude product was purified by column chromatography on silica gel (gradient elution: 5:1 petroleum ether/ethyl acetate to 20:1 dichloromethane/methanol) to afford **2a** as a white solid (9.96 g, 71 mmol, 71 %). ^{1}H NMR (300 MHz, $CDCl_3$) $\delta = 11.76$ (bs, 1 H, COOH), 5.18 (t, $J = 3.2$ Hz, 2 H, $CH_2{=}$), 2.26–2.16 (m, 2 H, $=CCH_2$), 1.51–1.25 (m, 4 H, $2\times CH_2$), 0.91 ppm (t, $J = 7.2$ Hz, 3 H, CH_3).

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Keywords: allenylation · carbon dioxide fixation · propargylation · regioselectivity · zinc

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