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ARTICLE

Effect of Noncovalent Interactions in Ion Pairs on Hypervalent Iodines: Inversion of Regioselectivity in Sulfonyloxylactonization

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We synthesized novel hypervalent iodines possessing cationic heterocyclic moieties nearby the iodine(III) center. The novel hypervalent iodines exhibited a totally different regioselectivity from common $PhI(OAc)_2$ during the sulfonyloxylactonization of 2-vinylbenzoic acids. The noncovalent interactions between the sulfonyloxy groups and the cationic heterocyclic moieties resulted in a significant change in the regioselectivity, which was revealed by the observation of intermediates and density functional theory studies including noncovalent interaction analysis.

Introduction

Organic hypervalent iodine compounds work as efficient oxidants and perform unique oxidative functionalizations of various substrates such as alkenes, ketones, and alkanes.[1] Modifications of the carbon backbones in organic hypervalent iodines strongly improved their properties such as stability, reactivity, and selectivity. Typically, the inductive effect of substituents is used for tuning the oxidizability (Fig. 1a).[1] The coordination of functional groups to an iodine center not only enhances stability and solubility (Fig. 1b).[2,3] The asymmetric induction effect by various types of chiral auxiliaries or chiral organic backbones has achieved enantioselective oxidative reactions (Fig. 1c).[1,4] For example, Ishihara and Muñiz reported that the hydrogen bond between an amide NH group in a chiral auxiliary and an AcO group located at the iodine center generated an effective reaction field for an asymmetric oxidation of alkenes.[5] Recently, Jacobsen, Sigman, Houk, and Xue revealed that multiple attractive non-covalent interactions, including CH-π and π-π interactions, between styrene substrates and the hypervalent iodine framework contributed to asymmetric induction in difluorinations of styrenes (Fig. 1d).[6] As described above, hypervalent iodine chemistry has progressed with the establishment of control methods of the properties and reaction fields. Therefore, to pioneer a novel area in tactics for the achievement of selective reactions with hypervalent iodine reagents has been of great significance even now. Recently, the control of regio- or stereoselectivity via noncovalent interactions in designed ion pairs has made amazing successes

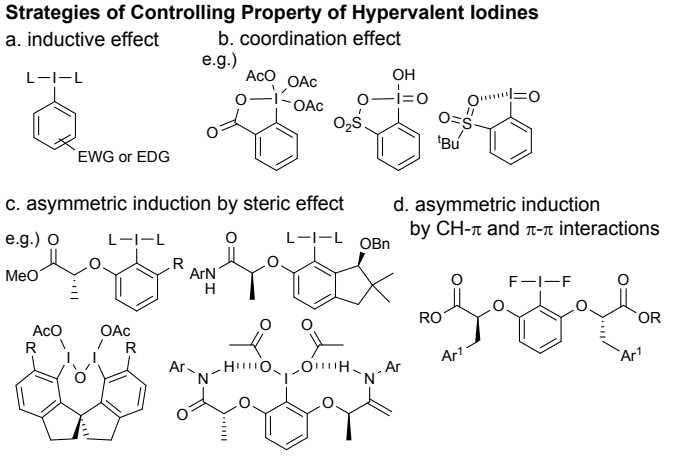

Fig. 1 Control of reaction fields on hypervalent iodines

in various fields such as transition metal catalysis,[7] phase-transfer catalysis,[8] counteranion-directed catalysis,[9] and ion-paring catalysis[10] because the noncovalent attractive forces in ion pairs are mainly constructed by electrostatic and induction interactions to be considerably long-range and strong by comparison with other noncovalent forces.[11] In hypervalent iodine chemistry, only Breslow reported a C-H chlorination of steroids catalyzed by an ion-paired template (Fig. 2a), wherein a regioselective chlorination is accelerated by the generation of ion pairs between ammonium and sulfonate moieties attached on steroids and hypervalent iodines.[12] Despite a large potential indicated by Breslow, other reaction systems via noncovalent attractive forces in ion pairs has been underdevelped even now. Thus, we envisioned the application of the noncovalent interactions in ion pairs to a dual functionalization of alkenes using two different nucleophiles (Nu^1 and Nu^2) which is a significant reaction in hypervalent iodine chemistry (Fig. 2b).[1,4] The control of regioselectivity in the addition of nucleophiles to iodonium intermediates is a vital issue for the success of a selective double functionalization (Fig. 2b, key step for

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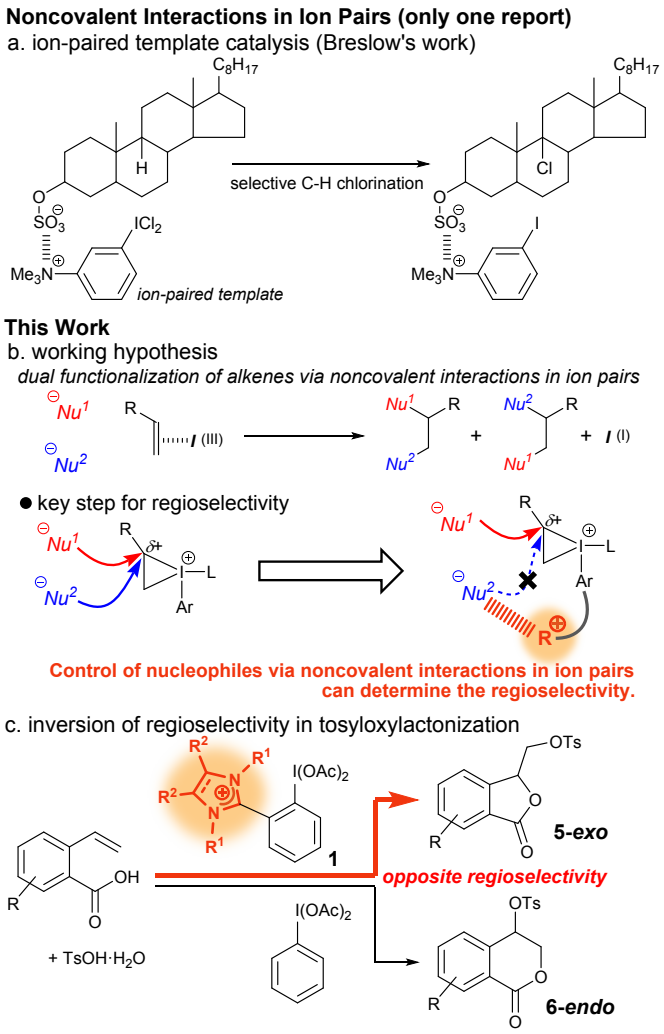


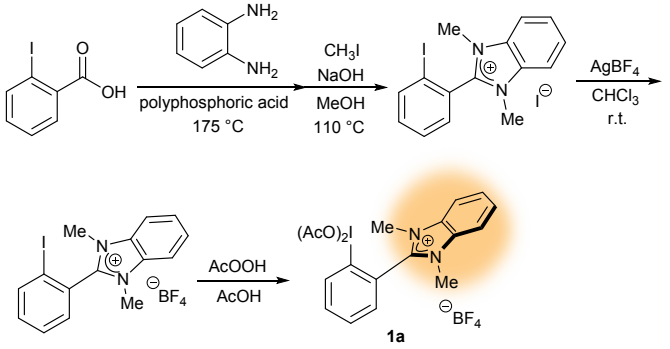
Fig. 2 Noncovalent interactions in ion pairs in hypervalent iodines

regioselectivity).[13] In our working hypothesis, noncovalent interactions between anionic nucleophiles (Nu^2) and the cationic substituents (R^+) of hypervalent iodine molecules affect the nucleophilicity in order to control regioselectivity. Herein, we report the synthesis of novel λ³-iodanes **1** bearing cationic nitrogen-containing heterocyclic moieties nearby the iodine(III) center (Fig. 2c). These hypervalent iodines and $PhI(OAc)_2$ exhibited an opposite regioselectivity in the sulfonyloxylactonization of 2-vinylbenzoic acids **2**. This is the first report of the control of regioselectivity by noncovalent interactions in dual functionalization of alkenes with hypervalent iodine reagents, which has enormous implications in terms of revealing the role of noncovalent interactions in hypervalent iodine-mediated reaction systems.

Results and discussion

We chose imidazolium structures as cationic moieties because of tolerance to oxidative conditions using hypervalent iodines.[14] Targeted $ArI(OAc)_2$ **1a** bearing an imidazolium moiety at the *ortho*-position in the ArI structure was prepared from commercially available 2-iodobenzoic acid by conventional methods (Scheme 1).[14] X-ray diffraction analysis of **1a** (Fig. 3) shows that the structure around the iodine atom adopts a T-shaped geometry with the benzene ring, which is located in a plane of the trigonal bipyramidal structure that occupies an equatorial position. Apical positions are occupied by AcO groups and both carbonyl oxygens coordinate to the iodine center. BF_4^- locates near the imidazolium moiety in a solid state. The imidazolium plane is almost perpendicular to the benzene ring.

By investigating various oxidative functionalizations using **1a**, we discovered that **1a** exhibited an interesting regio-divergence in tosyloxylactonization of 2-vinylbenzoic acids (Table 1). Fujita reported that asymmetric lactonization using *p*-toluenesulfonic acid (TsOH) and chiral iodoarene diacetate proceeded in a 6-*endo* cyclization fashion.[15] We performed lactonization using $PhI(OAc)_2$ and TsOH to preferentially obtain the 6-*endo* product **3a**, which is similar to that of Fujita's reagent (**4a**/**3a** = 17:83) (Entry 1). Generally, ArI(OTs)OH generated in situ is considered an intermediate in tosyloxylation using TsOH and iodoarene diacetates.[16] Examining Koser's reagent PhI(OTs)OH, the same regioselectivity as $PhI(OAc)_2$/TsOH was observed (Entry 2).[17] To our delight, synthesized hypervalent iodine **1a** exhibited a regioselectivity that was quite different from common hypervalent iodines to produce 5-*exo* **4a** in high-selectively



Scheme 1 Synthetic route of $ArI(OAc)_2$ **1a** bearing imidazolium moiety at *ortho*-position

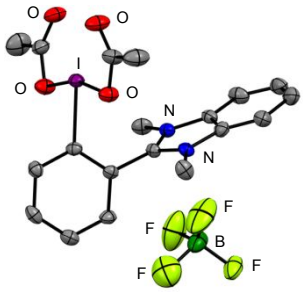
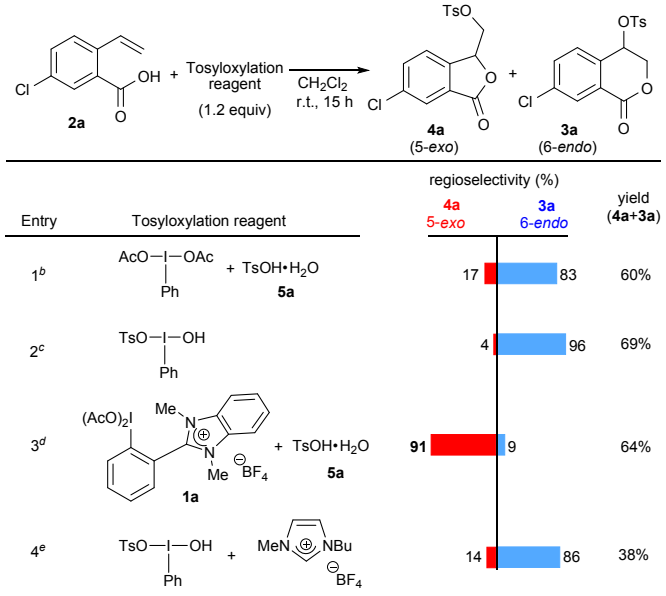


Fig. 3 ORTEP drawing of **1a**

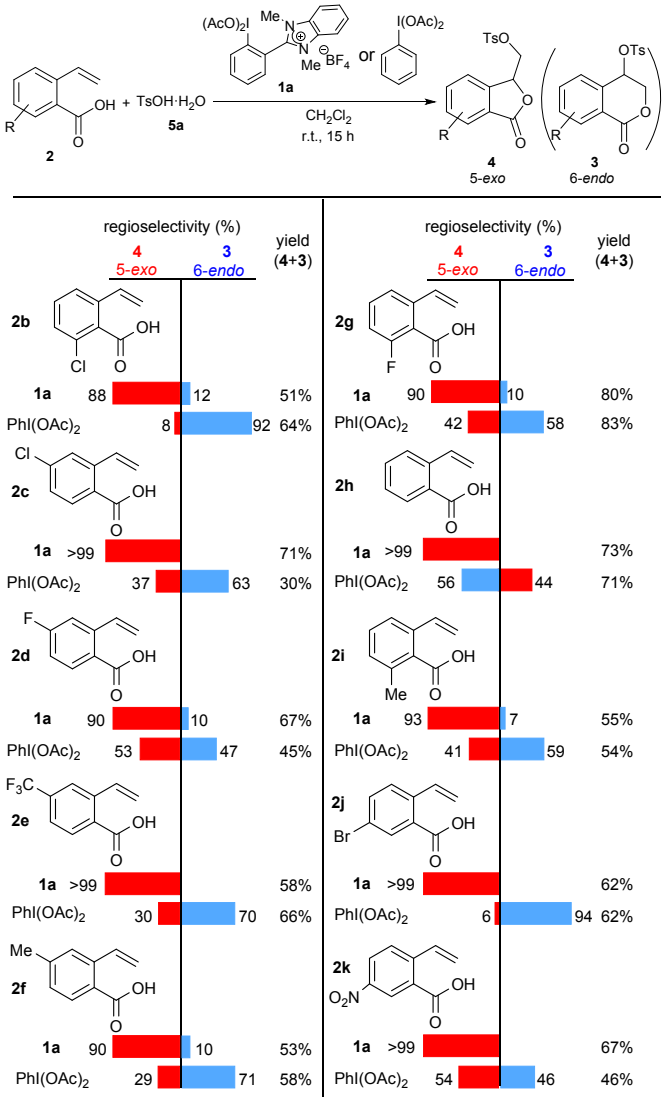
Table 1 Comparison of **1a** with common hypervalent iodine reagents on the regioselectivity of tosyloxylactonization of 2-vinyl benzoic acid **2a**[a]



[a]**2a** (0.15 mmol), CH_2Cl_2 (0.5 M), room temperature, 15 h. [b]$PhI(OAc)_2$ (0.18 mmol), $TsOH{\cdot}H_2O$ **5a** (0.15 mmol). [c]PhI(OTs)OH (0.18 mmol). [d]**1a** (0.18 mmol), $TsOH{\cdot}H_2O$ **5a** (0.15 mmol). [e]PhI(OTs)OH (0.18 mmol), *N*-butyl-*N*-methylimidazolium tetrafluoroborate (0.65 mmol).

(**4a**/**3a** = 91:9) (Entry 3).[18] Even when $CHCl_3$, PhCl, $ClCH_2CH_2Cl$, or CH_3CN instead of CH_2Cl_2 was used as solvents, **1a** and $PhI(OAc)_2$ exhibited the high level of 5-*exo* selectivity and 6-*endo* selectivity, respectively, regardless of the permittivity (Scheme S16 in ESI). In addition, we confirmed that the isomerization between 5-*exo* **4a** and 6-*endo* **3a** did not occur under tosyloxylactonization conditions (Scheme S18 in ESI). 1-Butyl-3-methylimidazolium tetrafluoroborate was used as an additive in the tosyloxylation of **2a** using PhI(OTs)OH, and preferentially afforded 6-*endo* **3a** (Entry 4). The selectivity (**4a**/**3a** = 14:86) approximated that in a no-additive examination (Entry 2). Thus, an outer-sphere cationic unit is ineffective and the intramolecular imidazolium moiety influences the change in regioselectivity.

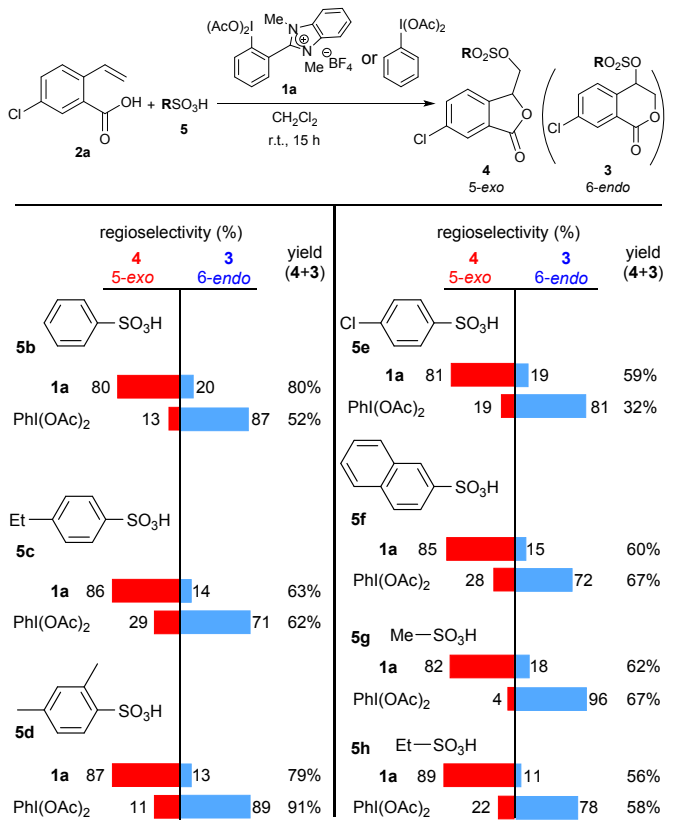
Table 2 Scope of 2-vinyl benzoic acids in 5-*exo* tosyloxylactonization using **1a**[a]



[a]Method with **1a**: **2** (0.15 mmol), **1a** (0.18 mmol), **5a** (0.15 mmol), CH_2Cl_2 (0.5 M), room temperature, 15 h. Method with $PhI(OAc)_2$: **2** (0.15 mmol), $PhI(OAc)_2$ (0.18 mmol), **5a** (0.15 mmol), CH_2Cl_2 (0.5 M), room temperature, 15 h.

Various 2-vinylbenzoic acids **2** underwent tosyloxylactonization mediated by **1a** to give 5-*exo* products **4** with high selectivity (Table 2). The present 5-*exo* cyclization was compatible to functional groups as demonstrated for fluoro (**2d** and **2g**), chloro (**2b** and **2c**), bromo (**2j**), trifluoromethyl (**2e**), and nitro (**2k**) ones. The cyclization of electron-neutral (**2h**), electron-rich (**2f** and **2i**), and electron-deficient substrates (for example, **2e** and **2k**) proceeded with high 5-*exo* selectivity in moderate to high yields. When $PhI(OAc)_2$ was applied to the tosyloxylation of these substrates (**2b**-**2k**), the cyclization did not exhibit high 5-*exo* selectivity but resulted either in 6-*endo* or in no selectivity.

Table 3 Scope of sulfonic acids in 5-*exo* sulfonyloxylactonization using **1a**[a]

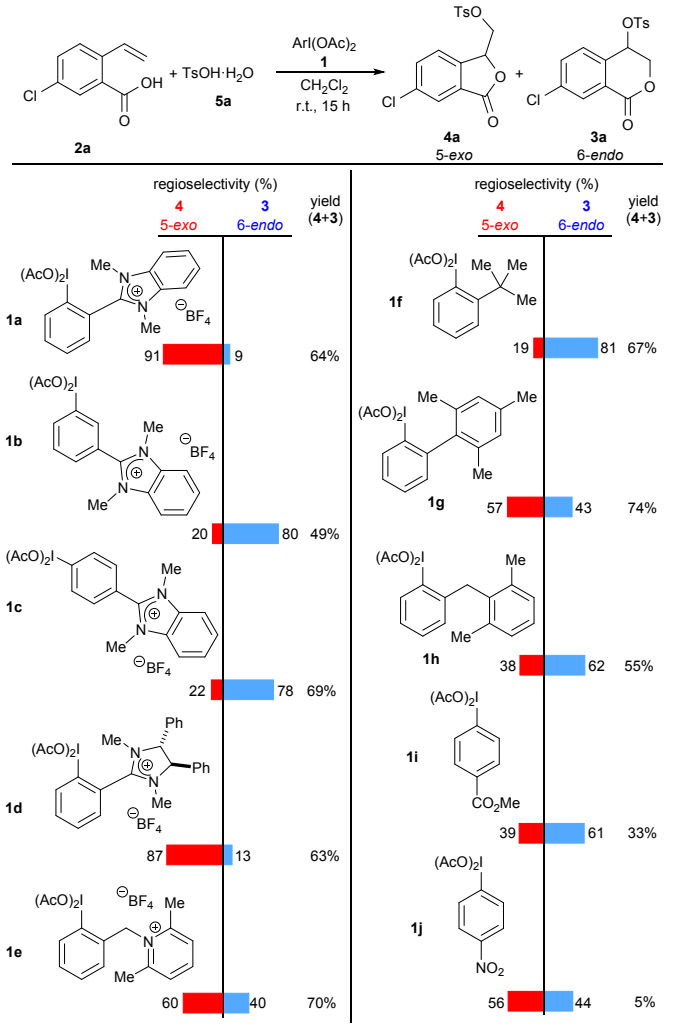


[a]Method with **1a**: **2** (0.15 mmol), **1a** (0.18 mmol), **5** (0.15 mmol), CH_2Cl_2 (0.5 M), room temperature, 15 h. Method with $PhI(OAc)_2$: **2** (0.15 mmol), $PhI(OAc)_2$ (0.18 mmol), **5** (0.15 mmol), CH_2Cl_2 (0.5 M), room temperature, 15 h.

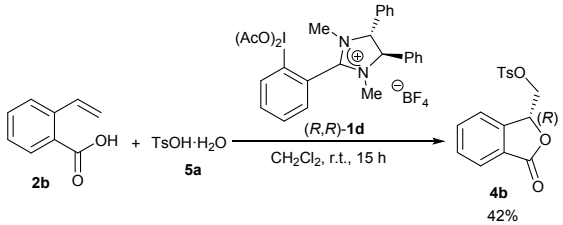
The generality of sulfonic acids in 5-*exo* cyclization using **1a** was examined (Table 3). Benzene-, *p*-ethylbenzene-, *m*-xylene-, 4-chlorobenzene-, naphthalenesulfonic acids (**5b**, **5c**, **5d**, **5e**, and **5f**) as well as TsOH selectively gave the corresponding 5-*exo* products **4**. Alkanesulfonic acids **5g** and **5h** were applicable to 5-*exo* selective cyclization. It is noted that $PhI(OAc)_2$ selectively led to 6-*endo* products in reactions using these sulfonic acids in contrast to **1a** in all cases.

To reveal the effect that the imidazolium moiety exerts on regioselectivity, various types of $ArI(OAc)_2$ were applied to the tosyloxylation (Table 4). In contrast to **1a**, regioisomers **1b** and **1c** bearing an imidazolium unit at *meta*- and *para*-positions, respectively, exhibited 6-*endo* selectivity. These results indicate that the structural arrangement between the iodine atom and the imidazolium moiety is an important factor for regioselectivity. The imidazolidinium moiety also worked as a trigger to lead to 5-*exo* selectivity (**1d**). $ArI(OAc)_2$ **1e** with a 2,6-dimethylpyridinium moiety at the *ortho*-position via a methylene spacer gave 5-*exo* **4a** although the selectivity was slightly decreased. The imidazolium moiety could be recognized as bulky and electron-withdrawing, and thus steric and inductive effects were investigated. Regardless of the steric hindrance of *t*Bu group, $ArI(OAc)_2$ **1f** gave 6-*endo* selectivity that was the same as that of $PhI(OAc)_2$. *ortho*-Mesityl-substituted $ArI(OAc)_2$ **1g** afforded 5-*exo* **4a** in slightly preference to 6-*endo* **3a**, and the selectivity was quite low. A 2,6-dimethylphenyl moiety (**1e**) was compared with a 2,6-dimethylphenyl moiety (**1h**) connected by a methylene spacer, and the regioselectivities were divergent despite having the same steric

Table 4 Effects of substituents on the benzene skeleton of $ArI(OAc)_2$[a]



[a]**2a** (0.15 mmol), **1** (0.18 mmol), **5a** (0.15 mmol), CH_2Cl_2 (0.5 M), room temperature, 15 h.



Scheme 2 Enantioselective tosyloxylactonization using optically active hypervalent iodine (*R,R*)-**1d**.

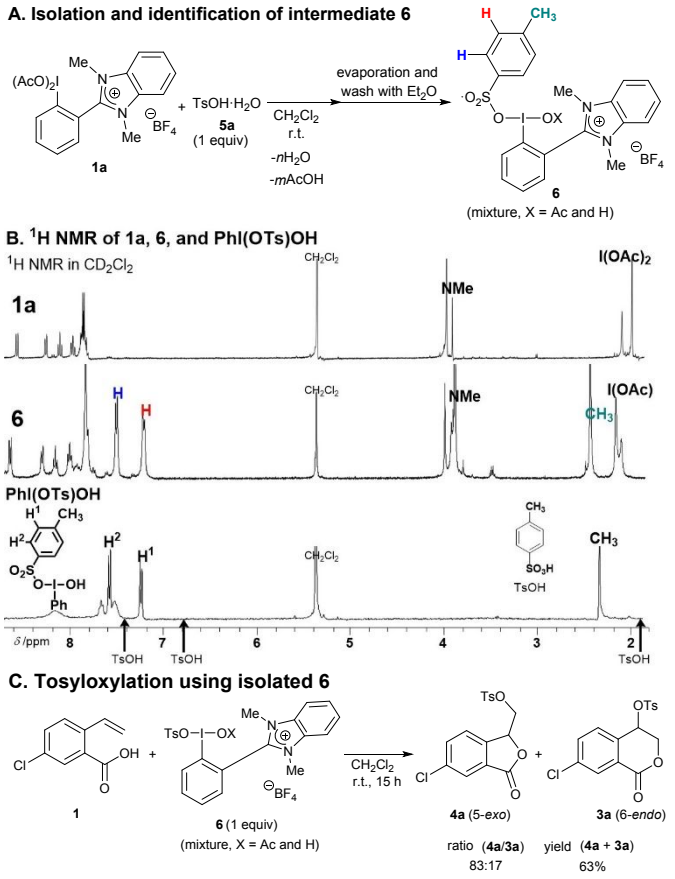


Fig. 4 Observation, isolation and reactivity of intermediate **6**

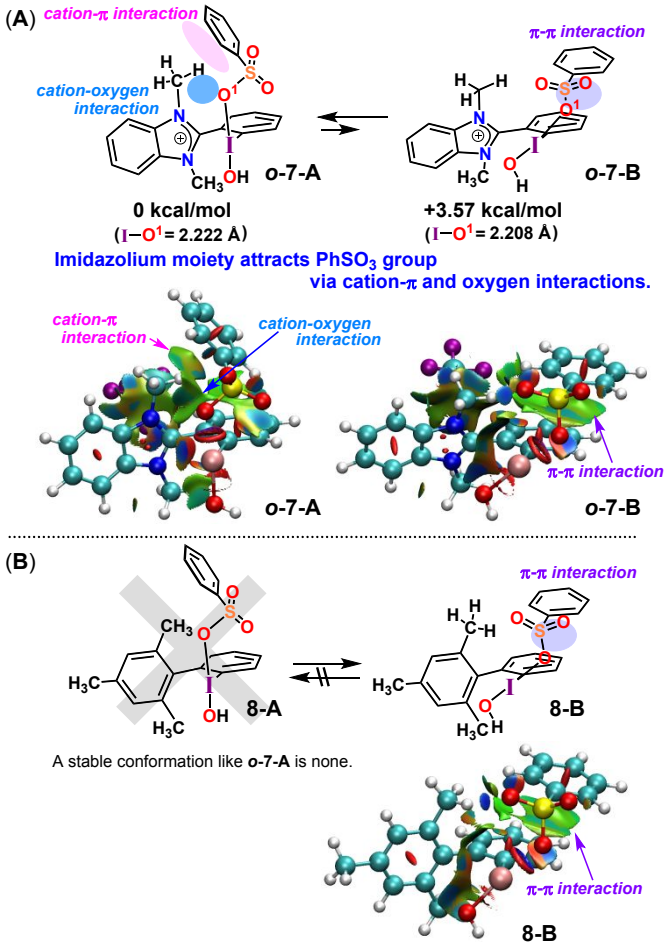
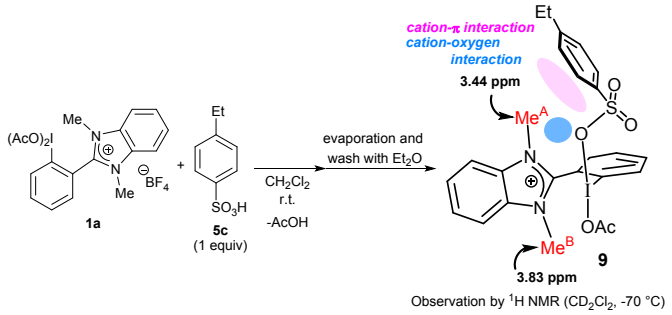


Fig. 5 Noncovalent interaction analysis for selected conformers of ArI(OH)OSO$_2$Ph **7**, **8**, and **9**. Color code for NCI analysis: red, repulsive; blue, attractive.



Scheme 3 Anisochronous two Me groups of ArI(OAc)(*p*-Et$C_6H_4SO_3$) **9** in ^{1}H NMR spectroscopy

hindrance; **1e** and **1h** exhibited 5-*exo* and 6-*endo* selectivity, respectively. Thus, the steric hindrance is not a critical factor in 5-*exo* selectivity. *para*-Substituents were investigated to verify electron-withdrawing effects, in which we adopted the *para*-position to avoid steric and coordination effects on the iodine center. The main product of *para*-(MeO)CO-substituted ArI(OAc)$_2$ **1i** was 6-*endo* **3a**. The examination of NO_2 group-substituted ArI(OAc)$_2$ **1j** resulted in a very low yield with no regioselectivity. Therefore, we established that the electron-withdrawing substituents on a phenyliodane backbone do not lead to effective 5-*exo* selectivity. These results suggested the importance of cationic moieties near the iodine(III) center in a manifestation of 5-*exo* cyclization. 2-Vinyl benzoic acid **2b** was subjected to the reaction conditions with optically active hypervalent iodine (*R*,*R*)-**1d** (Scheme 2). The corresponding 5-*exo* product **4b** was obtained in 69:31 e.r., which suggests the cationic nitrogen-containing heterocycle worked as a chiral auxiliary.

The reaction of ArI(OAc)$_2$ with TsOH·H_2O generally produces ArI(OTs)OX (X = Ac or H) species that serve as intermediates in various reactions.[1] When **1a** and TsOH·H_2O were mixed in CH_2Cl_2, the generation of AcOH was confirmed by in situ ^{1}H NMR (Scheme S1 in ESI). After evaporation of the volatiles and washing with Et_2O, the mixture of ArI(OTs)OH and ArI(OTs)OAc (= ArI(OTs)OX **6**) was isolated (Fig. 4A). The ^{1}H NMR spectra in Fig. 4B compares ArI(OTs)OX **6** with **1a** and PhI(OTs)OH.

Chemical shifts of the Ts signals in **6** differed from those of TsOH but were quite similar to those of PhI(OTs)OH. According to the spectra comparison, ArI(OTs)OX **6** is considered an intermediate. In fact, the tosyloxylation of **2a** using isolated **6** afforded almost the same result as that of the **1a**/TsOH·H_2O system (Fig. 4C and Scheme S3 in ESI).[19]

To gain insights into intermediate **6**, a density functional theory study (see ESI for full details) was performed with ArI(OH)OSO$_2$Ph ***o*-7** (Ar = 2-benzoimidazoliumylphenyl) used as a model of **6** (Fig. 5A). The ***o*-7** has two energetic local minimums, and conformer ***o*-7-A** is more stable than ***o*-7-B** by 3.57 kcal/mol. Noncovalent interaction analysis[20] shows that in

***o*-7-A** the Me group of the imidazolium moiety and the phenyl ring of the $PhSO_3$ group generates a cation–π interaction surface.[21,22,23] In addition, the same Me group forms an effective cation-oxygen interaction[10] with the oxygen atom of the $PhSO_3$ group, which is evident from the large isosurface. In minor conformer ***o*-7-B**, the π–π interaction of the $PhSO_3$ group with the iodobenzene framework helps stabilize the conformation. Notably, the I-O^1 bond of ***o*-7-A** (2.222 Å) is elongated by comparison with that of ***o*-7-B** (2.208 Å), which suggests that the iodine center in ***o*-7-A** is activated via the noncovalent interactions between the imidazolium moiety and the $PhSO_3$ group. In contrast to ***o*-7**, the most stable conformers of other regioisomers, *meta*-substituted ***m*-7** and *para*-substituted ***p*-7**, are the structures involving a π–π interaction like ***o*-7-B** (Schemes S25, S26, and S30 in ESI). This type of π–π interaction is a main factor in stabilizing the conformation of Koser-type reagents supported by crystalline structures,[24] and calculation studies.[25]

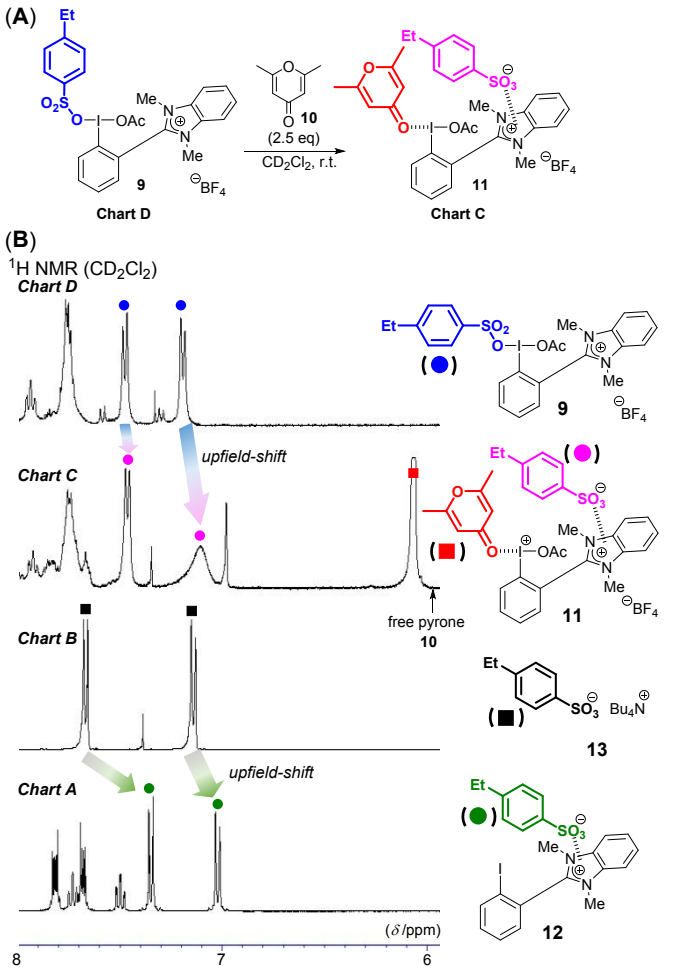
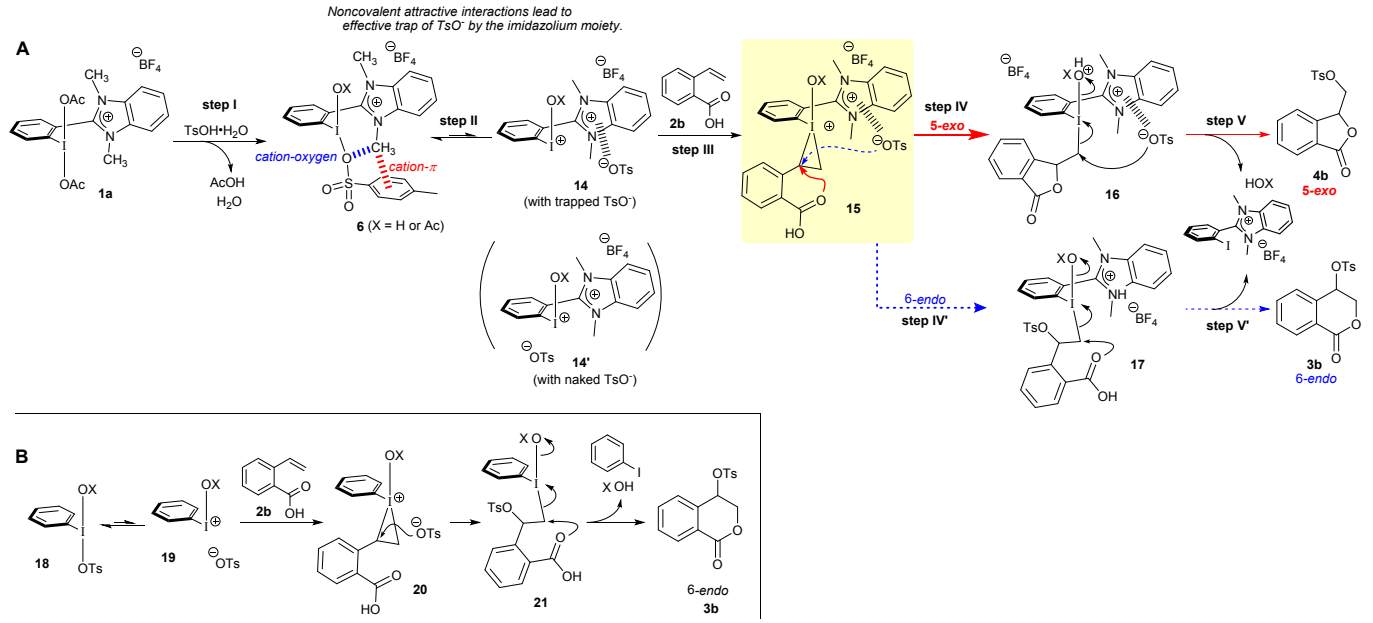


Fig. 6 (A) Reaction of ArI(OAc)OSO_2(4-EtPh) **9** with γ-pyrone **10** to give complex **11**. (B) Chart A: Bu_4N·4-EtPhSO_3 **13**. Chart B: Imidazolium 4-ethylbenzenesulfonate **12**. Chart C: Complex **11** generated from **9** with γ-pyrone **10**. Chart D: ArI(OAc)OSO_2Ph **9**.



Scheme 4 Proposed reaction mechanisms.

Additionally, we calculated the conformation of mesityl-substituted **8**, which has almost the same steric demand around the iodine atom as that of ***o*-7** (Fig. 5B). A local-minimum conformer possessing efficient interactions of mesityl and $PhSO_3$ groups like **8-A** was not found, and the optimized conformer **8-B** includes a π–π interaction like ***o*-7-B**. Thus, it is quite unusual that ***o*-7-A** would be a more stable conformer than ***o*-7-B** with a π–π interaction, which indicates that only the imidazolium moiety at the *ortho* position favorably attracts the $PhSO_3$ group via cation–π and cation-oxygen interactions.[26] When ArI(OAc)(*p*-$EtC_6H_4SO_3$) **9**, which was generated from the reaction of **1a** with 4-$EtC_6H_4SO_3H$[27], was observed by ^1H NMR spectroscopy, the two Me groups on nitrogen atoms are anisochronous and each of singlet signals appear at 3.44 and 3.83 ppm (Scheme 3).[28] The signal of Me^A group interacting with *p*-$EtC_6H_4SO_3$ group would shift upfield compared with that of Me^B group due to cation-π interactions.[29]

Tsuzuki revealed strong noncovalent attractive forces in ion pairs such as imidazolium trifluoromethanesulfonate by ab initio calculation, and found that electrostatic and induction interactions were contributors.[10] Thus, we thought, in the present sulfonyloxylactonization, the sulfonyloxy anion dissociating from the iodine atom and acting as a nucleophile was restrained by noncovalent interactions with the imidazolium moiety. Generally, sulfonyloxy groups on iodine(III) atoms are kicked out either by intramolecular coordinative functional groups or by external ligands.[30] Thus, when adding γ-pyrone **10** as an external ligand, we observed the behavior of the 4-$EtC_6H_4SO_3$ group of **9** by using ^1H NMR spectroscopy (Fig. 6A). Imidazolium sulfonate **12** was used as a reference compound to evaluate the interaction of the imidazolium cation with 4-$EtC_6H_4SO_3^-$ because two kinds of protons of the benzene ring of the 4-$EtC_6H_4SO_3$ group in **12** appear at a more upfield than those in Bu_4N salt **13** (Fig. 6B, Charts A and B).[31,32] The treatment of **9** (Chart D) with γ-pyrone **10** as an external ligand caused a downfield shift of signals of **10**, which shows that the carbonyl oxygen coordinated to the iodine center (Chart C).[33] More importantly, signals of the 4-$EtC_6H_4SO_3$ group appeared in a more upfield compared with those of **9**, and the chemical shift values approximated those of **12**.[34] Therefore, these results suggest that 4-$EtC_6H_4SO_3^-$ is kicked out and trapped by a noncovalent interaction with the imidazolium moiety, which generates complex **11**.[30d,35]

We propose a plausible reaction mechanism based on mechanistic studies (Scheme 4A). $ArI(OAc)_2$ **1a** reacts with $TsOH{\cdot}H_2O$ to give ArI(OTs)OX **6** (X = H or Ac) (step I).[36] Notably, the imidazolium moiety strongly attracts the TsO group via cation-π and cation-oxygen interactions in **6** (Fig. 5A). The noncovalent attractive interactions lead to abstraction and effective trap of TsO^- by the imidazolium moiety to generate the more electrophilic species **14** with trapped TsO^- (step II), and disturb the generation of **14´** with naked TsO^-. The electrophilic addition of **14** to the alkene moiety of **2b** gives iodonium intermediate **15** (step III).[37] A nucleophilic attack of the carboxyl group prior to TsO^- occurs at the benzylic carbon atom to afford intermediate **16** (step IV) because TsO^- is trapped by noncovalent attractive forces of the imidazolium moiety, which is supported by the experimental results shown in Fig. 6. Finally, a substitution of the iodine atom by TsO^- produces 5-*exo* **4b** (step V). In the case of step IV', a substitution of the iodine atom by the TsO^- in **15** gives intermediate **17**, and 6-*endo* **3b** is afforded as a minor product (step V'). On the other hand, a path involving species **14´** with naked TsO^- could be also possible, giving 6-*endo* **3b** because naked TsO^- in prior to the carboxyl group can attack iodonium intermediate **15**. But, the noncovalent attractive interactions in **6** lead to effective trap of TsO^- to disturb the generation of **14´**. Therefore, the noncovalent attractive interactions between TsO and imidazolium moieties in **6** is critical to the regioselectivity. In the present sulfonyloxylactonization, carboxylic acids with electron-withdrawing groups gives excellent regioselectivity, and the regioselectivity in the reactions using carboxylic acids with electron-donating groups is slightly decreased (Table 2). Electron-donating groups in carboxylic acids enhance the stability of the corresponding iodonium intermediate to increase the rate of steps IV and IV´ so the regioselectivity slightly deteriorates. In the case of PhI(OTs)OX **18** (Scheme 4B), naked TsO^- preferentially attacks the iodonium moiety in intermediate **20** to give 6-*endo* **3b**. Therefore, the trapping of TsO^- by noncovalent interaction with the cationic imidazolium moiety significantly changes the reaction course.

Conclusions

In conclusion, we discovered that the noncovalent interaction between the sulfonyloxy group and the cationic nitrogen-containing heterocyclic moiety substituted in the hypervalent iodines caused specific regioselectivity in the sulfonyloxylactonization of 2-vinyl benzoic acids. Hypervalent iodines bearing an imidazolium moiety exhibited 5-*exo* cyclization selectivity in contrast to the 6-*endo* selectivity shown by $PhI(OAc)_2$. ^1H NMR spectroscopy established ArI(OTs)OX **6** as the intermediate. DFT studies clarified the trapping of the sulfonyloxy group by the imidazolium moiety via noncovalent interactions such as cation-π and cation-oxygen interactions, which allowed a significant change in regioselectivity.

Conflicts of interest

There are no conflicts to declare.

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