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ARTICLE TYPE

Light and oxygen-enabled sodium trifluoromethanesulfinate-mediated selective oxidation of C-H bonds[†]

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Visible light-induced organic reactions are important chemical transformation in organic chemistry, and their efficiency highly depends on suitable photocatalysts. However, the commonly used photocatalysts are the precious transition-metal complexes and elaborate organic dyes, which hamper large-scale production for high cost. Here, we report a novel strategy for the first time: light and oxygenenabled sodium trifluoromethanesulfinate-mediated selective oxidation of C-H bonds, and high-value-added chemicals, aromatic ketones 10 and carboxylic acids, were easily prepared in high to excellent yields using readily available alkyl arenes, methyl arenes and aldehydes as the materials. The mechanism investigations showed that treatment of inexpensive and readily available sodium trifluoromethanesulfinate with oxygen under irradiation of light could in-situ form a pentacoordinate sulfide intermediate as the efficient photosensitizer. The methods are a highly efficient, economical and environmentally friendly strategy, and the light and oxygen-enabled sodium trifluoromethanesulfinate photocatalytic system breakthroughs the previous photochemical concepts.

Introduction

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Over the past decade, visible light photocatalysis has received great attention for its simplicity, economy and environmental friendliness,¹ and the efficiency of reactions is highly dependent 20 on photocatalysts.² The commonly used photocatalysts are the precious transition-metal complexes³ and elaborate organic dyes⁴ (Scheme 1A) that are previously prepared, which is not conducive to large-scale production for relative high cost. In addition, non-photosensitive donors and receptors form an 25 electron donor and acceptor (EDA) complexes that can absorb visible light to realize photocatalytic reactions (Scheme 1B).⁵ However, the EDA complexes are very limited thus far. Here, we want to explore a new strategy: an in-situ formed photocatalyst promotes the corresponding organic reactions. Sodium 30 trifluoromethanesulfinate (1) (Langlois reagent)⁶ is a readily available, inexpensive and easily stored reagent, and it is usually used as the trifluoromethyl source.7 We realized that many transition metals could form metal epoxides by interacting with oxygen (Scheme 1C).8 The pentacoordinate sulfides were

- ³⁵ reported although they were seldom developed.⁹ Atomic valence state of sulfur is +4 in **1**. We hypothesized that the photoinduced interaction of **1** with oxygen would form a pentacoordinate sulfide (**PS**) (**2**) with +6 valence state of sulfur (Scheme 1D), and the pentacoordinate sulfide (**2**) would act as a photosensitizer.
- ⁴⁰ Density functional theory (DFT) calculations show that formation of **2** from treatment of **1** with oxygen only needs 24.12 kcal/mol activation energy releasing a high energy (105.02 kcal/mol) (see Scheme 1D and Supporting Information for details).



45 Scheme 1 Previous photosensitizers and our design. (A) Transition-metal complexes and organic dyes. (B) Electron donor and acceptor (EDA) complexes as the photosensitizers. (C) Formation of transition-metal

epoxides. (D) Formation of pentacoordinate sulfide (**PS**, **2**). (E) Proposed mechanistic pathway of photoredox aerobic oxidation of ethylbenzene (**6**) to acetophenone (**9**).

The selective oxidation of saturated C-H bonds of readily 5 available alkanes to high-value-added chemicals¹⁰ using environmentally benign molecular oxygen¹¹ shows a great significance in industrial and research fields. In fact, the process catalyzed by enzymes is commonly seen in nature.¹² However, the selective aerobic oxidation of saturated C-H bonds is a great 10 challenge in chemistry. Ketones are versatile intermediates and important structural motifs in pharmaceuticals, natural products, and advanced organic materials.13 On the basis of our recent studies in visible light photocatalysis, we questioned if the pentacoordinate sulfide (2) could act as a photosensitizer as well 15 as a hydrogen atom grabbing catalyst under oxygen atmosphere and light irradiation, which might provide a new and useful strategy for selective oxidation of saturated C-H bonds. From a design perspective, a detailed description of our proposed mechanistic cycle for the aerobic oxidation of ethylbenzene (6) to 20 acetophenone (9) is outlined in Scheme 1E. We presumed that initial light-irradiation of 2 would produce the photoexcited state 2*, and a single-electron transfer (SET) of 2* to oxygen would generate two radicals 3 and 4. Treatment of 4 with 6 would deliver 5 and radical 7, and exchange of the proton in 5 with Na⁺ 25 would regenerate 2. Meanwhile, combination of 7 with 3 or oxygen in the presence of one proton would give 8, and

Results and discussion

Table 1 Optimization of reaction conditions^a

dehydration of 8 would provide the target product (9).

	F 10 CH ₃ 0.1 mmol S	SO ₂ Na (1) (25 mol%) O ₂ (1 atm) = LED (400-405 nm) CN (1.0 mL), rt, 12 h tandard condition	F 11, 10	00%
Entry	Variation of the standard conditions			Yield (%) ^b
1	air (1atm) instead of oxygen			100
2	Ar atmosphere instead of oxygen			nr
3	without light			nr
4	without CF ₃ SO ₂ Na			nr
5	CF ₃ SO ₃ Na instead of 1			nr
6	acetone instead of CH ₃ CN			100
7	DMF instead of CH ₃ CN			20
8	DMSO instead of CH ₃ CN			nr
9	blue LED (450-45: (400-405 nm)	5 nm) instead of bl	ue LED	64
10	blue LED (420-425 nm) instead of blue LED (400-405 nm)			88
11	blue LED (380-38: (400-405 nm)	5 nm) instead of bl	ue LED	100
^{<i>a</i>} Reaction conditions: 10 (0.1 mmol), 1 (25 mol%), solvent (1.0 mL), under O ₂ atmosphere (1 atm.) and light irradiation at room temperature (~25 °C) for 12 h. ^{<i>b</i>} The yields were determined by ¹⁹ F NMR using benzotrifluoride as the internal standard. nr = no reaction.				

Investigations on reaction conditions. With this mechanistic hypothesis in hand, we first tested the proposed aerobic oxidation

of 1-ethyl-4-fluorobenzene (10) under different conditions (see Tables S1-S8 in Supporting Information for details). To our 35 delight, we found that the conditions using 25 mol% sodium trifluoromethanesulfinate (1) as pre-photosensitizer, acetonitrile as the solvent with irradiation of a 3 W blue light emitting diode (LED) bulb (400-405 nm) under oxygen atmosphere (1 atm.), achieved the desired 1-(4-fluorophenyl)ethanone (11) in almost 40 quantitative yield (Table 1). The same yield was provided when oxygen was replaced with air (entry 1). However, the reaction did not work in the absence of oxygen, light or 1 (entries 2-4), which showed that none was dispensable for oxygen, light and 1 in the reaction. No reaction occurred when sodium 45 trifluoromethanesulfonate (CF₃SO₃Na) replaced 1 (entry 5). The effect of solvents was investigated (entries 6-8), and acetone also was a suitable solvent (giving 100% yield) (entry 6). We found that wavelength of light was of great concern for the reaction (entries 9-11), and wavelengths of 400-405 nm and 380-385 nm 50 were feasible. More conditions were performed in Tables S1-S8 of Supporting Information. Based on the results above, the aerobic oxidation of alkyl arenes to ketones only needed very simple conditions: light, oxygen or air, catalytic amount of sodium trifluoromethanesulfinate (1) and suitable solvents 55 without requirement of previously prepared precious transitionmetal complexes or elaborate organic dyes. Interestingly, sodium trifluoromethanesulfinate (1) itself is not a photosensitizer, and the activation of light and oxygen makes it become a photosensitizer, pentacoordinate sulfide (2).



Scheme 2 Aerobic oxidation of aryl arenes to ketones. Reaction conditions: alkyl arene (0.2 mmol), 1 (25 mol%), solvent (1.0 mL), under O_2 atmosphere (1 atm.) and light irradiation at room temperature (~25 °C) for 12 h. The yields were determined by GC-MS using dodecane as the internal standard. Using LED (400-405, 380-385 or 420-425 nm) as the light source. Isolated yield.

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Surveys of the alkyl arene scope on synthesis of ketones. Having established the optimal conditions for this aerobic oxidation of alkyl arenes, we surveyed the scope of substrates. As shown in Scheme 2, various ethyl arenes are amenable to this 5 light and oxygen-enabled sodium trifluoromethanesulfinatemediated selective oxidation strategy including neutral (9, 23-25, 92-100% yields), electron-rich (12, 100 % yield), weak electrondeficient (11, 13-17, 95-100% yields), strong electron-deficient ethyl arenes (18-22, 95-99% yields) and O-heterocycle (26, 51% 10 yield). Subsequently, arenes containing different alkyls were attempted under the standard conditions, and we found that length of alkyls and variation of substituents on the alkyls almost did not affect the reactivity of the substrates (27-31, 95-99% yields). Next, 1,4-diethylbenzene was used as the substrate under 15 irradiation of 3 W purple light emitting diode (LED) bulb (380-385 nm), and 1,4-diacetylbenzene (19) was obtained in 97% yield (see secondary 19 in Scheme 2). We tried the aerobic oxidation of 1,3,5-triethylbenzene and found that different light wavelength led to different products: irradiation with 420-425 nm blue light 20 gave 32 in 61% yield together with trace amount of 33 appearing, and irradiation with 380-385 nm purple light afforded 1,3,5triacetylbenzene (33) in 96% yield without 32 occurring. Finally, the aerobic oxidation of hydrocarbons containing two phenyls were investigated under the standard conditions, and they also 25 exhibited high reactivity (34-37). Diphenylmethane gave benzophenone (34) in 98% yield, 1,2-diphenylethane provided 2phenylacetophenone (35) in 97% yield, and 1,4-diphenylbutane and 1,5-diphenylpentane afforded diketones 36 and 37 in 89% and 86% yields, respectively. A gram-scale production of 30 acetophenone (9) was performed using ethylbenzene (6) (10 mmol, 1.06 g) as the material under the standard conditions with irradiation of 30 W blue LEDs (400 - 405 nm), and 1.07 g of 9 was obtained in 89% isolated yield. The reactions in Scheme 2 could tolerate various functional groups including C-F, C-Cl, C-35 Br and C-I bonds, ether, CF3, ester, acetyl, cyano and nitro groups. (A) Synthesis of 38



Scheme 3 Applications of the method.

- **Applications of the method.** To demonstrate synthetic ⁴⁰ practicability of this aerobic oxidative protocol, three applications were conducted. As shown in Scheme 3A, *O*-heterocycle **38** was easily prepared using synthesized **37** as the intermediate in the presence of boron trifluoride.¹⁴ Melperone (**42**) is an antipsychotic drug,¹⁵ so it is of important value to develop a conversiont and afficient surfative result. (A Baremediatel) 4
- ⁴⁵ convenient and efficient synthetic route. 1-(4-Bromobutyl)-4fluorobenzene (**39**) was used as the starting material, its aerobic oxidation under our standard conditions provided **40** in 93% yield, and coupling of **40** with 4-methylpiperidine (**41**) gave the drug

molecule (42) in 87% yield (Scheme 3B). Lenperone (44), an ⁵⁰ effective atypical antipsychotic drug used in the treatment of schizophrenia,¹⁶ was easily prepared in 82% yield through coupling of 40 with (4-fluorophenyl)(piperidin-4-yl)methanone (43) (Scheme 3C). Therefore, the results above showed that our environmentally friendly aerobic oxidative method from alkyl ⁵⁵ arenes to ketones was very effective, economical and practical.



Scheme 4 Investigations on the reaction mechanism.

Mechanistic investigations. To verify the proposed mechanistic 60 pathway of aerobic oxidation of alkyl arenes to ketones in Scheme 1E, some experiments were carried out as follows: (a) In order to confirm the active species of oxygen involved in the present reaction, and the electron paramagnetic resonance (EPR) experiments were performed. When a solution of 2,2,6,6-65 tetramethylpiperidin-4-one (TMPD) as the trapping agent of ¹O₂, 1 and ethylbenzene (6) in acetonitrile was irradiated with full wavelength light under oxygen atmosphere, a stronger characteristic signal of ¹O₂ adduct with TMPD was observed (Scheme 4Aa); When solution of 5,5-dimethyl-1-pyrroline N-70 oxide (DMPO), 1 and ethylbenzene (6) in acetonitrile was irradiated with full wavelength light under oxygen atmosphere, a characteristic signal of O2 - adduct with DMPO was found (Scheme 4Ab). (b) When ¹⁸O₂ replaced ¹⁶O₂ as the oxygen source using propylbenzene as the substrate, propiophenone (27) and 75 ¹⁸O-labelling propiophenone (27') were obtained in 24% and 76% yields (GC-MS determination), respectively (Scheme 4B), which indicated that molecular oxygen (O2) was a sole oxygen source in the oxidation of alkyl arenes to ketones. (c) Treatment of ethylbenzene (6) was carried out under argon atmosphere, and no

reaction occurred. Subsequently, the reaction system was conducted under oxygen atmosphere, product **9** was provided in almost quantitative yield (Scheme 4C). These results showed that O₂ is essential for this transformation. (d) Sodium trifluoromethanesulfinate (**1**) was performed under the standard conditions (¹⁹F NMR showed that **1** was consumed completely), then ethylbenzene (**6**) was added to the system, and a nearly quantitative yield was observed (Scheme 4D). (e) When sodium trifluoromethanesulfonate (CF₃SO₃Na) instead of **1** was added to reaction system of **6**, no reaction occurred (Scheme 4E). In addition, the reaction did not work in the presence of other sulfur-

addition, the reaction did not work in the presence of other sulfurcontaining compounds with +6 valence state (see Table S13 in Supporting Information). Therefore, we think that intermediate **2** could be the real photocatalyst. (f) Ethylbenzene (**6**) did not react ¹⁵ in the presence of 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) under the standard conditions (Scheme 4F), and the result exhibited that the aerobic oxidation of **6** to acetophenone (**9**) was



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Figure 1 Characterizations for pentacoordinate sulfide (2). (A) XPS spectra of 2: (a) XPS spectrum of the S 2p energy region; (b) XPS spectrum of the O 1s energy region. (B) PXRD patterns of 1, CF₃SO₃Na and 2. (C) UV-vis spectrum of 2. (D) FTIR-ATR spectra of 1, CF₃SO₃Na and 2.

Characterizations for pentacoordinate sulfide (2). To further ²⁰ identify the presumed pentacoordinate sulfide (2), sodium trifluoromethanesulfinate (1) (0.25 mmol) in 2 mL of acetonitrile was stirred with irradiation of blue LED (400-405 nm) under oxygen atmosphere (1 atm.) for 12 h, then the sediment was filtered to get a possible pentacoordinate sulfide (2) (see

- ²⁵ Supporting information). Subsequently, various characterizations were performed as follows: (a) Solid 2 was determined by X-ray photoelectron spectroscopy (XPS), and the binding-energy (BE) peak at 169.89 eV was observed in the XPS spectrum of the S 2p energy region (Figure 1Aa), that was assigned to +6 valence state
- ³⁰ of sulfur. Meanwhile, three strong peaks at 525.15, 533.02 and 537.49 eV were found in the XPS spectrum of the O 1s energy

region, that were assigned to three different binding forms of oxygen in **2** (Figure 1Ab). (b) Solid ¹⁹F NMR spectra of sodium trifluoromethanesulfinate (**1**), sodium trifluoromethanesulfonate ³⁵ (CF₃SO₃Na) and **2** were recorded, and they showed the chemical shifts at -86.244 ~ -88.701 ppm (m), -78.875 ppm (s) and -77.156 ppm (s), respectively (see Figure S5-S7 in Supporting Information), which indicated that **2** was different with **1** and CF₃SO₃Na. (c) Powder X-ray diffraction (PXRD) patterns of **1**, ⁴⁰ CF₃SO₃Na and **2** were also detected, and they gave different spectra (Figure 1B). (d) UV-visible absorption spectra of **1**, CF₃SO₃Na and **2** in MeCN in the range of 200-800 nm were recorded (Figure S9-S11 in Supporting Information), and **2** gave the obvious absorption peak in the range of visible light region ⁴⁵ (390 - 420 nm) (Figure 1C), which indicated **2** could act as a photosensitizer. (e) Fourier-transform attenuated total reflectance

- photosensitizer. (e) Fourier-transform attenuated total reflectance (FTIR-ATR) spectra of 1, CF₃SO₃Na and 2 were recorded, and they showed different peaks (see Figure 1D). According to the results above, intermediate 2 could be a pentacoordinate sulfide.
- ⁵⁰ Therefore, we think that the proposed mechanistic pathway of photoredox aerobic oxidation of alkyl arenes to ketones in Scheme 1E is reasonable.



Scheme 5 Aerobic oxidation of methyl arenes to carboxylic acids. Reaction conditions: methyl arene (0.2 mmol), 1 (50 mol%), solvent (1.0 mL), under O_2 atmosphere (1 atm.) and light irradiation at room temperature (~25 °C) for 12 h. Using blue LED (400-405 nm) as the light source. Isolated yield.

Aerobic oxidation of methyl arenes to carboxylic acids. Carboxylic acids are a kind of important organic compounds, and 55 they are used as the synthetic precursors for various high-valueadded chemicals.¹⁷ In the traditional oxidative methods, synthesis of the kinds of compounds was performed in the presence of stoichiometric loadings of hazardous oxidants such as dichromate/permanganate,18 oxone,19 periodate reagent20 with 60 large amounts of wastes containing heavy metals occurring, which is not environmentally benign. It is an important direction to develop simple, efficient and environmentally friendly methods to synthesize the high-value products from simple and readily available starting materials. To further demonstrate the light and 65 utility of this oxygen-enabled sodium trifluoromethanesulfinate-mediated selective oxidation strategy, we investigated aerobic oxidation of methyl arenes to carboxylic acids. As shown in Scheme 5, selective aerobic oxidation of methyl arenes was carried out in acetonitrile in the presence of 50

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mol% of 1 under oxygen atmosphere (1 atm.), and the reactions were satisfactory for methyl arenes containing different functional groups including neutral (45 and 61, 93% and 92% yields, respectively), electron-rich (46, 87% yield), weak 5 electron-deficient (47-53, 89-97% yields), strong electrondeficient groups (54-60, 87-95% yields), and O-, S-heterocycles (62 and 63, 52% and 68% yields, respectively). The present reactions could tolerate various functional groups including C-F, C-Cl and C-Br bonds, ether, CF3, acyl, ester, amide and cyano 10 groups, and O-, S-heterocycles. Notably, aerobic oxidation of 4fluorotoluene was performed with ¹⁸O₂ as the oxygen source under the standard conditions, 4-fluorobenzoic acid (47), single ¹⁸O-labelling 4-fluorobenzoic acid (47') and double ¹⁸O-labelling 4-fluorobenzoic acid (47") were obtained in 94% total yield with 15 a ratio of 4:32:64 for 47/47'/47". The result showed that molecular oxygen (O₂) was a sole oxygen source for oxidation of

methyl arenes to carboxylic acids.



Scheme 6 Aerobic oxidation of aldehydes to carboxylic acids. Reaction conditions: aldehyde (0.2 mmol), 1 (50 mol%), solvent (1.0 mL), under O_2 atmosphere (1 atm.) and light irradiation at room temperature (~25 °C) for 12 h. Using blue LED (400-405 nm) as the light source. Isolated yield.

Aerobic oxidation of aldehydes to carboxylic acids. The selective photocatalytic aerobic oxidation of aldehydes was ²⁰ surveyed using acetonitrile as the solvent in the presence of 25 mol% of **1** under oxygen atmosphere (1 atm.). As shown in

Scheme 6, the excellent results were provided for aromatic aldehydes containing different functional groups including neutral (45, 61 and 76, 86-95% yields), electron-rich (46, 64-66, 25 89-94% yields), weak electron-deficient (47-53, 67-72, 92-97% yields), and strong electron-deficient groups (54, 57-59, 73-75, 91-96% yields). Four heteroaryl aldehydes also provided the corresponding carboxylic acids 77-80 in 93-96% yields. Aliphatic aldehyde, decanal, was attempted to perform this aerobic 30 oxidation, and it afforded 81 in 91% yield. Notably, a gram-scale production of benzoic acid (45) was conducted under the standard conditions using benzaldehyde (82) (10 mmol, 1.06 g) as the example, and 1.15 g of 45 was obtained in 94% yield. The present reactions could tolerate various functional groups 35 including C-F, C-Cl and C-Br bonds, ether, hydroxyl, CF3, ester, amide and cyano groups, and N-, S-heterocycles. Aerobic oxidation of 4-fluorobenzaldehyde was also performed under the standard conditions with ¹⁸O₂ as oxygen source, 4-fluorobenzoic acid (47) and single ¹⁸O-labelling 4-fluorobenzoic acid (47') were 40 obtained in 97% total yield with a ratio of 13:87 for 47/47'.

Conclusions

We have developed a novel light and oxygen-enabled sodium trifluoromethanesulfinate-mediated selective oxidation of C-H bonds, and the high-value-added chemicals, aromatic ketones and 45 carboxylic acids, were prepared in high to excellent yields using readily available alkyl arenes, methyl arenes and aldehydes as the materials, in which the in situ formed pentacoordinate sulfide intermediate derived from sodium trifluoromethanesulfinate and oxygen under irradiation of light acted as the efficient 50 photosensitizer. The present methods show some advantages including inexpensive and readily available sodium trifluoromethanesulfinate as the precursor of photosensitizer, simple and easy operational reaction conditions, use of environmentally friendly chemicals and high selectivity of the 55 reactions. We believe that the light and oxygen-enabled sodium

trifluoromethanesulfinate photocatalytic system should breakthrough previous photochemical concepts and will find wide applications.

Conflict of interest

60 The authors declare no conflict of interest.

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Notes and references

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