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Silver-Catalyzed Decarboxylative Azidation of Aliphatic Carboxylic Acids

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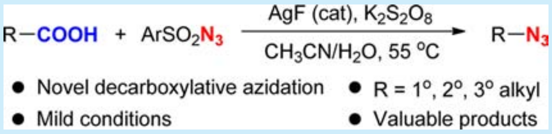
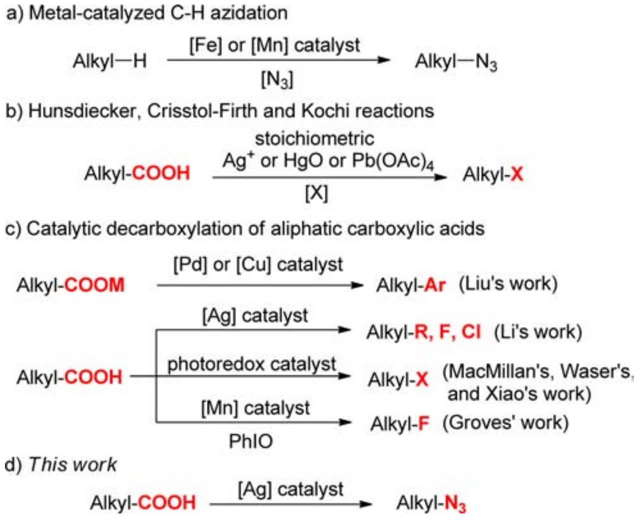
S *Supporting Information*

ABSTRACT: The catalytic decarboxylative nitrogenation of aliphatic carboxylic acids for the synthesis of alkyl azides is reported. A series of tertiary, secondary, and primary organoazides were prepared from easily available aliphatic carboxylic acids by using $K_2S_2O_8$ as the oxidant and $PhSO_2N_3$ as the nitrogen source. The EPR experiment sufficiently proved that an alkyl radical process was generated in the process, and DFT calculations further supported the SET process followed by a stepwise S_H2 reaction to afford azide product.



Aliphatic azides are highly synthetically useful and serve as direct precursors of various N-containing molecules within a single-step transformation.[1] Moreover, in drug discovery, lead compounds are designed by introducing the azido moiety to enhance biological activity.[2] Additionally, due to the development of "click" cycloaddition, azides have also achieved a significant position in bioconjugation and material science.[3] Therefore, chemists are always interested in more convenient and quick methods for the synthesis of aliphatic azides from readily available materials.[4] For some prominent examples, Hartwig's group[5a] and Groves' group[5b] independently developed aliphatic C−H azidation reactions using iron and manganese catalysis, respectively (Scheme 1a).

Scheme 1. Decarboxylation of Aliphatic Carboxylic Acids



On the basis of their stability, easy operability, ready availability, and low cost, carboxylic acids are frequently used as raw materials in organic synthesis.[6] During the numerous transformations of the carboxylic group to other functional groups, decarboxylative functionalization has become an important strategy to build new C−C or C−X bonds because of the excellent site selectivity of this strategy. For instance, decarboxylative reactions of alkynyl acids,[7] α-ketone acids,[8] alkenyl acids,[9] and benzoic acid derivatives[10] to construct new C(sp)−C (or X) or C(sp^2)−C bonds have been widely reported. Compared to the above success, the formation of C(sp^3)−C (or X) bonds via decarboxylation of aliphatic carboxylic acids remains a challenging subject.[11] The decarboxylative halogenation was achieved in many named reactions such as the Hunsdiecker reaction,[12] Crisstol−Firth reaction,[13] or Kochi reaction.[14]

However, stoichiometric metal (Ag, Hg, Pb) reagents are indispensable in these named reactions (Scheme 1b). Liu's group reported the decarboxylative coupling of activated aliphatic acids (Scheme 1c).[15] The catalytic decarboxylation of simple aliphatic acids was not achieved until Li's pioneering work.[16] Using catalytic silver as a catalyst, Li and co-workers realized the decarboxylative chlorination,[16a] fluorination,[16b] as well as alkynylation[16c] of various aliphatic carboxylic acids and provided an efficient approach to construct C(sp^3)−C (or X) bonds (Scheme 1c). MacMillan's,[17a] Xiao's,[17b] and Waser's[17c] groups employed photoredox chemistry as a powerful tool to realize decarboxylative reactions of aliphatic carboxylic acids (Scheme 1c). By developing the highly efficient Mn catalyst, Groves' group also reported decarboxylative fluorination with PhIO as oxidant (Scheme 1c).[18] Despite the significance of these methods to generate new C(sp^3)−C or C(sp^3)−halo bonds, the decarbox-

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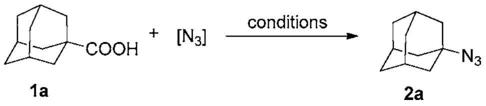
ylation of aliphatic carboxylic acid to form a C−N bond has been rarely reported.[19] Herein, as continuous efforts in developing azidation reactions,[4b,j,l] we describe the silver-catalyzed decarboxylative azidation of aliphatic carboxylic acids. A series of primary, secondary, and tertiary azides were prepared by the present approach. The mechanistic studies indicated that radical process was involved in this reaction.

Optimization studies using adamantane-1-carboxylic acid (**1a**) as the model substrate are summarized in Table 1. With $AgNO_3$ (20 mol %) as catalyst, $K_2S_2O_8$ (1 equiv) as oxidant, and DMSO/H_2O (1:1) as solvent, various azide reagents were tested (entries 1−5). When NaN_3, $TMSN_3$, or togni-N_3 was used as azide source, no product (**2a**) was detected (entries 1−3). However, 16% yield of **2a** was obtained with $EtSO_2N_3$ as the azidation reagent (entry 4), and this result encouraged us to test other sulfonyl azide reagents. When $EtSO_2N_3$ was changed to $PhSO_2N_3$, the yield was improved to 18% (entry 5). Other silver salts such as AgF showed almost the same catalytic efficiency compared to that of $AgNO_3$ (entry 6). With CuBr or $FeCl_2$ as the catalyst, only less than 5% yield of **2a** was detected (entries 7−8). When we screened other solvents (entries 9−11), to our delight, the yield increased to 72% in MeCN/H_2O (1:1) (entry 11). $AgNO_3$ exhibited similar catalytic behavior as AgF (entry 12), and we chose AgF because it more stable than $AgNO_3$ under light[20] (see the Supporting Information). It was demonstrated that $K_2S_2O_8$ was the best oxidant. When other oxidants such as PIDA or TBHP were used, **2a** was detected in very low yield (entries 13 and 14).

Table 1. Examination of Reaction Conditions[a]

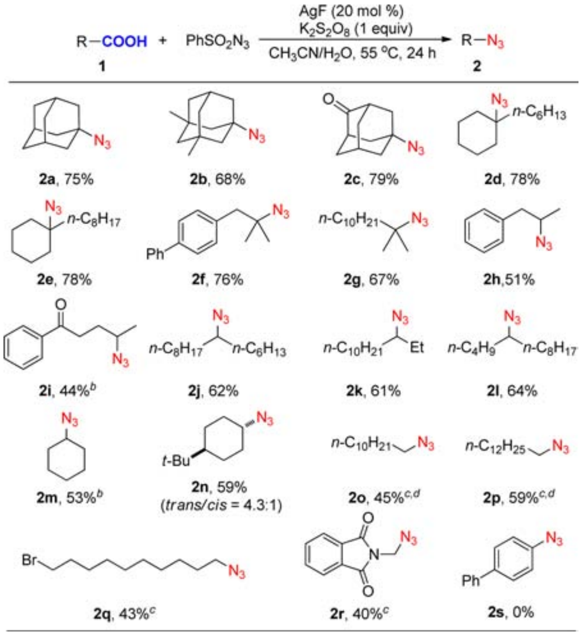


entry	catalyst	$[N_3]$	oxidant	solvent	yield[b] (%)
1	$AgNO_3$	NaN_3	$K_2S_2O_8$	DMSO/H_2O	nd
2	$AgNO_3$	$TMSN_3$	$K_2S_2O_8$	DMSO/H_2O	nd
3	$AgNO_3$	Togni-N_3	$K_2S_2O_8$	DMSO/H_2O	nd
4	$AgNO_3$	$EtSO_2N_3$	$K_2S_2O_8$	DMSO/H_2O	16
5	$AgNO_3$	$PhSO_2N_3$	$K_2S_2O_8$	DMSO/H_2O	18
6	AgF	$PhSO_2N_3$	$K_2S_2O_8$	DMSO/H_2O	18
7	CuBr	$PhSO_2N_3$	$K_2S_2O_8$	DMSO/H_2O	1
8	$FeCl_2$	$PhSO_2N_3$	$K_2S_2O_8$	DMSO/H_2O	2
9	AgF	$PhSO_2N_3$	$K_2S_2O_8$	DMSO	1
10	AgF	$PhSO_2N_3$	$K_2S_2O_8$	EA/H_2O	25
11	AgF	$PhSO_2N_3$	$K_2S_2O_8$	CH_3CN/H_2O	72 (75)[c]
12	$AgNO_3$	$PhSO_2N_3$	$K_2S_2O_8$	CH_3CN/H_2O	72 (72)[c]
13	AgF	$PhSO_2N_3$	PIDA	CH_3CN/H_2O	trace
14	AgF	$PhSO_2N_3$	TBHP	CH_3CN/H_2O	nd

[a] Reaction conditions: **1a** (0.3 mmol), catalyst (20 mol %), $[N_3]$ (0.6 mmol), oxidant (0.3 mmol), solvent (6 mL), stirred at 55 °C under argon atmosphere. [b] Yield was determined by ^1H NMR analysis of the crude reaction mixture using $Cl_2CHCHCl_2$ as an internal standard. [c] Isolated yield.

With AgF as the catalyst and $PhSO_2N_3$ as the azide source, we investigated the substrate scope of this useful decarboxylation. Aliphatic carboxylic acids **1a−c** bearing an adamantane skeleton reacted efficiently to give the corresponding azides **2a−c** in good yields (68−79%) (Scheme 2). The tertiary azides **2d−g** were obtained by the decarboxylative azidation of acids **1d−g** in good yields. Secondary acids showed slightly lower reactivity compared to that of tertiary carboxylic acid and were converted to secondary azides **2h−m** in 44−64% yields. The 1-azido-4-*tert*-butylcyclohexane (**2n**) was obtained in 59% yield (*trans*/*cis* = 4.3:1). The decarboxylative azidation of primary carboxylic acids afforded the products with only moderate yields even when 30 mol % of AgF was used as the catalyst. The bromo and phthalamide groups were tolerated under the conditions, affording the desired product **2q,r** in 43% and 40% yields, respectively. The decarboxylative azidation of benzoic acid derivative **1s** did not work under the present reaction conditions.

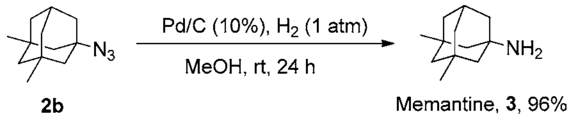
Scheme 2. Decarboxylative Azidation of Aliphatic Carboxylic Acids.[a]



[a] Reaction conditions: **1** (0.3 mmol), AgF (20 mol %), $PhSO_2N_3$ (0.6 mmol), $K_2S_2O_8$ (0.3 mmol), MeCN/H_2O (3 mL:3 mL), stirred at 55 °C under argon atmosphere for 24 h. Isolated yield. [b] Yield was determined by ^1H NMR analysis of the crude reaction mixture using $Cl_2CHCHCl_2$ as an internal standard. [c] AgF (30 mol %) was used, and the reaction time was 48 h. [d] $MesSO_2N_3$ was used instead of $PhSO_2N_3$.

In order to show the importance of the azidation products, we synthesized memantine **3**, whose hydrochloride is an antisenile dementis drug,[21] by the reduction of azide **2b** in the presence of H_2 (Scheme 3).

Scheme 3. Synthesis of Memantine



The results in Scheme 2 show that the reactivity of tertiary alkyl acids was higher than that of secondary or primary alkyl acids. Thus, we speculated that a radical process may be involved in the present decarboxylative reaction. To prove our hypothesis, 2 equiv of TEMPO was added to the standard reaction system. As expected, no azide **2a** was detected (eq 1). By treatment of 2-methyl-5-oxo-5-phenylpentanoic acid (**1i**) under the standard conditions, the cyclic product **4** was separated in 17% yield along with azidation product **2i** (eq 2). The two experiments strongly

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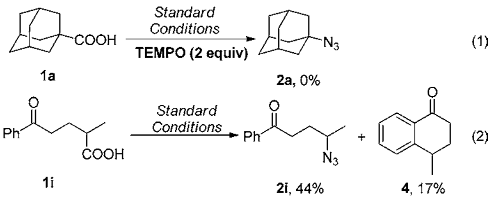


suggested the generation of carbon radical in the decarboxylative process.

Although the control experiments have provided indirect proof for a radical process, we still want to trap the carbon radical through EPR experiments. To our delight, when **1a** was exposed under standard conditions for 50 min, we successfully trapped the signal of carbon radical (Figure 1). This experiment directly proves the existence of carbon radical and indicates that the carbon radical is initially generated and then reacts with azide reagent.

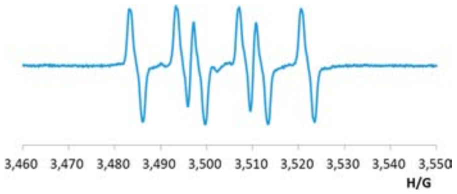


Figure 1. EPR experiment.

To further unravel the mechanism, a DFT calculation investigation into the Ag-catalyzed decarboxylative azidation of propionic acid as the model reaction was carried out (Figure 2).[22]

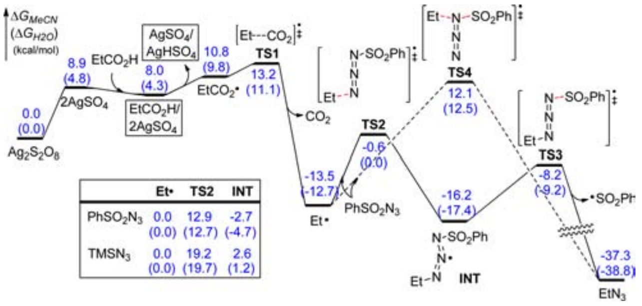
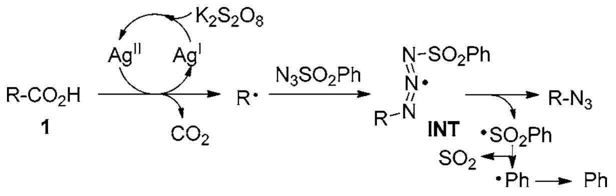


Figure 2. DFT-computed energy profiles for Ag-catalyzed decarboxylative azidation.

$Ag_2S_2O_8$ was in situ generated from AgF and $K_2S_2O_8$ as the starting point which undergoes O−O bond cleavage to oxidize Ag^I to Ag^{II}, as in the results for the dimer of $AgSO_4$. The oxidation process is endergonic by 8.9 kcal/mol. Once Ag^{II} was formed, it reacted with propionic acid through a SET process to deliver propionic acid radical. Although this is endergonic by 10.8 kcal/mol, it could occur as a reversible process under the condition used. The propionic acid radical undergoes decarboxylation through transition state **TS1** almost barrierlessly ($\Delta G^{\ddagger} = 2.4$ kcal/mol) to afford ethyl radical. This decarboxylation step is largely endergonic by 13.5 kcal/mol and is considered as an irreversible process. Ethyl radical reacts with benzenesulfonyl azide through two homolytic substitution (S_H2) pathways. When ethyl radical attacks the terminal N of benzenesulfonyl azide, the S_H2 process is stepwise. The first step corresponds to the C−N bond formation through **TS2** with an energy barrier of 12.9 kcal/mol to deliver the stable *N*-radical intermediate **INT** reversibly. The subsequent N−S bond cleavage through **TS3** requires only 8.0 kcal/mol in an activation free energy to give the azidation product. When ethyl radical attacks the alternative internal N of benzenesulfonyl azide, the S_H2 undergoes a concerted process without any intermediate to provide azidation product directly. However, this process through **TS4** requires an energy barrier of 25.6 kcal/mol, which is higher by 12.7 kcal/mol in energy than **TS2**. The stepwise S_H2 process via **TS2** is favored over the concerted one via **TS4**, which presumably is due to the existence of stable **INT**. When $TMSN_3$ was used as another azido source, the N-radical intermediate **INT** is less stable, leading to the higher energy barrier of 19.2 kcal/mol (6.3 kcal/mol higher than $PhSO_2N_3$). This difference is consistent with the experimental observations.

Based on the experiment results as well as DFT calculations, we proposed a plausible mechanism involving the catalytic generation of carbon radical. As Scheme 4 shows, Ag^I was first oxidized into Ag^{II} intermediate by $K_2S_2O_8$,[23] and then the aliphatic carboxylic acids underwent an SET process to generate the corresponding carbon radical and release CO_2. The carbon radical then attacked $PhSO_2N_3$ through a stepwise S_H2 process that implicated the intermediacy of N-radical INT to afford azide product and sulfonyl radical. The sulfonyl radical underwent a process of releasing SO_2 and generating aryl radical which was quenched by either H-abstraction or a reduction−protonation sequence to generate the corresponding aromatic compound (see the Supporting Information).

Scheme 4. Proposal Mechanism



In conclusion, silver-catalyzed decarboxylative nitrogenation of aliphatic carboxylic acids under mild conditions has been developed. Readily available aliphatic carboxylic acids with broad substrate scope were fully compatible to produce a series of tertiary, secondary, and primary organoazides by employing $PhSO_2N_3$ as the azide source. EPR experiments provided strong evidence for the SET process to deliver carbon radical and DFT calculations, further revealing the subsequent stepwise S_H2 process that implicates the intermediacy of *N*-radical species to afford the azide product.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.5b02155.

Experimental procedures, full characterization of products, and copies of NMR spectra (PDF)

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Notes

The authors declare no competing financial interest.

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