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Cooperative Photo-/Lewis Acid Catalyzed Tandem Intramolecular [3 + 2] Cross-Cycloadditions of Cyclopropane 1,1-Diesters with α,β-Unsaturated Carbonyls for Medium-Sized Carbocycles

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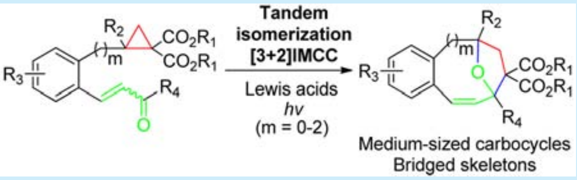
Ⓢ *Supporting Information*

ABSTRACT: A tandem isomerization/intramolecular [3 + 2] cross-cycloaddition (IMCC) of cyclopropane 1,1-diesters with α,β-unsaturated ketones/aldehydes under a cooperative catalysis of photo and Lewis acids has been successfully developed. This supplied a general and efficient strategy for construction of medium-sized carbocyclic (8-, 9-, and 10-membered) skeletons as well as such carbocycle-based bridged oxa-bicyclo[*n*.2.1] (*n* = 4−6) skeletons.



Medium-sized carbocyclic skeletons constitute the basic skeletons of many important biologically active natural products (Figure 1).[1] Developing general and efficient strategies for construction of such skeletons is important for synthesis of natural products and biologically active compounds.[2] Additionally, medium-sized carbocyclic skeletons are also useful building blocks in organic synthesis. However, due to entropic and enthalpic factors, medium-sized carbocyclic skeletons are much more difficult to assemble in high efficiency with conventional methods.[3]

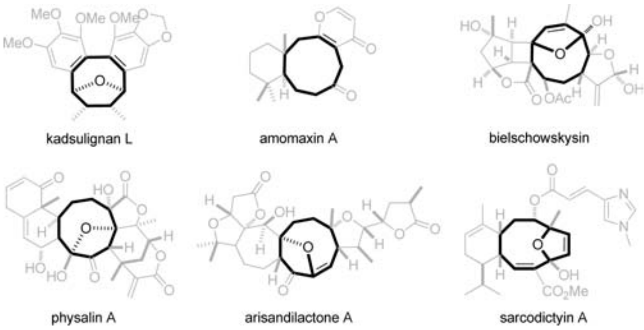
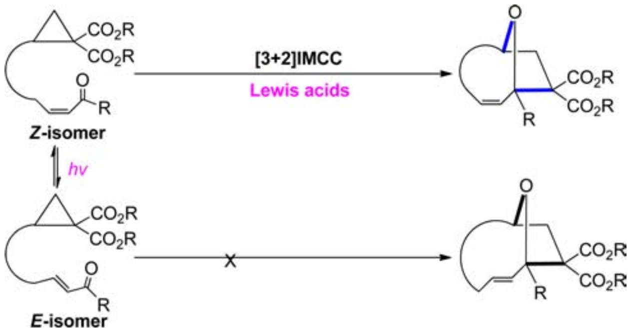


Figure 1. Representative natural products with medium-sized ring-derived polycyclic carbocycles.

Acid-promoted formal cycloadditions of donor−acceptor cyclopropanes can afford various carbo- or heterocycles.[4,5] We have developed intramolecular cross-cycloadditions (IMCC) of donor−acceptor cyclopropanes for construction of medium-sized skeletons.[6] To expand the scope of this strategy further and make it more general and efficient, we tried to explore the [3 + 2]IMCC of cyclopropane 1,1-diesters with α,β-unsaturated ketones/aldehydes (Scheme 1). This is mainly based on the following considerations: (1) There is a limitation in the size of the carbocyclic skeletons in our previously developed methods:[4f,6] while 6- to 8-membered skeletons could be constructed efficiently in excellent yields, 9-membered ones could be constructed but in moderate yields, and construction of 10-membered ones were quite difficult; (2) α,β-unsaturated ketones/aldehydes can be easily accessed through various methods, e.g., the most commonly used Horner−Wadsworth−Emmons olefination and aldol condensation/dehydration; (3) with consideration of the entropic and enthalpic factors, the conformationally rigid C$=$C is favorable to cycloaddition; (4) due to its rich chemistries, the C$=$C group can be efficiently and richly postmodified for further applications. However, there exists a big obstacle: from a conformational point of view, only the oxygen atom of the carbonyl in *Z*-isomer of α,β-unsaturated ketones/aldehydes can easily get close to the reaction site of cyclopropane to initiate the cycloaddition. However, the highly efficient and stereoselective synthetic methods for *Z*-α,β-unsaturated ketones/aldehydes are quite limited, and in most cases, the α,β-unsaturated ketones/aldehydes were prepared as a

Scheme 1. Our Assumption of the Tandem Enone Isomerization/[3 + 2]IMCC



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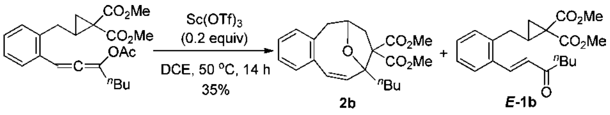
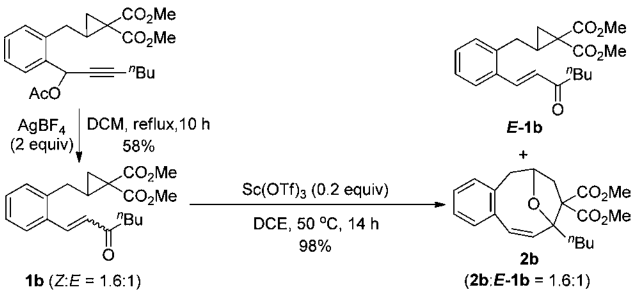
mixture of Z/E-isomers, and the E-isomer is usually the more preferable one.[7] To solve this problem, the photocatalyzed isomerization of the Z- and E-isomers of C=C was invoked.[8] We envisioned that under the irradiation of UV (ultraviolet) light the E-isomer could be isomerized to give a mixture of E- and Z-isomers, and the latter one would participate in the subsequent [3 + 2]IMCC. This process will be repeated until all of the substrate is involved in to make the reaction complete (Scheme 1).

Our initial investigation stemmed from an unexpected result in our previous research on the [3 + 2]IMCC/[3 + 2]IMPC of cyclopropane 1,1-diesters with allenes.[6e,9a] When we carried out the reaction of substrate cyclopropane−allene under catalysis of $Sc(OTf)_3$ (0.2 equiv) in 1,2-dichloroethane (DCE), instead of the expected result an oxa-bicyclo[5.2.1] cycloadduct was obtained together with an enone E-**1b** (Scheme 2). This was probably due to the generation of a mixture of Z-/E-isomer of enone **1b** from the hydrolysis of allenyl acetate, and the Z-isomer acted as the reactive one to take part in the subsequent domino [3 + 2]IMCC. To confirm this further, we prepared substrate **1b** as a mixture of the two isomers (Z/E = 1.6:1) through a $AgBF_4$-promoted rearrangement of propargyl acetate in dichloromethane (DCM) (Scheme 3).[9] Under catalysis of $Sc(OTf)_3$ (0.2 equiv), the Z-isomer was converted to the bridged cycloadduct **2b** almost quantitatively, and the E-**1b** was left unreactive. The ratio of **2b** to E-**1b** still remained 1.6:1.

Scheme 2. Unexpected Result in Our Previous Research on Cyclopropane−Allene

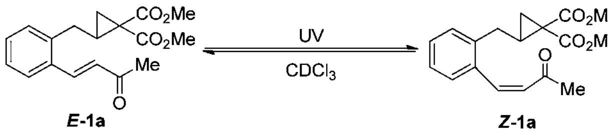


Scheme 3



The successful construction of the 9-membered carbocycle as well as the oxa-bicyclo[5.2.1] skeleton made us more confident of the proposed strategy with the help of the subsequent photopromoted isomerization of E/Z-α,β-unsaturated ketones/aldehydes (Scheme 1). Our initial investigation for the photoisomerization started from the reaction of substrate **1a**. The starting material **1a** was prepared as a single E-isomer via Wittig olefination (see the Supporting Information).[7] We found that under the irradiation of UV light (the most common one for detection of TLC in laboratory, see the Supporting Information), the isomerization proceeded successfully to afford a mixture of Z- and E-isomers (Table 1). With this positive result, we then added Lewis acids to test the tandem isomerization-[3 + 2]IMCC concept. We found that with the cooperative catalysis of UV light and Lewis acids the strategy was successfully carried out. The oxa-bicyclo[5.2.1] cycloadduct **2a** was obtained in an excellent yield under optimized conditions, the structure of which was unambiguously confirmed by NMR spectroscopy, HRMS, and X-ray crystal structure analysis (Scheme 4).[10]

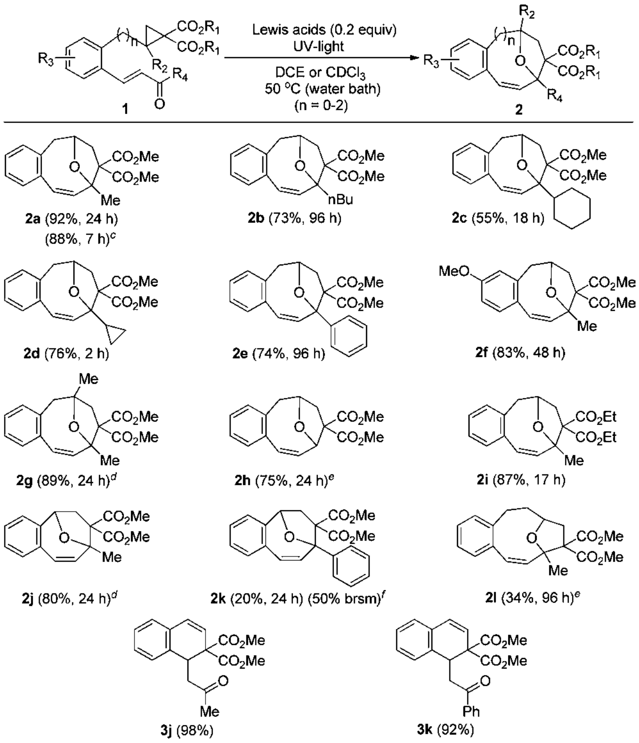
Table 1. UV Light-Promoted Isomerization of Enone 1a[a]



entry	time (h)	E/Z[b]
1	0	1.0:0
2	16	1.0:1.4
3	32	1.0:1.8
4	52	1.0:1.9
5	75	1.0:1.6
6	98	1.0:1.7

[a]Reaction conditions: 0.02 M in $CDCl_3$ in an NMR tube, water bath (50 °C). [b]The ratio was detected by ^{1}H NMR.

Scheme 4. Lewis Acid Catalyzed [3 + 2]IMCC of Cyclopropane 1,1-Diesters 1[a,b]

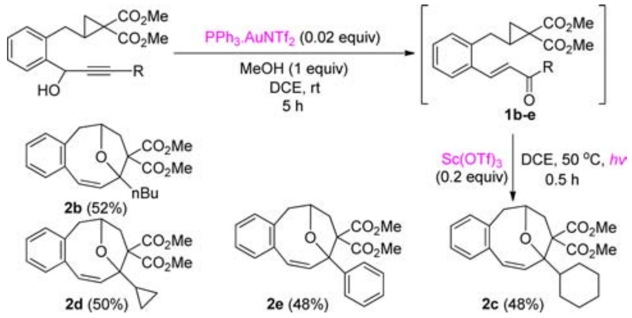


[a]Reaction conditions: in an NMR tube, **1** (0.04 mmol), $Sc(OTf)_3$ (0.2 equiv), DCE or $CDCl_3$ (2 mL), 50 °C (water bath). [b]Isolated yields. [c]In a quartz glass bottle, **1** (0.1 mmol), $Sc(OTf)_3$ (0.2 equiv), DCE or $CDCl_3$ (5 mL), 50 °C (water bath). [d]$Yb(OTf)_3$ (0.2 equiv) was used instead of $Sc(OTf)_3$, for **2g**, 50 °C, and for**2j**, rt. [e]$SnCl_4$ was used instead of $SC(OTf)_3$ in DCM. [f]$Eu(OTf)_3$ (0.2 equiv) was used, $CDCl_3$, rt, 60% starting material was recovered.

Following the successful example, the scope of the substrates was then examined (Scheme 4). Several other [3 + 2]IMCC for oxa-bicyclo[5.2.1] skeletons were carried out. [3 + 2]IMCC of various alkyl-substituted enones (**1b**, **1c** and **1d**) were also successfully carried out in moderate to good yields. Cycloadduct **2e** from the [3 + 2]IMCC of phenyl-substituted enone **1e** was obtained in 74% yield. This compound was sensitive to silica gel, and neutral Al_2O_3 was used in the column chromatographic purification. These examples showed that the steric hindrance of R^4 has less influence on the [3 + 2]IMCC. Substrate **1f** with a substituent on the benzene ring also gave the [3 + 2]IMCC cycloadduct **2f** in a good yield. Under catalysis of $Sc(OTf)_3$ (0.2 equiv), the tetrasubstituted cyclopropane **1g** was decomposed, probably due to its higher reactivity. When the less acidic $Yb(OTf)_3$ (0.2 equiv) was used as the catalyst, the [3 + 2]IMCC cycloadduct **2g** was obtained in an excellent yield. [3 + 2]IMCC of aldehyde **1h** also failed under the catalysis of $Sc(OTf)_3$ (0.2 equiv); however, $SnCl_4$ (0.2 equiv) made this reaction proceed successfully. Two examples were carried out for construction of the oxa-bicyclo[4.2.1] skeleton (**1j** and **1k**). However, the initial exploration did not give the corresponding cycloadducts (**2j** and **2k**). Instead, under the catalysis of $Sc(OTf)_3$ (0.2 equiv), 1,2-dihydronaphthalenes **3j** and **3k** were obtained. These reactions probably proceeded through the following tandem process: (1) generation of compact ion pairs from the ring-opening of cyclopropane and (2) intramolecular Michael additions/eliminations. Under catalysis of $Yb(OTf)_3$ (0.2 equiv), cycloaddcut **2j** was obtained in 80% yield. The successful [3 + 2]IMCC of **1k** was carried out under catalysis of $Eu(OTf)_3$ (0.2 equiv). One example was also successfully carried out for construction of the oxa-bicyclo[6.2.1] skeleton. The reactivity of **1l** seemed lower, and under catalysis of $Sc(OTf)_3$ (0.2 equiv) **1l** was unreactive. $SnCl_4$ (0.2 equiv) successfully promoted the [3 + 2]IMCC, and cycloadduct **2l** was obtained in 34% yield. This [3 + 2]IMCC could also be easily performed in a quartz glass bottle. For example, [3 + 2]IMCC of **1a** was carried out in a quartz glass bottle under irradiation of an UV disinfection lamp (see the Supporting Information) to afford **2a** in a yield (88%) similar to that in the NMR tube.

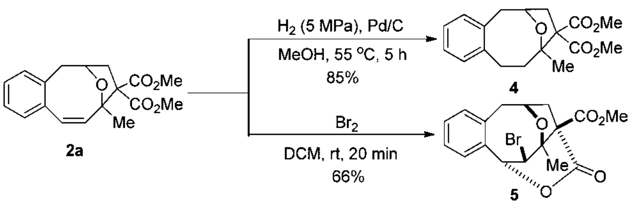
As enones can be easily prepared by a Meyer–Schuster rearrangement[11] from propargyl alcohol, which can be obtained by the nucleophilic addition of terminal alkyne to aldehyde, we designed a one-pot tandem Meyer–Schuster rearrangement/isomerization/IMCC process (Scheme 5). As a representative example, following the $AuNTf_2 \cdot PPh_3$-catalyzed Meyer–Schuster rearrangement, without separation of the enone **1b**, $Sc(OTf)_3$ (0.2 equiv) was added directly together with the irradiation of UV light to afford the [3 + 2]IMCC cycloadduct **2b** in 52% yield. Cycloadducts **2c**, **2d**, and **2e** were also obtained successfully through this tandem strategy.

Scheme 5. One-Pot Tandem Meyer–Schuster Rearrangement/Isomerization/IMCC



Two one-step postfunctionalizations on the C=C group of **2a** were carried out (Scheme 6). Hydrogenation afforded compound **4**. A regioselective and stereoselective bromoesterification of **2a** afforded a complex polycyclic compound **5**.

Scheme 6. Two One-Step Post-Functionalization Examples of 2a



In conclusion, we have developed a tandem isomerization/[3 + 2]IMCC of cyclopropane 1,1-diesters with α,β-unsaturated ketones/aldehydes under a cooperative catalysis of photo and Lewis acids. This supplied a general and efficient strategy for construction of medium-sized carbocyclic (8-, 9-, and 10-membered) skeletons as well as such carbocycle-based oxa-bicyclo[*n*.2.1] (*n* = 4, 5, and 6) skeletons. A one-pot tandem Meyer–Schuster rearrangement/isomerization/[3 + 2]IMCC process was also developed. We strongly believe that this strategy will find its potential in natural products synthesis and lead discovery.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.5b01928.

Experimental procedures and characterization data (PDF)
X-ray crystal structure of **2a** (CIF)
X-ray crystal structure of **5** (CIF)

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Notes

The authors declare no competing financial interest.

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