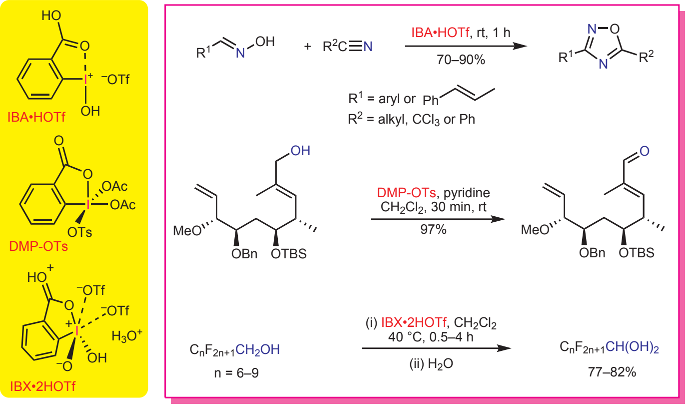
# Benziodoxole-Derived Organosulfonates: The Strongest Hypervalent Iodine Electrophiles and Oxidants

Mekhman S. Yusubov[a]
Pavel Postnikov[a]
Akira Yoshimura[a,1]
Viktor V. Zhdankin*[b]

[a] Research School of Chemistry and Applied Biomedical Sciences, Tomsk Polytechnic University, 634050 Tomsk, Russian Federation
[b] Department of Chemistry and Biochemistry, University of Minnesota Duluth, Duluth, MN 55812, USA
vzhdanki@d.umn.edu



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**Abstract** This account describes the development of organosulfonyloxy-substituted iodine(III) and iodine(V) benziodoxole derived reagents, which are thermally stable compounds with useful reactivity patterns. Iodine(III) benziodoxoles and pseudobenziodoxoles are powerful electrophiles and mild oxidants toward various unsaturated compounds. In particular, pseudocyclic benziodoxole-derived triflate (IBA-OTf) is an efficient reagent for oxidative heteroannulation reactions. Aldoximes react with nitriles in the presence of IBA-OTf at room temperature to give 1,2,4-oxadiazoles in high yields. Moreover, IBA-triflate is used as a catalyst in oxidative heteroannulations with *m*-chloroperoxybenzoic acid as the terminal oxidant. The iodine(V) benziodoxole derived tosylates, DMP-tosylate and IBX-tosylate, are superior oxidants for the oxidation of structurally diverse, synthetically useful alcohols, utilized as key precursors in the total syntheses of polyketide antibiotics and terpenes. And finally, the most powerful hypervalent iodine(V) oxidant, 2-iodoxybenzoic acid ditriflate (IBX·2HOTf), is prepared by treatment of IBX with trifluoromethanesulfonic acid. According to the X-ray data, the I–OTf bonds in IBX-ditriflate have ionic character, leading to the high reactivity of this reagent in various oxidations. In particular, IBX-ditriflate can oxidize polyfluorinated primary alcohols, which are generally extremely resistant to oxidation.

**Key words** hypervalent iodine, iodine, iodonium, 2-iodosylbenzoic acid (IBA), 2-iodoxybenzoic acid (IBX), oxidation

## 1 Introduction

Organohypervalent iodine compounds have found applications as environmentally sustainable and versatile reagents and catalysts for organic synthesis.[2] Aryliodine(III) dicarboxylates, in particular (diacetoxy)iodobenzene, are the most common hypervalent iodine(III) reagents and are widely used as oxidants. However, aryliodine(III) dicarboxylates typically have a relatively low electrophilic reactivity and tend to react according to radical pathways. In a series of groundbreaking research published in the 1980s,[3a–e] Gerald Koser demonstrated that the tosylate derivative of hypervalent iodine, PhI(OH)OTs (originally reported by Neilands[3f]), is a much stronger electrophile towards various unsaturated organic substrates. Since then, aryliodine(III) tosylates, ArI(OH)OTs (Koser's reagents), have received wide synthetic application as common hypervalent iodine electrophiles and oxidants.[4] At about the same time, researchers in Zefirov's lab at Moscow State University proposed that the electrophilic reactivity of hypervalent iodine reagents can be significantly increased by combining these reagents with strong acids, such as perchloric, tetrafluoroboric, or trifluoromethanesulfonic acids.[5] μ-Oxo-bis[(trifluoromethanesulfonato)(phenyl)iodine], PhI(OTf)O(OTf)IPh (Zefirov's reagent),[6] has the highest reactivity among such acid-activated hypervalent iodine reagents, as recently confirmed by computational studies.[6b] However, practical application of Zefirov's reagent is restricted by its low stability at room temperature and sensitivity to hydrolysis. In particular, it was reported that Zefirov's reagent readily self-condensed at room temperature forming *para*-phenylene-type oligomeric iodonium salts.[7] Kitamura has also report-

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ed the generation of another triflate, PhI(OH)OTf, from iodosobenzene and trifluoromethanesulfonic acid. PhI(OH)OTf is a thermally unstable and hydroscopic compound, which readily decomposes at room temperature producing an oligomeric iodonium salt as the final product.[8]

In this account, we overview our search for stable benziodoxole-derived tosylates and triflates with cyclic or pseudocyclic structures. Five-membered iodine–oxygen

## Biographical Sketches

**Akira Yoshimura** was born in Osaka (Japan) and completed his M.S. in 2007 and his Ph.D. in 2010, both from Tokushima University, under the supervision of Professor Masahito Ochiai. During 2010–2015 he carried his postdoctoral research with Professor Viktor V. Zhdankin at the University of Minnesota Duluth. Between 2016 and 2017 he worked as a Visiting Assistant Professor at Southern Methodist University (Dallas, USA). In 2019 he became a Researcher 5 at the University of Minnesota Duluth and also an Adjunct Professor at Tomsk Polytechnic University. His research interests are in the fields of synthetic and mechanistic organic chemistry of hypervalent main-group elements and heterocyclic chemistry. He has published over 60 research papers, mainly related to the chemistry of hypervalent iodine and bromine.

**Pavel S. Postnikov** was born in Anzhero-Sudzhensk, Russia (1984). His M.S. (2007) and his Ph.D. (2011) were earned at Tomsk Polytechnic University under the supervision of Professor Victor D. Filimonov. Currently, he is an Associate Professor at Tomsk Polytechnic University. His research interests are in the areas of hypervalent iodine chemistry and surface chemistry in the design of novel materials. He has published over 80 research papers, mainly related to the chemistry of hypervalent iodine, diazonium chemistry and surface chemistry.

**Mekhman S. Yusubov** was born in Georgia. His M.S. (1985), Ph.D. (1991), and Doctor of Chemical Sciences (1998) degrees were earned at Tomsk Polytechnic University in the laboratory of Professor Victor D. Filimonov. He is a currently a Professor at Tomsk Polytechnic University. Since 1994 he has been involved in international collaborative research programs with leading research laboratories in South Korea, Germany and the United Kingdom. In 2004 he started joint research in the area of hypervalent iodine chemistry with Professor Viktor V. Zhdankin at the University of Minnesota Duluth. His main research interests are in the fields of natural products and hypervalent iodine reagents. Professor M. S. Yusubov has published over 100 scientific papers.

**Viktor V. Zhdankin** was born in Ekaterinburg, Russian Federation. His M.S. (1978), Ph.D. (1981), and Doctor of Chemical Sciences (1986) degrees were earned at Moscow State University. He moved to the University of Utah in 1990, where he worked for three years as an Instructor of organic chemistry and Senior Research Associate with Professor Peter J. Stang. In 1993, he joined the faculty of the University of Minnesota Duluth, where he is currently a Professor of Chemistry. Dr. Zhdankin has published about 300 research papers, has given over a hundred research presentations in many countries, has edited several books, and co-authored the *Handbook of Heterocyclic Chemistry* (3rd Edition, 2010) with Professors A. R. Katritzky, C. A. Ramsden, and J. A. Joule, and authored a book on *Hypervalent Iodine Chemistry* (Wiley, 2013). His main research interests are in the areas of synthetic and mechanistic organic chemistry of hypervalent main-group elements and organofluorine chemistry. In 2011 he received the National Award of the American Chemical Society for *Creative Research & Applications of Iodine Chemistry*.

heterocycles, known under the common name 'benziodoxoles', are characterized by a generally improved stability compared to non-cyclic hypervalent iodine compounds. The improved thermal stability is usually explained by the lower reactivity of the hypervalent iodine center toward reductive elimination due to the bridging of the equatorial and the apical positions by a five-membered ring.[9] Stabilization of the hypervalent iodine center in the benziodoxole system made possible the synthesis of various stable derivatives of benziodoxoles, including azides,[10] cyanides,[11] and amides.[12] These stable substituted benziodoxoles have attracted significant recent interest as 'atom-transfer' reagents.[13] Similar to benziodoxoles, the pseudocyclic hypervalent aryliodanes bearing a coordinating group at the *ortho* position to the hypervalent center have improved thermal stability.[14] Based on such stabilizing effects of intramolecular coordination of hypervalent iodine derivatives, we have developed a series of organosulfonyloxy-substituted benziodoxoles and pseudobenziodoxoles (Figure 1). All these compounds are more stable compared to the non-cyclic analogs and have useful reactivity patterns. Iodine(III) benziodoxoles **1**–**4** and pseudobenziodoxoles **5** and **6** are powerful electrophiles and mild oxidants toward various unsaturated compounds, while iodine(V) derivatives **7**–**9** are powerful oxidants that can readily oxidize even the least reactive organic substrates such as fluorinated alcohols and others.

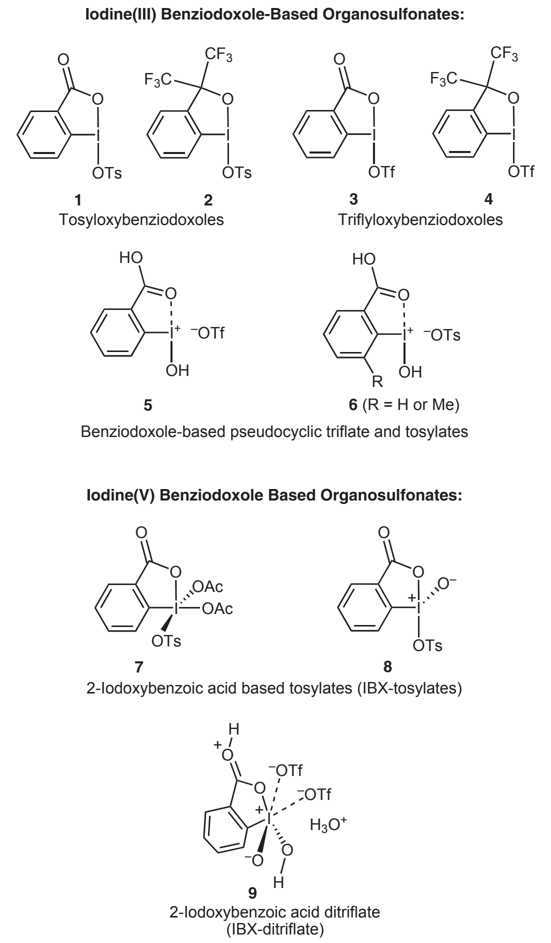
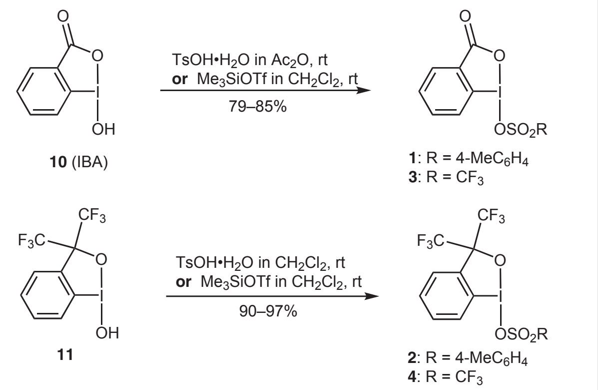


**Figure 1** Important examples of benziodoxole-derived organosulfonates

## 2 Iodine(III) Benziodoxole Based Organosulfonates

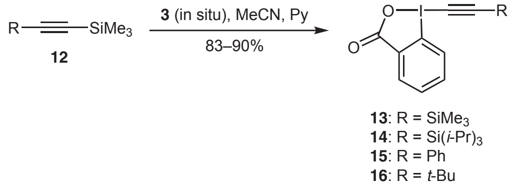
Benziodoxole-based tosylates **1** and **2** and triflates **3** and **4** were prepared by the reactions of 2-iodosylbenzoic acid (IBA) (**10**) or 1-hydroxy-3,3-bis(trifluoromethyl)-3(1*H*)-1,2-benziodoxole (**11**) with *p*-toluenesulfonic acid or trimethylsilyl triflate, respectively (Scheme 1).[15]

In particular, tosylate **1** was isolated as a white, microcrystalline precipitate from the reaction of IBA (**10**) with *p*-toluenesulfonic acid in acetic anhydride. The mesylate derivatives of the benziodoxoles were obtained by a similar method by dissolving 1-hydroxybenziodoxoles **10** or **11** in neat methanesulfonic acid.[15b] Tosylates **1** and **2** are relatively stable to hydrolysis, while triflates **3** and **4** are moisture-sensitive compounds that were isolated as hydrates, which probably have a pseudocyclic structure (see next section). We proposed cyclic structures for products **1**–**4** on the basis of spectroscopic data in comparison with spectra of other 1-substituted benziodoxoles. In particular, the cyclic structure of products **1** and **3** was in agreement with the IR absorption at about 1615 cm$^{-1}$, while the IR spectra of the noncyclic 2-iodosylbenzoate derivatives show a carbonyl signal at 1710 cm$^{-1}$.[16a] The structures of the benziodoxole-based tosylates were independently confirmed by X-ray structural studies in a report by Stuart and co-workers.[16b] Tosylate **1** can be used as an oxidant in Pd(II)-catalyzed C–H activation reactions.[16c]



**Scheme 1** Synthesis of benziodoxole-based tosylates and triflates

We expected that benziodoxole triflates **3** and **4** would be highly reactive electrophiles analogous to Zefirov's reagent, which is a particularly important reagent for the synthesis of alkynyliodonium salts by the reaction with alkynylsilanes.[17] Indeed, the in situ generated triflate **3** reacted with alkynylsilanes **12** in the presence of pyridine at room temperature producing alkynyliodonium derivatives **13–16** in high yields (Scheme 2). Triflate **4** reacted with alkynylsilanes **12** forming analogous alkynylbenziodoxole products.[15b]



**Scheme 2** Preparation of alkynylbenziodoxoles

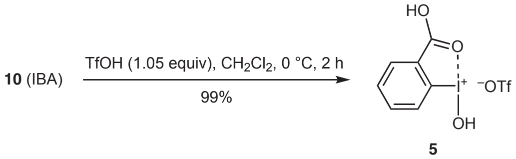
Alkynylbenziodoxoles **13** and **14** (also known as ethynylbenziodoxolones or EBXs) have recently found important synthetic applications as efficient electrophilic alkynylating reagents.[18] In particular, alkynylbenziodoxole **14** is a useful alkynyl transfer reagent to thiols,[19] arylsulfones,[20] *N*-sulfonylamides,[21] and phosphine derivatives.[22] EBX reagents were used for α-alkynylation of carbonyl derivatives,[23] direct alkynylation of olefinic or aromatic C–H,[24] and decarboxylative alkynylation of carboxylic acids.[25]

## 3 Pseudocyclic Iodine(III) Benziodoxole Triflate (IBA-triflate)

External or internal coordination of an iodine center may result in significant stabilization of an otherwise unstable hypervalent iodine compound. This strategy has been explored by several research groups in their efforts to develop new hypervalent iodine reagents. Ochiai and coworkers have found that the hydroxy(phenyl)iodonium ion is significantly stabilized by forming a complex with 18-crown-6 (18C6) ether.[26] The 18C6-complexes of aqua(hydroxy)(phenyl)iodonium and hydroxy(phenyl)iodonium ions are relatively stable compounds and useful electrophilic reagents.

The stability, solubility and reactivity of hypervalent iodine compounds can be improved by placing a coordinating group at the *ortho* position relative to the iodine atom.[2i,14,27] Protasiewicz originally reported highly soluble *ortho*-sulfonyl-substituted iodosylarenes and tosyliminoiodanes possessing useful electrophilic reactivity.[27a–c] More recently, our group reported the preparation and reactions of *ortho*-alkoxy-substituted hypervalent iodine reagents.[27d–f] Wirth has developed *ortho*-methoxymethyl-substituted chiral hydroxy(aryliodonium) tosylate reagents that are useful for enantioselective α-tosyloxylation of carbonyl compounds.[27g–i] Recently, the Wirth group reported the synthesis, characterization and reactions of pseudocyclic iodine(III) reagents bearing heteroaryl carbonyl groups.[27j] Legault and co-authors have reported an α-tosyloxylation reaction with *ortho*-amido-substituted tosylates.[27k] Several *ortho*-substituted aryliodonium salts with useful reactivity have also been described.[27l,m]

In a search for stable benziodoxole-derived triflates with pseudocyclic structure, we have investigated the preparation, structure, and reactions of 2-iodosylbenzoic acid triflate (IBA-OTf, structure **5** in Figure 1).[28,29] We have found that compound **5** can be conveniently prepared in excellent yield by a direct reaction of 2-iodosylbenzoic acid (**10**) with triflic acid in dichloromethane at 0 °C (Scheme 3). Product **5** was isolated in the form of a white solid by filtration from the reaction mixture and washing with ether and hexane at low temperature. IBA-OTf is a stable compound soluble in methanol and acetonitrile.



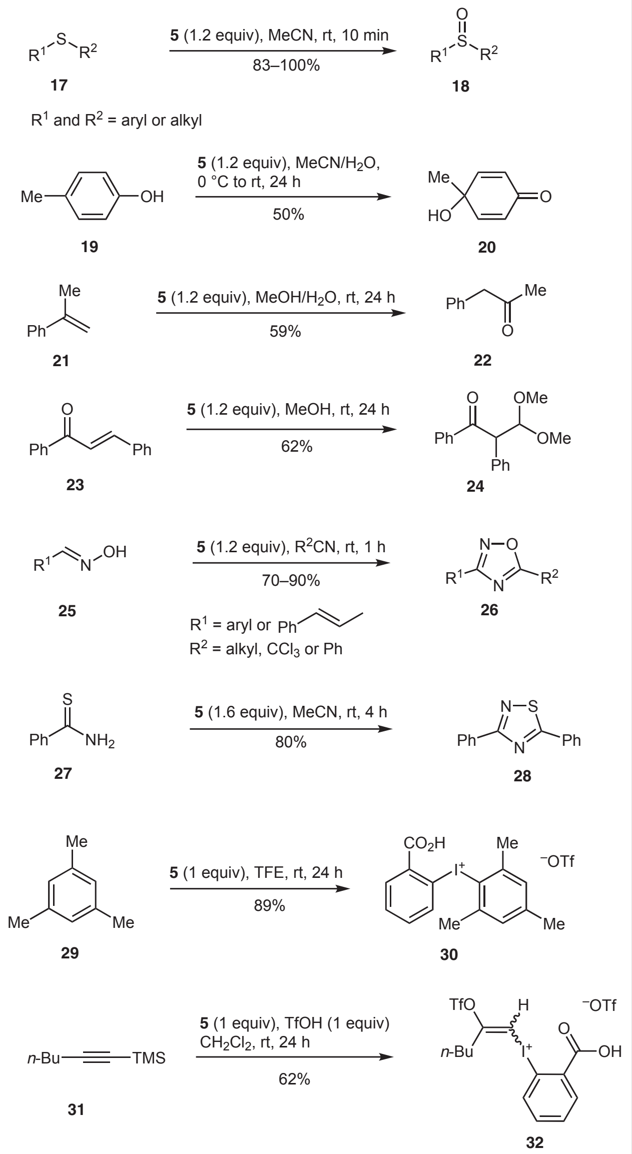
**Scheme 3** Preparation of IBA-OTf (**5**)

The structure of IBA-OTf (**5**) was confirmed by single crystal X-ray diffraction. The hydroxy(aryl)iodonium ion in **5** has a distorted T-shaped intramolecular geometry around the hypervalent iodine atom with an O–I–O angle of ~167°. The I–OH bond of 1.92 Å is significantly shorter than the dative secondary interaction between iodine and a carboxylate oxygen atom (2.34 Å), which is in agreement with the proposed pseudocyclic structure of **5**. The presence of an additional intermolecular iodine-triflate anion contact of 2.89 Å results in the overall square-planar coordination at the hypervalent iodine atom. We assume that such a coordination of the hypervalent iodine center stabilizes molecule **5** analogous to aqua(hydroxy)(phenyl)iodonium triflate.[26b,c]

The reactivity of IBA-triflate (**5**) as an effective oxidant and powerful electrophile is summarized in Scheme 4. The oxidation of sulfides **17** produces sulfoxides **18** in excellent yields.[29] *p*-Methylphenol (**19**) is oxidized to *p*-quinol **20** in a moderate yield.[28] α-Methylstyrene (**21**) and chalcone **23** are oxidized by reagent **5** to give products **22** and **24** as a result of oxidative rearrangement.[28] IBA-triflate (**5**) is a useful reagent for oxidative heteroannulation reactions. The oxidation of aldoximes **25** by reagent **5** in the presence of various nitriles affords 1,2,4-oxadiazoles **26** in high yields.[28] Thiobenzamide (**27**) reacts with IBA-triflate (**5**) producing oxidative dimer **28**.[28] For comparison, unactivated IBA (**10**) does not react with thiobenzamide (**27**) or benzaldoxime (**25**) ($R^1$ = Ph) at room temperature.

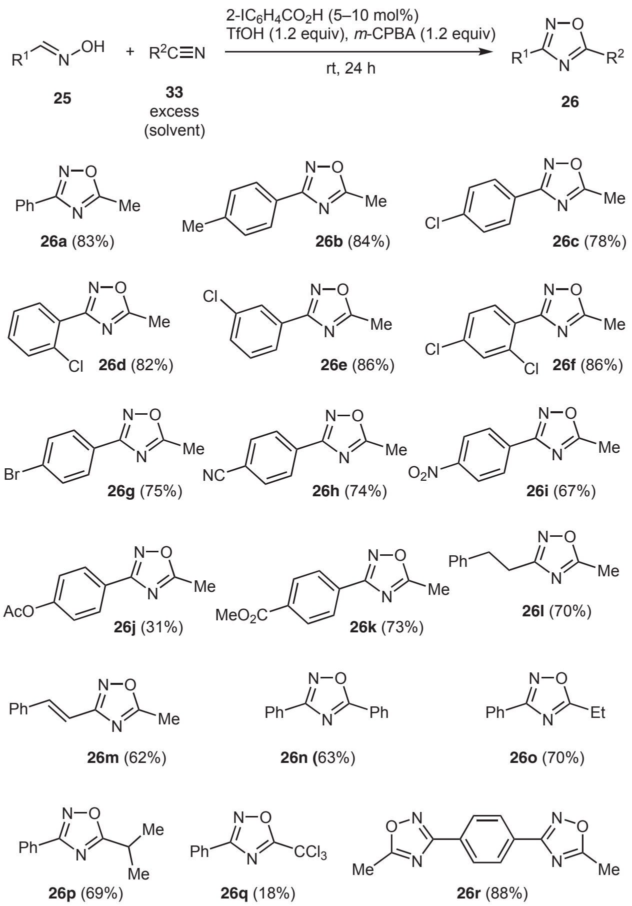
IBA-triflate (**5**) can be used as an efficient electrophilic reagent for the preparation of iodonium salts. In particular, diaryliodonium triflate **30** is obtained by reaction of compound **5** with mesitylene (**29**), and alkenyliodonium salt **32** is formed in the reaction of alkynylsilane **31**.[28]

In comparison to similar reactions of the previously reported hypervalent iodine reagents,[30] reactions of IBA-triflate (**5**) (Scheme 4) proceed smoothly under mild conditions. These reactions illustrate the broad range of potential synthetic applications of IBA-OTf. Furthermore, IBA-triflate (**5**) can be used as a recyclable reagent. 2-Iodobenzoic acid, which is the byproduct of all the oxidations shown in Scheme 4, can be conveniently recovered from reaction mixtures in 97% yield by treatment with aqueous sodium hydroxide followed by acidification of the aqueous solution.[28] The recovered 2-iodobenzoic acid can be easily oxidized to 2-iodosylbenzoic acid (**10**) and then converted back into IBA-triflate (**5**) according to the procedure shown in Scheme 3.



**Scheme 4** Reactions of IBA-OTf (**5**) as a versatile oxidant and powerful electrophile

In our further studies, we have found that IBA-triflate can be used as a catalyst in oxidative heteroannulations with *m*-chloroperoxybenzoic acid (*m*-CPBA) as terminal oxidant.[31] Thus, using 5–10 mol% of 2-$IC_6H_4CO_2H$ as a precatalyst and *m*-CPBA as the terminal oxidant in the presence of triflic acid, we have achieved oxidative heteroannulation of numerous aldoximes **25** and nitriles **33** to the corresponding 1,2,4-oxadiazoles **26** in high isolated yields (Scheme 5).[31a] We should emphasize that noncyclic aryl iodides did not work as effective precatalysts in this oxidative heteroannulation, and therefore generation of pseudocyclic IBA-OTf is an essential requirement for this important heteroannulation reaction.



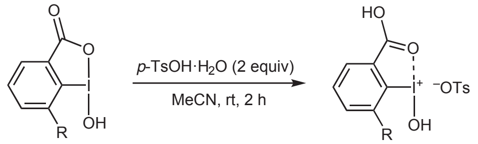
**Scheme 5** Oxidative heteroannulation of aldoximes and nitriles catalyzed by IBA-OTf

Bolm and co-workers have recently demonstrated that pseudocyclic IBA-OTf (**5**) can be used as an efficient precursor to novel sulfoximidoyl-substituted hypervalent iodine.[32]

## 4 Pseudocyclic Iodine(III) Benziodoxole Tosylates

In the next step of our search for stable and potentially useful benziodoxole-derived organosulfonates, we have investigated the synthesis, the X-ray crystal structures, and the reactions of new pseudocyclic benziodoxole tosylates,[33] which are the analogs of benziodoxole triflate (**5**).

Initially, we investigated the reactions of 2-iodosylbenzoic acids **10** and **34** with *p*-toluenesulfonic acid (2 equiv) in acetonitrile. The reactions were complete in 2 hours yielding benziodoxole-based tosylates **35** and **36** in high yields (Scheme 6). Tosylates **35** and **36** are stable crystalline solids soluble in acetonitrile and methanol. The composition of these products was established by elemental analysis, NMR spectroscopy and ESI mass spectrometry. In particular, their ESI mass spectra in positive mode demonstrated the presence of molecular ions $[ArI(OH)]^+$.[33]



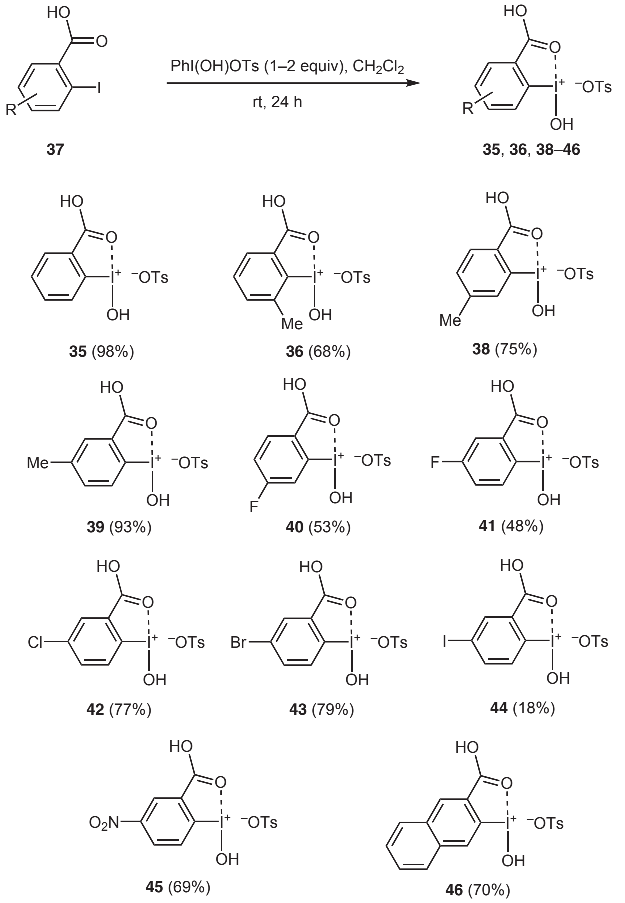
R = H: **10** (IBA)
R = Me: **34**

**35** (93%)
**36** (91%)

**Scheme 6** Preparation of benziodoxole-based tosylates from 2-iodosylbenzoic acids

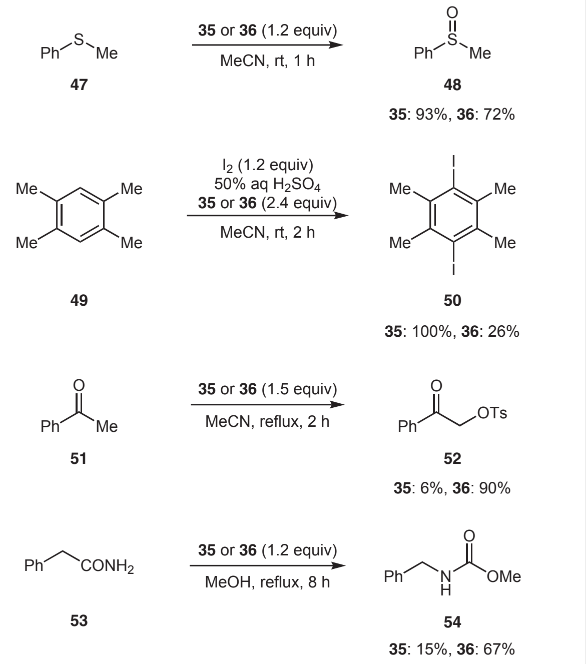
The structure of tosylate **36** was confirmed by single-crystal X-ray studies.[33] X-ray data revealed a pseudocyclic structure for compound **36** with a secondary bond of 2.362(3) Å between the hypervalent iodine and carboxylate oxygen. Molecule **36** has a tetracoordinated iodine center with an iodine–carbon covalent bond (1.926 Å), one I–O covalent bond (1.926 Å), and two iodine–oxygen secondary bonds to carboxylate and tosylate oxygen atoms. This geometry is analogous to the structure of benziodoxole triflate (**5**). The iodine center in the cationic fragment of **36** has a distorted T-shaped geometry typical of hypervalent iodine compounds. The intermolecular distance between iodine and the tosylate oxygen (2.947 Å) indicates the presence of a relatively weak non-covalent interaction. Taking into account primary and secondary bonding, the iodine(III) center in **36** has a pseudo square-planar coordination.

A convenient one-step procedure for the synthesis of benziodoxole-based tosylates is based on direct reaction of 2-iodobenzoic acids with a readily available [hydroxy(tosyloxy)iodo]benzene via a ligand transfer reaction.[3a] This general approach allows the conversion of various substituted *ortho*-iodobenzoic acids **37** into the respective [hydroxy(tosyloxy)]iodonium derivatives **35**, **36** and **38–46** (Scheme 7).[33]



**Scheme 7** Preparation of benziodoxole-based tosylates by ligand exchange between [hydroxy(tosyloxy)iodo]benzene and *ortho*-iodobenzoic acids

Reactions of benziodoxole-based tosylates as oxidants and electrophilic reagents toward several organic substrates are summarized in Scheme 8. For these studies we selected the readily available compound **35** and the *ortho*-substituted compound **36**. The oxidation of thioanisole (**47**) with reagent **35** produced the corresponding sulfoxide **48** in good yield. Arene **49** is oxidatively iodinated with $I_2$ and reagent **35** as the oxidant to give diiodoarene **50** in quantitative yield. In the analogous reactions of thioanisole (**47**) or arene **49** with reagent **36**, the corresponding products **48** and **50** were obtained in lower yields, probably because of partial decomposition of the reagent under the reaction conditions. Unreacted substrates were also recovered in these reactions. The oxidative α-tosyloxylation of acetophenone (**51**) or Hofmann rearrangement of phenylacetamide (**53**) with reagent **36** produced products **52** or **54** in good yields. However, similar reactions using reagent **35** gave the respective products only in very low yields. In these oxidations the reactivity of reagent **36** is higher than reagent **35**. We suggest that the presence of a methyl group at the *ortho*-position relative to the hypervalent iodine may lead to lower thermal stability and enhanced reactivity of compound **36** due to structural distortion. The effect of the *ortho*-methyl substituent on the stability and reactivity of benziodoxole-based tosylates **35** and **36** is in agreement with the experimental results reported by Legault and computational studies on the oxidative α-tosyloxylation of ketones.[27j]



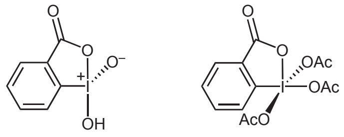
**Scheme 8** Reactions of benziodoxole-based tosylates as oxidants and electrophiles

Compared to Koser's reagent, pseudocyclic benziodoxole tosylates **35** and **36** have an additional advantage of being recyclable reagents. The reduced form of these reagents, 2-iodobenzoic acid or 3-methyl-2-iodobenzoic acid, can be effectively isolated from the reaction mixture in over 94% yield by treatment with aqueous base. Subsequent acidification and reoxidation with [hydroxy(tosyloxy)iodo]benzene according to Scheme 7 returns benziodoxole tosylates **35** and **36**.

IBA-tosylate (**35**) was recently used for the preparation of a novel phenol-substituted benziodoxole, namely, 1-(4-hydroxyphenyl)benziodoxole.[34]

## 5 Iodine(V) Benziodoxole Derived Tosylates

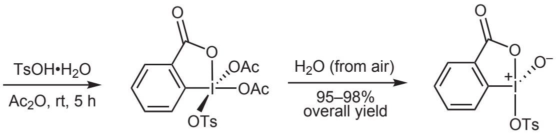
Hypervalent iodine(V) reagents are important oxidants widely utilized in organic synthesis.[2c,j,35] 2-Iodoxybenzoic acid (IBX, structure **55** in Figure 2) and the triacetoxy derivative **56** (known as Dess–Martin periodinane or DMP) have found wide application in organic synthesis as reagents for the oxidation of primary alcohols to aldehydes and numerous other important oxidative transformations.[35,36] Despite the significance of DMP and IBX as reagents, their practical applications are often restricted by low reactivity in many oxidations. Based on our experience of working with iodine(III) benziodoxoles (see previous sections), we expected that the organosulfonate derivatives of IBX would be thermally stable compounds with enhanced electrophilic and oxidative reactivity towards organic substrates.



**55** (IBX) **56** (DMP)

**Figure 2** Structures of IBX and DMP

We investigated a synthetic approach to IBX tosylate derivatives by interaction with tosic acid in acetic anhydride (Scheme 9),[37] similar to the preparation of 1-tosyloxybenziodoxolone (**1**) (Scheme 1). We have found that a suspension of IBX (**55**) and TsOH·$H_2O$ in acetic anhydride at room temperature completely dissolves after less than one hour of stirring. Then, a white solid of a mixed acetate-tosylate **7** (DMP-OTs) precipitates from the initially clear solution. DMP-OTs (**7**) can be separated by filtration in a dry atmosphere in the form of an extremely hygroscopic, white, crystalline solid. Handling compound **7** in open air leads to fast hydrolysis with the formation of IBX-OTs (**8**). Tosylate **8** is stable at room temperature and can be handled in open air without any special precautions. In contrast to the initial IBX, tosylate **8** does not show any explosive properties upon heating or impact; it has a melting point above 118 °C with partial decomposition.



**7** (DMP-OTs)
(can be isolated in 81% yield
under dry conditions)

**8** (IBX-OTs)
(isolated as the
monohydrate)

**Scheme 9** Preparation of the tosylate derivatives of DMP and IBX

The structure of IBX-tosylate (**8**) was assigned based on analytical and spectroscopic data. The presence of an I=O bond in molecule **8** was confirmed by the observation of a characteristic stretch at about 750 cm$^{-1}$ in the IR spectrum. Unfortunately, we were not able to obtain crystals of IBX-OTs (**8**) suitable for X-ray diffraction studies.

After numerous attempts, we were finally able to grow a single crystal of DMP-OTs (**7**) under dry conditions and analyze it by X-ray crystallography.[37a] The iodine(V) atom in **7** has four primary bonds to oxygens with bond distances between 1.99 and 2.21 Å. The bond to the tosylate oxygen atom is the longest of these I–O bonds (about 2.21 Å) and therefore has partial ionic character.

The bicyclic benziodoxole fragment in **7** is planar with square-pyramidal geometry at the iodine(V) atom formed by one carbon and four oxygen ligands. No significant intermolecular contacts are present at the hypervalent iodine center in **7**. Instead, the iodine atom in tosylate **7** has additional intramolecular coordination with carboxylic oxygens of two acetate ligands resulting in heptacoordinated geometry of the hypervalent center. It is interesting to compare the solid-state structure of tosylate **7** with Dess–Martin periodinane (**56**).[38] The five primary bonds to carbon and oxygen atoms in DMP (**56**) are arranged in a similar manner to tosylate **7**. However, instead of intramolecular coordination with carboxylic oxygens, the structure of DMP (**56**) has a weak intermolecular I–O contact with a neighboring molecule resulting in the overall pseudooctahedral geometry of the iodine(V) center.[38]

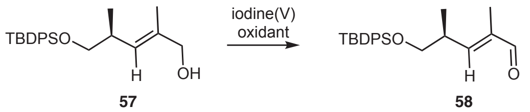
Compared to DMP and IBX, tosylates **7** and **8** have a higher reactivity toward alcohols. In particular, the oxidation of primary alcohols, such as benzyl alcohols and 1-octanol, by IBX-tosylate (**8**) at room temperature proceeds much faster with a quantitative conversion into the corresponding aldehydes in just 3 minutes.[37a] The high reactivity of tosylate **8** compared to IBX is probably explained by the stronger electrophilicity of the hypervalent iodine center because of the partial ionic character of the I–OTs bond.

In our further work,[37b] we have demonstrated that IBX-OTs and DMP-OTs are useful reagents for selective oxidation of structurally diverse, synthetically important alcohols, utilized as key precursors in the total syntheses of polyketide antibiotics and terpenes.

We initially investigated the oxidation of known allylic alcohol **57** as a model substrate for optimizing the reaction conditions and comparing with the common oxidants DMP, IBX, and the (diacetoxyiodo)benzene/TEMPO system that are widely used in the synthesis of natural products (Table 1).[37b]

These results (Table 1) clearly demonstrate that iodine(V) benziodoxole tosylate derivatives **7** and **8** are very effective oxidants in dichloromethane and also in acetonitrile (entries 1, 2 and 4–6). Pyridine as an additive can even further increase the yields of aldehyde **58** (entries 4–6). Both reagents **7** and **8** are stronger oxidants compared to Dess–Martin periodinane (**56**) (entries 7 and 8). IBX (**55**) (entry 9) and the combination PhI(OAc)$_2$/TEMPO (entry 10) show very low reactivity in this oxidation. It should be noted that a physical mixture of IBX and TsOH·H$_2$O is inactive, probably due to the low solubility of these compounds in CH$_2$Cl$_2$. A mixture of Dess–Martin periodinane (**56**) with toluenesulfonic acid has inconsistent reactivity.

**Table 1** Oxidation of (*S*,*E*)-5-[(*tert*-Butyldiphenylsilyl)oxy]-2,4-dimethylpent-2-en-1-ol **57** to Aldehyde **58** Using Different Iodine(V) Oxidants



| Entry | Conditions | Ratio[a] | Solvent | Conversion (%)[b] |
|---|---|---|---|---|
| 1 | **8**, rt, 3 min | 1.06 | CH$_2$Cl$_2$ | 96 |
| 2 | **8**, rt, 3 min | 1.06 | MeCN | 94 |
| 3 | **8**, rt, 3 min | 1.06 | DMSO | 72 |
| 4 | **8**, pyridine, rt, 3 min | 1.06 | CH$_2$Cl$_2$ | 96 |
| 5 | **7**, rt, 3 min | 1.1 | CH$_2$Cl$_2$ | 100 |
| 6 | **7**, pyridine, rt, 3 min | 1.1 | CH$_2$Cl$_2$ | 100 |
| 7 | DMP (**56**), rt, 3 min | 1.1 | CH$_2$Cl$_2$ | 63 |
| 8 | DMP (**56**), rt, 3 min | 1.1 | MeCN | 64 |
| 9 | IBX (**55**), rt, 10 min | 1.1 | CH$_2$Cl$_2$ | 0 |
| 10 | PhI(OAc)$_2$/TEMPO, rt, 10 min | 1.2 | CH$_2$Cl$_2$ | 6 |

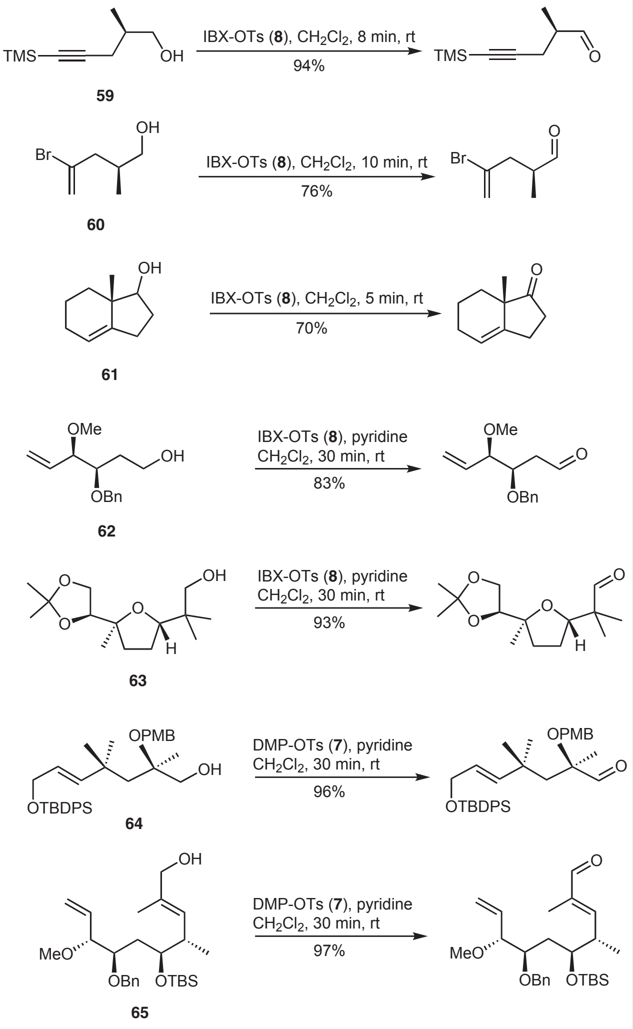
[a] Ratio of reagent/substrate.
[b] Conversion determined by $^1$H NMR spectroscopy.

At the next step, we extended the scope of the oxidations with IBX-OTs (**8**) and DMP-OTs (**7**) to several structurally complex alcohols **59**–**65** (Scheme 10).[37b] All these oxidations proceed rapidly at room temperature with selective formation of the final carbonyl products in high yields.

Therefore, we have demonstrated that the iodine(V) benziodoxole derived tosylates **7** and **8** are superior oxidants for the oxidation of protected complex alcohols, which serve as key intermediates in the total syntheses of terpenes and polyketide antibiotics.

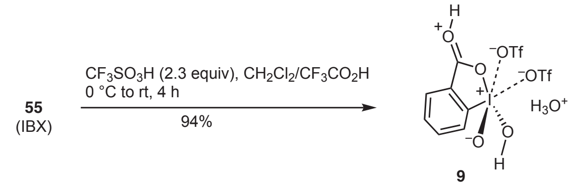
## 6 Iodine(V) Benziodoxole Derived Triflate (IBX-ditriflate)

Very recently, we reported the preparation and reactivity of the strongest iodine(V) oxidant, 2-iodoxybenzoic acid ditriflate (**9**).[39] IBX-ditriflate (**9**) was prepared by treatment of 2-iodoxybenzoic acid (**55**) with a slight excess of trifluoromethanesulfonic acid in CH$_2$Cl$_2$/CF$_3$CO$_2$H solution (Scheme 11). Product **9** precipitated from the solution as a sensitive to moisture, crystalline solid that could be isolated from the reaction mixture by filtration. IBX-ditriflate (**9**) is stable at room temperature and melts above 110 °C with gradual decomposition. In contrast to the initial IBX, triflate **9** does not show any explosive properties upon heating or impact.



**Scheme 10** Oxidation of structurally complex alcohols with reagents **7** and **8**

The procedure shown in Scheme 11 affords IBX-ditriflate (**9**) in high yields and can be reproduced on multigram scale. The composition of product **9** as IBX·2OTf was initially established based on elemental analysis and NMR spectroscopy.



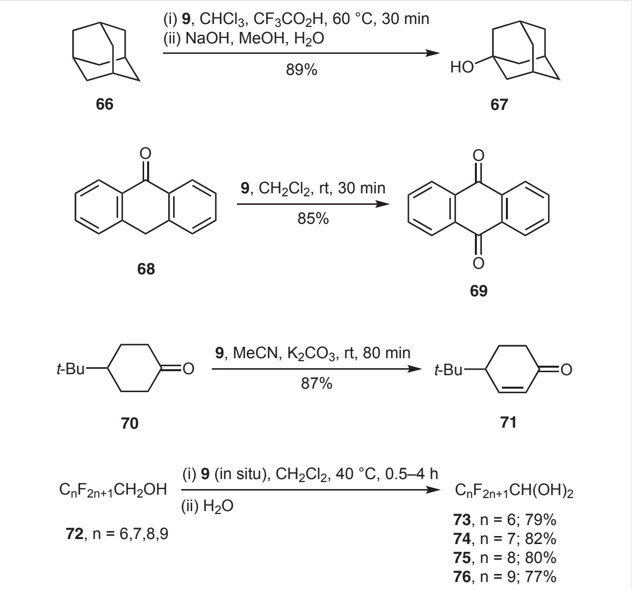
**Scheme 11** Preparation of IBX-ditriflate (**9**)

Performing X-ray structural studies of compound **9** was an extremely challenging task due to its exceptionally strong oxidizing reactivity. The X-ray measurements of **9**, which we have repeated many times, were technically very difficult. Because of the high reactivity of compound **9**, mounting crystals on the pin for diffraction studies was almost impossible as they reacted with any oil or glue commonly used in crystallography for crystal attachment! We selected and tested more than three dozen crystals before we could collect any dataset. Finally, we were able to obtain X-ray crystallographic data for **9** demonstrating a very complex solid-state assembly formed by primary bonds and various intermolecular secondary interactions.[39]

Structural formula **9** shown in Scheme 11 gives the best description of a simplified molecular structure of this compound. The hypervalent iodine atom in molecule **9** has short primary bonds to carbon and three oxygen atoms and secondary contacts to the oxygen atoms of two triflates (2.985 Å and 2.820 Å), which have a significant ionic character. In addition, there is a longer intermolecular I···O contact to the neighboring molecule. This set of four primary and three secondary contacts forms the overall pseudopentagonal bipyramidal geometry at the hypervalent iodine center. It is important to emphasize that because of the substantial ionic character, compound **9** can be expected to have an exceptionally high electrophilicity and oxidizing reactivity in reactions with organic substrates.

Indeed, we have found that triflate **9** is extremely reactive to organic compounds.[39] It readily reacts with many solvents including ether, hexane and acetonitrile, producing a mixture of oxidized products or black tar. According to $^{13}C$ NMR and mass spectrometry studies, triflate **9** in $CD_3CN$ solution is stable for about one hour and then is gradually reduced to iodine(III) benziodoxole derived triflate **5**. However, solutions of IBX-ditriflate (**9**) in trifluoroacetic acid or in dichloromethane are sufficiently stable.

We have investigated reactions of triflate **9** with numerous organic substrates. In many cases, these reactions were not selective and resulted in the formation of a complex mixture of products. Less reactive substrates, however, could be selectively oxidized to a single major product (Scheme 12).[39] The oxidation of adamantane (**66**) in trifluoroacetic acid was complete in 30 minutes to give 1-adamantanol (**67**) in excellent preparative yield. Several procedures for the preparation of 1-adamantanol from adamantane in a very low yield (under 5%) under catalysis by oxo-ruthenium complexes or iron(III) phthalocyanine complexes were previously reported in the literature.[40] Our procedure affords 1-adamantanol in a much better yield and does not involve the use of metal catalysts. Moreover, reagent **9** can be conveniently generated in situ from IBX and trifluoromethanesulfonic acid, which further simplifies this reaction.



**Scheme 12** Oxidations using IBX-ditriflate (**9**)

Ketone **68** is smoothly oxidized by triflate **9** under mild conditions to produce anthraquinone (**69**) in good yield. Substituted cyclohexanone **70** is oxidized with IBX-ditriflate under similar conditions in the presence of potassium carbonate to give α,β-unsaturated ketone **71**. In contrast, similar oxidations of ketones with IBX require 1–2 days of heating at about 85 °C in DMSO solutions.[41]

The exceptional reactivity of IBX-ditriflate (**9**) is best demonstrated by the oxidation of fluoroalcohols **70** (Scheme 12). Fluorinated alcohols, such as 2,2,2-trifluoroethanol (TFE) and 1,1,1,3,3,3-hexafluoroisopropanol (HFIP) are highly resistant to oxidation and are used as common solvents for the reactions of iodine(III) and iodine(V) reagents.[42] We were surprised to find that triflate **9** quickly reacts with TFE to give the corresponding aldehyde (as a hemiacetal) with quantitative conversion in a few hours. TFE is not oxidized by IBX (**55**) under similar conditions. HFIP is quantitatively oxidized by triflate **9** at 60 °C in just 0.5 hours.

Generated in situ, IBX-triflate can be used for effective oxidation of fluoroalcohols **72** to fluoroaldehydes that were isolated as *gem*-diols **73–76** (Scheme 12). We should note that fluoroaldehydes are usually synthesized by the reduction of fluorocarboxylic acids or by some different multistep transformations.[43] Fluoroaldehydes are practically important compounds;[44] however, their direct synthesis by oxidation of readily available fluoroalcohols was not previously reported, probably because of the lack of suitable oxidizing reagents.

## 7 Conclusions

In conclusion, we have developed new organosulfonyloxy-substituted hypervalent iodine(III) and iodine(V) benziodoxole derived reagents that are more stable than the noncyclic analogs and have useful reactivity patterns. Iodine(III) benziodoxoles and pseudobenziodoxoles are powerful electrophiles and mild oxidants toward various unsaturated compounds. In particular, pseudocyclic benziodoxole-derived triflate (IBA-OTf) is an efficient reagent for oxidative heteroannulation reactions. Aldoximes react with nitriles in the presence of IBA-OTf at room temperature to give 1,2,4-oxadiazoles in high yields. Moreover, IBA-triflate has been used as a catalyst in oxidative heteroannulations with *m*-chloroperoxybenzoic acid as the terminal oxidant. The iodine(V) benziodoxole derived tosylates, DMP-tosylate and IBX-tosylate, are superior oxidants for the oxidation of structurally diverse, synthetically useful alcohols, utilized as key precursors in the total syntheses of polyketide antibiotics and terpenes. And finally, the most powerful hypervalent iodine(V) oxidant, 2-iodoxybenzoic acid ditriflate (IBX·2HOTf) can be prepared by treatment of IBX with trifluoromethanesulfonic acid. According to the X-ray data, the I–OTf bonds in IBX-ditriflate have ionic character, leading to high reactivity of this reagent in various oxidations. In particular, IBX-ditriflate can oxidize primary fluoroalcohols, which are generally extremely resistant to oxidation.

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## References

(1) Current address: Department of Chemistry and Biochemistry, University of Minnesota Duluth, Duluth, Minnesota 55812, USA.

(2) (a) *Patai's Chemistry of Functional Groups: The Chemistry of Hypervalent Halogen Compounds*; Olofsson, B.; Marek, I.; Rappoport, Z., Ed.; John Wiley & Sons: Chichester, **2019**. (b) *Hypervalent Iodine Chemistry: Modern Developments in Organic Synthesis*, In *Topics in Current Chemistry, Vol. 373*; Wirth, T., Ed.; Springer: Switzerland, **2016**. (c) Zhdankin, V. V. *Hypervalent Iodine Chemistry: Preparation, Structure and Synthetic Applications of Polyvalent Iodine Compounds* 2014. (d) Hyatt, I. F. D.; Dave, L.; David, N.; Kaur, K.; Medard, M.; Mowdawalla, C. *Org. Biomol. Chem.* **2019**, *17*, 7822. (e) Ghosh, M. K.; Rajkiewicz, A. A.; Kalek, M. *Synthesis* **2019**, *51*, 359. (f) Flores, A.; Cots, E.; Berges, J.; Muniz, K. *Adv. Synth. Catal.* **2019**, *361*, 2. (g) Yoshimura, A.; Saito, A.; Zhdankin, V. V. *Chem. Eur. J.* **2018**, *24*, 15156. (h) Zhdankin, V. V.; Muñiz, K. *J. Org. Chem.* **2017**, *82*, 11667. (i) Yoshimura, A.; Yusubov, M. S.; Zhdankin, V. V. *Org. Biomol. Chem.* **2016**, *14*, 4771. (j) Yoshimura, A.; Zhdankin, V. V. *Chem. Rev.* **2016**, *116*, 3328.

(3) (a) Koser, G. F.; Wettach, R. H. *J. Org. Chem.* **1980**, *45*, 1542. (b) Koser, G. F.; Wettach, R. H.; Smith, C. S. *J. Org. Chem.* **1980**, *45*, 1543. (c) Koser, G. F.; Rebrovic, L.; Wettach, R. H. *J. Org. Chem.* **1981**, *46*, 4324. (d) Rebrovic, L.; Koser, G. F. *J. Org. Chem.* **1984**, *49*, 2462. (e) Koser, G. F.; Relenyi, A. G.; Kalos, A. N.; Rebrovic, L.; Wettach, R. H. *J. Org. Chem.* **1982**, *47*, 2487. (f) Neilands, O.; Karele, B. *Zh. Org. Khim.* **1970**, *6*, 885.

(4) For a review, see: Koser, G. F. *Aldrichimica Acta* **2001**, *34*, 89.

(5) (a) Zefirov, N. S.; Zhdankin, V. V.; Koz'min, A. S. *Izv. Akad. Nauk SSSR Ser. Khim.* **1983**, 1682. (b) Zefirov, N. S.; Zhdankin, V. V.; Dan'kov, Y. V.; Koz'min, A. S. *Zh. Org. Khim.* **1984**, *20*, 446. (c) Zefirov, N. S.; Zhdankin, V. V.; Dan'kov, Y. V.; Sorokin, V. D.; Semerikov, V. N.; Koz'min, A. S.; Caple, R.; Berglund, B. A. *Tetrahedron Lett.* **1986**, *27*, 3971. (d) Zhdankin, V. V.; Tykwinski, R.; Caple, R.; Berglund, B.; Koz'min, A. S.; Zefirov, S. *Tetrahedron Lett.* **1988**, *29*, 3717. (e) Zhdankin, V. V.; Tykwinski, R.; Berglund, B.; Mullikin, M.; Caple, R.; Zefirov, N. S.; Koz'min, A. S. *J. Org. Chem.* **1989**, *54*, 2609.

(6) (a) Hembre, R. T.; Scott, C. P.; Norton, J. R. *J. Org. Chem.* **1987**, *52*, 3650. (b) Izquierdo, S.; Essafi, S.; del Rosal, I.; Vidossich, P.; Pleixats, R.; Vallribera, A.; Ujaque, G.; Lledos, A.; Shafir, A. *J. Am. Chem. Soc.* **2016**, *138*, 12747.

(7) Kitamura, T.; Inoue, D.; Wakimoto, I.; Nakamura, T.; Katsuno, R.; Fujiwara, Y. *Tetrahedron* **2004**, *60*, 8855.

(8) (a) Kitamura, T.; Nagata, K.; Nakamura, T.; Furuki, R.; Taniguchi, H. *Tetrahedron* **1995**, *51*, 6229. (b) Kitamura, T.; Zheng, L.; Fukuoka, T.; Fujiwara, Y.; Taniguchi, H.; Sakurai, M.; Tanaka, R. *J. Chem. Soc., Perkin Trans. 2* **1997**, 1511. (c) Kitamura, T.; Furuki, R.; Taniguchi, H.; Stang, P. J. *Tetrahedron* **1992**, *48*, 7149.

(9) (a) Zhdankin, V. V. *Adv. Heterocycl. Chem.* **2015**, *115*, 1. (b) Zhdankin, V. V. *Adv. Heterocycl. Chem.* **2016**, *116*, 57.

(10) (a) Zhdankin, V. V.; Kuehl, C. J.; Krasutsky, A. P.; Formaneck, M. S.; Bolz, J. T. *Tetrahedron Lett.* **1994**, *35*, 9677. (b) Krasutsky, A. P.; Kuehl, C. J.; Zhdankin, V. V. *Synlett* **1995**, 1081. (c) Zhdankin, V. V.; Krasutsky, A. P.; Kuehl, C. J.; Simonsen, A. J.; Woodward, J. K.; Mismash, B.; Bolz, J. T. *J. Am. Chem. Soc.* **1996**, *118*, 5192. (d) Review: Olding, A.; Ho, C. C. *Aust. J. Chem.* **2019**, *72*, 646.

(11) (a) Zhdankin, V. V.; Kuehl, C. J.; Arif, A. M.; Stang, P. J. *Mendeleev Commun.* **1996**, 50. (b) Zhdankin, V. V.; Kuehl, C. J.; Krasutsky, A. P.; Bolz, J. T.; Mismash, B.; Woodward, J. K.; Simonsen, A. J. *Tetrahedron Lett.* **1995**, *36*, 7975.

(12) Zhdankin, V. V.; McSherry, M.; Mismash, B.; Bolz, J. T.; Woodward, J. K.; Arbit, R. M.; Erickson, S. *Tetrahedron Lett.* **1997**, *38*, 21.

(13) Brand, J. P.; Gonzalez, D. F.; Nicolai, S.; Waser, J. *Chem. Commun.* **2011**, *47*, 102.

(14) For a review, see: Zhdankin, V. V.; Protasiewicz, J. D. *Coord. Chem. Rev.* **2014**, *275*, 54.

(15) (a) Zhdankin, V. V.; Kuehl, C. J.; Bolz, J. T.; Formaneck, M. S.; Simonsen, A. J. *Tetrahedron Lett.* **1994**, *35*, 7323. (b) Zhdankin, V. V.; Kuehl, C. J.; Krasutsky, A. P.; Bolz, J. T.; Simonsen, A. J. *J. Org. Chem.* **1996**, *61*, 6547.

(16) (a) Panetta, C. A.; Garlick, S. M.; Durst, H. D.; Longo, F. R.; Ward, J. R. *J. Org. Chem.* **1990**, *55*, 5202. (b) Geary, G. C.; Hope, E. G.; Singh, K.; Stuart, A. M. *Chem. Commun.* **2013**, *49*, 9263. (c) Nappi, M.; He, C.; Whitehurst, W. G.; Chappell, B. G. N.; Gaunt, M. J. *Angew. Chem. Int. Ed.* **2018**, *57*, 3178.

(17) Zhdankin, V. V.; Stang, P. J. *Tetrahedron* **1998**, *54*, 10927.

(18) For reviews, see: (a) Hari, D. P.; Caramenti, P.; Waser, J. *Acc. Chem. Res.* **2018**, *51*, 3212. (b) Waser, J. *Synlett* **2016**, *27*, 2761. (c) Waser, J. *Top. Curr. Chem.* **2016**, *373*, 187. (d) Brand, J. P.; Waser, J. *Chem. Soc. Rev.* **2012**, *41*, 4165.

(19) (a) Frei, R.; Waser, J. *J. Am. Chem. Soc.* **2013**, *135*, 9620. (b) Frei, R.; Wodrich, M. D.; Hari, D. P.; Borin, P.-A.; Chauvier, C.; Waser, J. *J. Am. Chem. Soc.* **2014**, *136*, 16563.

(20) Chen, C. C.; Waser, J. *Org. Lett.* **2015**, *17*, 736.

(21) Aubineau, T.; Cossy, J. *Chem. Commun.* **2013**, *49*, 3303.

(22) Chen, C. C.; Waser, J. *Chem. Commun.* **2014**, *50*, 12923.

(23) (a) Fernandez Gonzalez, D.; Brand, J. P.; Waser, J. *Chem. Eur. J.* **2010**, *16*, 9457. (b) Fernandez Gonzalez, D.; Brand, J. P.; Mondiere, R.; Waser, J. *Adv. Synth. Catal.* **2013**, *355*, 1631. (c) Kamlar, M.; Cisarova, I.; Vesely, J. *Org. Biomol. Chem.* **2015**, *13*, 2884.

(24) (a) Collins, K. D.; Lied, F.; Glorius, F. *Chem. Commun.* **2014**, *50*, 4459. (b) Feng, C.; Feng, D.; Loh, T.-P. *Chem. Commun.* **2014**, *50*, 9865. (c) Finkbeiner, P.; Kloeckner, U.; Nachtsheim, B. J. *Angew. Chem. Int. Ed.* **2015**, *54*, 4949. (d) Brand, J. P.; Charpentier, J.; Waser, J. *Angew. Chem. Int. Ed.* **2009**, *48*, 9346. (e) Brand, J. P.; Waser, J. *Org. Lett.* **2012**, *14*, 744. (f) Feng, C.; Loh, T.-P. *Angew. Chem. Int. Ed.* **2014**, *53*, 2722.

(25) (a) Liu, X.; Wang, Z.; Cheng, X.; Li, C. *J. Am. Chem. Soc.* **2012**, *134*, 14330. (b) Vaillant, F. L.; Waser, J. *Chimia* **2017**, *71*, 226.

(26) (a) Ochiai, M.; Miyamoto, K.; Yokota, Y.; Suefuji, T.; Shiro, M. *Angew. Chem. Int. Ed.* **2005**, *44*, 75. (b) Miyamoto, K.; Yokota, Y.; Suefuji, T.; Yamaguchi, K.; Ozawa, T.; Ochiai, M. *Chem. Eur. J.* **2014**, *20*, 5447. (c) Ochiai, M. *Coord. Chem. Rev.* **2006**, *250*, 2771. (d) Ochiai, M.; Miyamoto, K.; Shiro, M.; Ozawa, T.; Yamaguchi, K. *J. Am. Chem. Soc.* **2003**, *125*, 13006.

(27) (a) Macikenas, D.; Skrzypczak-Jankun, E.; Protasiewicz, J. D. *J. Am. Chem. Soc.* **1999**, *121*, 7164. (b) Macikenas, D.; Skrzypczak-Jankun, E.; Protasiewicz, J. D. *Angew. Chem. Int. Ed.* **2000**, *39*, 2007. (c) Meprathu, B. V.; Protasiewicz, J. D. *Tetrahedron* **2010**, *66*, 5768. (d) Yoshimura, A.; Nemykin, V. N.; Zhdankin, V. V. *Chem. Eur. J.* **2011**, *17*, 10538. (e) Zhu, C.; Yoshimura, A.; Ji, L.; Wei, Y.; Nemykin, V. N.; Zhdankin, V. V. *Org. Lett.* **2012**, *14*, 3170. (f) Zhu, C.; Yoshimura, A.; Solntsev, P.; Ji, L.; Wei, Y.; Nemykin, V. N.; Zhdankin, V. V. *Chem. Commun.* **2012**, *48*, 10108. (g) Hirt, U. H.; Schuster, M. F. H.; French, A. N.; Wiest, O. G.; Wirth, T. *Eur. J. Org. Chem.* **2001**, 1569. (h) Altermann, S. M.; Richardson, R. D.; Page, T. K.; Schmidt, R. K.; Holland, E.; Mohammed, U.; Paradine, S. M.; French, A. N.; Richter, C.; Bahar, A. M.; Witulski, B.; Wirth, T. *Eur. J. Org. Chem.* **2008**, 5315. (i) Richardson, R. D.; Page, T. K.; Altermann, S.; Paradine, S. M.; French, A. N.; Wirth, T. *Synlett* **2007**, 538. (j) Qurban, J.; Elsherbini, M.; Alharbi, H.; Wirth, T. *Chem. Commun.* **2019**, *55*, 7998. (k) Guilbault, A.-A.; Legault, C. Y. *ACS Catal.* **2012**, *2*, 219. (l) Hamnett, D. J.; Moran, W. J. *Org. Biomol. Chem.* **2014**, *12*, 4156. (m) Yoshimura, A.; Fuchs, J. M.; Middleton, K. R.; Maskaev, A. V.; Rohde, G. T.; Saito, A.; Postnikov, P. S.; Yusubov, M. S.; Nemykin, V. N.; Zhdankin, V. V. *Chem. Eur. J.* **2017**, *23*, 16738.

(28) Yoshimura, A.; Nguyen, K. C.; Klasen, S. C.; Saito, A.; Nemykin, V. N.; Zhdankin, V. V. *Chem. Commun.* **2015**, *51*, 7835.

(29) Yoshimura, A.; Zhdankin, V. V. *ARKIVOC* **2017**, *(iii)*, 32.

(30) (a) Shah, A.-u.-H. A.; Khan, Z. A.; Choudhary, N.; Lohölter, C.; Schäfer, S.; Marie, G. P. L.; Farooq, U.; Witulski, B.; Wirth, T. *Org. Lett.* **2009**, *11*, 3578. (b) Dohi, T.; Ito, M.; Morimoto, K.; Minamitsuji, Y.; Takenaga, N.; Kita, Y. *Chem. Commun.* **2007**, 4152. (c) Bielawski, M.; Olofsson, B. *J. Chem. Soc., Chem. Commun.* **2007**, 2521. (d) Bouma, M. J.; Olofsson, B. *Chem. Eur. J.* **2012**, *18*, 14242.

(31) (a) Yoshimura, A.; Nguyen, K. C.; Klasen, S. C.; Postnikov, P. S.; Yusubov, M. S.; Saito, A.; Nemykin, V. N.; Zhdankin, V. V. *Asian J. Org. Chem.* **2016**, *5*, 1128. (b) Yoshimura, A.; Nguyen, K. C.; Rohde, G. T.; Saito, A.; Yusubov, M. S.; Zhdankin, V. V. *Adv. Synth. Catal.* **2016**, *358*, 2340.

(32) Wang, H.; Zhang, D.; Sheng, H.; Bolm, C. *J. Org. Chem.* **2017**, *82*, 11854.

(33) Yoshimura, A.; Klasen, S. C.; Shea, M. T.; Nguyen, K. C.; Rohde, G. T.; Saito, A.; Postnikov, P. S.; Yusubov, M. S.; Nemykin, V. N.; Zhdankin, V. V. *Chem. Eur. J.* **2017**, *23*, 691.

(34) Yoshimura, A.; Shea, M. T.; Guselnikova, O.; Postnikov, P. S.; Rohde, G. T.; Saito, A.; Yusubov, M. S.; Nemykin, V. N.; Zhdankin, V. V. *Chem. Commun.* **2018**, *54*, 10363.

(35) Zhdankin, V. V. *J. Org. Chem.* **2011**, *76*, 1185.

(36) (a) Duschek, A.; Kirsch, S. F. *Angew. Chem. Int. Ed.* **2011**, *50*, 1524. (b) Satam, V.; Harad, A.; Rajule, R.; Pati, H. *Tetrahedron* **2010**, *66*, 7659.

(37) (a) Yusubov, M. S.; Svitich, D. Y.; Yoshimura, A.; Nemykin, V. N.; Zhdankin, V. V. *Chem. Commun.* **2013**, *49*, 11269. (b) Yusubov, M. S.; Postnikov, P. S.; Yusubova, R. Y.; Yoshimura, A.; Juerjens, G.; Kirschning, A.; Zhdankin, V. V. *Adv. Synth. Catal.* **2017**, *359*, 3207.

(38) Schroeckeneder, A.; Stichnoth, D.; Mayer, P.; Trauner, D. *Beilstein J. Org. Chem.* **2012**, *8*, 1523.

(39) Yusubov, M. S.; Soldatova, N. S.; Postnikov, P. S.; Valiev, R. R.; Yoshimura, A.; Wirth, T.; Nemykin, V. N.; Zhdankin, V. V. *Chem. Commun.* **2019**, 7760.

(40) (a) Khan, M. M. T. *Stud. Surf. Sci. Catal.* **1991**, *66*, 31. (b) Neu, H. M.; Yusubov, M. S.; Zhdankin, V. V.; Nemykin, V. N. *Adv. Synth. Catal.* **2009**, *351*, 3168.

(41) Uyanik, M.; Akakura, M.; Ishihara, K. *J. Am. Chem. Soc.* **2009**, *131*, 251.

(42) Dohi, T.; Yamaoka, N.; Kita, Y. *Tetrahedron* **2010**, *66*, 5775.

(43) (a) Miller, A. O.; Peters, D.; Zur, C.; Frank, M.; Miethchen, R. *J. Fluorine Chem.* **1997**, *82*, 33. (b) Benefice-Malouet, S.; Commeyras, A. *J. Fluorine Chem.* **1995**, *70*, 103. (c) Hu, C.; Tang, X. *J. Fluorine Chem.* **1993**, *61*, 217. (d) Kolarikova, V.; Simunek, O.; Rybackova, M.; Cvacka, J.; Brezinova, A.; Kvicala, J. *Dalton Trans.* **2015**, *44*, 19663. (e) Ingrassia, L.; Mulliez, M. *Synthesis* **1999**, 1731. (f) Pierce, O. R.; Kane, T. G. *J. Am. Chem. Soc.* **1954**, *76*, 300.

(44) *Organofluorine Chemistry, Principles and Commercial Applications*; Banks, R. E.; Smart, B. E.; Tatlow, J. C., Ed.; Plenum Press: New York, **1994**.