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Construction of fused- and spiro-oxa-[n.2.1] skeletons by a tandem epoxide rearrangement/intramolecular [3+2] cycloaddition of cyclopropanes with carbonyls†

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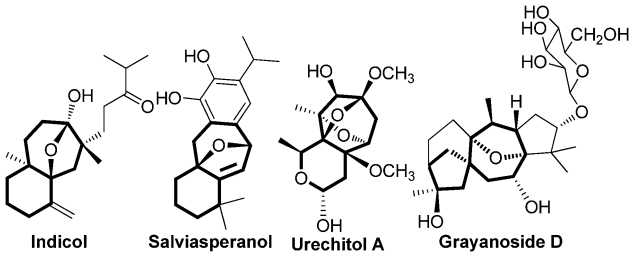
A Lewis acid promoted tandem reaction of epoxide rearrangement and intramolecular [3+2] cycloaddition reaction of cyclopropanes with carbonyls formed by epoxide rearrangement *in situ*, which were obtained with difficulty by a general method, is reported. A wide variety of fused- and spiro-oxa-[n.2.1] skeletons could be efficiently constructed.

Oxa-bridged carbocyclic skeletons are well-represented and widely found in natural products.[1] Such segments usually combined with fused- or spiro-structures exist in some high activity molecules. For example, indicol,[2] salviasperanol,[3] urechitol A,[4] and grayanoside D[5] (Scheme 1) represent two types of oxa-bridged carbocyclic containing fused- or spiro-systems. Highly efficient construction of these bridged skeletons is one of the most important themes in organic synthesis.[6] Several creative strategies such as the Diels–Alder reaction, transition-metal-catalyzed reactions, and radical reactions have been developed to construct the bridged carbocyclic skeletons.[7] However, there is still an urgent need of a strategy for the construction of these bridged oxa-[n.2.1] skeletons containing fused- or spiro-structures.

Cyclopropane derivatives were treated as important building blocks to build cyclic structures due to their facile preparation and high reactivity.[8] Recently, the intramolecular cross-cycloaddition reaction of D–A cyclopropanes with carbonyls, imines, alkenes, or allenes was carried out to construct the bridge-containing fused cyclic structures and applied to the total synthesis of natural products, as reported by Wang and co-workers.[9] But in this research study, there was less information on the construction the aliphatic bridged oxa-[n.2.1] skeletons. Inspired by high reaction efficiency and product diversity of cyclopropanes, we explored the tandem intramolecular [3+2] cycloaddition reaction of cyclopropanes with carbonyls generated from epoxides rearrangement *in situ*, which were obtained with difficulty by a general method, to construct the aliphatic bridged oxa-[n.2.1] skeletons containing fused- or spiro-structures. Also the strategy was applicable for the construction of the aromatic ones.



Scheme 1 Several representative natural products.

In this work, we chose the epoxide as the precursor of carbonyls because the catalytic rearrangement of epoxides to establish useful intermediates in organic synthesis has been widely elucidated,[10] and the ring opening reactions of epoxides could be catalyzed by a Lewis acid which could also be used as a co-catalyst in the following cycloaddition reaction.

Initially, preliminary evaluation of our strategy was carried out by using α,β-epoxy ketone **1a**/**1a**′, which is a mixture of the epimers, as the model substrate to screen the optimized reaction conditions for the tandem epoxide rearrangement/intramolecular [3+2] cycloaddition reaction (Table 1). When **1a**/**1a**′ was treated in a boron trifluoride ether complex ($BF_3{\cdot}Et_2O$) in DCE at −10 °C, the desired products **2a** and **3a** were detected in a combined yield of 50% in a ratio of 2 : 1 by isolating individual **2a** and **3a**, respectively (entry 1). Then different reaction conditions were explored. With DCE as the steady solvent, various Lewis acid catalysts were assessed (entries 2–7). Both the boron trifluoride acetic acid complex ($BF_3{\cdot}CH_3CO_2H$) and trimethylsilyl trifluoromethanesulfonate (TMSOTf) could promote the reaction to give **2a** and **3a** in a combined yield of 44% at −10 °C and the ratios were 2 : 1 and 1 : 1, respectively (entries 3 and 4). When the

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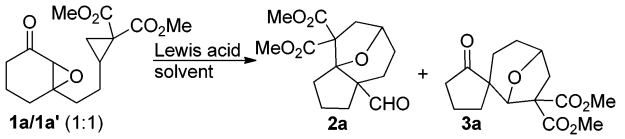
Table 1 Optimization of conditions of the tandem reaction of **1a**/**1a′**[a]



Entry[b]	Catalyst	Solvent	Temp. [°C]	Time [h]	Yield[d] [%]	**2a** : **3a**[e]
1	$BF_3{\cdot}Et_2O$	DCE	−10	12	50	2 : 1
2	$Sc(OTf)_3$	DCE	−10	12	Trace	
3	$BF_3{\cdot}CH_3CO_2H$	DCE	−10	12	44	2 : 1
4	TMSOTf	DCE	−10	12	44	1 : 1
5	$BF_3{\cdot}THF$	DCE	rt[c]	12	30	5 : 1
6	$SnCl_4$	DCE	50[c]	3	20	5 : 1
7	$Yb(OTf)_3$	DCE	50[c]	3	37	5 : 1
8	$BF_3{\cdot}Et_2O$	DCE	0	12	53	2 : 1
9	$BF_3{\cdot}Et_2O$	DCE	rt[c]	3	69	1 : 1
10	$BF_3{\cdot}Et_2O$	DCE	50[c]	3	50	1 : 1
11	$BF_3{\cdot}Et_2O$	$CHCl_3$	0	12	60	2 : 1
12	$BF_3{\cdot}Et_2O$	$CHCl_3$	rt[c]	3	71	1.4 : 1
13	$BF_3{\cdot}Et_2O$	$CHCl_3$	50[c]	3	71	1.4 : 1
14	$BF_3{\cdot}Et_2O$	DCM	0	12	60	1 : 1
15	$BF_3{\cdot}Et_2O$	DCM	rt[c]	3	72	1 : 1
16	$BF_3{\cdot}Et_2O$	DCM	Reflux[c]	3	74	1 : 1
17	$BF_3{\cdot}Et_2O$	THF	0	12	Trace	
18	$BF_3{\cdot}THF$	DCM	rt[c]	12	50	6 : 1
19	$BF_3{\cdot}THF$	DCM	Reflux[c]	12	54	2 : 1
20	$BF_3{\cdot}Bu_2O$	DCM	Reflux[c]	3	86	1 : 1

[a] The diastereomeric ratio (d.r.) values were confirmed by ^{1}H NMR spectroscopy. [b] All the reaction were carried out with **1a**/**1a′** (47.4 mg, 0.15 mmol) in the presence of a Lewis acid (0.30 mmol) in solvent (2.0 mL) under an argon atmosphere. [c] The Lewis acid was added to the reaction system at 0 °C, stirred for 5 min at 0 °C and then the temperature was raised. [d] Total yields of **2a** and **3a**. [e] The ratio of **2a** and **3a** was confirmed by the isolated yield of individual **2a** and **3a**.

boron trifluoride tetrahydrofuran complex ($BF_3{\cdot}THF$), $SnCl_4$, and $Yb(OTf)_3$ were used as catalysts, the reaction did not occur at low temperature (−10 °C and 0 °C). When the temperature was increased, they gave us low product yields but higher isomer ratios (**2a** : **3a** = 5 : 1, entries 5–7). By considering entries 1 to 7, $BF_3{\cdot}Et_2O$ was used as the optimized catalyst to explore the solvent and temperature effects. Different solvents such as DCE, $CHCl_3$, and DCM were used at different temperatures (entries 8–15). Fortunately, when the reaction was performed in the refluxing DCM, **2a** and **3a** were obtained in a combined yield of 74% (**2a** : **3a** = 1 : 1, entry 16).

At the same time, the reaction was attempted using $BF_3{\cdot}Et_2O$ or $BF_3{\cdot}THF$ as promoters in THF or DCM (entries 17–19), but satisfactory results were not obtained. In the end, when the reaction was performed with $BF_3{\cdot}Bu_2O$ in the refluxing DCM (entry 20), the combined yield of **2a** and **3a** was up to 86% with the same ratio as given in entry 16 (1 : 1). Hence the use of 2 equiv. of $BF_3{\cdot}Bu_2O$ in the refluxing DCM was determined to be the optimized reaction condition based on the yield.

Under the optimized reaction conditions, the substrate scope and limitation of the tandem reaction were explored by using **1** as substrates in the presence of $BF_3{\cdot}Bu_2O$ (2 equiv.) in the refluxing DCM (Table 2). When the two methyl groups in the cyclopropane 1,1-diester moiety were substituted by two ethyl groups (entry 1), or two germinal methyl groups were introduced into the six-membered ring of the substrate (entry 2), the reaction proceeded

Table 2 Scope of the $BF_3{\cdot}Bu_2O$-mediated [3+2] tandem reaction of **1**

Entry[a]	Substrate[b]	Product		Yield [%]	**2** : **3**[d]
1	**1b**/**1b′** (1 : 1)	**2b**	**3b**	86[c]	1 : 1
2	**1c**/**1c′** (1 : 1)	**2c**	**3c**	88[c]	1 : 1
3	**1d**/**1d′** (1 : 1)	**2d**	**3d**	62[c]	1 : 9
4	**1e**/**1e′** (1 : 1)	**2e**	**3e**	75[c]	4 : 1
5	**1f**/**1f′** (1 : 1)	**2f**		54	
6	**1g**/**1g′** (1.5 : 1)	**2g**		43	
7	**1h**/**1h′** (1 : 1)	NR			
8	**1i**/**1i′** (1 : 1)	**2i**		43	
9	**1j**/**1j′** (2 : 1)	**2j**		92	
10	**1k**/**1k′** (3 : 1)	**2k**/**2k′** (2 : 1)[b]		87	
11	**1l**/**1l′** (1 : 1)	**2l**		41	
12	**1m**/**1m′** (3 : 1)	**2m**		87	

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Table 2 (*continued*)

Entry[a]	Substrate[b]	Product	Yield [%] 2 : 3[d]
13	**1n**/**1n′** (1.5 : 1)	**2n**	83

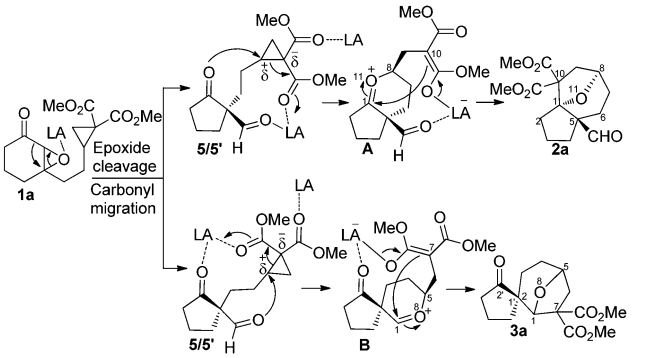
[a] All the reactions were carried out with **1** (0.15 mmol) in the presence of $BF_3{\cdot}Bu_2O$ (0.21 mL, 0.30 mmol) in DCM (5.0 mL) for 3 h under an argon atmosphere, as given in Table 1. [b] The diastereomeric ratio (d.r.) values were confirmed by ^1H NMR spectroscopy. [c] Total yields of **2** and **3**. [d] The ratio of **2** and **3** was confirmed by the isolated yield of individual **2** and **3**.

smoothly to give the fused-bridged product **2** and spiro-bridged product **3** in similar yields (**2** : **3** = 1 : 1, which was confirmed by the isolated yield of individual **2** and **3**). The reaction of substrate **1d**/**1d′**, including a quaternary carbon center in the cyclopropane ring (entry 3), also occurred smoothly giving the product in a medium yield. It was supposed that the steric hindrance between the methyl group of cyclopropane and the carbonyl group of cyclohexanone reduced the reactivity of the intramolecular [3+2] cycloaddition reaction, which led to the ratio of **2d** to **3d** as 1 : 9. The reaction of substrate **1e**/**1e′** (entry 4), having a α,β-epoxy cycloheptanone structure, also afforded adducts **2e** and **3e** in 75% yield (**2e** : **3e** = 4 : 1). Substrates **1f**/**1f′** and **1g**/**1g′** with a quaternary carbon center in the epoxide ring gave only fused cyclic products in moderate yields (entries 5 and 6). Substrate **1h**/**1h′** being activated by one ester group was less active and its reaction did not proceed to give the desired product (entry 7). Substrate **1i**/**1i′** with one more methylene was examined and gave only product **2i** in medium yield along with the loss of one formyl group (entry 8). We suspected that the low efficiency of **2i** formation is probably due to the conformational flexibility of the eight-membered ring structure in **2i**.

A series of aromatic substrates (entries 9–13) were constructed to assess the [3+2] cycloaddition reaction of phenylacetaldehydes and propiophenone intermediates, which were difficult to prepare by a common reaction, with cyclopropanes. Then the tandem protocol was applied to the aromatic substrates **1j**/**1j′** and **1k**/**1k′** (entries 9 and 10). To our delight, the desired products were produced in excellent yields by using these substrates. But substrate **1l**/**1l′** (entry 11) gave a low product yield, probably because of its conformational flexibility. When compounds **1m**/**1m′** and **1n**/**1n′** were used as substrates, propiophenone intermediates were first generated through epoxide rearrangements and the reactions proceeded smoothly in excellent yields (entries 12 and 13).

X-ray crystallography of **4** (formed from **2c** by air oxidation) and **3c** (ESI,† Fig. S1)[11] confirmed the relative configuration of **2** and **3**. This suggested that the bridge oxygen and carbonyl in **2a–g** and **3a–e** are on the different sides of the carbon rings.

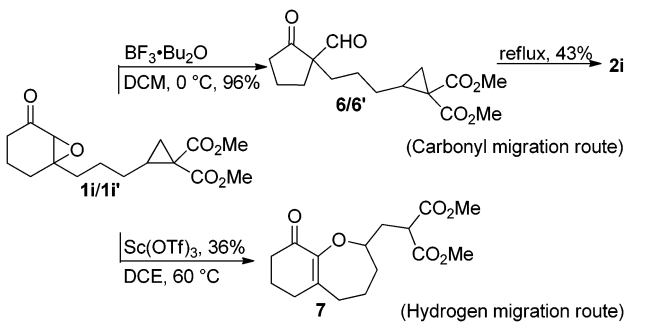
A plausible reaction-mechanism was proposed (Scheme 2).[7g] The first step involved the epoxide-ring rupture from the quaternary carbon side followed by carbonyl migration to generate intermediate **5**/**5′**. Then the carbonyl of an aldehyde or the carbonyl of a ketone could be trapped together with a



Scheme 2 Proposed reaction mechanism.

diester moiety through Lewis acid binding interactions. Meanwhile, another free carbonyl attacked the asymmetric cyclopropane dipole, which was activated by a Lewis acid-binded diester motif to generate oxonium intermediate A or B, respectively, and these C=O groups in the intermediate were located on the same side of the tetrahydropyrylium, which would control the nucleophilic cyclization between enolate and oxoniums on one side. Consequently the single relative configuration of the cyclization products **2a** and **3a** were obtained with the bridge oxygen and carbonyl on the opposite side. Furthermore, the intermediate **5**/**5′** was isolated when the reaction was adopted at 0 °C, and the isolated **5**/**5′** could also be transformed to **2a** and **3a** under the same conditions described in Table 2, which strongly supported the dicarbonyl-involved process.

To further demonstrate the first step of the tandem reaction involving the epoxide rearrangement process, we chose compound **1i**/**1i′** as a substrate in our research because its low activity would be accessible to trap the reaction intermediate. When the substrate **1i**/**1i′** was promoted by $BF_3{\cdot}Bu_2O$ in DCM at 0 °C, only the epoxide rearrangement product **6**/**6′** was detected and could also be isolated, subsequently the corresponding desirable product **2i** was obtained in modest yield when the reaction was further heated to reflux (Scheme 3), which proved that the first step of the tandem reaction is a carbonyl migration in the epoxide rearrangement to generate intermediate **6**/**6′**. Then the [3+2] cross-cycloaddition of the cyclopropane with the carbonyl of the ketone in **6**/**6′** gave product **2i**. Also, metal catalyst $Sc(OTf)_3$ in 1,2-dichloroethane (DCE) was investigated (Scheme 3), and fused product **7** was detected; the hydrogen



Scheme 3 Further reactions of **1i**.

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migration in the epoxide rearrangement to form the 1,2-dione intermediate was followed by isomerization to enol to form fused product **7** by the nucleophilic ring-opening reaction (Scheme 3). The hydrogen migration also strongly supported the epoxide rearrangement process.

In summary, we have successfully developed a tandem epoxide rearrangement/intramolecular [3+2] cycloaddition reaction of cyclopropane with carbonyls for the efficient construction of fused- or spiro-oxa-[n.2.1] skeletons under mild reaction conditions. The carbonyls for the [3+2] cycloaddition were produced *in situ* by the epoxide rearrangement, which were not easily obtained by general methods. This reaction is applicable for both aliphatic and aromatic epoxide compounds. Further studies towards the application of this tandem reaction to the synthesis of structure-related natural products are still in progress in our laboratory.

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