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Mild Ring Contractions of Cyclobutanols to Cyclopropyl Ketones via Hypervalent Iodine Oxidation

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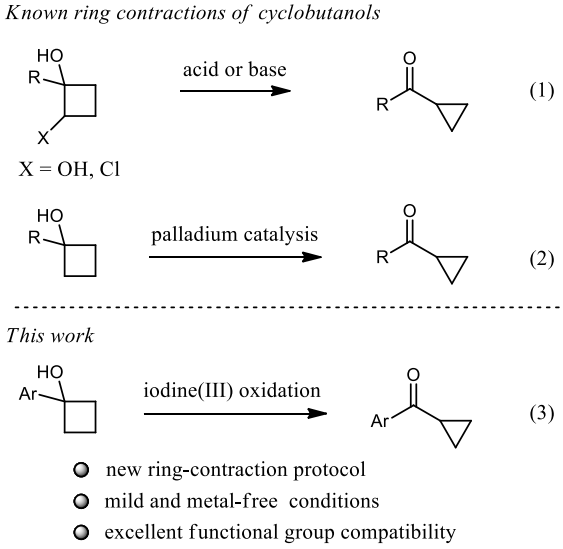
Abstract. An iodine-mediated oxidative ring contraction of cyclobutanols has been developed. The reaction allows the synthesis of a wide range of aryl cyclopropyl ketones under mild and eco-friendly conditions. A variety of functional groups including aromatic or alkyl halides, ethers, esters, ketones, alkenes, and even aldehydes are nicely tolerated in the reaction. This is in contrast with traditional synthetic approaches for which poor functional group tolerance is often a problem. The practicality of the method is also highlighted by the tunability of iodine oxidation system. Specifically, combining the iodine(III) reagent with an appropriate base allows the reaction to accommodate a range of challenging electron-rich arene substrates. The facile scalability of this reaction is also exhibited herein.

Keywords: ring contraction; hypervalent iodine; cyclopropyl ketone; cyclobutanol



Scheme 1. Ring contractions of cyclobutanols to cyclopropyl ketones

Cyclopropyl ketones are core structures in many natural products and bioactive compounds.[1] They have also been used in the synthesis of a variety of invaluable cyclic compounds[2] and are intriguing structures in mechanistic studies.[3] The synthetic routes to these compounds include cyclopropanation of alkenes,[4] ring closure of γ-halogenated ketones,[5] ring contractions of cyclobutanes,[6-8] and diverse elaborations of cyclopropyl derivatives.[9] Among these routes, the contraction of strained cyclobutanols contracted to even smaller cyclopropyl ketones, which proceeds via C-C bond cleavage and reconnection, is mechanistically appealing but rarely studied.[6,7] Only two protocols for this ring-contraction process can be found in the literature (Scheme 1): (1) acid or base promoted ring contraction of vicinally disubstituted cyclobutanols (eq 1)".[6] (2) palladium catalyzed oxidative ring contraction of cyclobutanols (eq 2).[7] Despite considerable advances made in the synthesis of cyclopropyl ketones, the development of a mild and eco-friendly reaction with good functional group compatibility is highly desirable.

Hypervalent iodine reagents have emerged as important and unique oxidants in organic synthesis due to their diverse reactivities, low toxicities, accessibility and easy handling.[10] Numerous iodine(III)-mediated transformations have been developed over the past few decades. An iodine oxidation protocol has also been applied to the ring contractions of cyclic ketones and alkenes.[11] Unlike the reported reactions, we herein disclose an iodine-mediated ring contraction of cyclobutanols to cyclopropyl ketones (eq 3).

We commenced the study by using cyclobutanol **1a** as a model substrate (Table 1). After thoroughly surveying reaction conditions (temperature, concentration, solvent, etc.),[12] $PhI(OAc)_2$/TMSOTf (1/2) in DCM at -50 ℃ for 6 h were identified as the optimum conditions for the reaction of **1a**. The

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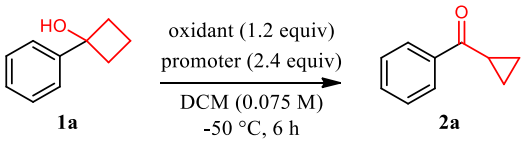
Table 1. Effect of oxidants and electrophilic promoters[a]



1a **2a**

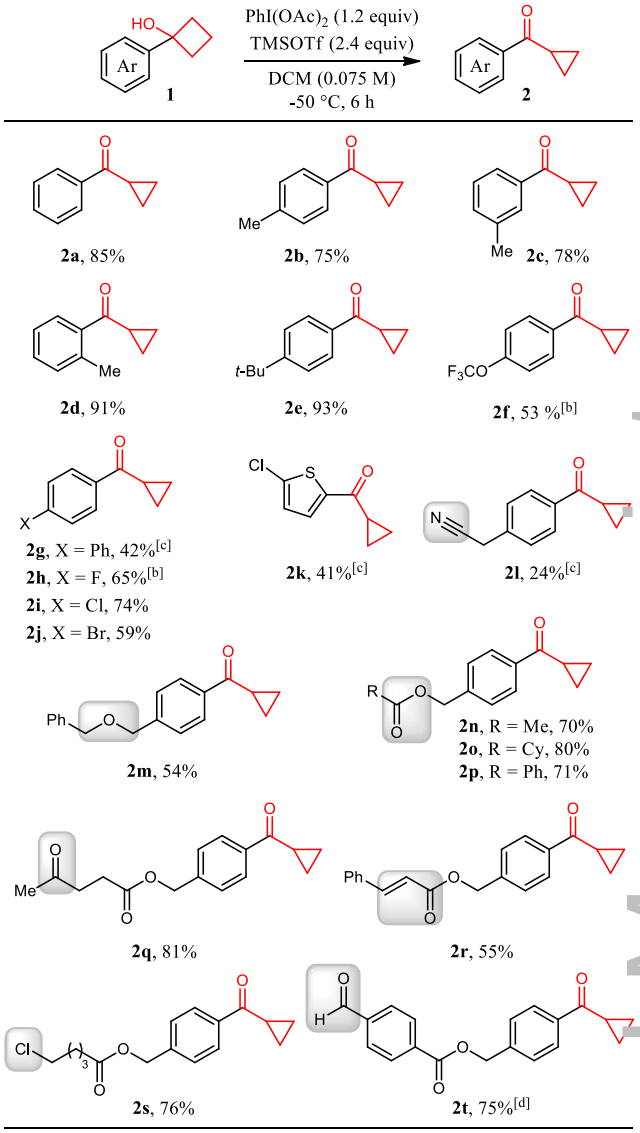
entry	oxidant	promoter	yield (%)[b]
1	$PhI(OAc)_2$	TMSOTf	85
2	none	TMSOTf	0[c]
3	$PhI(OAc)_2$	none	0[d]
4	$PhI(CF_3CO_2)_2$	TMSOTf	17[c]
5	PhI(OH)OTs	TMSOTf	24[c]
6	$PhI(OAc)_2$	TMSOAc	0[d]
7	$PhI(OAc)_2$	$BF_3{\cdot}Et_2O$	0[c]
8	$PhI(OAc)_2$	Tf_2O	37
9	PhI(OH)OTs	Tf_2O	43
10	Only PhI=O	Tf_2O	59
11	PhI(OH)OTs	none	0[c]
12	$PhI(CF_3CO_2)_2$	none	0[d]

[a] Reactions were performed on 0.3 mmol scale.
[b] Isolated yield.
[c] Complex mixture was obtained.
[d] 85% of **1a** (entry 3), 61% of **1a** (entry 6) and 70% of **1a** (entry 12) were recovered.

effects of oxidants and electrophilic promoters were examined as shown in Table 1. It was found that the reaction requires both $PhI(OAc)_2$ and TMSOTf (entries 2 and 3). Compared to other iodine reagents ($PhI(CF_3CO_2)_2$ or PhI(OH)OTs), $PhI(OAc)_2$ is the most suitable for the reaction (entries 4 and 5). TMSOTf was then found to be the best Lewis acid of all tested compounds (TMSOAc, $BF_3{\cdot}Et_2O$) (entries 6 and 7). Notably, the combination of Tf_2O with iodine reagents ($PhI(OAc)_2$, PhI(OH)OTs or PhI=O) could also promote the transformation in modest yields (entries 8-10). In contrast, in the absence of electrophilic promoters, hypervalent iodine compounds themselves (PhI(OH)OTs or, $PhI(CF_3CO_2)_2$) proved ineffective for the reaction (entries 11 and 12).

With the best conditions in hand, we next examined the substrate scope. As shown in Table 2, a wide range of cyclobutanols were tolerated in the reaction. Substrates bearing a methyl group, regardless of the position on arene (*p*-, *m*-, *o*-), gave rise to the desired cyclopropyl ketones **2b-2d** in good to excellent yields (75%, 78% and 91%, respectively). It seemed that steric hindrance had little impact on the reaction since the sterically hindered **1d** provided the corresponding product in excellent yield (91%). Compared to methyl and *t*-butyl groups (**1b-1e**), electron withdrawing groups (**1f-1j**) have a slight detrimental effect on the reaction, and the desired cyclopropyl ketones (**2f-2j**) were furnished in relatively low yields (42-74%). This result might be attributable to the lower nucleophilicity of electron-deficient substrates. Heteroarene **1k** is also well tolerated in the reaction, although **2k** is produced in modest yield (41%). Remarkably, a wide variety of

Table 2. Substrate scope[a]



[a] Unless otherwise noted, all reactions were performed on 0.3 mmol scale under the optimum conditions.
[b] -50 ℃ for 18 h.
[c] Cyclobutanols **1g**, **1k** and **1l** were completely consumed.
[d] HCl was used during work up.[12]

functional groups are compatible with the reaction conditions including ethers (**2f** and **2m**), esters (**2n-2t**), a nitrile (**2l**), a ketone (**2q**), an alkene (**2r**), and an aldehyde (**2t**); functional group compatibility is a common challenge faced by conventional methods.[4-9] The substrates **1g**, **1k** and **1l** were completely consumed to produce the desired cyclopropyl ketones in low yields and inseparable complex mixtures. It is worth noting that the use of aryl and alkyl halides **(2i-2k** and **2s**) as substrates provides a platform for later manipulations.

When we switched to cyclobutanol **1u** bearing a phenoxyl group, cyclopropyl ketone **2u** was generated in very low yield even though most of substrate **1u** had been consumed (eq 4). This poor

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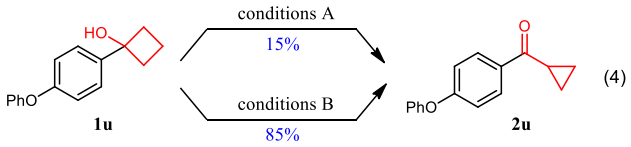
selectivity might be due to the strong background iodine(III)-mediated arene oxidation.[13] To solve the region-selectivity issue, we sought to tune the electrophilicity of $PhI(OTf)_2$ by introducing an organic base to the oxidation system.[14] To our delight, through a rapid base screen (for details, see Supporting Information), we found the combination of 2,6-



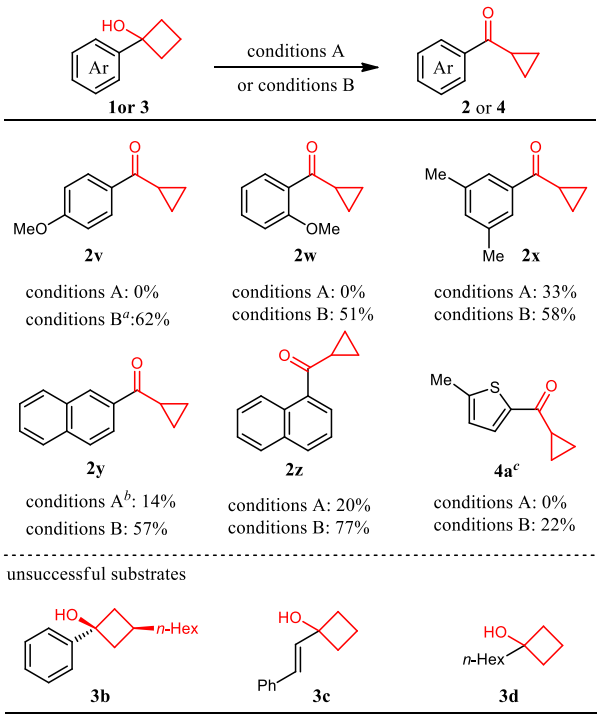
(4)

conditions A[12]: $PhI(OAc)_2$ (1.2 eq), TMSOTf (2.4 eq), -50 °C, 6 h

conditions B[12]: $PhI(OAc)_2$ (1.2 eq), TMSOTf (2.4 eq), -30 °C, 12 h
2,6-dichloropyridine (2.4 eq)

dichloropyridine with iodine(III) enabled an efficient ring contraction of **1u** and provided **2u** in very good yield (85%). The pyridine base likely decreased the electrophilicity of the iodine(III) reagent, thus essentially inhibiting the undesired oxidation of the electron-rich phenyl ring of **1u**. We believe that this discovery is significant for the future development of hypervalent iodine-mediated transformations.

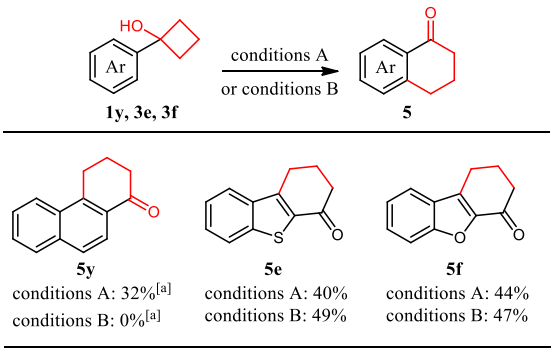
Table 3. Ring contraction reactions of **1v-1z** and **3a-3d** under conditions A or B



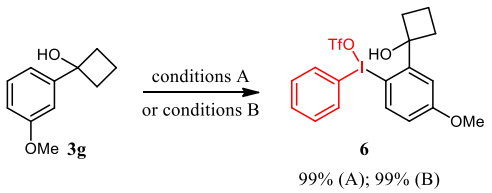
[a] Performed at -50 ℃ for 12 h. [b] 2,3-Dihydrophenanthren-4(1H)-one (**5y**) was obtained in 32% yield.
[c] Cyclobutanol **3a** was used as the substrate.

Inspired by the subtle base effect in the reactions of **1u**, we were curious to compare conditions A with conditions B by evaluating their performance with a variety of electron-rich arene substrates (Table 3). Methoxyl-substituted arenes **1v** and **1w** completely decomposed under conditions A; However under conditions B, which involve the assistance of base, provided **2v** and **2w** in synthetically useful yields (62% and 51%, respectively). The use of 2,6-dichloropyridine also changed the outcome of the reactions of **1x-1z** by significantly improving their chemical yields. In addition, electron-rich thiophenyl **3a**, which was not tolerated under conditions A, afforded the desired **4a** by using extra organic base, albeit in a relatively low yield (22%). However, even submitted to the newly developed conditions B, **1l** still provided poor chemical yield of **2l** (20%), which is similar to the reaction under conditions A (Table 2). Unfortunately, further efforts to expand the substrate scope to alkyl phenyl cyclobutanol **3b**, vinyl cyclobutanol **3c** and alkyl cyclobutanol **3d** failed; reactions with these three substrates in either conditions A or B merely resulted in complex mixtures. To date, we have no rational explanation for these results.

Table 4. Reactions of **1y**, **3e** and **3f** under conditions A or B



[a] **2y** was obtained in 14% yield from conditions A and 57% yield from conditions B, respectively.

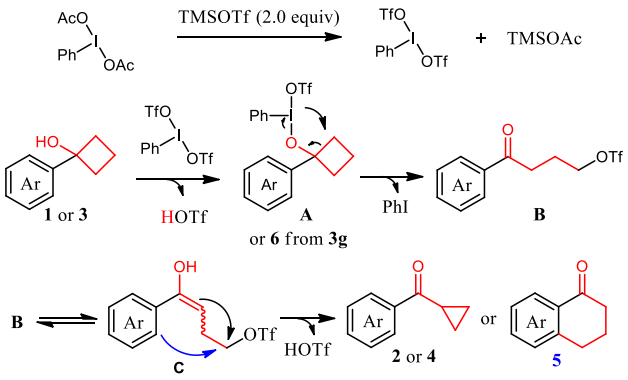


(5)

Interestingly, the reaction of 2-naphthalene **1y** under conditions A afforded cyclohexanone **5y** as the major product in relatively low yield (Table 4.). Similar transformations were also observed when using benzo[b]thiophene **3e** and benzofuran **3f** as substrates. Cyclohexanones **5e** and **5f** were obtained in modest yields, and none of the corresponding cyclopropyl ketone products could be identified. The formation of cyclohexanones might be due to an

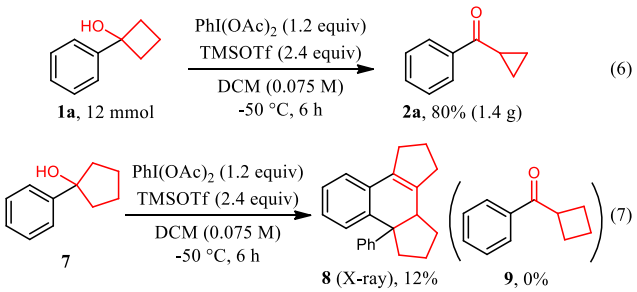
intramolecular electrophilic aromatic substitution (see mechanistic discussion below). Surprisingly, when we switched to *meta*-methoxy-substituted phenyl cyclobutanol **3g** (eq 5), in lieu of expected cyclopropyl ketone **4g**, diaryl iodane **6** appeared as the sole product with quantitative yields under either conditions A or B. This result can be attributed to the strong substituent effects of substrate **3g**. Similar transformations for the synthesis of diaryl iodanes can be found in the literature.[15]

Based on these experimental observations, a reaction mechanism was postulated (Scheme 2). According to Wirth's NMR studies[14b], $PhI(OTf)_2$ is formed by mixing $PhI(OAc)_2$ with two equiv of TMSOTf. Cyclobutanol **1** (or **3**) interacts with $PhI(OTf)_2$ affording intermediate **A**. In the case of **3g**, diaryl iodane **6** is formed through electrophilic aromatic substitution with iodine(III). Subsequent internal nucleophilic addition of $^-$OTf to the cyclobutyl ring of **A** results in its ring opening while simultaneously delivering **B**.[16,17] In the presence of a strong acid (HOTf), **B** tautomerizes to its enol form, **C**. Through an intramolecular SN_2 process, **C** is converted to **2** (or **4**). Alternatively, **C** may undergo an intramolecular electrophilic aromatic substitution to produce cyclohexanone **5** (blue arrow). Although the use of extra base has significantly improved the reactions of some electron-rich arene substrates (Table 3), a detailed mechanistic interpretation of the subtle base effect cannot be provided due to lack of promising evidence.



Scheme 2. Proposed mechanism

To examine the practicality of the method, a gram scale reaction was performed. As shown in eq 6, model substrate **1a** was submitted to the optimum conditions and efficiently produced 1.4 g of cyclopropyl ketone **2a** (80% yield). Unfortunately, the current methodology cannot be applied to cyclopentanol **7**. Interestingly, in lieu of **9**, tetracyclic compound **8** was isolated albeit in very low yield (eq 7). Its structure was confirmed by X-ray crystallography.



In summary, an iodine(III)-mediated oxidative ring contraction of aryl cyclobutanols to aryl cyclopropyl ketones has been developed. The reaction proceeds under mild conditions and has a broad substrate scope and superb functional group compatibility. Notably, the addition of an organic base (2,6-dichloropyridine) to the iodine(III) oxidation system allows the transformation to tolerate more challenging electron rich-arene substrates. In addition, the gram-scale reaction proceeding with high efficiency demonstrates the practicality of the method. Further expansion of the substrate scope, detailed mechanistic studies and application of the technology to some practical synthesis are currently under way.

Experimental Section

A mixture of $PhI(OAc)_2$ (1.2 equiv) in DCM (3 mL) was charged in a Schlenk flask under nitrogen atmosphere. TMSOTf (2.4 equiv) was added dropwise. After stirring for 10 min at room temperature, the mixture was cooled to -50 ℃. A solution of cylcobutanol **1** (44.5 mg, 0.3 mmol) in DCM (1 mL) was added dropwise. After stirring under the same temperature for 6 h, the mixture was quenched with $NaHCO_3$ (sat., 1 mL). Then the mixture was diluted with DCM (15 mL). The organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. After removal of the solvent in vacuo, the crude material was purified by flash column chromatography on silica gel to give the cyclopropyl ketone **2**.

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Mild Ring Contractions of Cyclobutanols to Cyclopropyl Ketones via Hypervalent Iodine Oxidation

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