

# Lewis Acid/Rhodium-Catalyzed Formal [3 + 3]-Cycloaddition of Enoldiazoacetates with Donor–Acceptor Cyclopropanes

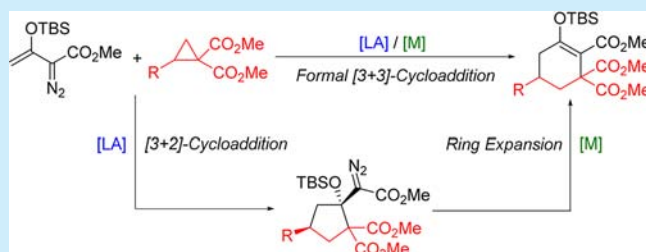
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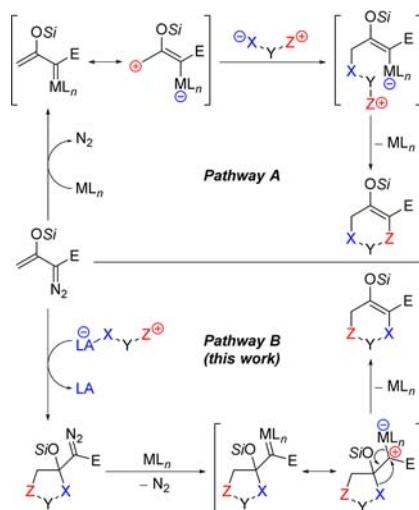
**S** Supporting Information

**ABSTRACT:** A formal [3 + 3]-cycloaddition of enoldiazoacetates with donor–acceptor cyclopropanes was realized by the combination of a Lewis acid-catalyzed diastereoselective [3 + 2]-cycloaddition and a subsequent rhodium-catalyzed chemoselective ring expansion. This tandem transformation provides an efficient approach to highly functionalized cyclohexenes.



Formal [3 + 3]-cycloaddition has attracted burgeoning interest over the past decade.<sup>1,2</sup> Silyl-protected enoldiazoacetates have proven to be one of the most effective participants in this transformation, which contribute to the efficient and highly selective construction of six-membered heterocycles.<sup>3</sup> In previous studies metallo-enolcarbenes were found to undergo vinylogous association at the nucleophilic site of stable dipoles followed by ring closure with the dipole's electrophilic site to form the cycloaddition products (Scheme 1, Pathway A).<sup>2,3</sup> We envisioned that diverse products could be obtained through a new pathway, which is constituted of Lewis acid-promoted [3 + 2]-cycloaddition between enoldiazoacetates and dipoles,<sup>2d,4</sup> metal-catalyzed dinitrogen extrusion, and subsequent 1,2-migration to the electrophilic carbene center<sup>4,5</sup> (Pathway B).

**Scheme 1. Divergent Pathways for Formal [3 + 3]-Cycloaddition of Enoldiazoacetates**



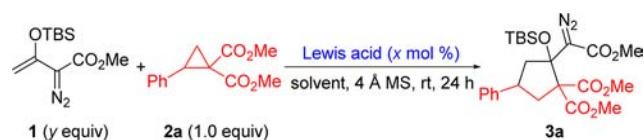
The dipolar attachment (XYZ) in Pathway B is opposite of that in Pathway A.

Donor–acceptor cyclopropanes have been shown to be versatile and reactive partners in Lewis acid-catalyzed [3 + 2]-cycloaddition reactions<sup>6,7</sup> which make them ideal candidates for Pathway B. Initial efforts were directed to reactions of *tert*-butyldimethylsilyl (TBS)-substituted enoldiazoacetate **1** with a stoichiometric amount of donor–acceptor cyclopropane **2a** catalyzed by different Lewis acids in dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>) at room temperature (Table 1, entries 1–6), and Yb(OTf)<sub>3</sub> proved to be a superior promoter, providing highest conversion of cyclopropane **2a** in that solvent with 5 mol % catalyst (entry 6). Alternative solvents were then investigated for this transformation (entries 7–10), and 1,2-dichloroethane (DCE) stood out as the optimal choice with a markedly increased conversion (to 71%, entry 8). With observations that unreacted **2a** remained after all of the enoldiazoacetate had been consumed,<sup>8</sup> we increased the amount of **1**. Using 1.5 equiv of enoldiazoacetate **1** provided complete conversion of cyclopropane **2a**, affording the desired [3 + 2]-cycloaddition product **3a** in 84% isolated yield with a diastereomeric ratio of 10:1 (entry 11). However, reducing the catalyst loading to 2 mol % significantly lowered the reactivity (entry 12). As expected, removal of the TBS group by treatment of **3a** with TBAF (1 M in THF) or with water in the presence of Lewis acids resulted in quantitative ring opening to the malonic ester linked  $\epsilon$ -phenyl- $\alpha$ -diazo- $\beta$ -ketoester that underwent formal intramolecular C–H insertion<sup>9</sup> to form the corresponding  $\beta$ -tetralone derivative.

The generality of this process was evaluated under these optimized conditions with a selection of donor–acceptor cyclopropanes **2** (Table 2). Neither electron-withdrawing nor electron-donating substituents at the para-position of the phenyl

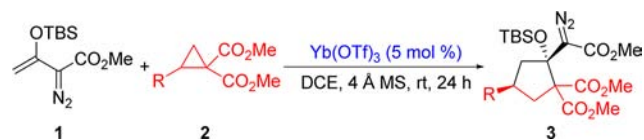
Received: June 8, 2015

Published: June 30, 2015

**Table 1. Lewis Acid-Catalyzed [3 + 2]-Cycloaddition of Enoldiazoacetate 1 with Cyclopropane 2a: Optimization of Reaction Conditions<sup>a</sup>**

entry	Lewis acid	x	solvent	y	conversion (%) <sup>b</sup>
1	Sc(OTf) <sub>3</sub>	5	CH <sub>2</sub> Cl <sub>2</sub>	1.0	42
2	Mg(OTf) <sub>2</sub>	5	CH <sub>2</sub> Cl <sub>2</sub>	1.0	<5
3	Zn(OTf) <sub>2</sub>	5	CH <sub>2</sub> Cl <sub>2</sub>	1.0	<5
4	In(OTf) <sub>3</sub>	5	CH <sub>2</sub> Cl <sub>2</sub>	1.0	38
5	La(OTf) <sub>3</sub>	5	CH <sub>2</sub> Cl <sub>2</sub>	1.0	<5
6	Yb(OTf) <sub>3</sub>	5	CH <sub>2</sub> Cl <sub>2</sub>	1.0	45
7	Yb(OTf) <sub>3</sub>	5	CHCl <sub>3</sub>	1.0	35
8	Yb(OTf) <sub>3</sub>	5	DCE	1.0	71
9	Yb(OTf) <sub>3</sub>	5	toluene	1.0	40
10	Yb(OTf) <sub>3</sub>	5	THF	1.0	<5
11	Yb(OTf) <sub>3</sub>	5	DCE	1.5	>95 (84) <sup>c,d</sup>
12	Yb(OTf) <sub>3</sub>	2	DCE	1.5	61 (38) <sup>c</sup>

<sup>a</sup>Reaction conditions: Lewis acid/1/2a = 0.003x:0.3y:0.3 (mmol), with 4 Å molecular sieves (150 mg) in specified solvent (2 mL) at room temperature for 24 h. <sup>b</sup>Conversions of 2a were determined by <sup>1</sup>H NMR analysis of the reaction mixtures with internal standards. <sup>c</sup>Isolated yields after flash column chromatography. <sup>d</sup>Diastereomeric ratio was 10:1 determined by <sup>1</sup>H NMR analysis of the reaction mixture.

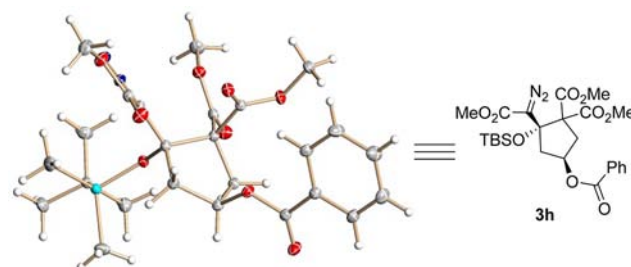
**Table 2. Lewis Acid-Catalyzed [3 + 2]-Cycloaddition of Enoldiazoacetate 1 with Cyclopropanes 2: Substrate Scope<sup>a</sup>**

entry	substrate	R	product	yield (%) <sup>b</sup>	dr <sup>c</sup>
1	2a	Ph	3a	84	10:1
2	2b	4-BrC <sub>6</sub> H <sub>4</sub>	3b	76	12:1
3	2c	4-MeOC <sub>6</sub> H <sub>4</sub>	3c	87	15:1
4	2d	4-MeC <sub>6</sub> H <sub>4</sub>	3d	84	>20:1
5	2e	3-MeC <sub>6</sub> H <sub>4</sub>	3e	72	6:1
6	2f	(E)-styryl	3f	77	10:1
7	2g	2-furyl	3g	72	9:1
8	2h	BzO	3h	81	>20:1
9	2i	PhthN	3i	82	>20:1

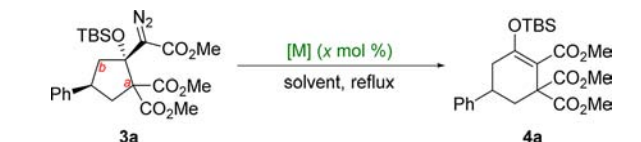
<sup>a</sup>Reaction conditions: Yb(OTf)<sub>3</sub>/1/2 = 0.015:0.45:0.3 (mmol), with 4 Å molecular sieves (150 mg) in DCE (2 mL) at room temperature for 24 h. <sup>b</sup>Isolated yields after flash column chromatography. <sup>c</sup>Diastereomeric ratios were determined by <sup>1</sup>H NMR analysis of the reaction mixtures.

rings affected the efficiency of this reaction, and the corresponding products 3b–3d were obtained in good yields with high diastereoselectivities (entries 2–4). Also, a *meta*-methyl substituent on the phenyl ring was well tolerated (entry 5), although diastereoselectivity in this case was the lowest observed in this series. Cyclopropanes derived from cinnamaldehyde (2f) and furfural (2g) gave results similar to those obtained with cyclopropane 2a (entries 6 and 7). Moreover, cyclopropanes 2h (R = OBz) and 2i (R = NPhth) smoothly underwent the reaction to afford cyclopentanol derivative 3h and

cyclopentylamine derivative 3i, respectively (entries 8 and 9).<sup>10</sup> The relative configuration of 3h, and others in this series by analogy, was determined by single-crystal X-ray diffraction (XRD) analysis (Figure 1);<sup>11</sup> the trans-relationship between the TBSO group and R is opposite of that found for the Lewis acid-catalyzed diastereoselective [3 + 2]-cycloaddition of 1 with azomethine imines.<sup>4</sup>

**Figure 1.** Single-crystal structure of compound 3h. The benzoyloxy and 1-diazo-2-methoxy-2-oxoethyl functionalities are on the same side of the cyclopentane ring.

Having prepared a series of [3 + 2]-cycloaddition products 3, we next investigated the transition metal-catalyzed ring expansion of these compounds (Table 3). In the reaction of 3a

**Table 3. Transition Metal-Catalyzed Ring-Expansion of 3a: Screening of Catalysts<sup>a</sup>**

entry	[M]	x	solvent	time (h)	yield (%) <sup>b</sup>
1	Rh <sub>2</sub> (OAc) <sub>4</sub>	2	toluene	24	76
2	Rh <sub>2</sub> (cap) <sub>4</sub> <sup>c</sup>	2	toluene	24	88
3	Rh <sub>2</sub> (pfb) <sub>4</sub> <sup>d</sup>	2	toluene	24	46
4	[Pd(allyl)Cl] <sub>2</sub>	2	toluene	3	74
5	Cu(MeCN) <sub>4</sub> PF <sub>6</sub>	5	DCE	3	79
6	Cu(OTf) <sub>2</sub>	5	DCE	3	69
7 <sup>e</sup>	Cu(hfacac) <sub>2</sub> <sup>f</sup>	5	DCE	30	73

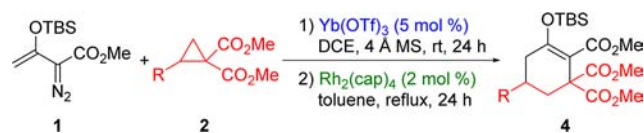
<sup>a</sup>Reaction conditions: [M]/3a = 0.003x:0.3 (mmol), in specified solvent (2 mL) under reflux. <sup>b</sup>Isolated yields after flash column chromatography. <sup>c</sup>cap = caprolactamate. <sup>d</sup>pfb = perfluorobutyrate. <sup>e</sup>The reaction was performed at 40 °C. <sup>f</sup>hfacac = hexafluoroacetylacetonate.

with Rh<sub>2</sub>(OAc)<sub>4</sub> in refluxing toluene, the ring-expansion product 4a was formed in good yield through 1,2-migration of the quaternary carbon C<sub>a</sub> (entry 1). The less Lewis acidic Rh<sub>2</sub>(cap)<sub>4</sub> further increased the yield of 4a to 88% (entry 2), whereas use of the more Lewis acidic Rh<sub>2</sub>(pfb)<sub>4</sub> provided a much lower yield of 4a (entry 3).<sup>12</sup> [Pd(allyl)Cl]<sub>2</sub> was also an efficient catalyst for this process, and a 74% yield of 4a was achieved within 3 h (entry 4). In contrast to rhodium and palladium catalysts, copper catalysts gave 4a in good yields at much lower temperatures (entries 5–7). For example, 4a was obtained in 73% yield in the presence of 5 mol % Cu(hfacac)<sub>2</sub> even at 40 °C, although a longer reaction time was required (entry 7). However, none of these catalysts achieved the high yield obtained with the use of Rh<sub>2</sub>(cap)<sub>4</sub>. It should be noted that no 1,2-migration of the secondary carbon

$C_b$  or the TBSO moiety, as was observed in a related system,<sup>4</sup> was observed in those cases reported in Table 3.

With the optimized conditions for both the [3 + 2]-cycloaddition and ring expansion reactions in hand, we performed the formal [3 + 3]-cycloaddition by the tandem combination of the two steps,<sup>13</sup> and the substrate scope of this transformation was investigated. As shown in Table 4, all of the

**Table 4. Lewis Acid/Rhodium-Catalyzed Formal [3 + 3]-Cycloaddition of Enoldiazoacetate 1 with Cyclopropanes 2: Substrate Scope<sup>a</sup>**



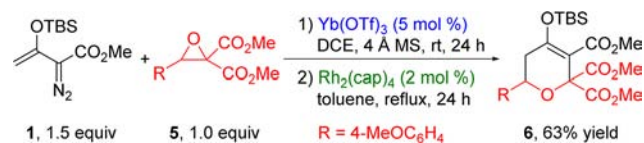
entry	substrate	R	product	yield (%) <sup>b</sup>
1	2a	Ph	4a	68
2	2b	4-BrC <sub>6</sub> H <sub>4</sub>	4b	61
3	2c	4-MeOC <sub>6</sub> H <sub>4</sub>	4c	73
4	2d	4-MeC <sub>6</sub> H <sub>4</sub>	4d	68
5	2e	3-MeC <sub>6</sub> H <sub>4</sub>	4e	66
6	2f	(E)-styryl	4f	66
7	2g	2-furyl	4g	56
8	2h	BzO	4h	60
9	2i	PhthN	4i	64

<sup>a</sup>Reaction conditions: (1) Yb(OTf)<sub>3</sub>/1/2 = 0.015:0.45:0.3 (mmol), with 4 Å molecular sieves (150 mg) in DCE (2 mL) at room temperature for 24 h; (2) after filtration and concentration, with Rh<sub>2</sub>(cap)<sub>4</sub> (0.006 mmol) in toluene (2 mL) under reflux for 24 h. <sup>b</sup>Isolated yields after flash column chromatography.

cyclopropanes (2a–2i) underwent this tandem process smoothly, and the substituents (R) can be not only aromatic rings or a styryl group but also protected hydroxy and amino groups (entries 1–9). Replacement of Rh<sub>2</sub>(cap)<sub>4</sub> with Rh<sub>2</sub>(OAc)<sub>4</sub> gave results that were only moderately different.

In addition to cyclopropanes, epoxide 5, prepared by the dirhodium(II)-catalyzed reaction of dimethyl diazomalonnate with *p*-anisaldehyde,<sup>14</sup> was also a suitable substrate for this process, furnishing the highly substituted dihydropyran 6 in 63% yield (Scheme 2). Diastereoselectivity for the initial [3 + 2]-

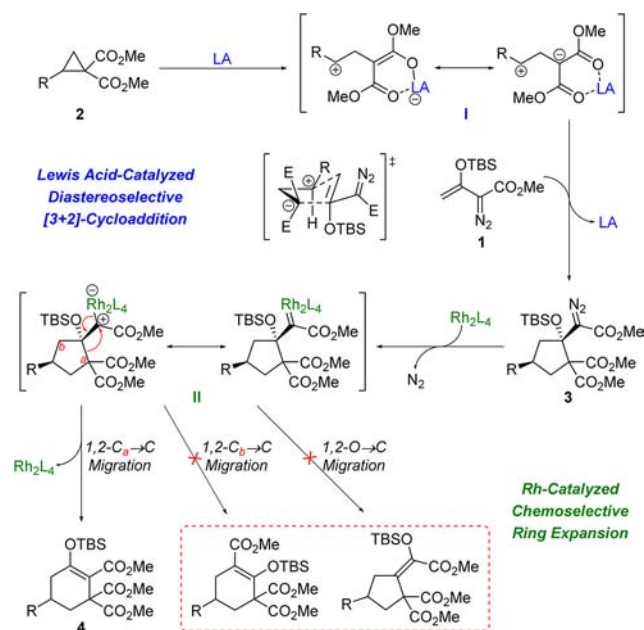
**Scheme 2. Lewis Acid/Rhodium-Catalyzed Formal [3 + 3]-Cycloaddition of Enoldiazoacetate 1 with Epoxide 5**



cycloaddition was 5:1. This example indicates the potential for further applications of this formal [3 + 3]-cycloaddition strategy; and, as structural analogues to 1,1,2-tricarboxylic acids that include citric acid,<sup>15</sup> these compounds may have related applications.

The mechanism of this formal [3 + 3]-cycloaddition (Scheme 3) is proposed in accord with the general process given in Scheme 1. The Lewis acid catalyst first activates the donor–acceptor cyclopropane 2 to generate the zwitterionic intermediate I, which then reacts with the enoldiazoacetate 1 to form the [3 + 2]-cycloaddition product 3. Subsequent ring expansion

**Scheme 3. Proposed Mechanism of the Lewis Acid/Rhodium-Catalyzed Formal [3 + 3]-Cycloaddition**



of 3, which is triggered by rhodium-catalyzed dinitrogen extrusion followed by 1,2-migration of the quaternary carbon C<sub>a</sub> to the electrophilic carbene carbon, produces six-membered ring products 4. The exclusive migration of the dicarboxylate-substituted carbon to the electron-deficient metal carbene center defines the net dipolar arrangement in the overall [3 + 3]-cycloaddition process. 1,1,2-Tricarboxylic acid derivatives of organic compounds have been mainly restricted to those of 1,1,2-ethanetricarboxylate derivatives,<sup>16</sup> and we are aware of only one prior procedure to access such structures in a cyclohexane ring.<sup>17</sup>

In summary, we have developed a formal [3 + 3]-cycloaddition of enoldiazoacetates with donor–acceptor cyclopropanes whose versatility in other cycloaddition reactions is well documented.<sup>6</sup> This tandem transformation consists of a Lewis acid-catalyzed diastereoselective [3 + 2]-cycloaddition reaction of enoldiazoacetates with donor–acceptor cyclopropanes and a subsequent rhodium-catalyzed chemoselective ring expansion of diazoacetates with β-quaternary centers. Studies focused on asymmetric processes, as well as on selective product transformations,<sup>15</sup> are underway.

## ■ ASSOCIATED CONTENT

### Supporting Information

General experimental procedures, the X-ray structure of 3h, and spectroscopic data for all new compounds. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.5b01674.

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### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

Support for this research from the National Science Foundation (CHE-1212446) is gratefully acknowledged. The HRMS used in

this research was supported by a grant from the National Institutes of Health (G12MD007591).

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(8) 24% of cyclopropane **2a** was recovered after flash column chromatography when using one molar equivalent of enoldiazoacetate **1**.

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(10) 2-<sup>n</sup>BuO-substituted cyclopropane-1,1-dicarboxylates also underwent cycloaddition with **1** under the same conditions, albeit in only

moderate yield, but diastereoselectivities were low and this approach was not pursued with these compounds.

(11) CCDC 1401683 contains the supplementary crystallographic data of **3h** for this Letter. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

(12) 42% of [3 + 2]-cycloaddition product **3a** was recovered after flash column chromatography when Rh<sub>2</sub>(pfb)<sub>4</sub> was used as the catalyst.

(13) See the Supporting Information for details.

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