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Zefirov's reagent and related hypervalent iodine triflates

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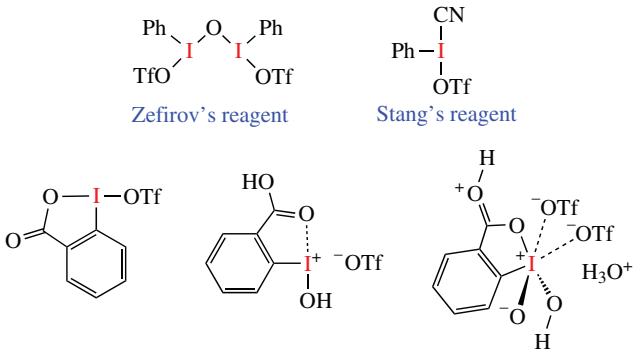
This minireview describes chemistry of hypervalent organoiodine triflates, which have received wide synthetic application as powerful electrophilic reagents and oxidants. The first representative of these compounds, μ-oxo-bis[(trifluoromethanesulfonato)(phenyl)iodine], was originally prepared and investigated in N. S. Zefirov's laboratory at Moscow State University in the early 1980s. This compound, now commonly known as Zefirov's reagent, is a useful reagent for the synthesis of various iodonium salts from the corresponding organic precursors. Recently, thermally stable and highly reactive triflates derived from cyclic hypervalent iodine compounds, benziodoxoles, have been reported and utilized in organic synthesis. The strongest iodine(V) oxidant, IBX-ditriflate, has been prepared from 2-iodoxybenzoic acid (IBX) and triflic acid. IBX-ditriflate can readily oxidize organic substrates that are generally resistant to oxidation.



Benziodoxole-derived iodine(III) and iodine(V) triflates

Keywords: iodine, hypervalent iodine, Zefirov's reagent, iodonium, iodine triflates, benziodoxoles, benziodoxole triflate, IBX.

In memory of Professor N. S. Zefirov (1935–2017)

Introduction

Since the beginning of the 20th century, the chemistry of hypervalent iodine compounds has attracted a surging research interest.[1–10] Derivatives of iodine(III) and (V) have emerged as versatile and environmentally friendly reagents widely employed in academic research and in industry. Hypervalent iodine compounds are widely used as selective oxidants and electrophilic group transfer reagents in organic synthesis[1–10] and also as initiators of polymerization with numerous industrial applications.[11,12]

Out of the numerous structural types known for hypervalent iodine compounds, iodonium salts ($R_2I^+ X^-$), have received the most important practical application in industry, medicine, and pharmaceutical research.[1,3,11–13] The preparation of iodonium salts usually involves a reaction between electrophilic iodine reagent with the corresponding organic precursor.[14] Hypervalent

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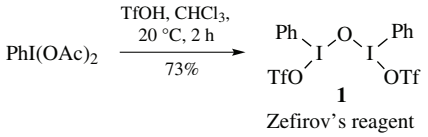
Viktor V. Zhdankin was born in Ekaterinburg, Russian Federation. His MS (1978), PhD (1981), and Doctor of Chemical Sciences (1986) degrees were earned at Moscow State University in the laboratory of Nikolay S. Zefirov. He moved to the University of Utah in 1990, where he worked for three years as Instructor of organic chemistry and Senior Research Associate with Peter J. Stang. In 1993, he joined the faculty of the University of Minnesota Duluth, where he is currently a Professor of Chemistry. In the last 10 years, he has visited Tomsk Polytechnic University numerous times as a visiting Professor. Dr. Zhdankin has published more than 300 research papers, gave over a hundred research presentations in many countries, edited several books, 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*. Professor V. V. Zhdankin is a Member of Editorial Board of *Mendeleev Communications* and a Chair of Editorial Board of *ARKIVOC*.

organoiodine triflates are derived from the strongest trifluoromethanesulfonic (triflic) acid and represent the most powerful iodine electrophiles due to a significant positive charge on the hypervalent iodine center. Therefore, organoiodine(III) triflates (as individual compounds or generated *in situ*) have found wide application as effective reagents for the synthesis of various aryliodonium salts. The first representative of hypervalent organoiodine triflates, μ-oxo-bis[(trifluoromethanesulfonato)-(phenyl)iodine], was originally prepared and investigated in N. S. Zefirov's laboratory at Moscow State University in the early 1980s. This compound, now commonly known as Zefirov's reagent, is a particularly useful reagent for the synthesis of various aryliodonium salts from the corresponding organic precursors. Numerous other hypervalent iodine triflate derivatives have been reported following the discovery of Zefirov's reagent. These triflates are utilized in organic synthesis as individual, stable reagents, or can be generated *in situ* in the case of thermally unstable derivatives.

The present minireview summarizes chemistry of hypervalent organoiodine triflates, starting from Zefirov's reagent and through the recent studies of the most powerful organoiodine(V) oxidant, IBX-ditriflate, that has been prepared from 2-iodoxybenzoic acid (IBX) and triflic acid.

Preparation and chemistry of Zefirov's reagent

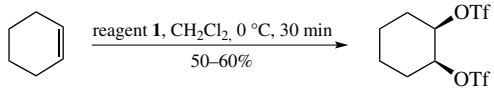
The preparation of μ-oxo-bis[(trifluoromethanesulfonato)-(phenyl)iodine] **1** was originally reported in 1983 by treatment of (diacetoxyiodo)benzene with triflic acid in chloroform (Scheme 1).[15,16] Compound **1** precipitates from the reaction mixture as a yellow solid (mp 119–121 °C) that can be handled for brief periods in open air at room temperature. The structure of μ-oxo-bis[(trifluoromethanesulfonato)(phenyl)iodine] **1** was initially assigned on the basis of elemental analysis, spectroscopic data, and by analogy with the previously known iodine(III) derivatives of strong acids.[17] Recently, the structure of compound **1**, prepared from $PhI(OAc)_2$ and TMSOTf in dichloromethane, was unambiguously confirmed by single crystal X-ray analysis.[18]



Scheme 1 Originally reported preparation of Zefirov's reagent.

In 1987, Norton and coworkers reported a new procedure for the preparation of triflate **1** from iodosylbenzene (PhIO) and triflic anhydride (Tf_2O) in dichloromethane and suggested the name 'Zefirov's reagent' for this highly reactive compound.[19] Generated by this reaction Zefirov's reagent **1** can be isolated as a yellow solid or can be conveniently used *in situ* as a bright yellow suspension. It was demonstrated in early publications that Zefirov's reagent **1** is a powerful electrophile capable of reacting with alkenes with formation of 1,2-ditriflates.[16,19–21] This reaction proceeds with high degree of stereoselectivity as *syn*-addition (> 99%), as illustrated by the reaction of cyclohexene (Scheme 2).

In modern synthetic works, Zefirov's reagent is usually generated *in situ* from PhIO, $PhI(OAc)_2$ or $PhI(OCOCF_3)_2$ and triflic acid, triflic anhydride, or trimethylsilyl triflate in dichloromethane. Solutions or suspensions of Zefirov's reagent

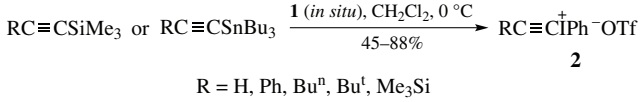


Scheme 2 Reaction of Zefirov's reagent **1** with cyclohexene.

in dichloromethane have a relatively low stability at room temperature and are sensitive to hydrolysis. In particular, it was reported that solutions of $PhI(OAc)_2$ in the presence of triflic acid at room temperature can readily form *para*-phenylene type oligomeric iodonium salts as products of self-condensation of the initially formed hypervalent iodine triflate.[22] Therefore, it is important to perform reactions of Zefirov's reagent *in situ* at lower temperatures, usually at 0 °C. In some publications, the structure of triflate species, generated *in situ* from PhIO or $PhI(OAc)_2$, is shown as $PhI(OTf)_2$. However, recent spectroscopic and computational studies of Dutton and coworkers have clearly indicated that $PhI(OTf)_2$ does not exist.[23] These studies are in agreement with Shafir's work on the isolation of compound **1** and its precursor PhI(OAc)OTf from solutions of $PhI(OAc)_2$ and TMSOTf in dichloromethane.[18] According to computational studies, Zefirov's reagent has the highest electrophilic reactivity among other acid-activated hypervalent iodine reagents.[18]

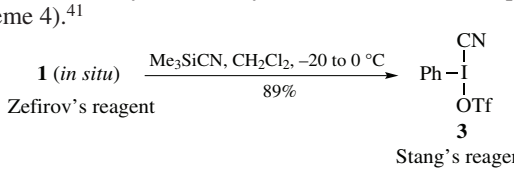
Hypervalent iodine triflates, generated *in situ* from $ArI(OAc)_2$ and triflic acid or TMSOTf, have found wide application in organic chemistry. Examples of these applications are represented by the preparation of hydrazones,[24] oxyamination reactions,[25] formation of bicyclic diazenium salts,[26] synthesis of functionalized cyclopropane rings,[27,28] cyclization of hydroxystilbenes or carboxylic acids,[29,30] functionalization of acetylenes,[31] aryl C–H alkylations,[32,33] alpha arylations,[34] and preparation of the Weiss' reagent, $[PhI(Pyr)_2]^{2+}$.[35,36]

Most importantly, the generated *in situ* Zefirov's reagent has found wide application in the synthesis of various iodonium salts. The preparation of iodonium salts from hypervalent iodine triflates and the corresponding nucleophilic organic substrates has been extensively covered in numerous books, book chapters and reviews. Stang and coworkers have first demonstrated in 1990–1991 that the novel and synthetically valuable alkynyliodonium salts **2** can be prepared by the reaction of Zefirov's reagent *in situ* with alkynylsilanes or alkynylstannanes (Scheme 3).[37,38] A similar procedure for the preparation of alkynyliodonium salts **2** employs the reaction of alkynylboronates with Zefirov's reagent.[39]



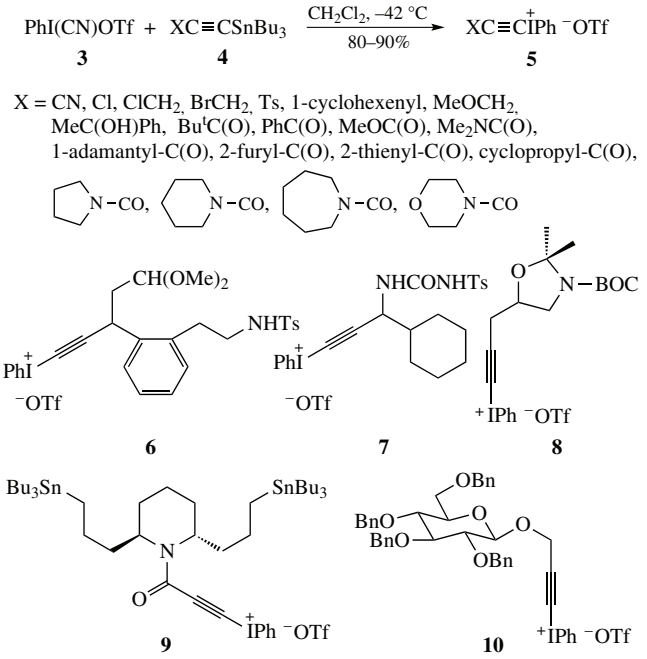
Scheme 3 Preparation of alkynyliodonium salts using Zefirov's reagent **1**.

A particularly useful reagent **3**, known in modern literature as Stang's reagent,[40] can be prepared by the treatment of Zefirov's reagent with cyanotrimethylsilane at low temperature (Scheme 4).[41]



Scheme 4 Preparation of Stangs's reagent from Zefirov's reagent.

Stang's reagent has found broad synthetic application as a versatile iodonium transfer reagent useful for the preparation of various iodonium salts under mild conditions.[1–3] In particular, the interaction of a large variety of readily available functionalized alkynylstannanes **4** with reagent **3** under very mild conditions provides ready access to diverse functionalized alkynyliodonium salts **5** in excellent yields (Scheme 5).[42–44] This procedure is particularly useful for the preparation of various complex, functionalized alkynyliodonium derivatives, such as compounds **6** and **7**,[45] **8**,[46] **9**,[47] and **10**.[48] Products **5**–**10** are formed under



Scheme 5 Examples of alkynyliodonium salts prepared using Stangs's reagent **3**.

these very mild conditions in high yields (80–90%) and can be used in subsequent transformations without additional purification. The synthesized by this procedure structurally complex alkynyliodonium triflates have found wide application in the synthesis of natural products.[49]

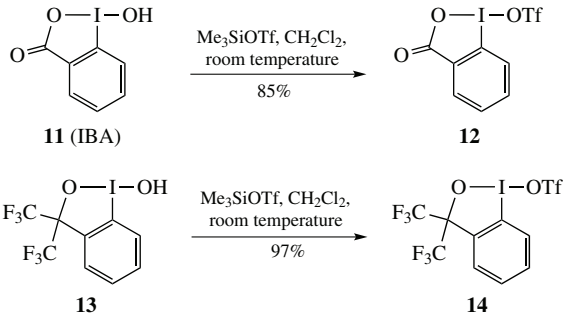
The reactions of Zefirov's and Stang's reagents with the corresponding organostannanes were also used for the preparation of a wide variety of practically useful alkenyliodonium,[50,51] and also aryl- and heteroaryliodonium triflate salts.[52,53]

Benziodoxole triflate

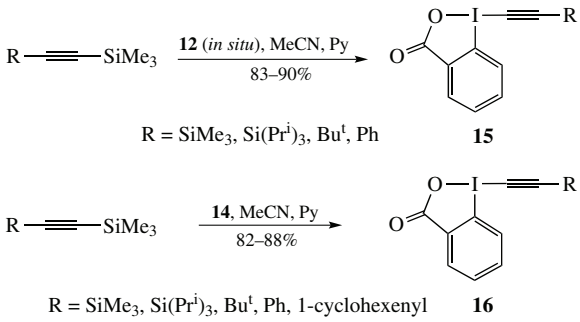
Zefirov's reagent and other noncyclic hypervalent iodine triflates have a relatively low stability at room temperature and are sensitive to hydrolysis, which restricts their application as common oxidizing reagents. The triflate derivatives of cyclic or pseudocyclic hypervalent iodine compounds are characterized by enhanced stability. Particularly important are the five-membered iodine–oxygen heterocycles known under the general name of 'benziodoxoles'. Benziodoxoles are characterized by a higher thermal stability compared to the non-cyclic hypervalent iodine compounds, which is explained by the lower reactivity of hypervalent iodine center toward reductive elimination because of the link between apical and equatorial positions *via* the five-membered ring.[54] Such a stabilization of hypervalent iodine in a cyclic system made it possible to prepare several important, stable benziodoxole-derived reagents, including azidobenziodoxole (Zhdankin reagent),[55–57] trifluromethylbenziodoxole (Togni reagent),[8] and ethynylbenziodoxole (Waser reagent).[7] These stable benziodoxoles are known under the general name of 'atom-transfer' reagents.[58]

Benziodoxole triflates **12** and **14** were prepared by the reactions of 1-hydroxybenziodoxole (IBA) **11** or 1-hydroxy-3,3-bis(trifluoromethyl)-3(1*H*)-1,2-benziodoxole **13** with trimethylsilyl triflate (Scheme 6).[59]

Benziodoxole triflates **12** and **14** were isolated in the form of thermally stable, yellow solids (mp 166–168 °C for compound **12** and 143–145 °C for compound **14**). Similar to Zefirov's reagent, benziodoxole triflates can readily react with alkynylsilanes producing alkynylbenziodoxoles **15** and **16** in high yields (Scheme 7).[59]



Scheme 6 Synthesis of benziodoxole triflates.

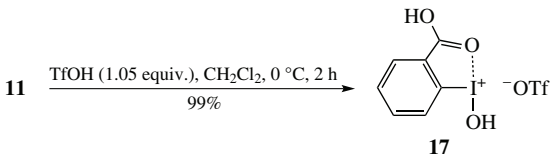


Scheme 7 Preparation of alkynylbenziodoxoles.

Alkynylbenziodoxoles **15** (also known as ethynylbenziodoxolones, EBXs or Waser reagents) are used in organic synthesis as efficient electrophilic alkynylating reagents.[7,60–62] For example, TIPS-EBX [reagent **15**, R = $Si(Pr^i)_3$] readily transfers alkynyl group to thiols,[63] arylsulfones,[64] *N*-sulfonylamides,[65] and phosphine derivatives.[66] Alkynylbenziodoxoles were used for α-alkynylation of carbonyl compounds,[67] direct alkynylation of olefinic or aromatic C–H bonds,[68] and decarboxylative alkynylation of carboxylic acids.[69]

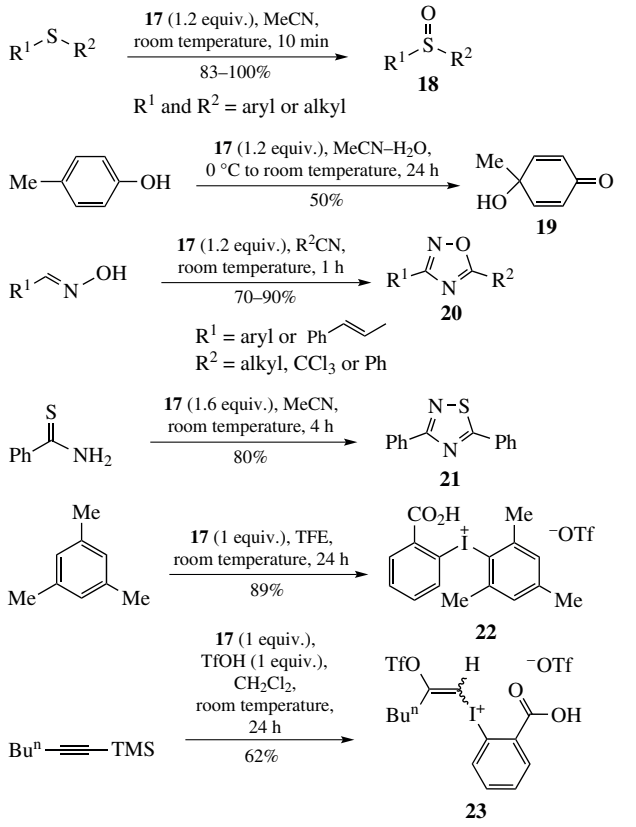
Pseudobenziodoxole triflate

The pseudocyclic hypervalent iodine compounds with a coordinating group in the *ortho* position to the hypervalent center also have enhanced thermal stability compared to the noncyclic hypervalent iodine derivatives.[70] Such stabilization due to intramolecular coordination of hypervalent iodine made possible the preparation of the stable pseudobenziodoxole triflate **17** (Scheme 8).[71] Compound **17** can be conveniently prepared in excellent yield by a direct reaction of 1-hydroxybenziodoxole with triflic acid in dichloromethane at 0 °C. Pseudobenziodoxole triflate **17** was isolated in the form of a stable white solid soluble in methanol and acetonitrile.

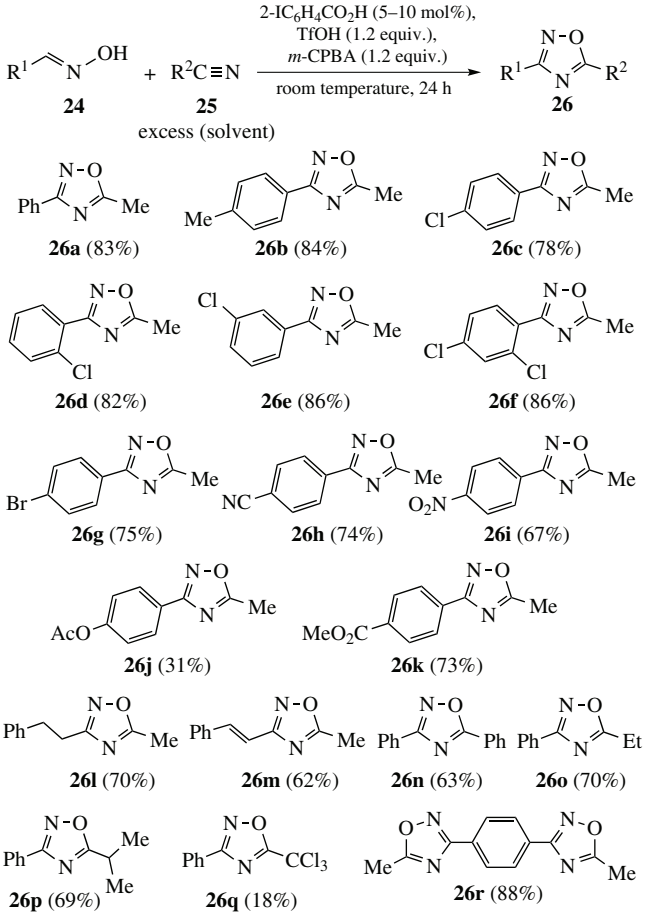


Scheme 8 Preparation of pseudobenziodoxole triflate.

Pseudobenziodoxole triflate **17** is an effective oxidant and powerful electrophile as exemplified in Scheme 9. For example, it can readily oxidize organic sulfides to sulfoxides **18**,[72] and *p*-methylphenol is oxidized to *p*-quinol **19** in a moderate yield.[71] Triflate **17** is a useful reagent for oxidative heterocyclization reactions. The oxidation of aldoximes in the presence of various nitriles by reagent **17** affords 1,2,4-oxadiazoles **20** in high yields.[71] Thiobenzamide reacts with reagent **17** producing product **21** as a result of oxidative dimerization.[71]



Scheme 9 Reactions of pseudobenziodoxole triflate **17** as versatile oxidant and powerful electrophile.



Scheme 10 Oxidative heterocyclizations of aldoximes and nitriles catalyzed by IBA-OTf.

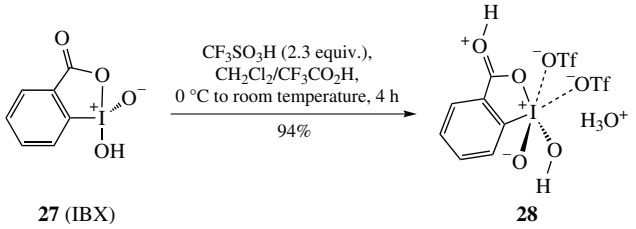
Triflate **17** is a useful electrophilic reagent for the preparation of iodonium salts as illustrated by the formation diaryliodonuim triflate **22** and alkenyliodonium salt **23**.[71]

Furthermore, pseudobenziodoxole triflate **17** can be used as a catalyst in oxidative heterocyclization reactions with *m*-chloroperoxybenzoic acid as terminal oxidant.[73–75] Thus, using 2-$IC_6H_4CO_2H$ (5–10 mol%) as a precatalyst and *m*-chloroperoxybenzoic acid as the terminal oxidant in the presence of triflic acid allows oxidative heterocyclization of aldoximes **25** and nitriles **33** to the corresponding 1,2,4-oxadiazoles **26** to occur in high yields (Scheme 10).[73]

Bolm and coworkers have recently demonstrated that pseudobenziodoxole triflate **17** can be used as an efficient precursor to the novel sulfoximidoyl-substituted hypervalent iodine compounds.[76]

2-Iodoxybenzoic acid ditriflate: the most powerful iodine(V) oxidant

The exceptional oxidizing properties of hypervalent iodine triflates are best illustrated by a recent study on preparation and reactivity of the strongest iodine(V) oxidant, 2-iodoxybenzoic acid ditriflate (IBX-ditriflate) **28**.[77] Compound **28** was prepared by the reaction of 2-iodoxybenzoic acid (IBX, **27**) with slightly excessive triflic acid in the presence of trifluoroacetic acid (Scheme 11). Product **28** was isolated as a moisture sensitive, microcrystalline, white solid that is stable at room temperature and melts at 110 °C with partial decomposition.

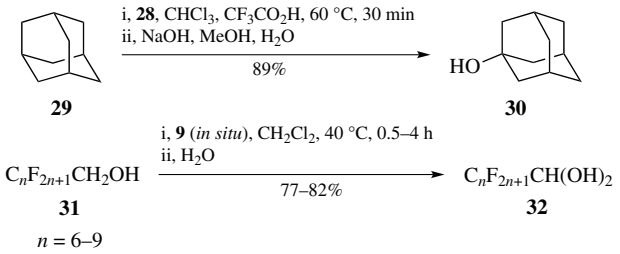


Scheme 11 Preparation of IBX-ditriflate **28**.

X-ray crystallographic data for IBX-ditriflate revealed a very complex solid-state assembly formed by primary bonds and various intermolecular secondary interactions, which can be illustrated by a simplified molecular structure **28** shown in Scheme 11.[77] It is important to emphasize that the significant ionic character of compound **28** leads to the exceptionally high electrophilic and oxidizing reactivity towards organic substrates. IBX-ditriflate readily reacts with common organic solvents, such as ether, hexane and acetonitrile, producing a mixture of oxidized products or black tar. According to ^{13}C NMR and mass-spectrometry studies, triflate **28** in acetonitrile solution is stable for about one hour and then is gradually reduced to iodine(III) benziodoxole-derived triflate **17**. However, solutions of IBX-ditriflate **28** in trifluoroacetic acid or in methylene chloride are sufficiently stable.

Triflate **28** reacts with many organic substrates non-selectively producing complex mixture of products. However, the less reactive substrates can be selectively oxidized to a single major product (Scheme 12).[40] For example, the oxidation of adamantane **29** in trifluoroacetic acid is complete in 30 min to give 1-adamantanol **30** in excellent preparative yield. This reaction represents a relatively uncommon case of C–H activation in a saturated hydrocarbon.

The exceptional reactivity of IBX-ditriflate is best demonstrated by the oxidation of fluoroalcohols. 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



Scheme 12 Oxidations using reagent **28**.

iodine(III) and iodine(V) reagents. Triflate **28** quickly reacts with TFE to give the corresponding aldehyde (as a hemiacetal) with quantitative conversion in a few hours. HFIP is quantitatively oxidized by triflate **28** at 60 °C just in 0.5 h.

Generated *in situ* IBX-triflate can be used for effective oxidation of fluoroalcohols **31** to fluoroaldehydes that are isolated as *gem*-diols **32** (see Scheme 12). Fluoroaldehydes are practically important compounds; however, their direct synthesis by oxidation of readily available fluoroalcohols was not previously reported, probably because of the lack of suitable oxidizing reagents.

Conclusion and outlook

This short review summarizes synthetic applications of Zefirov's reagent and related hypervalent organoiodine triflates as powerful electrophilic reagents and oxidants. Zefirov's reagent is a useful reagent for the synthesis of various iodonium salts from the corresponding organic precursors. The thermally stable and highly reactive benziodoxole triflates are utilized in organic synthesis as versatile oxidants and precursors to alkynylbenziodoxoles. The most powerful iodine(V) oxidant, IBX-ditriflate, can be conveniently prepared from 2-iodoxybenzoic acid (IBX) and triflic acid. The development of all these synthetically important reagents originated from pioneering research in N. S. Zefirov's laboratory at Moscow State University in the early 1980s.

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