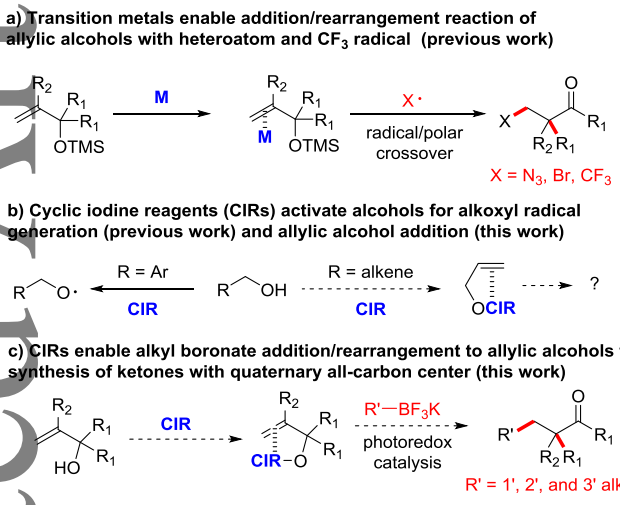
Cyclic Iodine Reagents Enable Allylic Alcohols for Alkyl Boronate Addition/Rearrangement by Photoredox Catalysis

Mingshang Liu[a,b], Hanchu Huang[a], and Prof. Dr. Yiyun Chen[a,b]*

ABSTRACT All-carbon quaternary centers are prevalent in bioactive small molecules. However, their efficient construction remains a formidable synthetic challenge. Here we report cyclic iodine(III) reagents enable the synthesis of cyclopentanones, cyclohexanones, and dihydrofuranones bearing α-quaternary centers by photoredox catalysis. The reaction proceeds by the formation of the novel cyclic iodine(III) reagent-allylic alcohol complex, which enables the first alkyl boronate addition and semi-pinacol rearrangement of allylic alcohols with dual alcohol and olefin activation. The reaction is suitable for gram scale synthesis and is transformable to alcohols, olefins, oximes, and lactones with an α-quaternary center in one step.

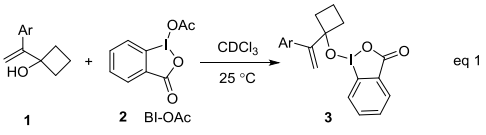
KEYWORDS allylic alcohol, cyclic iodine reagents, quaternary all-carbon center, photoredox catalysis, alkyl boronate

All-carbon quaternary centers are prevalent in bioactive small molecules. However, their efficient construction remains a formidable challenge for synthetic chemists.[1] The allylic alcohols are versatile synthetic building blocks, and the semi-pinacol rearrangement of allylic alcohols provides a valuable entry to synthesize ketones with α-quaternary centers.[2] The transition metals are known to coordinate and activate allylic alcohols for the radical addition/semi-pinacol rearrangement reactions,[3] and the use of heteroatom and stabilized carbon radicals have been reported in these reactions (Scheme 1a).[3c, 3f-h, 4]

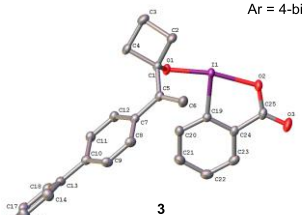


Scheme 1. Transition Metal and Cyclic Iodine Activa-tion of Allylic Alcohols

Hypervalent iodine reagents are widely used oxidants in organic synthesis, among which the cyclic iodine(III) reagents (CIR, such as hydroxybenziodoxoles) demonstrate different and unique transition-metal-like reactivity.[5] Recently, the CIRs are reported to form the CIR-benzyl alcohol complexes under photoredox catalysis conditions for alkoxyl radical generation.[6] We hypothesize the allylic alcohols may also be activated by CIR. However, the CIR-allylic alcohol complex is unknown, and the reactivity of CIRs with allylic alcohols remains unexplored (Scheme 1b). Alkyl boronates are readily available and stable alkyl radical precursors,[7] and the concerted addition/rearrangement of alkyl boronates to allylic alcohols will enable the synthesis of ketones with sterically congested quaternary centers.[8] In this letter, we report the discovery of a novel cyclic iodine(III) reagent-allylic alcohol complex, which enables alkyl boronate addition/rearrangement to allylic alcohols for the synthesis of ketones with quaternary centers (Scheme 1c).



Ar = 4-biphenyl



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We started the investigation by studying the interaction between tertiary allylic alcohol **1** and cyclic iodine(III) reagents acetoxylbenziodoxole (BIOAc) **2**. Upon mixing in chloroform, the ligand exchange reaction occurred on the cyclic iodine(III) center, and the new benziodoxole-vinyl cyclobutanol complex **3** was isolated as an air-stable white solid (eq 1). The X-ray crystallography of **3** showed a new O-I bond formation on the cyclic iodine(III) center. As a result, both the hydroxyl and olefin bond lengths were elongated in the new complex (1.43 and 1.33 Å in **1** to 1.46 and 1.34 Å in **3**). The IR spectra of **3** were measured and indicated that the alkene stretch shifted to lower wavenumbers compared to vinyl cyclobutanol **1**. We also performed the cyclic voltammetry experiments and found the oxidation potential of **3** (E_p = 1.38 V vs SCE in MeCN) was significantly decreased compared to that of **1** (E_p = 1.76 V vs SCE in MeCN). These crystallography, spectrometry and cyclic voltammetry experiments suggest the coordination to the CIR significantly affected both the hydroxyl and olefin groups of allylic alcohols.[9]

We next tested the reaction of alkylboronic acid **4** with vinyl cyclobutanol **1** under $[Ru(bpy)_3](PF_6)_2$ **7** ($E^0_{1/2}{}^{III/II}$ = 1.29 V vs SCE in MeCN) photoredox catalysis conditions. Among various alkyl radical generation methods,[10] the potassium persulfate and noncyclic iodine(III) reagents gave no cyclopentanone product **5** amid little conversion (entries 1-3, Table 1).[11] In contrast, the use of BIOAc **2** gave the desired cyclopentanone **5** in 67% yield, which suggested the critical benziodoxole coordination. In addition, the

[a] State Key Laboratory of Bioorganic and Natural Products Chemistry, Center for Excellence in Molecular Synthesis, Shanghai Institute of Organic Chemistry, University of Chinese Academy of Sciences, Chinese Academy of Sciences, 345 Lingling Road, Shanghai 200032 China.

[b] School of Physical Science and Technology, ShanghaiTech University, 100 Haike Road, Shanghai 201210 China.
E-mail: yiyunchen@sioc.ac.cn

+Dedicated to Professor Xiyan Lu on the occasion of his 90th birthday.

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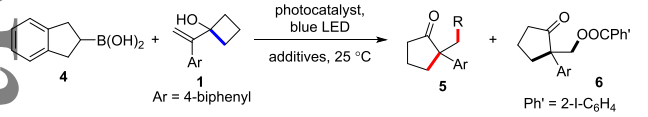
o-iodobenzoate addition adduct **6** was observed in 4% yield (entry 4).[11] The solvent optimization using acetonitrile improved the yield of **5** to 75%, together with an increased 8% yield of **6** (entry 5). The use of $[Ir(dtbbpy)(ppy)_2]PF_6$ **8** ($E^0_{1/2}{}^{IV/III}$ = 1.21 V vs SCE in MeCN) gave **5** in an optimal 89% yield (81% isolated yield, entry 6).[12-13] In contrast, the use of *fac*-Ir(ppy)$_3$ **9** ($E^0_{1/2}{}^{IV/III}$ = 0.77 V vs SCE in MeCN) with low oxidation potential was not effective (entry 7).[8d] We further tested different acetoxylbenziodoxole derivatives (3,4-difluoro acetoxylbenziodoxole (3,4-F-BIOAc) **10** and 3,4-dimethoxy acetoxylbenziodoxole (3,4-MeO-BIOAc) **11** and observed similar reaction outcomes (entries 8-9).[6b, 6c, 14] The photocatalysts and light irradiation were both required for the reaction (entries 10-11).

Table 1 Optimization of the Alkyl Boronate Addition to Allylic Alcohols

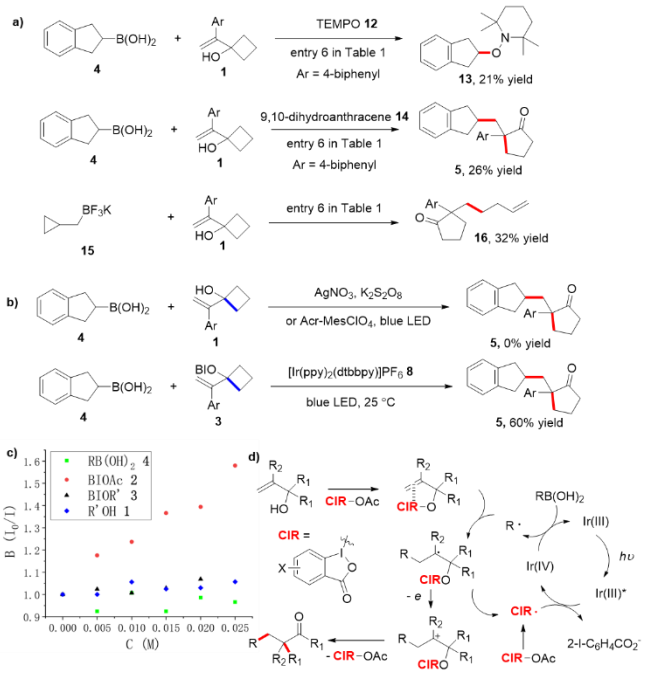


entry	conditions	conversion	yield **5**	yield **6**
1	$[Ru(bpy)_3](PF_6)_2$ **7**, $K_2S_2O_8$, CH_2Cl_2	<10%	<5%	0
2	$[Ru(bpy)_3](PF_6)_2$ **7**, $PhI(OAc)_2$, CH_2Cl_2	<5%	0	0
3	$[Ru(bpy)_3](PF_6)_2$ **7**, $PhI(O_2CCF_3)_2$, CH_2Cl_2	<5%	0	0
4	$[Ru(bpy)_3](PF_6)_2$ **7**, BIOAc **2**, CH_2Cl_2	>95%	67%	4%
5	$[Ru(bpy)_3](PF_6)_2$ **7**, BIOAc **2**, CH_3CN	>95%	75%	8%
6	$[Ir(ppy)_2(dtbbpy)]PF_6$ **8**, BIOAc **2**, CH_3CN	>95%	89% (81%)	0
7	*fac*-Ir(ppy)$_3$ **9**, BIOAc **2**, CH_3CN	<5%	0	0
8	entry 6, 3,4-F-BIOAc **10**	78%	75%	1%
9	entry 6, 3,4-MeO-BIOAc **11**	79%	77%	0
10	entry 6, no [Ir]	<5%	0	0
11	entry 6, no hv	<5%	0	0

[a] Reaction conditions: 4 (0.3 mmol, 1.5 equiv), 1 (0.20 mmol, 1 equiv), and photo-catalysts [Ru] (0.004 mmol, 0.02 equiv) or [Ir] (0.002 mmol, 0.01 equiv) in 2.0 mL solvents under nitrogen with 4 W blue LED irradiation at 25 oC for 36 h, unless otherwise noted. [b] Conversions and yields were determined by 1H NMR analysis, and isolated yields are in parentheses. BI = benziodoxole.

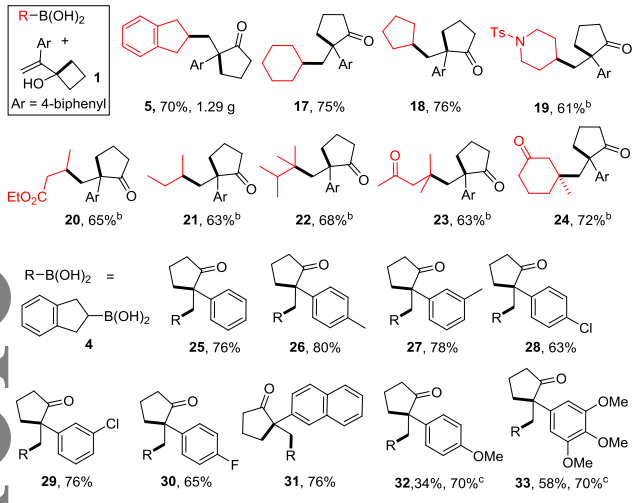
To gain mechanistic insights, we added TEMPO **12** to the optimal reaction conditions and observed the inhibition of the reaction together with the alkyl-TEMPO addition adduct **13** in 21% yield (Scheme 2a).[11] In addition, the radical scavenger 9,10-dihydroanthracene slowed down the formation of **5** to 26% yield.[15] We also use the cyclopropyl methylene trifluoroborate **15** as the radical clock and observed the ring-opening addition product **16** in 32% yield, which is consistent with the radical addition mechanism. We next used the silver salts / persulfates or Fukuzumi catalyst conditions to generate alkyl radicals from alkylboronic acids, and did not observe the desired product **5** (Scheme 2b).[16] In contrast, the use of benziodoxole-vinyl cyclobutanol complex **3** gave **5** in 60% yield, which suggests the essential role of benziodoxole coordination for alkyl boronate additions. We also performed the luminescence quenching experiments and observed BIOAc **2** quenched the photoexcited $[Ir(dtbbpy)(ppy)_2]PF_6$ **8*** most effectively, while the alkylboronic acid **4** was ineffective (Scheme 2c).

Based on the mechanistic investigations above, we propose that $[Ir(dtbbpy)(ppy)_2]PF_6$ is photoexcited to Ir(III)* and oxidized by CIR-OAc or its resulting CIR radical to Ir(IV) (Scheme 2d).[17] The Ir(IV) oxidizes the alkyl boronates for alkyl radical generation,[18] which then undergoes radical addition to the new CIR-allylic alcohol complex, the suitable radical acceptor upon CIR coordination. After the subsequent oxidation to carbocation and polar rearrangement, the substituted ketone with an α-quaternary center is generated. The CIRs have triple roles for the desired reaction pathway: *i)* the redox-active reactivity for the alkyl radical formation and the cation intermediate formation, *ii)* the activation of the allylic alcohol, and *iii)* the *in situ* protection of alcohols for the inhibition of the epoxide formation.[19]



Scheme 2. Mechanistic Investigations and Proposals

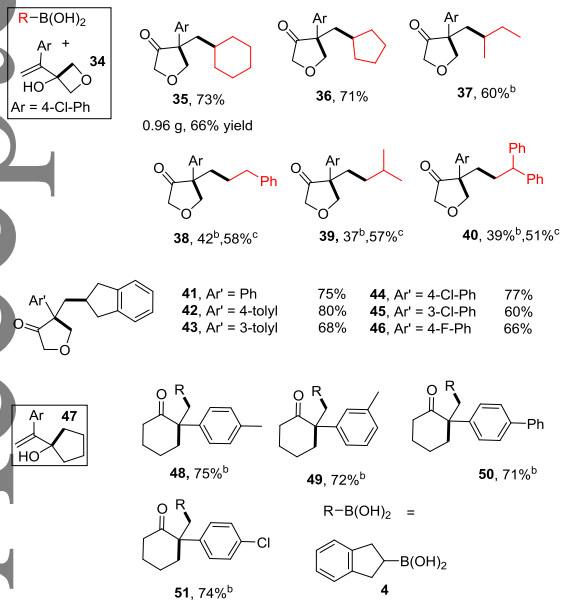
We next explored the alkyl boronate scope for the reaction (Scheme 3). The gram scale reaction of the model substrates **1** and **4** gave cyclopentanone **5** in 1.29 g in 70% yield. Various cyclohexyl, cyclopentyl, and tosylpiperidinyl boronates all worked well to give substituted cyclopentanones **17**-**19** in 61-76% yields. The noncyclic alkyl boronates reacted smoothly to give **20**-**21** in 63-65% yields. Notably, tertiary alkyl boronates reacted uneventfully to give **22**-**24** with two quaternary centers in 63-72% yields. We also prepared different vinyl cyclobutanol derivatives, which could be obtained easily in two steps from commercially available methyl ketones.[4a] These various aryl substitutions did not affect the reaction to give **25**-**31** in 63-80% yields. The vinyl cyclobutanols substituted with electron-rich methoxyl groups yielded **32** and **33** in 34% and 58% yields, respectively, together with o-iodobenzoate addition adducts. In this regard, 3,4-MeO-BIOAc **11** gave **32** and **33** in improved 70% and 70% yields, respectively.[20]



[a]Reaction conditions: entry 6 in Table 1, [b]3 equiv of alkyl boronates, [c]3,4-MeO-BIOAc used.

Scheme 3. Substrates Scope of Vinyl Cyclobutanols[a]

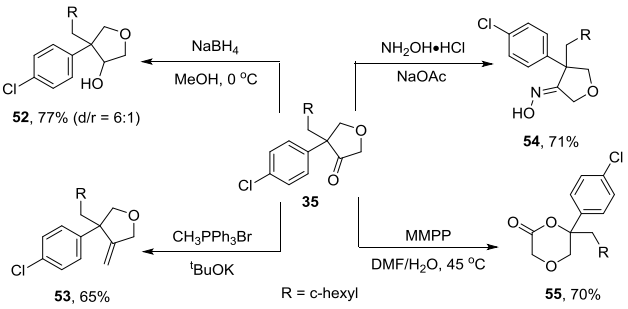
We then challenged the vinyl oxetanol **34** for alkyl boronate addition/rearrangements, which are difficult substrates for previously reported transition-metal-catalyzed reactions to synthesize dihydrofuranones (Scheme 4).[4a-h] Various alkyl boronates reacted smoothly to give dihydrofuranones with α-quaternary centers **35**-**40** in 51-73% yields, including the gram scale reaction of **35** in 0.96 g in 66% yield.[21] Methyl, phenyl, chloride, and fluoride substitutions on the vinyl oxetanols were all tolerated and did not affect the reactions, providing **41**-**46** in 60-80% yields. The reaction is not limited to strained vinyl cyclobutanols, and vinyl cyclopentanol **47** reacted uneventfully to give substituted cyclohexanones **48**-**51** in 71-75% yields.[4a]



[a]Reaction conditions: entry 6 in Table 1, [b]3 equiv of alkyl boronates. [c]$Ru(bpy)_3(PF_6)_2$ was used in condition b.

Scheme 4. Substrates Scope of Allylic Alcohols[a]

To demonstrate the synthetic potential of this alkyl radical addition/rearrangement reaction, we performed post-synthetic modifications of the dihydrofuranone **35** (Scheme 5). Sodium borohydride treatment yielded the dihydrofuran-2-ol **52** in 77% yield (d/r = 6/1); the Wittig reaction afforded the dihydrofuran with an exocyclic olefin **53** in 65% yield; the hydroxyamine addition provided the oxime **54** in 71% yield; and the Baeyer-Villiger oxidation resulted in the ring-expanded dioxan-2-one **55** in 70% yield. It is worth noting that dihydrofuranones with sterically congested quaternary centers are difficult to synthesize by other methods, and subsequent derivation provides an expedient synthetic route for these structurally diverse and difficult-to-approach molecules.



Scheme 5. Post-Synthetic Transformations of Dihydrofuranones

Conclusions

In conclusion, we have developed the first CIR-enabled ketone synthesis with α-quaternary centers by alkyl boronate addition/rearrangement reactions under photoredox conditions. The cyclic iodine(III) reagents formed the novel CIR-allylic alcohol complexes, which are critical to the alkyl boronate addition, polar rearrangements, and *in situ* alcohol protection, and provided complementary reactivity comparing to transition metals. The tunable reactivity of CIRs with alcohols for alkoxyl radical generation or alkyl radical addition to allylic alcohols demonstrate the versatile reactivity of CIR. Further investigations are underway in our laboratory.

Supporting Information

The supporting information for this article is available on the WWW under https://doi.org/10.1002/cjoc.2018xxxxx.

Acknowledgement

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[11] See supporting information for details.

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[18] The oxidation of alkylboronic acids by photoexcied Ir(III)* was unlikely, see Supporting Information for details.

[19] The formation of oxirane in the reaction mixture was less than 5%. In addition, when the oxirane was added to the reaction conditions, the ring-opening adduct was only obtained in 32% yield after 36 hours. The oxirane may be the reaction intermediate, however, it is not the major reaction pathway.

[20] The use of 3,4-MeO-BIOAc **8** with lower oxidation potential slowed down the reaction of BI-allylic alcohol complex with Ir(IV) for intramolecular o-iodobenzoate addition, see ref. 6b,c.

[21] The $[Ru(bpy)_3](PF_6)_2$ was required with some primary alkyl boronates due to their higher oxidation potentials.

[22] CCDC 1868549 (**3**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www. Ccdc.cam.ac.uk/data_request/cif.

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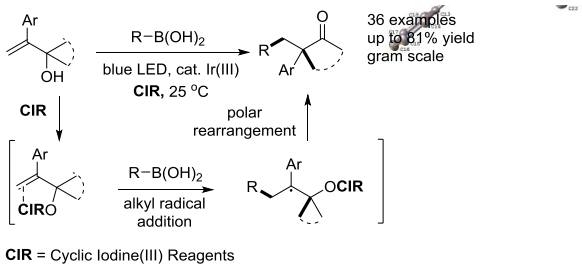

Here we report cyclic iodine(III) reagents enable the synthesis of cyclopentanones, cyclohexanones, and dihydrofuranones bearing α-quaternary centers by photoredox catalysis. The reaction proceeds by the formation of the novel cyclic iodine(III) reagent-allylic alcohol complex, which enables the first alkyl boronate addition and semi-pinacol rearrangement of allylic alcohols with dual alcohol and olefin activation.