

Decarboxylative Borylation of mCPBA-Activated Aliphatic Acids

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Supporting Information

ABSTRACT: A decarboxylative borylation of aliphatic acids for the synthesis of a variety of alkylboronates has been developed by mixing *m*-chloroperoxybenzoic acid (*m*CPBA)activated fatty acids with bis(catecholato)diboron in N,Ndimethylformamide (DMF) at room temperature. A radical chain process is involved in the reaction which initiates from



the B-B bond homolysis followed by the radical transfer from the boron atom to the carbon atom with subsequent decarboxylation and borylation.

 ${f B}$ oron-containing compounds are widely used in many fields due to their unique charge distribution and strong transformation ability.¹ For example, organoboron derivatives have proven to be a powerful coupling agent with the advancement of Suzuki-Miyaura cross-coupling reaction in the synthesis of pharmaceuticals and organic functional materials.² In addition, organic boronic acids and boronic esters also exhibit certain biological activities because they have enough electrophilicity of binding to amino acid residues.³ This brings new opportunities for discovery of boroncontaining drugs such as Velcade,⁴ Dutogliptin,⁵ and An-2690.⁶ Given the importance of organic boron compounds, their efficient synthesis has attracted more and more attention from chemists. Traditionally, sensitive organolithium reagents' and Grignard reagents⁸ are used to synthesize organoborons. To expand the applicability of borylation, a number of methods, including borylation of alkenes,9 transition-metalcatalyzed borylation of organohalides,¹⁰ and activation of C–X $(X = H, C, N, O, F)^{11-15}$ bonds, have been developed. Although these strategies have yielded good results, harsh and complex reaction conditions are still required. With the further advancement of chemistry, it is urgent to solve the problems of energy and ecological environment brought about by chemical agents.¹⁶

Carboxylic acid, an important biomass platform compound, has attracted the attention of chemists because of its abundant reserves, wide sources, and low toxicity.¹⁷ Therefore, the synthesis of boron derivatives using carboxylic acid derivatives has boomed.¹⁸ Recently, phenol-, amine-, and mercaptanactivated carboxylic acids have been transformed into boronic esters through transition-metal-catalyzed oxidative addition and reductive elimination (Scheme 1a).^{12d-g} With the development of base-promoted and photoinduced methods in radical borylation reaction, some novel protocols for radical decarboxylative borylation have also been explored by using phthalimide-activated carboxylic acids.^{19,20} Baran's group first realized nickel- or copper-catalyzed radical decarboxylative borylation under strong alkaline conditions.²¹ The Lewis base-

Scheme 1. Strategies for the Decarboxylative Borylation

a) decarboxylative borylation using phenol, amine and mercaptan-activated carboxylic acids (Rueping's, Shi's and Hosoya's works) 0 Δ

$$Ar = B_2(OR')_4$$

$$FG = OPh, N(Boc)Me, SEt$$

$$Iigand$$

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b) decarboxylative borylation using phthalimide-activated carboxylic acids



catalyzed protocol was developed under metal-free thermal conditions by Fu's group.^{19g} Li's group finished this transformation utilizing a photoredox strategy under mild conditions.^{20f} Glorius²⁰ⁱ and Aggarwal's^{20a} groups independently developed ingenious protocols to construct C-B bonds by combining Lewis base activation with optical excitation. In these reported reactions, transition metal, high temperature, light irradiation, or long reaction time are ineluctable (Scheme 1b). Inspired by Aggarwal's work, we envisioned that diacyl peroxides might be used as a substitute of phthalimide esters to

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realize the borylation without extra light irradiation on account of the motif of sustainable chemistry. Compared with stable carboxylic phthalimide esters, peroxides exhibit relative low stability and more activity since the BDE of the O-O bond in peroxides $(\sim 34 \text{ kcal/mol})^{22a}$ is weaker than that of the N–O bond in carboxylic phthalimide esters (~55-65 kcal/mol).^{22b} Such properties of peroxides provide the possibility of the reaction. In addition, although diacyl peroxides have been widely used as a radical initiator, employing them as the alkyl radical precursors in organic transformations is still unappreciated.²³ Herein, we wish to report a metal- and light-free protocol for the radical decarboxylative borylation of diacyl peroxides under ambient temperature using *m*-chloroperoxybenzoic acid (mCPBA) as the activator of carboxylic acids (Scheme 1c). These diacyl peroxides could be easily accessed from the condensation of a variety of carboxylic acids with cheap and commercially available mCPBA. This protocol not only represents a new and efficient mode for carboxylic acid activation but also realizes the decarboxylative borylation of carboxylic acids in a more rapid and convenient mode.

We initiated this study by stirring peroxide 1a (0.3 mmol) and organodiboron compound 2 (0.39 mmol) in DMAc (1 mL) under argon atmosphere for 20 min. Then pinacol and Et₃N were charged, and the corresponding mixture was stirred for an additional 1 h. No reaction took place when B₂pin₂ 2a and $B_2(OH)_4$ 2b were used (Table 1, entries 1-2). Encouragingly, when B_2cat_2 2c was used as the borating reagent, the desired product 3a was acquired in 83% yield (Table 1, entry 3). By screening solvents such as DMF, CH₃CN, dioxane, THF, HMPA, and DMPU, we found that amides were specific solvents for an efficient transformation. The yield of 3a was further increased to 89% in DMF, whereas the reaction was inert in CH₃CN, dioxane, and THF (Table 1, entries 4-9). Increasing or decreasing the usage amount of 2cdid not gave better results (Table 1, entries 10 and 11). When this transformation was carried out under air, the yield of 3a was significantly reduced to 76%, suggesting that this reaction is sensitive to air (Table 1, entry 12). In addition, the reaction was immune to light since the yield of 3a was not affected neither by blue LED irradiation nor in the dark (Table 1, entries 13 and 14). Moreover, when symmetric diacyl peroxide 1a' was tested in reaction, the desired product 3a could be produced in 80% yield as well (Table 1, entry 15). Unfortunately, 3a could not be produced when perester 1a" was used in the protocol (Table 1, entry 16).

With the optimal conditions in hand, we investigated the reaction applicability by treating a variety of activated aliphatic acids with B₂cat₂. As shown in Scheme 2, primary acid derivatives were first explored. Both linear and branched aliphatic peroxyanhydrides were efficiently converted to the expected primary alkylboronates 3b-d in 58-96% yields. Peroxides containing alkenyl and alkynyl groups were also compatible in the reaction, giving rise to the corresponding products 3e and 3f in medium yields. 5-Chloro- and 5bromopentanoic acid derivatives transformed smoothly in the protocol, delivering haloalkyl boronates 3g and 3h in 74% and 84% yields, respectively. Peroxide containing an ester group, as in the case of 1i, also participated well in the reaction, producing 3i in 54% yield. When aliphatic peroxides incorporating aromatic rings such as phenyl and indole were involved, the reaction gave the corresponding alkylboronates 3j-l in good yields. Notably, heptanediacid bisperoxide reacted very well in the reaction, affording 1,5-bis(boronic

Table 1. Optimization of the Reaction Conditions^a

<i>n</i> C ₁ -	H ₂₃ COOR + B ₂ 1	(OR') ₄ DMF, rt, Ar, then pinacol, E 2	$ \begin{array}{c} \underline{20 \text{ min}} \\ t_3 \text{N, rt, 1 h} \end{array} n \text{C}_{11} \text{H}_{23} \\ \textbf{3}. \end{array} $,−Bpin a
	R =	0 nC ₁₁ H	0 ≝ H ₂₃ C∽∽ ∽ 1a' 1a"	
entry	substrate	$B_2(OR')_4^h$	solvent ⁱ	yield (%) ^b
1	1a	B_2Pin_2 (2a)	DMAc	0
2	1a	$B_2(OH)_4$ (2b)	DMAc	0
3	1a	B_2cat_2 (2c)	DMAc	83
4	1a	B_2cat_2 (2c)	DMF	89
5	1a	B_2cat_2 (2c)	CH ₃ CN	0
6	1a	B_2cat_2 (2c)	dioxane	0
7	1a	B_2cat_2 (2c)	THF	0
8	1a	B_2cat_2 (2c)	HMPA	64
9	1a	B_2cat_2 (2c)	DMPU	78
10 ^c	1a	B_2cat_2 (2c)	DMF	83
11 ^d	1a	B_2cat_2 (2c)	DMF	87
12 ^e	1a	B_2cat_2 (2c)	DMF	76
13 ^f	1a	B_2cat_2 (2c)	DMF	89
14 ^g	1a	B_2cat_2 (2c)	DMF	87
15	1a'	B_2cat_2 (2c)	DMF	80
16	1a"	B_2cat_2 (2c)	DMF	0

^{*a*}All reactions were carried out by stirring 1a (0.3 mmol) and 2 (1.3 equiv) in solvent (1 mL) under argon atmosphere at room temperature for 20 min. Then pinacol (4 equiv) and Et₃N (0.6 mL) were added, and the reaction mixture was stirred for an additional 1 h, except as noted. ^{*b*}Isolated yield. ^{*c*}2c (1.2 equiv) was used. ^{*d*}2c (1.4 equiv) was used. ^{*c*}The reaction was carried out under air. ^{*f*}The reaction was stirred in dark. ^{*g*}The mixture was stirred under blue LED irradiation. ^{*h*}B₂pin₂ = bis(pinacolato)diboron. B₂cat₂ = bis(catecholato)diboron. ^{*i*}DMF = *N*,*N*-dimethylformamide. DMAc = *N*,*N*-dimethylacetamide. THF = tetrahydrofuran. HMPA = hexamethyl phosphoryl triamide. DMPU = 1,3-dimethyltetrahydropyrimidin-2(1H)-one.

ester) 3m in 59% yield. Next, the tolerance of secondary aliphatic acid derivatives was tested. Cycloalkyl acid peroxides encompassing cyclopropyl, cyclopentyl, cyclopentenyl, cyclohexyl, indene, as well as bridged hydrocarbon were all suitable for the decarboxylative borylation, yielding the desired secondary alkylboronates 3n-t in good yields. It is noteworthy that the present decarboxylative borylation provided excellent stereoselectivity in the cases of 3n, 3s, and 3t where new stereoisomeric centers were produced. Decarboxylative borylation of peroxides bearing the gem-difluoro group and pyran ring proceeded very well, delivering 3u and 3v in moderate yields. In addition, open-chain secondary acid derivative α methyl-hydrocinnamic acid peroxide was also a good candidate in the present tactics, producing the open-chain secondary alkylboronate 3w in 83% yield. Regrettably, when mCPBAactivated 1-adamantanecarboxylic acid was subjected to the standard conditions, the reaction failed to deliver alkylboronate 3x, probably because such a kind of mixed tertiary diacyl peroxide was unstable. Instead, unlike primary and secondary peresters, which were ineffective in the reaction, tertiary peresters 1x transformed smoothly under standard conditions, generating tertiary alkylboronate 3x in 51% yield. The aforementioned decarboxylative borylation only exhibited the regioselectivity on the aliphatic moiety of peroxides, which is probably because aliphatic acids were easier to decarboxylate than aryl acids. To see if this method is suitable for the



Scheme 2. Scope of Aliphatic Peroxides^{*a,b*}

^{*a*}A mixture of 1 (0.3 mmol) and 2c (1.3 equiv) in DMF (1 mL) was stirred for 20 min under argon atmosphere at room temperature. Then pinacol (4 equiv) and Et₃N (0.6 mL) were added, and the reaction mixture was stirred for an additional 1 h, except as noted. ^{*b*}Isolated yield. ^{*c*}Ia (1 mmol) was used. ^{*d*}Ik (4 mmol, 1.52 g) was used. ^{*e*}B₂cat₂ (3 equiv), pinacol (8 equiv), and Et₃N (1.2 mL) were used. ^{*f*}*tert*-Butyl-adamantane-1-carboperoxoate (0.3 mmol) was used. ^{*g*}*tert*-Butyl peroxybenzoate (0.3 mmol) or dibenzoyl peroxide (0.3 mmol) were used.

decarboxylative borylation of aromatic acids, the standard conditions were applied to dibenzoyl peroxide (BPO) and *tert*butyl peroxybenzoate (TBPB). However, neither of them gave the desired product 3y, probably because the decarboxylation of the benzoic acid radical was a thermodynamic adverse process. In order to further demonstrate the applicability of the strategy, several natural carboxylic acid derivatives including monounsaturated and polyunsaturated fatty acids as well as lithocholic acid were investigated in the reaction. Consequently, the corresponding alkylboronates 3z-ac were generated in excellent yields. In addition, the reaction could also be conducted on a gram scale without any difficulty, as in the case of 3k, promising the practicability and application of this protocol. To investigate the reaction mechanism, some control experiments were conducted as shown in Scheme 3. The

Scheme 3. Mechanistic Studies



blank experiment revealed that no reaction took place, and 1a was almost quantitatively recovered when B₂cat₂ was absent under the standard conditions (Scheme 3a). This result suggests that the alkyl radical is generated by the reaction of peroxide 1 with DMF-ligated B2cat2 rather than the spontaneous decomposition of 1 itself. In addition, radical clock experiments were performed as shown in Scheme 3b. When 6-heptenoic acid derivative 1ad was carried out under the standard reaction conditions, the direct radical decarboxylative borylation product 3ad and the tandem cyclized borylation product 3ad' were obtained as a mixture in 75% yield in a ratio of 2.75:1. When cyclopropylacetic acid peroxide lae was subjected to this reaction, ring-opening product 3e was obtained in 30% yield as a sole product. These results clearly demonstrate that a free radical process was involved in the reaction by the treatment of 1 with 2c in DMF.

Based on the pertinent work of decarboxylative borylation^{19d,20a} and our experimental results, it is assumed that a radical chain process is involved in this transformation as shown in Figure 1. The reaction is initiated by the thermal homolysis of the B–B bond, which is caused by the reaction of peroxide 1 and DMF-ligated B_2cat_2 A, providing DMFstabilized boron-center radical C and carbon-center radical



Figure 1. Proposed mechanism.

D. Then, the unstable intermediate **D** resolves into an alkyl radical **E** with the release of CO_2 and **F**. The low strength of the O–O bond makes the radical propagation process more favorable and spontaneous so that no additional energy supply is required. Radical **E** is trapped by DMF-ligated B_2cat_2 **A** to yield product **G** and radical **C**. The latter can also react with peroxide **1** to yield alkyl radical **E**, CO_2 , and **F** to realize the propagation of radical species. On the other hand, radical **C** can be initiated by the thermal homolysis of bi-DMF-ligated B_2cat_2 **H** as well. Finally, product **3** is produced by the replacement of the catechol moiety in unstable compound **G** by pinacol. On the other hand, a single electron transfer (SET) might be involved for the tertiary perester (see Supporting Information).

With the preliminary cognition of reaction mechanism, we tried to construct C–C bonds by utilizing the generated alkyl radical in this protocol. It was gratifying to detect that quinones 4 such as vitamin K3 4a and 2-chloro-1,4-naphthoquinone 4b could be used in the protocol to produce the desired C–C bond-forming products 5a and 5b in moderate yields (Scheme 4). Apparently, this method possesses the potential to construct C–C bonds under mild conditions besides C–B bonds.

Scheme 4. C–C Bond Formation a,b



^{*a*}Reaction conditions: the mixture of 1d (0.9 mmol), 4 (0.3 mmol), and 2c (0.6 mmol) in DMF (1 mL) was stirred for 20 h at room temperature under an argon atmosphere. ^{*b*}Isolated yield.

In conclusion, a new approach for decarboxylative borylation has been developed by the treatment of *m*CPBA-activated fatty acids with B_2cat_2 . This strategy provides effective and handy access for the synthesis of a variety of alkylboronates without the need for metal, additive, and illumination. In addition, this strategy can also be applied to the forging of C–C bonds. For details of mechanism and applications of this reaction, further in-depth studies are being conducted.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.9b04218.

Experimental details and copies of spectra (PDF)

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