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Lewis Acid and (Hypo)iodite Relay Catalysis Allows a Strategy for the Synthesis of Polysubstituted Azetidines and Tetrahydroquinolines

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Supporting Information

ABSTRACT: A catalytic [3 + 1]-annulation reaction between cyclopropane 1,1-diester and aromatic amine is developed based on the relay catalysis strategy. Lewis acid-catalyzed nucleophilic ring opening of cyclopropane 1,1-diester with aromatic amine and (hypo)iodite-catalyzed C−N bond formation are combined successfully in one reaction. Using this reaction, biologically important azetidines and tetrahydroquinolines can be prepared directly.

Cyclopropane 1,1-diesters, a typical class of donor−acceptor (D−A) cyclopropane,[1] have been widely used in organic synthesis. Under Lewis acid catalysis, cyclopropane 1,1-diesters are usually used as homo-Michael acceptors or three-carbon zwitterion equivalents. Therefore, the representative reactions of cyclopropane 1,1-diesters are Lewis acid-catalyzed ring-opening reactions[1,2] and [3+*n*]-annulation reactions.[1,3−5] To date, various annulation reactions have been developed, and most focused on the [3 + 2]- and [3 + 3]-annulations, which were convenient for the synthesis of five- and six-membered cyclic compounds. However, to the best of our knowledge, the synthesis of four-membered cyclic compounds via [3 + 1]-annulation of cyclopropane 1,1-diesters has rarely been reported. It is due to the lack of suitable corresponding reactants that should contain the reactive center with both electrophilicity and nucleophilicity. From another perspective, [3 + 1]-annulation of cyclopropane 1,1-diesters could be achieved by the sequential ring-opening/ring-closing strategy.

Azetidines form an important class of biological compounds, and a variety of synthetic methods have been developed.[6] In 2014, our group reported the synthesis of azetidines from cyclopropane 1,1-diesters in two steps (Figure 1).[7] In view of the important biological and pharmacological properties of azetidine and our interest in relay catalysis,[8] we attempted to develop a more efficient synthetic method for azetidines via the relay catalytic [3 + 1]-annulation reaction of cyclopropane 1,1-diesters.

It is well-known that catalytic nucleophilic ring opening of cyclopropane 1,1-diesters with amines has been intensively studied during past decades.[9] According to the previously mentioned synthetic strategy, it is possible to achieve the synthesis of azetidines by the combination of above ring-opening reaction with a suitable amination reaction. Recently, iodine-catalyzed oxidative α-amination of carbonyl compounds has developed rapidly[10] and has attracted our attention. Herein, we disclose a relay catalytic [3 + 1]-annulation reaction between aromatic amines and cyclopropane 1,1-diesters (Figure 1). In this reaction, Lewis acid catalyzed ring opening, and (hypo)iodite generated in situ catalyzed oxidative amination.[11]

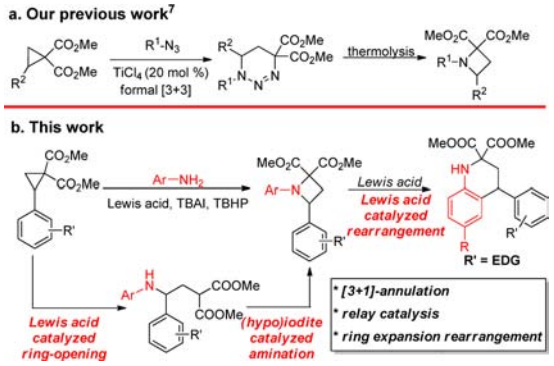

Figure 1. Synthesis of azetidines from cyclopropane 1,1-diesters.

In our initial trials, dimethyl 2-phenylcyclopropane-1,1-dicarboxylate **1a** and 4-methylaniline **2a** were employed to optimize the reaction conditions, and the results are summarized in Table 1. At first, we employed 20 mol % of $Ni(ClO_4)_2{\cdot}6H_2O$ as the catalyst for the ring-opening procedure and *t*-Bu_4NI/*t*-BuOOH (TBAI/TBHP) to promote the amination to screen the solvents. Using MeCN as the solvent, the reaction proceeded smoothly to give the desired azetidine

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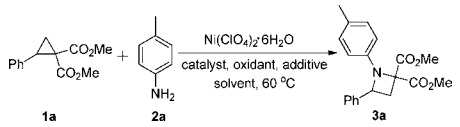
Table 1. Optimization of the Reaction Conditions



1a 2a 3a

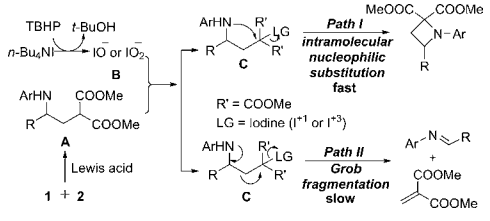
entry[a]	cat.	oxidant[b]	additive	solvent	time (h)	yield[d] (%)
1	TBAI	TBHP		CH_3CN	24	48
2	TBAI	TBHP		AcOEt	48	12
3	TBAI	TBHP		toluene	48	trace
4	TBAI	TBHP		DCE	48	trace
5	TBAI	TBHP		MeOH	48	30
6	KI	TBHP		CH_3CN	24	54
7	NIS	TBHP		CH_3CN	40	65
8	I_2	TBHP		CH_3CN	46	70
9	I_2	TBHP	$Al(OTf)_3$	CH_3CN	60	72
10	TBAI	TBHP	$Al(OTf)_3$	CH_3CN	65	76
11	TBAI	TBHP	$BF_3{\cdot}Et_2O$	CH_3CN	60	64
12	TBAI	TBHP	*m*-CBA[c]	CH_3CN	60	68
13	TBAI	TBHP	AcOH	CH_3CN	60	70
14	TBAI	$K_2S_2O_8$	$Al(OTf)_3$	CH_3CN	60	trace
15	TBAI	H_2O_2[e]	$Al(OTf)_3$	CH_3CN	60	47
16	TBAI	DTBP[f]	$Al(OTf)_3$	CH_3CN	60	0
17[g]	TBAI	TBHP	$Al(OTf)_3$	CH_3CN	30	77

[a]Reaction conditions: **1a** (0.3 mmol), **2a** (1.5 equiv, 0.45 mmol), $Ni(ClO_4)_2{\cdot}6H_2O$ (20 mol %, 0.06 mmol), catalyst (10 mol %, 0.03 mmol), oxidant (2.0 equiv, 0.6 mmol), additive (10 mol %, 0.03 mmol), solvent (c = 0.1 M). [b]TBHP (70% aqueous solution). [c]*m*-CBA (3-chlorobenzoic acid). [d]Isolated yield. [e]H_2O_2 (30% aqueous solution). [f]DTBP (di-*tert*-butyl peroxide). [g]TBAI (20 mol %, 0.06 mmol).

3a in 48% yield (Table 1, entry 1). Other solvents, such as AcOEt, toluene, 1,2-dichloroethane (DCE), and MeOH, required longer reaction time or gave product in lower yields (Table 1, entries 2−5).

Then, several other iodine sources, such as potassium iodide (KI), *N*-iodosuccinimide (NIS), and I_2, were also employed in this reaction, respectively (Table 1, entries 6−8). To our delight, when 10 mol % of I_2 was used, the yield increased to 70%. Analyzing the byproducts suggested that some ring-opening product decomposed via Grob fragmentation in the amination process.[12] Plausible mechanisms of ring closing and side reactions are summarized in Scheme 1. In order to prohibit

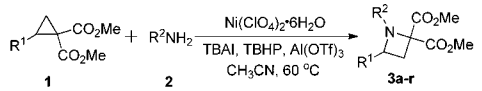
Scheme 1. Proposed Mechanism for the Reaction



the undesired Grob fragmentation, some acidic additives were added to reduce the nucleophilicity of the nitrogen atom in the intermediate **C**. In addition, acidic additives will adjust the equilibration between active species (hypoiodite or iodite) and inert species such as triiodide salts.[11d] When 10 mol % of $Al(OTf)_3$ was added the yield increased slightly (Table 1, entry 9). Replacing I_2 with TBAI, the yield increased to 76% (Table 1, entry 10). Other additives such as AcOH, *m*-Cl-C_6H_4COOH, and $BF_3{\cdot}Et_2O$ also showed some inhibiting effects (Table 1, entries 11−13). Meanwhile, the addition of acidic additives led to an obvious decrease in the rate of ring-closing reaction. Subsequently, different peroxides were investigated. Using $K_2S_2O_8$, H_2O_2, and DTBP, the yield decreased obviously (Table 1, entries 14−16). At last, we adjusted the loading of TBAI from 10 to 20 mol %, the reaction was accelerated, and the yield increased to 77% (Table 1, entry 17). Under conditions without $Ni(ClO_4)_2{\cdot}6H_2O$ or TBAI, no desired product was obtained. The structure of **3a** was determined by X-ray crystallographic analysis.[13]

To demonstrate the generality of this method, the scope of this relay catalysis reaction was investigated under the optimal conditions. A variety of cyclopropanes and anilines with different substituents were examined, and the results are summarized in Scheme 2. For 2-aryl-substituted cyclopropanes,

Scheme 2. Scope Investigation of the Synthesis of Azetidines[a,b]



1 2 3a-r

3a, R^1 = Ph, R^2 = 4-MeC_6H_4 (77%)
3b, R^1 = 4-MeC_6H_4, R^2 = 4-MeC_6H_4 (61%)
3c, R^1 = 3-MeC_6H_4, R^2 = 4-MeC_6H_4 (80%)
3d, R^1 = 2-MeC_6H_4, R^2 = 4-MeC_6H_4 (57%)
3e, R^1 = 4-FC_6H_4, R^2 = 4-MeC_6H_4 (78%)
3f, R^1 = 4-ClC_6H_4, R^2 = 4-MeC_6H_4 (63%)
3g, R^1 = 4-BrC_6H_4, R^2 = 4-MeC_6H_4 (63%)
3h, R^1 = 2-naphthyl, R^2 = 4-MeC_6H_4 (61%)
3i, R^1 = vinyl, R^2 = 4-MeC_6H_4 (35%)
3j, R^1 = Ph, R^2 = 4-*t*-BuC_6H_4 (80%)
3k, R^1 = Ph, R^2 = Ph (51%)
3l, R^1 = Ph, R^2 = 4-FC_6H_4 (72%)
3m, R^1 = Ph, R^2 = 4-ClC_6H_4 (61%)
3n, R^1 = Ph, R^2 = 4-BrC_6H_4 (59%)
3o, R^1 = vinyl, R^2 = 4-FC_6H_4 (51%)
3p, R^1 = Ph, R^2 = 3-MeC_6H_4 (50%)[c]
3q, R^1 = Ph, R^2 = 2-MeC_6H_4 (23%)[c]
3r, R^1 = Ph, R^2 = 4-$OMeC_6H_4$ (60%)[d]

[a]Unless otherwise noted, reaction was performed with 0.3 mmol of **1** under optimized reaction conditions. [b]Isolated yield. [c]Reaction was performed without $Al(OTf)_3$. [d]TBAI, TBHP and $Al(OTf)_3$ were added after the ring-opening reaction finished.

this protocol was found to be tolerant to both electron-withdrawing and electron-donating substituents on aryl and gave the corresponding azetidines **3a−h** in moderate to good yields. The position of the substituent on the aryl group slightly influences the reactivity, and sterically demanding *ortho*-substituted cyclopropanes always gave relatively lower yields of the desired products. 2-Vinylcyclopropane gave the product **3i** in low yield. It might be ascribed to the instability of the vinyl group under these oxidative conditions.

To avoid the oxidation of aromatic amine before ring opening, a series of selected anilines with certain oxidative stability were employed in this reaction. For *para*-substituted anilines, the desired products were obtained in moderate to good yields (**3j−o**) (Scheme 2). Among them, the anilines bearing electron-donating groups always gave higher yield than the others. Furthermore, *o*- and *m*-methylanilines were used to investigate the steric effects (**3p,q**) (Scheme 2), and the reactions did not occur under the optimal conditions. However, products **3p** and **3q** could be obtained under the conditions without addition of $Al(OTf)_3$, and 2-methylaniline gave lower yield than 3-methylaniline due to the larger steric hindrance. In addition, for the amines with poor oxidative stability, such as *p*-methoxyaniline, the corresponding azetidine can also be prepared by the stepwise one-pot procedure (**3r**) (Scheme 2).

During the above scope screening, when 2-(4-methoxyphenyl)cyclopropane diester was used, tetrahydroquinoline derivative **4a**[13] was obtained rather than the expected azetidine

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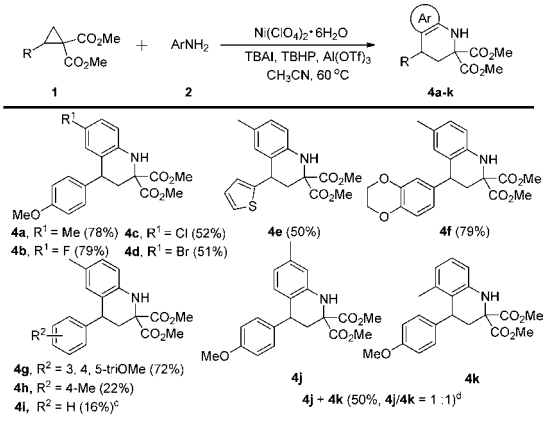
(Scheme 3). Tetrahydroquinoline derivatives are the key subunits found in various complex molecules that show

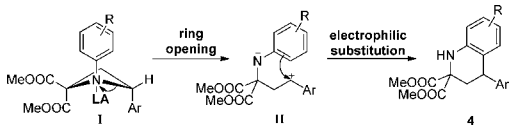
Scheme 3. Relay Catalysis for the Synthesis of Tetrahydroquinolines[a,b]



[a]Unless otherwise noted, the reaction was performed with 0.3 mmol of **1** under optimized reaction conditions. [b]Isolated yield. [c]Performed at 130 °C. [d]Reaction was performed without $Al(OTf)_3$.

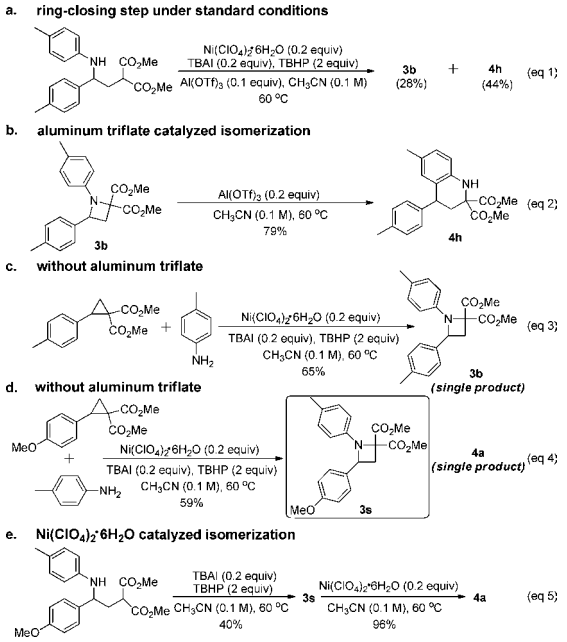
interesting biological activity.[14] Therefore, these attracted our interest to carry out continuous research on this reaction. Screening of different cyclopropanes and anilines suggested that the presence of an electron-rich aryl group on cyclopropane is necessary for the generation of tetrahydroquinoline. The cyclopropanes containing alkoxyphenyl or 2-thienyl at C-2 all afforded tetrahydroquinolines (**4a**–**g**) (Scheme 3) in moderate yields. Moreover, regioisomers **4j** and **4k** could be obtained as a separable mixture from 3-methylaniline under the conditions without $Al(OTf)_3$. Based on this discovery, we carefully analyzed the reaction mixture of dimethyl 2-(4-methylphenyl)-cyclopropane 1,1-dicarboxylate with *p*-methylaniline again and isolated the tetrahydroquinoline **4h** and azetidine **3b** in 22% and 61% yields, respectively. This result demonstrated that the tetrahydroquinolines may be derived from azetidines via ring expansion. We speculated that under the catalysis of the Lewis acid the ring opening of azetidine would form benzylic cation **II**. A subsequent electrophilic substitution afforded the tetrahydroquinoline (Scheme 4).[15]

Scheme 4. Postulated Mechanism for the Isomerization of Azetidine



Verification experiments were carried out to prove our postulation (Scheme 5). At first, under the standard conditions, the ring-opening product could be transferred to azetidine, which clearly support the mechanism of the reaction as a ring-closing step (Scheme 5, eq 1). Second, in the presence of 20 mol % of $Al(OTf)_3$, the azetidine **3b** transformed into tetrahydroquinoline **4h** in 79% yield (Scheme 5, eq 2). Third, under the conditions without $Al(OTf)_3$, azetidine **3b** can be prepared as single product (Scheme 5, eq 3). This proved that the $Al(OTf)_3$ is the efficient catalyst for this isomerization. Thus, we attempted to prepare the azetidine **3s**,

Scheme 5. Verification Experiments



precusor of **4a**, under the conditions without $Al(OTf)_3$. However, the tetrahydroquinoline **4a** was obtained in 59% yield as a single product (Scheme 5, eq 4). By that time, we realized and verified that $Ni(ClO_4)_2·6H_2O$ has enough ability to catalyze the isomerization of azetidines bearing more electron-rich phenyl groups (Scheme 5, eq 5), which could form more stable benzylic cations by the ring opening. For this reaction, $Al(OTf)_3$ is still necessary because the addition of $Al(OTf)_3$ could obviously improve the yield.

According to the above understanding, the reaction between cyclopropane **1a** and *p*-toluidine **2a** was examined again at higher temperature and higher catalytic loading of Al $(OTf)_3$, respectively, and expected to generate the tetrahydroquinoline directly. Using 50 mol % of $Al(OTf)_3$ did not give satisfactory results. When the reaction temperature was increased to 130 °C, the expected tetrahydroquinoline **4i** (Scheme 3) was obtained only in 16% yield.

In summary, based on the ring-opening/ring-closing strategy, a relay catalytic [3 + 1]-annulation reaction between cyclopropane 1,1-diesters and aromatic amines was developed for the synthesis of azetidines. This relay catalysis consists of Lewis acid-catalyzed nucleophilic ring opening of cyclopropane 1,1-diester with amine and (hypo)iodite-catalyzed oxidative α-amination of carbonyl compounds. For some cyclopropane 1,1-diesters containing an electron-rich aryl group, the obtained azetidines rearranged to tetrahydroquinolines under the catalysis of Lewis acid. This reaction offers a convenient method for the synthesis of some azetidines and tetrahydroquinolines.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.6b02430.

X-ray data for **3a** (CIF)
X-ray data for **4a** (CIF)

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Detailed experimental procedures and full spectroscopic data for all new compounds (PDF)

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Notes

The authors declare no competing financial interest.

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