Chemoselective Decarboxylative Oxygenation of Carboxylic Acids to Access Ketones, Aldehydes and Peroxides

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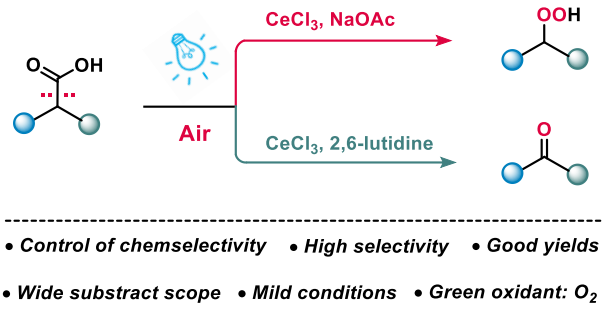
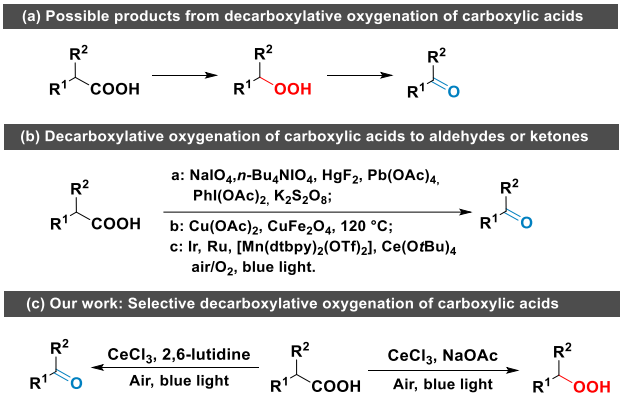


ABSTRACT: Reported here is a photocatalytic strategy for the chemoselective decarboxylative oxygenation of carboxylic acids using Ce(III) catalysts and O_2 as the oxidant. By simply changing the base employed, we demonstrate that the selectivity of the reaction can be channeled to favor hydroperoxides or carbonyls, with each class of products obtained in good to excellent yields and high selectivity. Notably, valuable ketones, aldehydes and peroxides are produced directly from readily available carboxylic acid without additional steps.

Control of chemoselectivity is one of the most important and enduring topics in organic synthesis.[1] A case in point is decarboxylative oxygenation of carboxylic acids, which could afford two different products, a carbonyl and a peroxide in a de-homologation manner (Scheme 1a). This is potentially a tremendously interesting reaction, because of the easy availability of the substrate and the huge importance of each product. Carboxylic acids are probably the most easily accessible functionality in biological and chemical synthesis.[2] Many of them are widespread in nature, e.g. amino acids, fatty acids and keto-acids, or are produced at large industrial scale, e.g. formic acid, acetic acid, benzoic acid and acrylic acid, and they are easy to store and simple to handle.[3-6] The importance of ketones and aldehydes can hardly be overstated. They are widely used as precursors and starting materials in the synthesis of a wide variety of chemicals including vitamins, drugs and fragrances.[7] In comparison, organic peroxides are less featured in organic synthesis. However, they play important roles in many biological processes, e.g. biodegradation and aging, and in drug development, e.g. as antimalarial agents, and they feature widely in oxidation reactions as oxidants and in polymerization processes as initiators.[8, 9]

Thus, developing a method for selective decarboxylative oxygenation of carboxylic acids to carbonyls and peroxides is of significant practical value. The transformation of carboxylic acids to aldehydes or ketones has been well documented (Scheme 1b). Earlier methods often rely on the use of stoichiometric amounts of oxidants, such as $NaIO_4$,[10] *n*-Bu_4NIO_4,[11] HgF_2,[12] $Pb(OAc)_4$,[13] $PhI(OAc)_2$[14] and $K_2S_2O_8$,[15] or high temperature. Photocatalytic oxidative decarboxylation of carboxylic acids with O_2 has recently been reported, using catalysts such as acridiniums, $[Ir(F(Me)ppy)_2(bpy)]PF_6$, $[Ru(bpy)_3]Cl_2$, $[Mn(dtbpy)_2(OTf)_2]$ or $Ce(OtBu)_4$ under blue or visible light irradiation.[16-19]

Scheme 1. Decarboxylative oxygenation of carboxylic acids to form various products.



Whilst various methods exist for the synthesis of ketones and aldehydes via decarboxylation of carboxylic acids, much fewer methods have been developed to access organic peroxides, and those that have been reported usually suffer from a limited substrate scope and/or rely on harsh conditions.[20] For instance, there appears to be few methods that are feasible for the formation of both benzylic and aliphatic

peroxides using benign and economic oxidants, i.e. O_2[21] or H_2O_2.[22] Indeed, although a lot of work has been reported on oxidative decarboxylation[4, 23] and peroxides are generally believed to be a key intermediate in the reaction,[16, 19, 24] only one example has shown the possibility of synthesis of peroxides from decarboxylation and their use in intramolecular cyclization.[19]

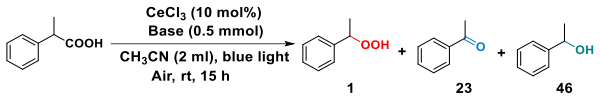
In continuing our interest in selective oxidation,[18, 25-28] we report herein a photocatalytic method that enables selective formation of aldehydes/ketones and peroxides, via aerobic decarboxylative oxygenation of carboxylic acids with simple, cheap cerium halides as catalyst (Scheme 1c). Remarkably, the selectivity of the reaction can be tuned by a simple change of the base used.

We started by searching for conditions that would allow for selective decarboxylative oxygenation of carboxylic acids. Inspired by the remarkable ability of Ce(III/IV) in engaging photoredox reactions,[29-32] at the outset we examined $CeCl_3$ as a potential catalyst, which is much cheaper and more easily available than Ce(O*t*Bu)$_4$,[19] for the model reaction of *α*-methylphenylacetic acid with 1 bar of air under the irradiation of blue light (465 nm, 9 W). The results are shown in Table 1. As can be seen, in the presence of 1 equivalent of a base, NaOAc, the hydroperoxide **1** was obtained, much to our surprise, in an excellent yield of 94%. The formation of hydroperoxides has been observed before, but in a significantly lower yield.[19] Interestingly, without the addition of the base, α-methylphenylacetic acid was transformed to a mixture of **1** and 1-phenylethanone (**23**) in 49% and 22% yield, respectively (entry 2).

Aiming to alter the reaction selectivity, we screened a range of bases in the reaction. As is clear, the base plays a decisive role in affecting the selectivity of products (entries 1, 3-11). Whilst NaOAc led to almost exclusive formation of the peroxide **1**, replacing it with 2,6-lutidine afforded the ketone **23** and alcohol **46** in yields similar to those obtained with Ce(O*t*Bu)$_4$.[19] Lower yields were observed with other bases, such as Na_2CO_3, NaOH, KOAc, CsOAc, LiOAc, Et_3N and pyridine (entries 4-11). It is interesting to note that the formation of the peroxide is suppressed by amine bases but strongly promoted by NaOAc and to a less degree by Na_2CO_3. The difference in yield observed with the different acetate bases (entries 1 and 4-6) may be at least partly due to their varying solubilities in the solvent used (Table S2). This dramatic effect of bases on the chemo-selectivity of decarboxylative oxygenation has not been noted in previous studies. Taking NaOAc and 2,6-lutidine as the optimum base for the formation of **1** and **23**, respectively, we also examined the effect of other cerium compounds as possible catalysts (Table S1). As may be expected, blue light, $CeCl_3$, and air are all essential components for the decarboxylative oxygenation to occur (entries 12-14).

To demonstrate the generality of our strategy, we investigated the decarboxylative oxygenation of a variety of carboxylic acids. Firstly, the scope for the formation of hydroperoxides was examined. As shown in Scheme 2, a variety of phenylacetic acids underwent selective decarboxylative oxygenation, affording the corresponding hydroperoxide products in good yields (46-94%). All the halogen-substituted (*p*-CF_3-, *p*-Br-, *p*-Cl-, and *p*-F-) phenylacetic acids were tolerated; they afforded the corresponding hydroperoxide products (**4-7**) in good yields. A thiopheneacetic acid also worked, without poisoning the catalyst, so did 2-naphthylacetic acid, albeit in moderate yields. The position of substitutes affects the yields, as *m*-substituted (**9**) and *o*-substituted (**10**) hydroperoxide products showed lower yields (61% and 59%). This might result from some steric hindrance.[33] Worth noting is that the secondary (**1**) and tertiary peroxides (**11**) were obtained in significantly higher yields (94%) than the primary analogue (**2**), indicating the involvement of benzylic radical in the formation of the peroxide products. The reaction could also be run at a larger scale, albeit with a reduced yield (**1**).

Table 1. Optimization of selective transformation of carboxylic acids[a]



Entry	Catalyst	Base	Yield (%)[b]		
			1	**23**	**46**
1	$CeCl_3$	NaOAc	94	2	0
2	$CeCl_3$	/	49	22	0
3	$CeCl_3$	2,6-lutidine	0	74	22
4	$CeCl_3$	KOAc	37	8	0
5	$CeCl_3$	LiOAc	38	42	0
6	$CeCl_3$	CsOAc	33	9	0
7	$CeCl_3$	Na_2CO_3	37	2	0
8	$CeCl_3$	NaOH	9	1	0
9	$CeCl_3$	Pyridine	0	51	10
10	$CeCl_3$	Et_3N	0	37	0
11	$CeCl_3$	DBU	0	10	0
12[c]	$CeCl_3$	NaOAc	0	0	0
13	/	NaOAc	0	0	0
14[d]	$CeCl_3$	NaOAc	0	0	0

[a]Reaction conditions: α-methylphenylacetic acid (0.5 mmol), $CeCl_3$ (10 mol%), base (0.5 mmol), CH_3CN (2 mL), air, blue light (465 nm, 9 W), room temperature, 15 h. [b]NMR yields are given, determined using mesitylene (20 μL) as internal standard. [c]Reaction in dark. [d]N_2 instead of air.

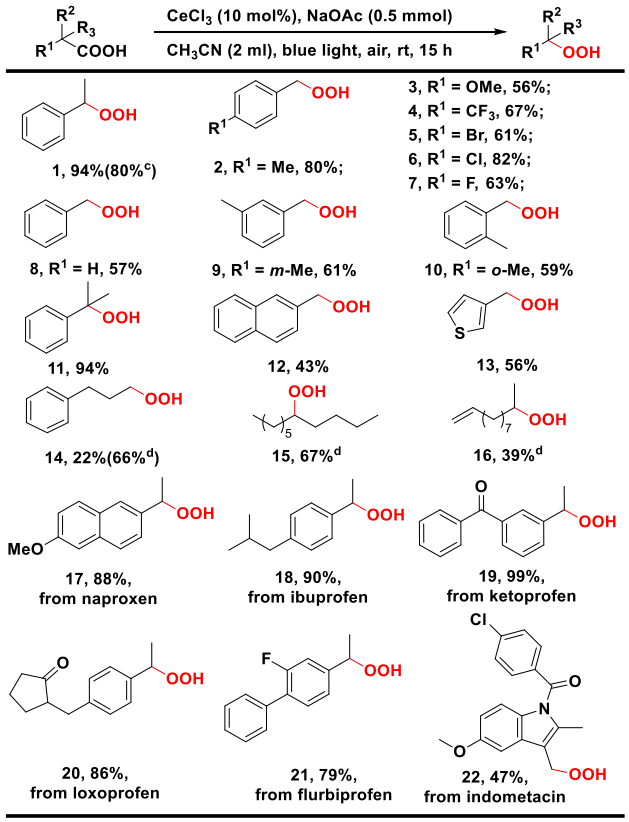
The more challenging aliphatic acids are also feasible, as showcased by the peroxides **14-16**; however, a higher O_2 concentration (N_2/O_2 volume: 1:2; 1 bar) and Na_2CO_3 as the base were necessary. As shown in Scheme 2, a lower yield of **14** was obtained under the condition of using air and NaOAc. Remarkably, the oxidation-prone C=C bond remained intact in **16**, and byproducts were formed in very low yields (Scheme S1, eq. 1). There was no benzylic oxidation in **14**.

Furthermore, a series of anti-inflammatory drugs, such as naproxen, ibuprofen, ketoprofen, loxoprofen, flurbiprofen and indomethacin, could be oxidatively decarboxylated, furnishing the corresponding hydroperoxide products (**17-22**) in moderate to high yields (47-99%). Such peroxides could provide metabolites for drug study, as they may form under enzymatic oxidation.[34] We note that whilst the formation of peroxyl species from the reaction of the carbon radical with triplet O_2 is generally assumed,[16, 19, 24, 35] this is the first time

a range of peroxides have been isolated as potently useful products in oxidative decarboxylation.

A simple change of the base from NaOAc to 2,6-lutidine allows the selectivity of the oxidative decarboxylation to be channeled to carbonyl products. The scope of aldehydes and ketones resulting from the selective decarboxylative oxygenation of acids is shown in Scheme 3, demonstrating the adaptability and practicability of the method. As can be seen, a variety of phenylacetic acids bearing different functional groups were converted to the corresponding aldehyde and ketone products (**23-35**) in moderate to good yields (43-75%). *O*-Tolylacetic acid was selected as the example substrate to showcase the chemoselectivity of this transformation. As shown in Scheme S1, only trace of alcohol byproduct was detected. Phenylacetic acids bearing electron withdrawing halide substituents, including -CF_3, -Br, -Cl, and -F, were tolerated in the decarboxylative oxygenation, so were those bearing electron donating substitutes, e.g. *m*-Me and *o*-Me (**34** and **35**). Moreover, an acid bearing a heteroatom ring, i.e. thiophene, showed good reactivity, affording **36** in a good yield (70%). Interestingly, 2-(phenylmethoxy)acetic acid with an oxygen atom in the carbon chain also reacted smoothly, without the weak benzylic C-H bond being compromised (**37**). An amino acid derivative was also tolerated, giving the corresponding amide product **38** in a good yield (66%).

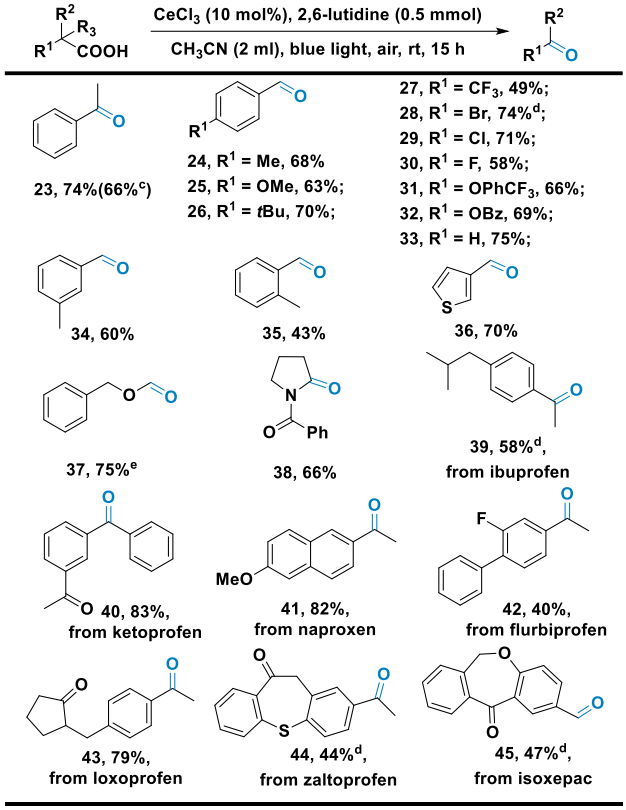
Scheme 2. Decarboxylative oxygenation of carboxylic acids to hydroperoxides[a, b]



[a]Reaction conditions: acid (0.5 mmol), $CeCl_3$ (10 mol%), NaOAc (0.5 mmol), CH_3CN (2 mL), blue light (465 nm, 9 W), air, room temperature, 15 h. [b]Isolated yields are given. [c]Acid (1 mmol). [d]Na_2CO_3 (0.5 mmol) instead of NaOAc, and N_2/O_2 (1:2) mixture instead of air.

As with the reaction leading to peroxides, a wide range of drug molecules, including ibuprofen, ketoprofen, naproxen, flurbiprofen, loxoprofen, zaltoprofen and isoxepac, underwent the decarboxylative oxygenation to yield the corresponding aldehyde or ketone products (**39-45**) in moderate to excellent yields (40-83%). Apart from possible use in the study of drug metabolism, these derivatives may serve as useful scaffolds to build new bioactive molecules or as substrates for further reactions.[36, 37]

Scheme 3. Decarboxylative oxygenation of carboxylic acids to aldehydes and ketones[a, b]



[a]Reaction conditions: acid (0.5 mmol), $CeCl_3$ (10 mol%), 2,6-lutidine (0.5 mmol), CH_3CN (2 mL), blue light (465 nm, 9 W), air, room temperature, 15 h. [b]Isolated yields are given. [c]Acid (1 mmol). [d]Pyridine (0.5 mmol) instead of 2,6-lutidine. [e]UV (365 nm, 9 W) instead of blue light.

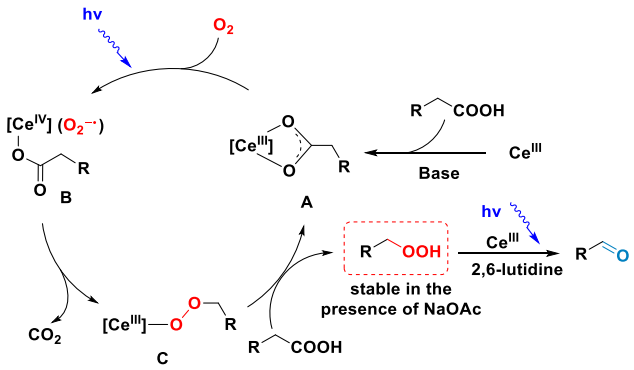
Whilst the mechanism of decarboxylative oxygenation of carboxylic acids has been widely accepted,[17-19] the chemoselective formation of isolable peroxides, aldehydes and ketones prompted us to look into the mechanism concerning particularly what controls the selectivity of the reaction. Firstly, the coordination of carboxylic acids with cerium catalysts was explored by mass spectroscopy with phenylacetic acid (PA) as a standard substrate and $CeCl_3$ as catalyst. As shown in Figure S3, mixing $CeCl_3$ with PA appears to lead to, as indicated by HRMS measurement, a cerium species $[Ce(PA\text{-}H)_2]^+$, which could result from the coordination of two PA molecules with a Ce(III) centre.[38, 39] It is thus likely that the selective decarboxylative oxygenation starts from the coordination of carboxylic acids to $CeCl_3$. Indeed, esters do not engage in the reaction (Scheme S2).

As with other decarboxylative oxygenation reactions,[19] alkyl hydroperoxides are likely to be a key intermediate.

The kinetic profile of the reaction of α-methylphenylacetic acid reveals that this is the case. As is seen in Figure S4(a), the formation of the hydroperoxide **1** is rapid and precedes that of the ketone **23** and alcohol **46**, and its decrease is coincided with the rise of the latter two. Furthermore, subjecting the isolated **1** to the conditions of $CeCl_3$, 2,6-lutidine and blue light afforded **23** in 78% yield (Figure S4(b)). It is thus reasonable to conclude that the carbonyl products result from the peroxide intermediate.

The question then is why the peroxides are not reacting further, as is usually observed? Table 1 indicates that the base plays a critical role. This is more clearly manifested when the isolated peroxide **1** was subjected to blue light irradiation, in which **1** remained largely intact when using NaOAc as the base but fully converted to **23** and **46** when 2,6-lutidine was used (Scheme S3, eqs 1-2). A possible explanation is that the acetate anion coordinates to cerium, preventing that of the peroxide and hence its further transformation, whereas 2,6-lutidine could not play such a role. This conjecture finds support in UV-Vis experiments (see Figure S5(b) and related explanation). [40,41]

Scheme 4. Proposed mechanism of selective decarboxylative oxygenation of carboxylic acids ([Ce^n] species)



Based on the above observations and previous literature,[17-19] a plausible mechanism of this selective decarboxylative oxygenation reaction is suggested (Scheme 4). Firstly, a Ce(III) compound reacts with a carboxylic acid, forming the complex **A**. Under light irradiation, **A** is oxidized by O_2 to afford a Ce(IV)-superoxide species **B**.[19] Ce(IV) carboxylate is well known to undergo facile decarboxylation via light-promoted homolysis of the Ce-oxygen bond. The resulting alkyl radical would be easily trapped by the superoxide radical, giving rise to a Ce(III) peroxide specie **C**, metathesis of which with a free carboxylic acid then releases the observed alkyl hydroperoxide. However, light may not be necessary for the conversion of **B** to **C**, as indicated by the oxidation of α-methylphenylacetic acid in the dark with pre-irradiated $CeBr_3$ mentioned above. The decarboxylation could be facilitated by the superoxide radical attacking the α carbon, a process reminiscent of an iron catalysed oxidation of ethers.[42] The peroxide product from **C** is stable in the presence of NaOAc, but is transformed to a carbonyl or an alcohol when using 2,6-lutidine as base. Light is necessary to promote the single-electron reduction of O_2 by Ce(III) species and the transformation of the peroxide to the aldehyde.[18,19]

In conclusion, a Ce(III)-catalyzed selective decarboxylative oxygenation of carboxylic acids to widely different products has been developed. The selectivity of this decarboxylative oxygenation process can be tuned with a simple change of base. With this protocol, a wide range of carboxylic acids have been selectively transformed to hydroperoxides, aldehydes and ketones in good yields with O_2 under mild conditions.

ASSOCIATED CONTENT

Data Availability Statement

The data underlying this study are available in the published article and its Supporting Information.

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.
General information, preparation of substrates, optimization of reaction conditions and characterization data. (DOCX)

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The manuscript was written through contributions of all authors.

Notes

The authors declare no competing financial interest.

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