Diazo Compounds

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Indium-Catalyzed Cycloisomerizations of Cyclopropene-3,3-Dicarbonyl Compounds: Efficient Access to Benzo-Fused Heteroaromatics and Heterobiaryls**

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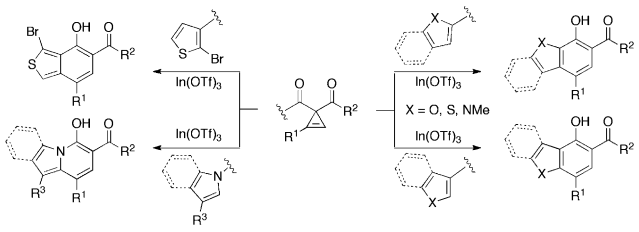
Benzo-fused heteroaromatics and heterobiaryls[1] are common structural motifs termed as "privileged"[2] by medicinal chemists because of their presence in a diverse range of pharmaceutically relevant small molecules and bioactive natural products. Both have been used as probes to explore biochemical pathways and to understand biological function. Because of their interesting photophysical properties, each has found application in materials science as organic light-emitting diodes (OLEDs) and organic photovoltaics (OPVCs).[3] Furthermore, they both serve as ligands for many metal complexes. Given this diverse utility, the development of efficient methods for the synthesis of benzo-fused heteroaromatics and heterobiaryls has been an important goal for synthetic chemists. Whereas alkynes have been widely used as reactive units to generate benzo-fused substrates,[4] cyclopropenes have received limited attention in this area despite their unique reactivity that results from their substantial ring strain.

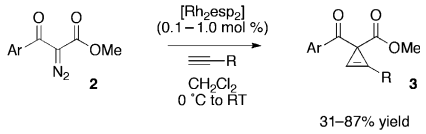
Cyclopropenes readily participate in an assortment of additions, substitutions, cycloadditions, and metal-promoted transformations.[5] In particular, the metal-catalyzed rearrangement, or cycloisomerization, of 2-acyl- and 2-iminocyclopropenes to afford heterocyclic compounds has recently garnered a lot of attention from both a synthetic and mechanistic viewpoint. This method has become a powerful way to prepare furans,[6] indolizines,[7,8] imidazopyridines,[7] and pyrrolo[2,1-*b*]oxazoles.[8] In contrast, only few examples of the analogous metal-catalyzed cycloisomerizations to form benzenoid rings have been disclosed. In a seminal report, Shi and co-workers demonstrated that arylvinylcyclopropenes rearrange in the presence of Lewis acids to give functionalized naphthalenes.[9] While this example (and subsequent publications)[10] has provided invaluable insight into the potential of using cyclopropenes as substrates for benzannulation reactions, only carbocyclic products were generated.

As part of our ongoing efforts toward the reactions of small strained rings in the presence of Lewis acids,[11] we were keenly interested in utilizing cyclopropene-3,3-dicarbonyl compounds as templates for intramolecular cyclizations. Although this class of cyclopropenes has not been employed as a substrate for cycloisomerizations, it has been shown to undergo ring-opening reactions in the presence of halides[12] or organometallic reagents.[13] These reagents serve as nucleophiles to promote an S_N2-like ring-opening of the cyclopropene. However, to the best of our knowledge, ring-opening of cyclopropene-3,3-dicarbonyl compounds promoted by Lewis acids have not been disclosed. Herein, we report the first example of a Lewis acid catalyzed cycloisomerization of cyclopropene-3,3-dicarbonyl compounds to give a wide array of benzo-fused heteroaromatics and heterobiaryls (Scheme 1).



Scheme 1. In(OTf)$_3$-catalyzed cycloisomerizations of 3,3-dicarbonyl cyclopropene substrates. Tf = trifluoromethanesulfonyl.

Cyclopropene-3,3-dicarbonyl substrates (**3**) were readily synthesized by using the general protocol disclosed by Gonzales-Bobes et al.[14] in which the corresponding α-diazo-β-keto esters **2** are added to solutions of alkynes in the presence of Dubois' catalyst,[15] [Rh_2esp_2] (dirhodium α,α,α′,α′-tetramethyl-1,3-benzene dipropanoate; Scheme 2).



Scheme 2. Rhodium(II)-catalyzed cyclopropenation.

However, while the expected cyclopropenes **3** were observed as the major products in all cases, varying amounts of the cycloisomerization products **4** (for structure see Table 1) were also obtained.[16] Attempts to reverse the product ratio by

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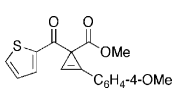
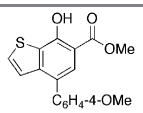
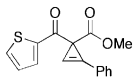
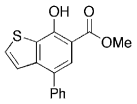
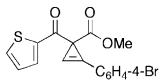
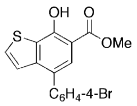
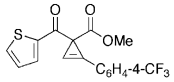
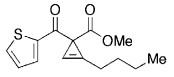
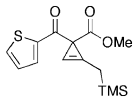
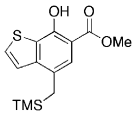
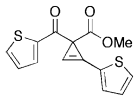
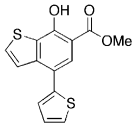
increasing the catalyst loading (2.5 to 5.0 mol%) only provided a ratio of approximately 1.4:1 in favor of the cycloisomerization product.[17] Encouraged by the ability of Gevorgyan and co-workers to selectively modulate product ratios in his reported cycloisomerizations of 3-iminocyclopropenes,[7] we examined other rhodium(II) dimers as catalysts. However, in the end, these efforts failed to give appreciable amounts of the desired cycloisomerization products.

Consequently, we focused our efforts on probing the cycloisomerizations of the cyclopropenes in the presence of Lewis acids. Given our success in the homo-Nazarov cyclizations of heteroaryl cyclopropyl ketones, $In(OTf)_3$ was the first Lewis acid screened. To optimize the reaction conditions, we chose to utilize the cyclopropene-3,3-dicarbonyl compound **3a**, derived from 2-thiophene, as the model substrate.[18] To our delight, $In(OTf)_3$ effectively catalyzed the cycloisomerization of the cyclopropene **3a** to give the anticipated heterobiaryl benzo[*b*]thiophene derivative **4a** in 86% yield (Table 1, entry 1).[19]

Table 1: $In(OTf)_3$-catalyzed cyclopropene cycloisomerizations.[a]

	3		4		*t* [h]	Yield [%][b]
1		**3a**		**4a**	9	86
2		**3b**		**4b**	10	86
3		**3c**		**4c**	10	86
4		**3d**	–		24	–[c]
5		**3e**	–		24	–[c]
6		**3f**		**4f**	7.5	68[d]
7		**3g**		**4g**	7	83

[a] Reactions run with cyclopropene (1 equiv) and $In(OTf)_3$ (5 mol%) in CH_2Cl_2 at 25 °C. [b] Yield of product isolated after column chromatography. [c] No reaction after 24 h. [d] Performed in 1,2-dichloroethane at reflux. TMS = trimethylsilyl.

Next, the effects of the cyclopropene substituent were studied by changing the alkyne used during the cyclopropenation. Both the phenyl and 4-bromophenyl cyclopropenes **3b** and **3c** afforded their respective cycloisomerization products in 86% yield (Table 1, entries 2 and 3). When a strongly electron-deactivating substituent is employed on the aryl ring, such as the 4-CF_3 group in **3d**, no cycloisomerization product is obtained (Table 1, entry 4). Similarly, having an *n*-alkyl substituent on the cyclopropene, as in **3e**, provided no benzannulated product (Table 1, entry 5). Attempts to promote cyclization by increasing the temperature (1,2-dichloroethane or toluene at reflux) or catalyst loading (up to 30 mol%) failed to yield any appreciable conversion.

This lack of reactivity can be explained in terms of localized charge stabilization. If we envision the extreme case of the actual formation of a vinylic cation and consider reaction enthalpies (energies of stabilization), a phenyl substituent provides approximately 25 kcal mol^{-1} of increased stability, over a simple *n*-alkyl substituent, on the positively charged vinylic position.[20] While we do not believe a formal vinyl cation is being generated, we argue that there must be a significant partial positive charge at C1 for cycloisomerization to occur. Hence, aryl substituents (ones that can stabilize the charge) will promote the reactions, whereas simple *n*-alkyl substituents will not. To probe this hypothesis, we synthesized the cyclopropene **3f**, derived from propargyltrimethylsilane. Localization of positive charge at C1 should be favorable, as it will be stabilized by the β-silyl effect. We were pleased to find that although the cycloisomerization did not proceed at room temperature, upon heating **3f** in 1,2-dichloroethane, the desired product **4f** was obtained in 68% yield (Table 1, entry 6).

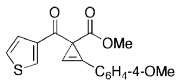
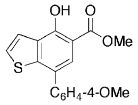
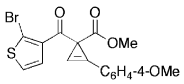
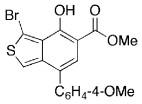
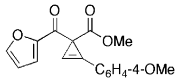
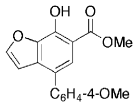
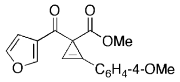
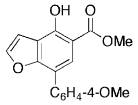
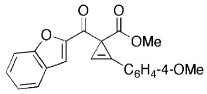
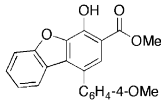
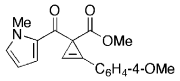
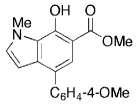
Lastly, when the cyclopropene **3g**, derived from 2-ethynyl thiophene was employed, the anticipated heterobiaryl thiophene derivative **4g** was afforded in 83% yield (Table 1, entry 7).

After establishing the reactivity of the cyclopropenes derived from 2-thiophene, the cycloisomerization reactions with cyclopropenes containing different heteroaromatic substituents were subsequently investigated (Table 2). Given that the 2-thiophene substrate **3a** served as our model substrate, other thiophene derivatives were examined first. The 3-thienyl cyclopropene **3h** readily cyclized to give the isomeric benzo[*b*]thiophene **4h** in 82% yield (Table 2, entry 1). When the 2-bromo-3-thienyl cyclopropene **3i** was employed, the anticipated benzo[*c*]thiophene (isobenzothiophene) product **4i** was obtained in 55% yield (Table 2, entry 2). This represents an important result given that benzo[*c*]thiophene analogues have been extensively utilized in the field of organic materials as components in OLEDs, as well as photovoltaics.[21]

Given the established importance of the benzofuran moiety in medicinal chemistry, we were interested in examining the reactivity of various furanyl derivatives in the cycloisomerization reaction. Both 2-furyl and 3-furyl cyclopropenes **3j** and **3k** provided the functionalized benzo[*b*]furans **4j** and **4k** in 78 and 82% yield, respectively (Table 2, entries 3 and 4). Similarly, the 2-benzofuranyl cyclopropene **3l** readily generated dibenzofuran **4l** in 69% yield (Table 2, entry 5). It is important to note that the dibenzofuran moiety is present in a number of natural products.

Along the same lines, N-methylpyrrole was employed as the heteroaryl substituent. Upon subjecting cyclopropene **3m**

Table 2: Effects of changing the heteroaryl moiety.[a]

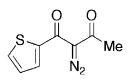
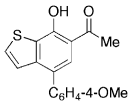
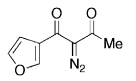
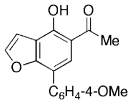
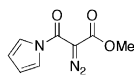
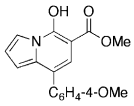
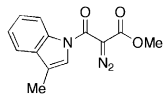
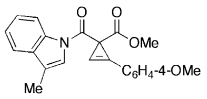
	3		4		t [h]	Yield [%][b]
1		**3h**		**4h**	9	82
2		**3i**		**4i**	8	55
3		**3j**		**4j**	9	78[c]
4		**3k**		**4k**	10	82
5		**3l**		**4l**	12	69
6		**3m**		**4m**	12	78

[a] Reactions run with cyclopropene (1 equiv) and $In(OTf)_3$ (5 mol%) in CH_2Cl_2 at 25 °C. [b] Yield of product isolated after column chromatography. [c] Performed in 1,2-dichloroethane at reflux.

to the reaction conditions, the highly functionalized *N*-methylindole **4m** was obtained in 78% yield (Table 2, entry 6). This result was particularly satisfying given that indole is considered a privileged scaffold by medicinal chemists and our method allows the facile formation of indolyl derivatives with a high degree of substitution.[22]

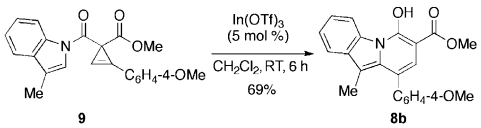
Finally, we wanted to probe the effects of varying the carbonyl groups on the cyclopropenes to include ketones and amides (Table 3). We anticipated that these groups would have some effects on the reaction based on changes in the Lewis basicity of the carbonyl groups. During our attempts to synthesize cyclopropene-3,3-diketones (containing a ketone in place of an ester), we obtained an unforeseen result. Treatment of the α-diazo 1,3-diketones **5a** and **5b** (derived from 2-thiophene and 3-furan, respectively) with $[Rh_2esp_2]$ and 4-ethynylanisole, only provided the benzo[*b*]thiophene **6a** and benzo[*b*]furan **6b** in 62 and 31% yield, respectively (Table 3, entries 1 and 2).[23]

Table 3: Effects of varying the carbonyl acceptor groups.[a]

	Substrate		Product		t [h]	Yield [%][b]
1		**5a**		**6a**	4	62[c]
2		**5b**		**6b**	5	31
3		**7a**		**8a**	2	51
4		**7b**		**9**	2.5	67

[a] Reactions run with diazo compound (1.3 equiv), 4-ethynylanisole (1 equiv), and $[Rh_2esp_2]$ (0.1 mol%) in CH_2Cl_2 at 25 °C. [b] Yield of product isolated after column chromatography. [c] 1 mol% $[Rh_2esp_2]$ was employed.

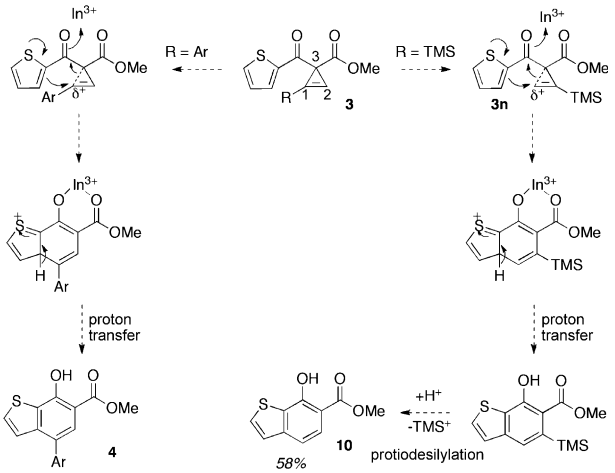
Similarly, when the *N*-pyrrolyl α-diazo β-amidoester **7a** was used,[24] only the cycloisomerization product **8a**, a functionalized indolizine, was generated in 51% yield (Table 3, entry 3). Surprisingly, when the *N*-indolyl α-diazo β-amidoester **7b** was employed, only the cyclopropene **9** was produced in 67% yield (Table 3, entry 4). Ultimately, **9** could be cycloisomerized in the presence of $In(OTf)_3$ to afford the pyrido[1,2-*a*]indole product **8b** in 69% yield [Eq. (1)]. Given



(1)

that the electronics of the *N*-pyrrolyl and *N*-indolyl α-diazo β-amidoesters should be similar, this dramatic difference in reactivity can be rationalized based on steric interference or a π-stacking interaction that may arise between the ligands on the rhodium catalyst and the benzenoid portion of the indole.

Mechanistically, we envisioned that the heteroaryl group can serve as an intramolecular nucleophile according to a Friedel–Crafts-type mechanism (Scheme 3). The Lewis acid catalyst will polarize the C1–C3 bond upon coordination with the carbonyl groups in the cyclopropene to form a six-membered chelate. Next, the pendant heteroaryl moiety will initiate an intramolecular S_N1-like nucleophilic cyclopropene ring-opening. This sequence ultimately generates the final



Scheme 3. Mechanistic rationalization for the indium-catalyzed cycloisomerization.

cycloisomerized product **4**. This represents novel reactivity given that the reported ring-opening reactions of cyclopropene-3,3-dicarbonyl compounds occur by S_N2-like processes or through the formation of carbenoids.

An interesting result was observed when cyclopropene **3n** (derived from TMS acetylene) was subjected to the reaction conditions (Scheme 3). The only product observed was the 4-unsubstituted benzo[*b*]thiophene derivative **10** (58% yield), which does not contain the TMS group. We postulate that heteroaryl attack on the cyclopropene occurs with an inverse regioselectivity to afford the corresponding TMS-substituted aromatic product, which under the reaction conditions, will undergo protiodesilylation[25] to afford the benzo[*b*]thiophene product **10**.

In summary, we have developed a novel Lewis acid catalyzed cycloisomerization of heteroaryl cyclopropene-3,3-dicarbonyl compounds. The method is efficient (up to 86% yield), highly modular (amenable to various heteroaromatics, N-acylindoles, and N-acylpyrroles), and allows the facile formation of functionalized benzo-fused heteroaromatics and heterobiaryls, including aryl- or heteroaryl-substituted benzothiophenes, benzofurans, dibenzofurans, indoles, indolizines, and pyrido[1,2-*a*]indoles. Efforts to employ cyclopropenes derived from internal alkynes are currently underway.

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[17] Attempts to add in more Rh^{II} catalyst failed to generate more cycloisomerization product. Similarly, adding a Lewis acid to the mixture of cyclopropene and cycloisomerization product failed to promote further cycloisomerization.

[18] This approach was motivated in part by our recent publication on the $In(OTf)_3$-catalyzed ring-opening/intramolecular Friedel – Crafts alkylation (known as the heteroaromatic homo-Nazarov cyclization) of donor – acceptor cyclopropanes containing pendant heteroaryl groups: L. H. Phun, D. V. Patil, M. A. Cavitt, S. France, *Org. Lett.* **2011**, *13*, 1952 – 1955.

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