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Rhodium(III)-Catalyzed Annulative Coupling of Sulfoxonium Ylides and Allenoates: An Arene C–H Activation/Cyclopropanation Cascade

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Supporting Information

ABSTRACT: Rhodium(III)-catalyzed annulative coupling of sulfoxonium ylides with allenoates was achieved, forming highly functionalized cyclopropanes with a quaternary carbon center by means of the sulfoxonium ylide functionality as a traceless bifunctional directing group and C4 synthon via an arene C–H activation and cyclopropanation cascade. The protocol features simultaneous formation of three new C–C bonds in one pot with



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excellent diastereoselectivity. The resultant cyclopropanation products could be further transformed to diverse synthetically useful compounds.

C yclopropane is a structural element in many biologically active compounds, and it can also act as a versatile building block in organic synthesis.¹ Many efforts have been devoted to the synthesis of cyclopropane derivatives by means of Simmons–Smith cyclopropanation reaction and the welldefined and most widely used transition-metal-catalyzed carbene transfer processes.² However, the carbene precursors, that is, diazo compounds, face the potential explosion issue and inconvenience to preserve, and the monosubstituted and aliphatic diazo compounds are hardly applicable.^{2,3} Thus, development of new cyclopropanation methods with the suitable surrogates of diazo compounds has been highly desirable.

Sulfoxonium ylides have been widely used as the carbene surrogates in organic transformations under transition-metal catalysis due to their facile preparation and operational safety. In this regard, a domino reaction strategy of transition-metalcatalyzed C-H activation and cyclization with sulfoxonium ylides has recently attracted much attention. Diverse carbeneinvolving methods have been developed to realize the acylmethylation of arenes⁵ and synthesis of acyclic,⁶ carbocyclic,⁷ and heterocyclic compounds such as furans, indoles,⁹ quinolines,¹⁰ pyrroles,¹¹ pyrimidines,¹² and others¹³ by means of iridium, rhodium, ruthenium, cobalt, palladium, and other metal catalytic systems. In all these cases, sulfoxonium ylides served as the C1 or C2 synthons with the assistance of a nucleophilic directing group (Scheme 1a).⁴⁻¹³ In 2017, Li et al. disclosed Rh(III)-catalyzed [4 + 2] annulation of sulfoxonium ylides with alkynes to afford naphthols by using sulfoxonium ylides as the C4 synthons,¹⁴ and the Fan group reported the synthesis of highly function-



(a) Sulfoxonium ylides as C1 and C2 synthons⁴⁻¹³



(b) [4+2] Annulation with alkynes¹⁴ and diazo compounds¹⁵



(c) [4+1] Annulation with anthranils16

(d) This work: annulative coupling with allenoates



alized naphthalenones via rhodium(III)-catalyzed [4 + 2] reaction of sulfoxonium ylides with α -diazocarbonyls¹⁵ (Scheme 1b). Recently, rhodium(III)-catalyzed [4 + 1] annulation of sulfoxonium ylides with anthranils toward

Received: October 11, 2019 Published: November 5, 2019 indoloindolones was also achieved by Cheng et al. (Scheme 1c).¹⁶ Continuous efforts have been made to explore the coupling partners for these reactions, including internal alkynes, diazo compounds, or *N*,*O*-heterocycles. Although much progress has been achieved, the development of other coupling partners is still highly desirable. Allenes have been proved to be highly valuable building blocks for the construction of complex molecules.¹⁷ However, transition-metal-catalyzed cyclopropanation of allenes has seldomly been documented.^{17,18} All the attempts within this category were focused on the intramolecular cyclization of allenes¹⁹ and their intermolecular reactions with diazo compounds.²⁰

Taking into account the development of new cyclopropanation methods, the potential application of sulfoxonium ylides in the synthesis of cyclic compounds, and our interest in domino reactions of allenes involving C–H and C–S bond activation,²¹ we envisioned that a transition-metal-catalyzed C–H activation and cyclopropanation cascade might be established by the precise combination of the allene and sulfoxonium ylide substrates and rendering the latter to serve as both the traceless bifunctional directing group and a carbene precursor. Herein, we disclose rhodium(III)-catalyzed annulative coupling of sulfoxonium ylides with allenoates through an arene C–H activation/cyclopropanation cascade toward the synthesis of 2*H*-cyclopropa[*b*]-naphthalen-2-ones bearing three continuous stereogenic centers including a quaternary carbon atom (Scheme 1d).

Initially, the reaction of benzoyl sulfoxonium ylide (1a) with benzyl 2-methylbuta-2,3-dienoate (2a) was conducted to screen the reaction conditions (Table 1). After systematic

Table 1. Optimization of the Reaction Conditions ^a		
~	0 0 4 mol % [Cp*RhCl ₂]	
	40 mol % PivOH	CO ₂ Bn
	1a 2a DCE, 110 °C, N ₂ , 12	h 3a
entry	variation	yield ^{b} (%)
1	none	$66 (62)^c$
2	[Cp*RhCl ₂] ₂ (5 mol %), AgSbF ₆ (20	mol %) 66
3	[Cp*RhCl ₂] ₂ (3 mol %), AgSbF ₆ (12	mol %) 59
4	PivOH (1 equiv)	62
5	PivOH (2 equiv)	55
6	2a (3 equiv)	63
7	120 °C	66
8	100 °C	57
9	without [Cp*RhCl ₂] ₂	0
10	without AgSbF ₆	trace
11	without PivOH	trace
12	without CsOPiv	40
a -		

^aConditions: **1a** (0.3 mmol), **2a** (0.6 mmol), [Cp*RhCl₂]₂ (4 mol %), AgSbF₆ (16 mol %), PivOH (40 mol %), CsOPiv (10 mol %), DCE (3 mL). ^bIsolated yields. ^c**1a** (1 mmol), **2a** (2 mmol), and DCE (10 mL). DCE = 1,2-dichloroethane.

experiments, the optimal reaction conditions were identified (see the Supporting Information for details). In the presence of 4 mol % of $[Cp*RhCl_2]_2/16$ mol % of AgSbF₆ with 40 mol % of PivOH and 10 mol % of CsOPiv as the additives in 1,2-dichloroethane (DCE) at 110 °C, the reaction gave the target product 3a as a single diastereomer in 66% yield, and 3a could be obtained in 62% yield on a 1 mmol scale (Table 1, entry 1). The yield could not be further improved by increasing the

catalyst loading (Table 1, entry 2) but using less amount of the catalyst, or an excessive amount of the acid PivOH diminished the yield to 55-62% (Table 1, entries 3-5). Increasing the loading of allenoate 2a or elevating the reaction temperature could not further enhance the reaction efficiency either, while lowering the temperature to 100 °C led to the product in 57% yield (Table 1, entries 6-8). Other acids and additives proved to be much less effective (see the Supporting Information for details). The control experiments revealed that the rhodium-(III) catalyst, silver salt, and acid were essential for the reaction (Table 1, entries 9-11). It is noteworthy that the reaction was obviously inhibited to form 3a in only 40% yield in the absence of cesium trimethyl acetate (CsOPiy) (Table 1, entry 12). The asymmetric synthesis of polysubstituted cyclopropanes was also tried by adding various chiral ligands such as chiral BINOL-based Brønsted acids, C2-symmetric carboxylic acids, and chiral phosphine ligands in the reaction system,²² but no enantioselectivity was observed for the isolated product (see the Supporting Information for details).

Under the optimized reaction conditions, the protocol generality was explored by means of a variety of aroyl- and heteroaroyl-based sulfoxonium ylides to react with 2a (Scheme 2). A negative steric effect was observed from the *o*-Me substituent in the aroyl moiety of the *ortho*-methyl-benzoyl



^aConditions: 1 (0.3 mmol), 2a (0.6 mmol), [Cp*RhCl₂]₂ (4 mol %), AgSbF₆ (16 mol %), PivOH (40 mol %), CsOPiv (10 mol %), and DCE (3 mL).

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sulfoxonium ylide 1b, and its reaction with 2a gave the target product **3b** in 40% yield. The *ortho*-fluoro group only exhibited a negligible steric effect, leading to the corresponding product 3c (64%), while ortho-chloro-functionalized sulfoxonium ylide 1d gave the target product 3d in 53% yield. meta-Methyl- and fluoro-substituted benzoyl sulfoxonium ylides could be effectively converted to products 3e and 3f (57-62%). Introducing an electron-donating group such as methoxy, methyl, and tert-butyl or a fluoro substituent to the paraposition of the phenyl ring rendered the reaction to give products 3g-3j in 57-65% yields, whereas 4-Br and the electron-withdrawing groups such as trifluoromethoxy, trifluoromethyl, and acetyl showed an obvious negative electronic impact on the product yields of 3k-3n (30-41%), suggesting that the reaction is highly dependent on the steric and electronic effects from the aroyl-based sulfoxonium ylide substrates. Dimethyl- and dimethoxy-substituted benzoyl sulfoxonium ylides afforded the corresponding cyclopropanation products 30-3q in moderate yields (47-58%). 2-Naphthoyl sulfoxonium ylide (1r) could also efficiently react with 2a to execute the C-H activation at the less sterically hindered 3-position, affording product 3r in 62% yield. The heterocyclic substrates, that is, N-benzyl-2-indoloyl, 2-thienoyl, and 3-thienoyl-based sulfoxonium ylides, reacted under the same conditions to form the target products 3s-3u in 42-62% yields. The 4-(2-pyridyloxy)-bearing benzoyl sulfoxonium ylide (1v) underwent the cyclopropanation reaction selectively at the ortho position of the carbonyl group, giving 3v in 48% yield, although the pyridyloxy moiety could act as a potential directing group for the C-H activation procedure. This result implicates that the C-H activation/cyclopropanation sequence can overcome the limitation of C-H activation involving strong coordinating N-heterocycle functionalities.² The potential utility of the synthetic protocol was exemplified by functionalizing the ylide substrates 1w and 1x derived from the drug molecules such as probenecid and adapalene, affording the target products 3w and 3x in 42-61% yields.

Next, the scope of allenoates was investigated in the reaction with benzoyl sulfoxonium ylide (1a) (Scheme 3). 2-Ethyl- and *n*-butyl-substituted allenoates 2b and 2c underwent the reaction smoothly to afford the target products 4a (60%) and 4b (60%), respectively, while 2-(n-heptyl) and benzyl substituents exhibited a negative steric effect on the product yields of 4c and 4d (50-52%). Both ethyl and n-propyl 2methylbuta-2,3-dienoates 2f and 2g also reacted with 1a under the stated conditions, giving the corresponding cyclopropanation products 4e (63%) and 4f (61%). iso-Propoxycarbonyl and tert-butoxycarbonyl functionalities on the allene backbone exhibited an obvious steric impact on the reaction efficiency to render the formation of 4g and 4h in low to moderate yields (25–48%). However, phenyl 2-methylbuta-2,3-dienoate (2j) could efficiently react to give the target cyclopropanation product 4i in 60% yield. Unexpectedly, neither allenone 2k nor the unsubstituted allenoate 2l could undergo the cyclopropanation reaction to afford the products 4j and 4k, respectively, under the standard conditions, indicating the necessity of both the alkyl and ester groups at the same terminus of the allene backbone. The ester group may weakly coordinate with the catalytically active metal center, and the alkyl group exhibits a steric effect, which ensures the regioselectivity of the reaction. The 4-methyl-substituted allenoate 2m exhibited a negative steric effect, leading to the target product 4l in 21% yield. It is noteworthy that all the

Scheme 3. Scope of Allenoates $(2)^a$



"Conditions: 1a (0.3 mmol), 2 (0.6 mmol), $[Cp*RhCl_2]_2$ (4 mol %), AgSbF₆ (16 mol %), PivOH (40 mol %), CsOPiv (10 mol %), and DCE (3 mL).

cyclopropanation products **3** and **4** were obtained as the single diastereomers. In addition, the molecular structures of the target products were further confirmed by the X-ray singlecrystal structural determination of compound **4e** (see the Supporting Information for details).

Further derivatizations of the cyclopropanation products were performed to demonstrate the potential applications of the present synthetic method (Scheme 4). Treatment of 3a

Scheme 4. Derivatizations of Cyclopropanation Product 3a^a



[&]quot;Conditions: (a) **3a** (3 mmol), NH₂OH·HCl (2 equiv), pyridine (1 mL), EtOH (2 mL), 60 °C, 1 h, then Ac₂O (2 equiv), DMAP (10 mol %), pyridine (3 mL), rt, 1 h; (b) **5** (0.2 mmol), diphenylacetylene (1.2 equiv), $[Cp*RhCl_2]_2$ (2.5 mol %), NaOAc (30 mol %), MeOH (1 mL), 60 °C, N₂, 12 h; (c) **3a** (2 mmol), TsNHNH₂ (1 equiv), MeOH (5 mL), 60 °C, 36 h; (d) **3a** (0.2 mmol), *p*-toluenesulfonyl azide (1 equiv), $[Cp*IrCl_2]_2$ (4 mol %), AgNTf₂ (16 mol %), HOAc (15 mol %), Li₂CO₃ (15 mol %), DCE (1 mL), 50 °C, N₂, 12 h; (e) **3a** (0.2 mmol), *n*-butyl acrylate (3 equiv), $[Cp*RhCl_2]_2$ (2 mol %), AgSbF₆ (8 mol %), Cu(OAc)₂ (1.2 equiv), 1,4-dioxane (1 mL), 120 °C, N₂, 5 h; (f) **3a** (0.2 mmol), NaBH₄ (1.01 equiv), MeOH (2 mL), rt, N₂, 20 min; (h) **3a** (0.2 mmol), methyltriphenylphosphonium bromide (1.5 equiv), 'BuOK (1.5 equiv), THF (3 mL), rt, N₂, 40 min.

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with hydroxylamine hydrochloride and acetic anhydride afforded O-acetyl oxime ester 5 in 75% yield, which proved to be a useful building block in transition-metal-catalyzed cross coupling.²⁴ Thus, fused 8,9-dihydro-7*H*-benzo[de]quinoline (6) was efficiently synthesized in 92% yield via rhodium(III)catalyzed ortho-C-H activation of the intermediate compound 5. 3a was quantitatively converted to N-tosylhydrazone 7, which can serve as a versatile carbene precursor.² The ketone carbonyl of 3a can act as an effective directing group which enabled efficient amination and alkenvlation at the ortho-C-H position of the aryl moiety under iridium(III) or rhodium(III) catalysis, giving the corresponding products 8 and 9 in 88-91% yields, respectively. The ketone carbonyl of 3a was selectively reduced to hydroxyl with NaBH₄ as the reductant, and the ester group could be further reduced by LiAlH₄ to give diol 11 (90%). Compound 3a underwent the Wittig reaction with methyltriphenylphosphonium bromide to afford alkene 12 (72%) with tolerance of the ester group. It is noteworthy that all the products 5-12 were obtained as the single diastereomers.

Control experiments were then conducted to probe into the reaction mechanism (Scheme 5). Deuterium incorporation was

Scheme 5. Control Experiments



observed at the *ortho*-C–H position of the phenyl functionality and the α -position of the carbonyl in **1a** when it was treated with deuterated pivalic acid (PivOD, 2 equiv) in the absence of an allenoate substrate (eq 1), while no deuterium incorporation occurred in the absence of the Rh(III) catalyst (eq 2). These results indicate that the C–H bond cleavage process is reversible during the reaction.^{14–16} The kinetic isotope effect (KIE) was measured from the parallel reactions of **1a** and its deuterated form **1a**[D] with **2a** (eq 3), and a primary isotope effect was observed with $k_{\rm H}/k_{\rm D} = 0.85$, suggesting that C–H bond activation/cleavage is not likely involved in the ratedetermining step in the overall catalytic cycle.

A plausible mechanism is proposed in Scheme $6^{.14-16}$ Initially, interaction of benzoyl sulfoxonium ylide 1a and the Rh(III) catalyst generates the five-membered rhodacycle complex A via arene C-H activation. Coordination of allenoate 2a to the rhodium center forms species B, followed by C=C insertion into the Rh-C bond to form the Rh(III)-sulfoxonium ylide complex intermediate C. Intramolecular rearrangement gives species D which releases DMSO to yield the rhodium carbenoid intermediate E. Intramolecular cyclopropanation thus occurs to form species F (Path A), which is then protonated to produce the target product 3a and regenerate the catalyst, establishing a catalytic annulative

Scheme 6. Proposed Mechanism



coupling cycle. Species E may also undergo migratory insertion to furnish the [4 + 2] annulation toward intermediate **G** (Path B), followed by intramolecular nucleophilic attack of the α -C at the proximal carbon to give the target product **3a**.

In summary, a Rh(III)-catalyzed annulative coupling of sulfoxonium ylides with allenoates was successfully developed to access 2H-cyclopropa[b]naphthalen-2-ones with excellent diastereoselectivity via an arene C–H activation/cyclopropanation cascade. The protocol features construction of three new C–C bonds to deliver highly functionalized tricyclic carbocycles in one pot, exhibiting high compatibility with functional groups and broad substrate scopes. The resultant cyclopropanation products can be readily converted to potentially important synthetic intermediates under mild conditions. This work provides a useful method to access carbocycle-fused cyclopropane derivatives.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.or-glett.9b03589.

Experimental materials and procedures, NMR of compounds, and X-ray crystallographic analysis (PDF)

Accession Codes

CCDC 1868910 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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