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Rhodium(III)-Catalyzed C−H Activation/Alkyne Annulation by Weak Coordination of Peresters with O−O Bond as an Internal Oxidant

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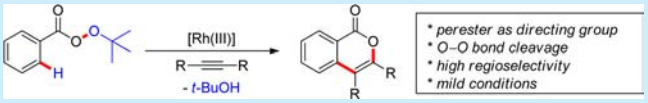
Supporting Information

ABSTRACT: A redox-economic strategy has been developed, involved in an efficient Rh(III)-catalyzed oxidative C−H activation and alkyne annulation with perester as the oxidizing directing group. In this process, the cleavage of an oxidizing O−O bond as an internal oxidant is described for the first time. This reaction could be carried out under mild conditions and exhibits excellent regioselectivity and wide functional groups tolerance.

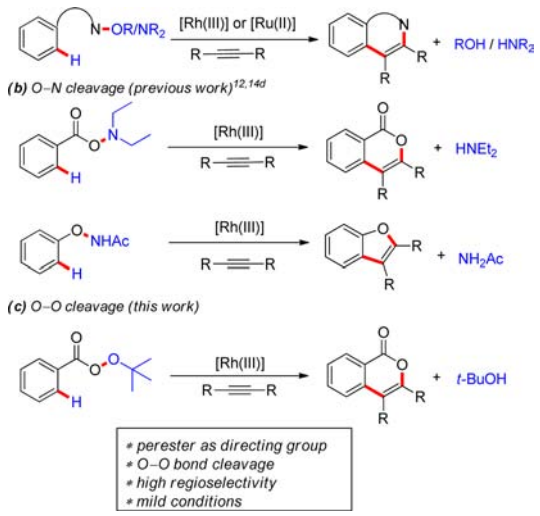


Transition-metal-catalyzed functionalization of inert C−H bonds by oxidative couplings of substrates bearing C−C multiple bonds has attracted significant interest since it avoids the multistep preparation of preactivated starting materials and thus allows an overall streamlining of organic synthesis.[1] Concerning the catalytic mechanism, it generally involves a high-oxidation-state metal species as a promoter and generates the desired products as well as low-oxidation-state metal species produced by reductive elimination. Therefore, stoichiometric or excessive amounts of oxidants are generally required to regenerate the active catalyst, which would provide a stoichiometric amount of waste and reduce the overall "greenness" of the process. To overcome this drawback, a novel redox-neutral strategy via the use of an oxidizing directing group (internal oxidant)[2] has been recently pioneered by Hartwig,[3] Yu,[4] Glorius,[5] Guimond and Fagnou,[6] Ackermann[7] and our group.[8] So far, internal oxidants are limited to the oxidizing potential of N−O, N−N, and O−N bonds in oximes,[9] *N*-pivaloxybenzamide,[6b,10] hydrazines,[11] phenoxyamides,[12] *N*-oxides,[8,13] and others.[14] Exploitations of other covalent bonds containing heteroatoms in the redox-neutral C−H activation are extremely rare.[15]

Peresters are easily available and widely applied as oxidants or radical initiators in organic synthesis[16] due to their weak O−O bond and the strong dependence of the decomposition time in their structures.[17] We deduced that the O−O bond from the easily available aryl peresters could serve as an internal oxidant for the transition-metal-catalyzed direct C−H activation. In this view, using a perester as an oxidizing directing group will be of great value compared to the ones using O−N or N−N bonds as an internal oxidant (Scheme 1a, b), with the leaving *O*-containing moiety resulting in a more environmentally friendly alcohol as the sole byproduct (Scheme 1c). In addition, isocoumarins are important structural motifs of various bioactive natural products.[18]

Transition-metal-catalyzed oxidative annulations of arylcarboxylic acids and alkynes have recently been developed for the isocoumarins construction, which requires stoichiometric external oxidants and high temperatures.[19] Moreover, C−O bond formation involved in an internal oxidant is rarely explored,[12b,d,14d] partly owing to the large energy gap between M−O HOMO and M−C LUMO frontier orbitals.[20] Thus, there would be some formidable challenges in this redox-economic process: (1) The coordination of the oxygen atom in aryl peroxides is weak.[1d,h] To the best of our knowledge, aryl peroxides have not been successfully used as directing groups in the directed C−H activations. (2) The O−O bond of aryl peroxides is thermally labile and would undergo decomposition to generate free radicals under various factors, such as temperature or ultraviolet radiation. (3) The initial C−H activation via metal catalysis and the subsequent O−O bond cleavage need to be compatible, and the leaving moiety at the late stage should not inhibit the active metal species. As a consequence, we hence became intrigued by developing

Scheme 1. Strategies for the Redox-Neutral C−H Activation



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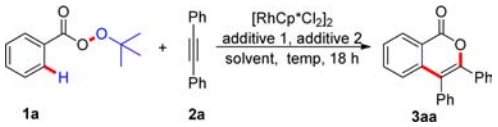
Rh(III)-catalyzed direct coupling of *tert*-butyl peroxybenzoate (TBPB) with alkynes through C−H/O−O bonds functionalization with a perester as an efficient oxidizing directing group (Scheme 1c).

We commenced our study on the condensation of TBPB (**1a**) with diphenylacetylene (**2a**) (Table 1). Varieties of metal salts as additives were screened (entries 1−5). CsOPiv was found to promote the transformations most efficiently, delivering isocoumarin **3aa** in 72% yield (entry 5). Further investigation showed that the yield increased to 80% when the temperature decreased to 80 °C (entry 6), which might be attributed to the decomposition of peresters at the higher temperature. Furthermore, we were pleased to find that reducing the loading of $[RhCp^*Cl_2]_2$ from 2.5 to 1 mol % preserved a similar catalytic activity in the presence of PivOH (entries 7 and 8). Moreover, the isolated yield was improved to 93% by simply switching the ratio of **1a** and **2a** to 1.0:1.5 (Table 1, entry 9). Attempts to lower the catalyst loading further as well as to decrease the reaction temperature resulted in reduced yields (entries 10 and 11). No target product was observed in the absence of rhodium catalyst (entry 12).

Table 1. Optimizing Various Parameters for the Condensation of TBPB with Diphenylacetylene[a]

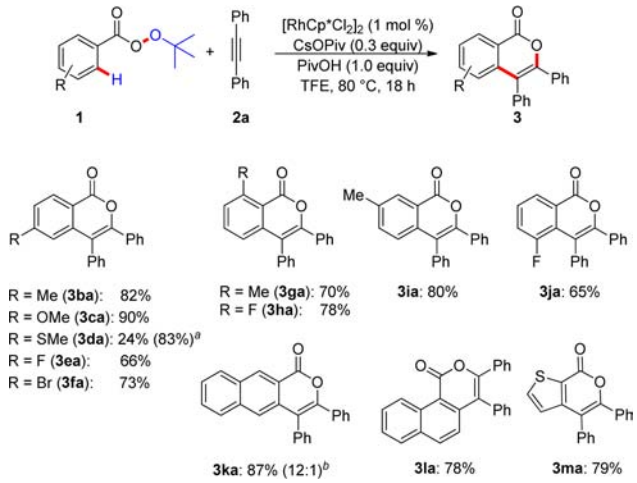


entry	$[Rh]_2$ (mol %)	additive 1 (equiv)	additive 2 (equiv)	solvent	temp (°C)	**3aa** (%)
1	2.5	AgOAc (0.3)		TFE	100	63
2	2.5	CsOAc (0.3)		TFE	100	55
3	2.5	NaOAc (0.3)		TFE	100	65
4	2.5	KOAc (0.3)		TFE	100	59
5	2.5	CsOPiv (0.3)		TFE	100	72
6	2.5	CsOPiv (0.3)		TFE	80	80
7	1	CsOPiv (0.3)		TFE	80	68
8	1	CsOPiv (0.3)	PivOH (1.0)	TFE	80	80
9[b]	1	CsOPiv (0.3)	PivOH (1.0)	TFE	80	93
10[b]	0.5	CsOPiv (0.3)	PivOH (1.0)	TFE	80	50
11[b]	1	CsOPiv (0.3)	PivOH (1.0)	TFE	60	22
12[b]	0	CsOPiv (0.3)	PivOH (1.0)	TFE	80	0

[a]Reaction conditions: **1a** (0.5 mmol), **2a** (0.6 mmol), solvent (2.0 mL), 18 h under N_2. [b]**1a** (0.5 mmol), **2a** (0.75 mmol). TFE: 2,2,2-trifluoroethanol.

With the optimized reaction conditions in hand, the scope of aryl peresters for the synthesis of isocoumarins was explored (Scheme 2). A variety of *para*-substituted TBPB were tested first. The desired products were obtained in good to excellent yields for donating groups (**3ba**−**fa**). It is known that sulfur is easily coordinated with transition metals, making them inactive. However, *tert*-butyl 4-(methylthio)benzoperoxoate (**1d**) was a suitable substrate in this catalytic system and delivered the desired product in 84% yield in the presence of 2.5 mol % of $[RhCp^*Cl_2]_2$. The withdrawing groups resulted in lower yields. For instance, TBPB substituted by 4-CO_2Me, 4-NO_2, 4-COMe, and 4-CN gave the corresponding products in 40%, 38%, 10%, and less than 5% yields, respectively. No target products were found when 4-OH- and NH_2-substituted TBPB as well as *tert*-butylpyridine-2-carboperoxoate were used as the substrates. Moreover, good yields were obtained for *ortho*-substituted TBPB. For instance, -*o*-methyl and fluoro-*tert*-butyl benzoperoxoate (**1g** and **1h**) gave the corresponding products **3ga** and **3ha** in 70% and 78% yields, respectively. It is worth noting that only a single isomer was obtained, although two chemically inequivalent *ortho* C−H bonds exist in *meta*-substituted TBPB. The redox-economic C−H bond annulation occurred at the less hindered C−H bond (**3ia**, Scheme 2). In contrast, *tert*-butyl 3-fluorobenzoperoxoate (**1j**) gave product **3ja** as the sole product, perhaps because of a secondary directing group effect.[21] Naphthyl peresters **1k** and **1l** afforded the fused target products **3ka** and **3la** in 87% and 78% yields, respectively. In addition, high regioselectivity was achieved by using *tert*-butyl naphthalene-2-carboperoxoate (**1k**) as the coupling substrate. It is worth noting that *tert*-butyl thiophene-2-carboperoxoate also reacted smoothly under the standard reaction conditions, delivering the target product **3ma** in 79% yield.

Scheme 2. Scope of Aryl Peresters 1[ab]



[a]$[RhCp^*Cl_2]_2$ (2.5 mol %). [b]Ratio of regioselectivity was determined by ^{1}H NMR.

We next examined the scope of the internal alkynes in this redox-economic C−H bond annulation. As shown in Scheme 3, various internal alkynes reacted smoothly with TBPB and afforded the desired 3,4-disubstituted isocoumarins in moderate to good yields. Both electron-rich, such as bis(4-methoxylphenyl)acetylene (**2b**) and di(4-methylphenyl)-acetylene (**2c**), and electron-deficient tolanes, such as bis(4-trifluoromethylphenyl)acetylene (**2f**), were compatible and gave the corresponding products (**3ab**, **3ac**, and **3af**) in 68%, 82% and 55% yields, respectively. Halogens were tolerated well. Yields of 80% and 66% were obtained for bis(4-chlorophenyl)acetylene (**2d**) and bis(4-fluorophenyl)acetylene (**2e**). Similarly, when fluorine was substituted at the 3-position of the aryl group, the yield decreased slightly (**3ag**), while only trace amounts of the desired products were detected for 4-COMe-, NO_2-, 4-CO_2Me-, CN-, OH-, and NH_2-substituted 1,2-diphenylethyne as well as 1,2-di(pyridin-2-yl)ethyne as substrates. Importantly, this catalytic system was not restricted to aryl-substituted alkynes

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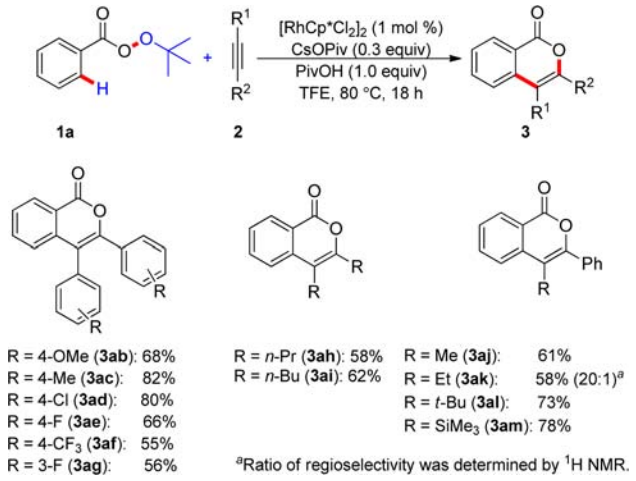
Scheme 3. Scope of Internal Alkynes 2[a]

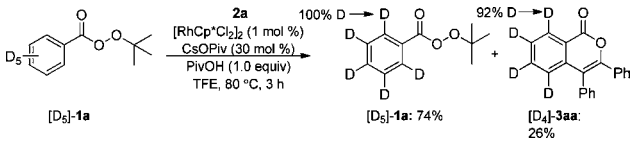


[a]Ratio of regioselectivity was determined by ^{1}H NMR.

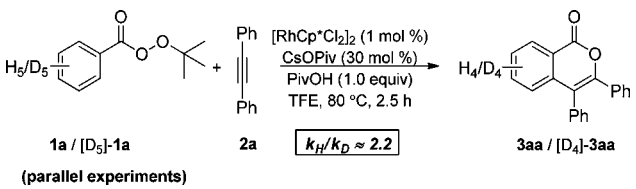
but also allowed the oxidative annulation of dialkylalkynes. For instance, 4-octyne (**2h**) and 5-decyne (**2i**) smoothly reacted with TBPB (**1a**) under the standard reaction conditions, furnishing the desired products in 58% and 62% yields, respectively (**3ah**, **3ai**). When unsymmetrical alkynes were employed, excellent regioselectivity was achieved. Isocoumarins **3aj**, **3al**, and **3am** were formed in 61%, 73%, and 78% yields as the exclusive regioisomers, and **3ak** was produced in 58% yield as two isomers in 20:1 ratio.

To probe the reaction mechanism, isotope experiments were carried out (Schemes 4 and 5). First, [D_5]-TBPB ([$\mathbf{D_5}$]-**1a**) was

Scheme 4. C−H Functionalization with Labeled Compound [$\mathbf{D_5}$]-1a



Scheme 5. Kinetic Isotope Effect Studies with Labeled Compound [$\mathbf{D_5}$]-1a

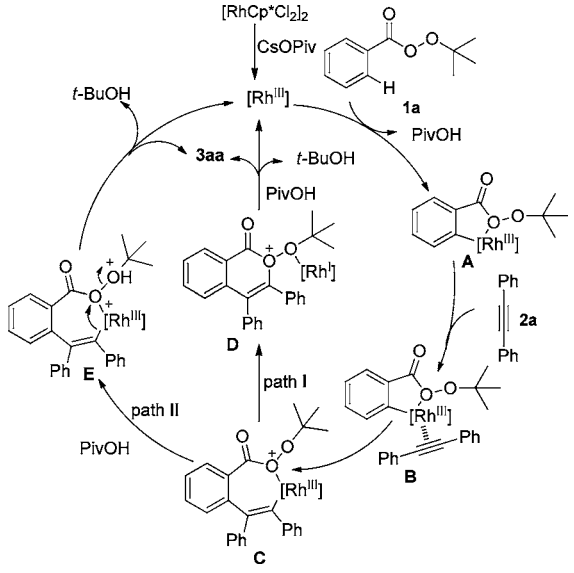


subjected to the standard reaction conditions (Scheme 4). No significant loss of deuterium was observed for the product [$\mathbf{D_4}$]-**3aa** or recycled substrate [$\mathbf{D_5}$]-**1a**, indicating that the step of cyclorhodation was irreversible.

Then, we conducted parallel experiments using substrates **1a** or [$\mathbf{D_5}$]-**1a** with diphenylacetylene (**2a**) under the standard reaction conditions. A significant kinetic isotope effect ($k_H/k_D \approx 2.2$) was found, suggesting the irreversible C−H cleavage to be the rate-determining step (Scheme 5).[22]

On the basis of the experimental results obtained above and the literature,[2−14,19] a proposed catalytic cycle for this novel oxidative annulation reaction is depicted in Scheme 6. The first

Scheme 6. Plausible Reaction Mechanism



step was the generation of the active [Rh^{III}] species. Then an irreversible C−H activation of aryl perester **1a**[23] was catalyzed by the active rhodium species through cyclorhodation[14d,19] to give intermediate **A**, which was coordinated and inserted with diarylalkyne **2a** to form intermediate **C**. C−O bond formation by elimination of intermediate **C** gave intermediate **D**.[9h,11f,14c,d] Product **3aa** was released through the redox process of intermediate **D** and regenerated the active [Rh^{III}] species (path I). Another possible pathway (path II) is also possible which involves a pivalic acid promoted intramolecular nucleophilic substitution leading to a C−O bond formation and O−O bond cleavage to afford product **3aa**, *tert*-butyl alcohol, and a [Rh^{III}] species.[11f,14d] Since the protonation of *O*,*O*-*tert*-butyl group of intermediates **E** by pivalic acid makes it a better leaving group in path II, while the migration of the [Rh^{I}] to the adjacent oxygen would require a high energy 3-ring transition state in path I, path II seems to be more favorable in this transformation.

In summary, we have developed a mild and efficient Rh(III)-catalyzed redox-neutral C−H activation of peresters with alkynes to synthesize various isocoumarins. This is the first example employing peresters as the oxidizing directing groups in directed C−H activation reactions. Using this rare oxidizing perester directing group will broaden the scope of metal-catalyzed C−H bond functionalizations and may find further applications in the efficient synthesis of useful complex molecules.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.5b02291.

Experiemental procedures and NMR spectra (PDF)

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Notes

The authors declare no competing financial interest.

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